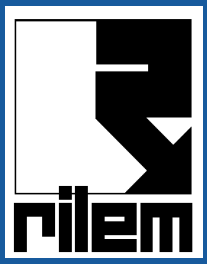

Proceedings
PRO 78

Historic Mortars and RILEM TC 203-RHM Final Workshop HMC2010

Proceedings of the
2nd Conference and of the
Final Workshop of RILEM TC 203-RHM

Edited by J. Válek, C. Groot, J. J. Hughes

RILEM Publications S.A.R.L.

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THEME IV: REPAIR MORTARS FOR HISTORIC MASONRY

RILEM TC 203-RHM 'REPAIR MORTARS FOR HISTORIC MASONRY' FINAL WORKSHOP

Preface

The 1st Historical Mortars Conference which took place in Lisbon, 2008, chaired by Dr. Rosario Veiga from LNEC was a very successful meeting and it gave rise to an idea that such a specialised event on historic mortars should be repeated. During the conference it became clear that sharing knowledge, creating new contacts and interdisciplinary collaborations are very much required in this topic. Mortars are not seen as a single discipline, but attract attention from a wide range of professions. This was confirmed by the number and variety of research projects on mortars which were presented.

Research has been focusing on historic mortars for some time. Demand for an improved scientific and technical guidance for conservation field led to the formation of the RILEM Technical Committee TC 167-COM on 'Characterisation of old mortars with respect to their repair' and its follow-up TC 203-RHM 'Repair mortars for historic masonry'. The later committee is now in its final stage. The final workshop of the TC 203-RHM will be incorporated as part of the conference and the resulting documents promise interesting material for discussions during the conference.

An objective of the 2nd Historic Mortars Conference is to bring together scientists, technicians and professionals involved in research and studies of historic mortars to present and discuss advances in this topic. The main theme of the conference is the conservation of historic buildings and works of art, i.e. studying mortars with respect to repair. This is a unifying field where a truly interdisciplinary collaboration is needed and where contributions of archaeologist, architects, civil and structural engineers, geologists, material scientists, chemists, conservation scientists and art restorers interested in mortars should have their place. The special focus of the conference will be on the application of research and technical knowledge to conservation practice and vice versa in its reflection on such recommendations.

A number of contributions, representing the whole world have been collected under the following four main conference themes:

I *Characterisation of historic mortars*
(architectural, material, archaeological, construction and technological aspects)

II *Assessment of mortars and masonry*
(diagnostics and testing methods, complex evaluation of masonry and mortars, structural issues, damage and deterioration)

III *Conservation and restoration issues*

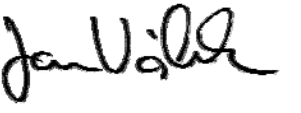
(case studies, values, authenticity and compatibility of mortars, restoration and conservation techniques)

IV Repair mortars for historic masonry
(design and requirements for repair mortars, testing and evaluation of repair mortars, emerging materials and technologies).

The conference was organised by the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of the Czech Republic (ITAM AV ČR) in cooperation with the International Union of Laboratories and Experts in Construction Materials (RILEM). The conference administration was managed by Congress Business Travel, ltd. The Organising Committee greatly appreciate the financial support of Vicat from France and VAS v.o.s. building restoration and property management company from the Czech Republic. The prize for the best student presentation was supported and awarded by Lafarge, France. The conference was organised under the auspice of Mr. Ondřej Pecha, Member of the Committee of Prague City Council for Monument Care and Tourism.

The organisation was a team effort of the staff of the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of the Czech Republic, with special thanks going to Dr. Claire Moreau who made the key contribution to the efficient organisation of the event and all the members of the Organising Committee. The papers were reviewed and edited by the members of the Scientific Committee and their great effort was greatly appreciated and in particularly I wish to thank Dr. John Hughes of University of the West of Scotland and Dr. Caspar Groot of TU Delft. The full papers were proof read and edited by Jennifer Wehby, Dorn Carran and Dr. John Hughes. I also wish to thank Mr. Martin Pavala, Dr. Eva Čechová, Mr. Jiří Novotný, Mr. Josef Jiroušek for leading the excursions following the conference.

In Prague, September 2010



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RILEM TC 203-RHM Final Workshop Preface

At the successful first Historic Mortars Conference at Lisbon in 2008 (HMC08) it was concluded that there is a clear need for continuity in the exchange of experience and knowledge in this specialized field of restoration.

To this end the second Historic Mortar Conference (HMC 2010) was organized by the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of the Czech Republic, chaired by Dr Jan Valek, in cooperation with the RILEM TC 203 RHM: Repair Mortars for Historic Masonry.

As part of the conference members of RILEM TC 203 presented in a workshop the final deliverables of the TC on performance requirements of repair mortars for historic masonry.

More than 140 papers were submitted after the call in which the conference themes are covered in a wide range of topics and views: fundamental aspects of mortar characterization with a view to repair, property development of binders and repair choices are discussed in the contributions as well as how to realize performance and repair requirements in restoration practice.

From this it may be expected that an interesting and useful interdisciplinary exchange of knowledge and experience will take place at HMC10.

It may as well be hoped that the findings of these conference proceedings will find their way to the field and that they may contribute to an improved restoration and conservation practice.

Caspar Groot
Chair RILEM TC 203-RHM
Delft, 29Aug10

Theme I

Characterisation of historic mortars

architectural, material, archaeological, construction and technological aspects

I.01

Gypsum Mortars of the Khoja Zainuddin Mosque in Bukhara (Uzbekistan) – A Contribution to Building Archaeological Studies

Jasmin Badr[1], Christiane Huck-Stiasny[2] and Rainer Drewello[2]

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Abstract The Old City of Bukhara (Uzbekistan), protected as UNESCO world cultural heritage, is one of the most important historical urban fabrics in Central Asia. In the northwest of the city lies the Khoja Zainuddin Mosque – a monument of overarching art historical importance and an outstanding state of preservation. A building archaeological survey has shown that the whole building was erected in one single phase in the middle of the 16th century [1]. However, several later modifications can be clearly determined in the prayer hall and the adjoining rooms. For the classification within the historical context, a detailed analysis of the mortars was executed. Pure gypsum, gypsum-lime and clay mortars were identified. In some samples, the analyses also provided evidence of organic add-ons, probably to improve the mortar's properties.

1 Architectural context

The Khoja Zainuddin Mosque (Fig. 1) is dominated by a domed prayer hall that is surrounded by a wooden portico in the north and east. The western part of the building is occupied by four small rooms and a monumental niche with the tomb of the saint Khoja Zainuddin.

According to the different layers of paintings in the prayer hall, at least three phases of decoration can be distinguished. Whereas the first layer probably dates to the construction phase in the middle of the 16th century, the second and third layer point to the middle of the 17th century [1]. Unlike the richly decorated prayer hall, the adjoining rooms are mostly painted in a uniform white or grey beige

colour without any ornaments or other decorative elements. However, damaged spots on the walls show that these rooms have also been plastered several times.

Fig. 1 First floor plan of the Khoja Zainuddin Mosque with sampling locations

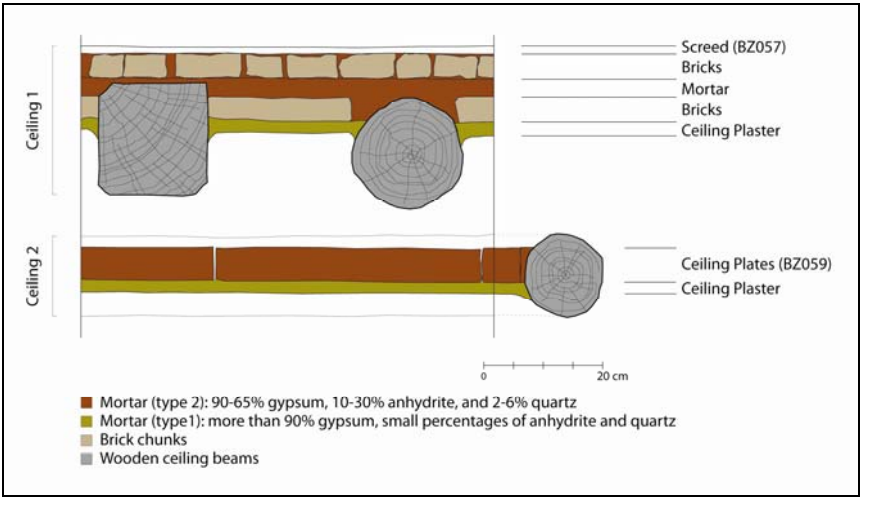

Fig. 2 Cross section of the ceiling construction in room 5

Fig. 3 Ceiling constructions in room 5

Fig. 4 Mortar sample taken in room 7

A particularly interesting element is represented by the ceiling construction in room 4 and 5 (Fig. 3): In between the wooden ceiling beams, brick chunks are fixed with different layers of very delicate mortars. This construction is covered from both the upper and lower side by further layers of mortar. In room 5, a second ceiling was constructed under the original one that burnt through to some extent. Substantially, the same construction system was applied for the new ceiling; the only difference is the usage of mortar plates (Fig. 2) in place of the brick chunks.

Also the niche in the east wall of room 7 marks a special point of interest. The original opening towards the northern portico was later closed with reused mortar chunks (Fig. 4) that still bear traces of ornaments and paintings.

2 Geological background

Even though there is only little historical evidence for mineral deposits in Central Asia, it can be assumed that many of them have been known and exploited from the 16th century to this day.

An overview shows the most relevant raw materials and their deposits in the region of Bukhara (Fig. 5).

Gypsum and anhydrite: Large Paleogene gypsum deposits are situated in Mamzhurgat (thickness 4-15 m) [2, 3] in the region of Kagan, about 12 km southeast of Bukhara. This gypsum is of white or greyish-white colour, fine-grained and crystalline.

Celestine: Beside the deposits of the Fergana Valley another celestine deposit is situated in the Surkhandaryo Province within sulphur deposits [4].

Quartz: A large deposit (thickness 18 m) of very pure quartz (content of SiO_2 is up to 99.3%) is situated in Tozbulak in the southern Kulzhuktaw Mountains. The deposit of Bitab in the southern mountains of Nurataw also contains microcline deposits, convenient for the production of fine ceramics [2, 3].

Limestone: The deposits of Korovulbazar (about 43 km in the southwest of Bukhara) and Proletarabad (about 25 km in the southwest of Bukhara) are characterized by grey or greyish and fine grained limestone [2, 3].

Thermal waters: The deepwater sources in the region of Bukhara contain a high percentage of strontium (> 300mg/l).

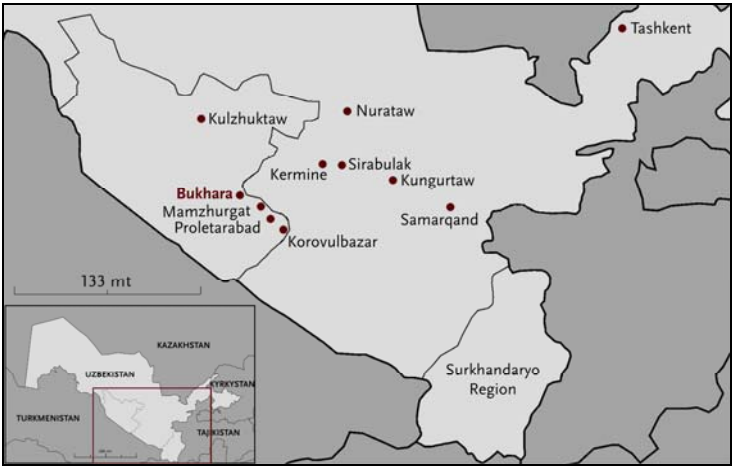

Fig. 5 Gypsum, celestine, quartz and limestone deposits in the region of Bukhara

3 Mortar analysis

The investigation of the mortars began with a macroscopic study of all the samples. Polished and thin sections of the most significant mortars were analysed using reflected-light microscopy. For the determination of specific components and compound percentages, x-ray diffraction (PW 1800 by Philips, detector: Xenon proportional counter, SemiQuant), FTIR-spectrometry (Spektrum 2000 and Auto Image System by Perkin Elmer, diamond cell, aperture 100 x 100 µm, wavenumbers 4000-550 cm^{-1}) and scanning electronic microscopy were used (SEM, Philipps XL 40). The latter was fitted with an energy-dispersive x-ray spectroscopy application (EDS, microanalysis system Quantax by Bruker, HV 20kV, WD 11.5, Spot size 6).

As the macroscopic and microscopic analyses already show different compositions, the x-ray diffraction permits a more detailed classification of the mortars. Five types could be distinguished:

1) More than 90% gypsum, small percentages of anhydrite and quartz.
2) 90-65% gypsum, 10-30% anhydrite, and 2-6% quartz.
3) 64-55% gypsum, 35-42 anhydrite, and 1-5% quartz.
4) Less than 55% gypsum, 45% of lime, quartz, charcoal and brick chippings in variable concentrations.

5) Clay mortar, mixed with gypsum, lime, charcoal and brick chippings.

The spectrum of compositions is presented in Table 1.

Table 1 Analysis results of the x-ray diffraction, the scanning electronic microscope (SEM) and the FTIR-spectrometry

Sample No.	Room	Type	X-ray Diffraction	SEM-EDS	FTIR-Spectrometry	Remarks
BZ028	roof	2	80% gypsum, 15% quartz, 5% anhydrite	*main components*: C, O, S, Ca *secondary component*: Mg, Si	*main component*: gypsum *secondary components*: calcite, quartz, long-chain unsaturated fatty acids, calcium oleate, protein, calcium oxalate	the occurrence of acids, oleates, oxalates and proteins indicate the addition of an organic compound; most probably whey
BZ050.1	4.1	2	78% gypsum, 18% anhydrite, 4% quartz	*main components*: O, S, Ca *secondary components*: C, Na, Al, Si, Cl, Fe, Sr	*main component*: gypsum *secondary components*: hemihydrate/ anhydrite, calcite, calcium oxalate	-
BZ058.2h	5	4	65% gypsum, 32% anhydrite, 3% quartz	*main components*: O, S, Ca *secondary components*: C, Si	*main component*: gypsum *secondary components*: quartz, calcite, hemihydrate/ anhydrite	-
BZ058.2d	5	3	41% gypsum, 27% quartz, 15% calcite, 8% anhydrite, 3% albite, 3% clinochlore, 3% muscovite	*main components*: C, O, S, Ca *secondary components*: Na, K, Al, Si, Fe, Sr	*main component*: gypsum, calcite (mol ratio 1:1), clay minerals, quartz	-
BZ059	5.0	4	45%gypsum, 29%quartz, 15% calcite ; 5% albite, 2% muscovite, 2% clinochlore	*main components*: C, O, S, Ca *secondary components*: Na, Mg, Al, Si, P, Cl, K, Fe	*main components*: gypsum, calcite and quartz *secondary components*: long-chain unsaturated fatty acids, calcium oleate and protein, calcium oxalate, potassium and sodium nitrate	the detected nitrates and phosphorous may be due to infiltration of excrements; the acids, oleates, oxalates and proteins probably indicate the addition of whey

BZ065.1	4.0	1	99% gypsum, < 1% anhydrite, < 1% quartz	*main components*: O, S, Ca *secondary components*: C, Na, Mg, K, Sr	*main component*: gypsum *secondary components*: calcite and quartz	the detected strontium (celestine) may indicate the addition of celestine crystals
BZ071h	7	1	95% gypsum, 2% quartz, 2% anhydrite, 1% muscovite	*main components*: O, S, Ca *secondary components*: Na, Al, Si, K	*main component*: gypsum *secondary components*: calcite (varying percentages), quartz, calcium oxalate	-
BZ071d	7	1	94% gypsum, 3% anhydrite, 3% quartz	*main components*: O, S, Ca *secondary components*: Na, Al, Si, K	*main component*: gypsum *secondary components*: hemihydrate/ anhydrite, calcite, quartz	-
BZ076	7	5	53% quartz, 17% calcite, 13% albite, 8% gypsum, 4% anhydrite, 3% clinochlore, 2% muscovite	*main components*: C, O, Al, Si, S, K, Ca, Fe *secondary components*: Na, Mg, Cl	clay minerals, clusters of lime, gypsum, iron silicates	-

3.1 Characteristics of particular samples

In Table 1, examples of the five defined groups are briefly presented. The results show the composition of the mortars and the percentages of crystalline components. However, some samples show additional features. Three samples have been chosen for further analyses. Sample BZ028, a joint mortar, was taken on the exterior of the building, BZ059 from one of the mortar plates in the ceiling construction (Fig. 2). Sample BZ065.1 represents a pure gypsum mortar which was affected by heat.

BZ028 (Table 1, Fig. 6): The white outdoor gypsum mortar shows moderately sorted grains in a homogeneous matrix with low porosity. The aggregates consist of natural xenomorphic and partly idiomorphic gypsum and anhydrite crystals (approximately 80%) measuring up to 0.2 cm.

Using FTIR microscopic spectroscopy, a residue of the organic add-on could be identified. The extraction of the powder using organic solvents (methanol, methyl ethyl ketone) resulted in a mixture of long-chain unsaturated fatty acids, calcium oleate and protein. The spectrum of substances is a strong hint for the

addition of an organic compound. Most probable is the add-on of whey. The organic modified binder might have been used to refine the plaster and to improve its properties. The detected oxalates are assumed to be the result of the microbially induced corrosion of calcite forming a precipitation of calcium oxalate underneath the surface layer of secondary precipitated gypsum.

Fig. 6 Sample no. BZ028, 50x

Fig. 7 Sample no. BZ059, 50x

BZ059 (Table 1, Fig. 7): the FTIR-spectrum bears great resemblance with sample no. BZ028. The occurrence of calcium oxalate in combination with calcium oleate and proteins indicates the use of whey.

BZ065.1 (Table 1, Fig. 8): This sample represents an extremely pure and homogeneous gypsum mortar of very low porosity. Only few gypsum crystals were added, measuring up to 0.5 cm. Celestine was detected in the sample using SEM and EDS. The yellowish-brownish colour of the white mortar is a result of its location at the bottom side of a chimney opening [5].

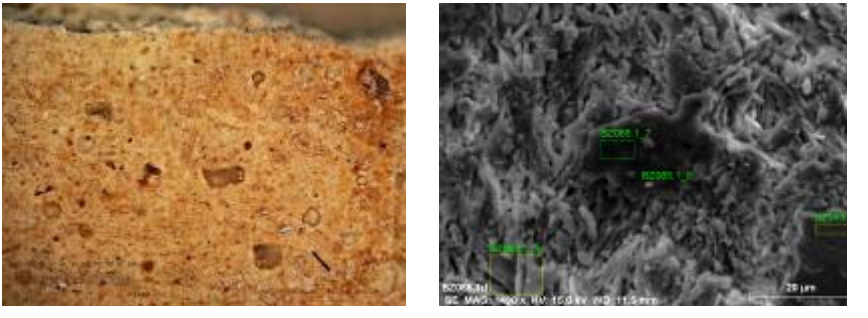

Fig. 8 Sample no. BZ065.1, polished section, 50x (left), SEM image (right)

4 Conclusion

Regarding all samples taken at the Khoja Zainuddin Mosque, it can be stated that the mortars contain important percentages of gypsum. As the geographical

factor surely played an essential role in the 16th and 17th century, it can be assumed that the natural deposits in the region of Bukhara were consistently exploited.

A great number of samples show a rather homogeneous gypsum matrix with gypsum and anhydrite as aggregates in different proportions (type 1-3). In some cases, gypsum-lime mortars (gypsum-lime ratio nearly equals 1:1) were applied (type 4). The high lime percentage is due to lime clusters that were intentionally added [6]. They can be clearly identified within the homogeneous matrix using cross section analysis (Fig. 7). In addition, clay mortars were mainly used for the masonry. In contrast to the extremely hard and well preserved gypsum mortars, the latter contain only small percentages of binding material (type 5).

Considering the mortar samples in the historical context and comparing the different compositions, it is evident that the pure gypsum mortars were applied in early construction phases while the composite mortars appear in later phases. The latter are mostly situated in the ceilings and particularly in the lower layers (Fig. 2). Organic compounds were obviously added (see BZ059) in order to improve the properties of the mortar, namely its mechanical stability and water resistance [7, 8]. However, the same components were also applied for external mortars (see BZ028). The use of whey is suggested, although animal milk products are still – and surely were – an extremely valuable addition for simple building materials. If so, the thesis of the importance of the Khoja Zainuddin Mosque as one of the most significant buildings of 16th century in Bukhara might be supported.

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I.02

Understanding Historic Mortars and their Variations – a Condition for Performing Restorations with Traditional Materials

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Abstract In order to design a restoration mortar with properties and composition similar to the original mortar, it is important to analyze the historic mortar in several ways. A combination of analyses give information about the mixing ratio between binder and aggregates, chemical composition of the mortar, additives, tool marks, application technique etc. This paper shows the variations in Swedish medieval lime mortars with a high content of binder. By analysing historic mortar with a combination of ocular investigations, microscopically studies of thin section specimens, Scanning Electron Microscopy and X-Ray Powder Diffraction, all the information needed for designing a restoration mortar, with composition and properties similar to the historic mortar, is gained.

1 Introduction

When adding new materials in conservation and restoration of an architectural heritage, the new materials should be compatible with the old materials in order to preserve them. Old mortar remaining on historical buildings is an important source of knowledge that can be used in the restoration work. In order to design a restoration mortar with properties and composition similar to the original mortar, it is important to analyze the historic mortar in several ways. A combination of analyses gives information about the mixing ratio between binder and aggregates, chemical composition of the mortar, additives, tool marks and application technique [1]. This paper show the difference between several medieval lime mortars from different regions of Sweden. The geological variation of the country is reflected in the historic mortars. Only by knowing and understanding the differences they can be restored with traditional mortars with similar properties.

A simple ocular examination can show:

- If the mortar were made for joints or plaster, the colour of the binder.

- If it is a mortar rich in lime or not.
- The content of small or large particles in the aggregate.
- Impurities or additives such as crushed bricks, coal or pieces of wood and fibres of different kinds.
- Tool marks, lime wash residues and residues of other paint

Optical and spectroscopic methods, such as Scanning Electron Microscopy (SEM), optical microscopy analysis of thin section samples and X-ray powder diffraction analysis (XRD), can be used to investigate the following important aspects more in detail:

- The type of binder, such as clay, lime, hydraulic lime or cement, used in the mortar.
- The geographic origin of the raw material used for lime burning.
- The lime slaking method and storing of the lime putty [2].
- The origin of the aggregate, their mineral composition and particle size distribution.
- Any additives used when making the mortar.
- The methods used in the application and working of the plaster, by traces of tools.
- The number of lime wash layers applied to the surface.
- The mixing ratio of the mortar.
- The pore structure and durability of the plaster.

2 Materials and methods

The historic mortar was original material collected from the attics or the masonry of medieval churches and church ruins from different areas in Sweden. All of them are lime rich traditional lime mortars.

2.1 Methods for material analyses

To analyze mortar, new as well as old, there are several useful techniques such as Scanning Electron Microscopy, thin sections studied in light microscope and X-ray powder diffraction analyses.

Mortar samples were studied using Environmental Scanning Electron Microscopy (ESEM). The microscope used was a Quanta 200 SEM FEG from FEI. The samples were mounted on a carbon adhesive tape without further treatment.

SEM is a valuable technique for studying the structure and crystal sizes in lime [5, 6]. In addition, it gives information about the pore structure of the mortar and the size and appearance of the sand particles.

Optical microscopy studies of thin section mortar specimens were used to obtain information about the type of binder, the pore structure, the blending ratio, the minerals and grain sizes of the sand particles etc. [4, 7, 8].

Thin section specimens were prepared from historic mortar. An UV-fluorescent epoxy was used in a vacuum impregnation of the samples before they were polished down to a thickness of ca 3 μm and studied in an Olympus Bh-2 polarization microscope. The magnification of the pictures is shown for each picture.

The mineralogical composition of mortar was determined qualitatively by X-Ray Powder Diffraction (XRD). Only crystalline species can be detected by this method and the detection limit is 1-3 % (w/w). The instrument used was a Siemens D5000 powder diffractometer applying Cu characteristic radiation and a scintillation detector. The scanned 2-theta range was 10 to 70 degrees. The identification of components was carried out using the Joint Committee for Powder Diffraction Standards database.

3 Results and discussion

Examples of historical mortar investigated ocular are shown in Figs. 1-6. By performing an ocular investigation lots of information can be read. Tool marks, additives as well as bigger binder and aggregate particles are visible. Those surfaces have been found on the medieval churches on Gotland both outdoors in the joints and indoors on the attics.

Fig. 1 Medieval joints in the tower of Linde church. Hard lime rich white mortar with very fine graded sand. Traces of tools used when applying the mortar.

Fig. 2 Remaining plaster on a Romanesque choir still left on the attic of Norrlanda church. Very lime rich with fine graded sand. Traces from tools.

Fig. 3 Two types of old mortar on the west façade of Othem church. They are both white and lime rich. One with fine graded sand and the other with larger rounded sand particles.

Fig. 4 Remains of wood and coal in an extremely lime rich mortar on Norrlanda church. A very hard and compact mortar.

Fig. 5 Joint on Fardhem church containing crushed red bricks. Pink secondary mortar based on lime.

Fig. 6 The joints at the ruin from a citadel at Gothem. A bit yellowish lime mortar with large sand particles and remains of large coal particles.

The Scanning Electron Microscope gives information about the type of lime and the structure of the mortar. At a magnification of 100 x the air pore structure is visible as well as how the sand particles are embedded in the lime. At a magnification of about 2500 x the micro pore structure of the binder becomes visible. In even larger magnifications each crystal of the lime can be studied in detail. The shape and size of the crystals as well as how they are packed together give information for identifying the slaking and storing process of the lime [2]. For example, the earth slaking technique give large particles arranged in an airy structure while the wet slaking technique give smaller particles arranged in a dense and well packed structure.

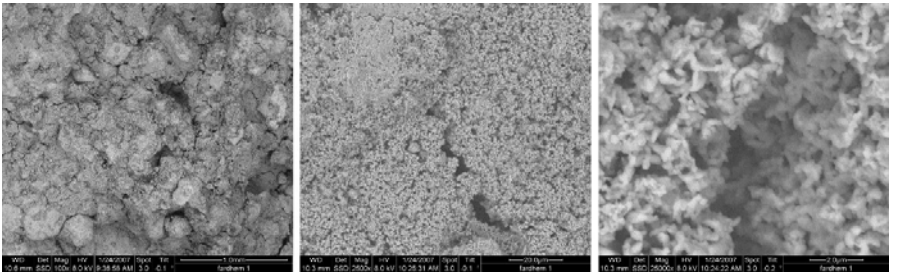

Fig. 7 Medieval lime mortar from Fardhem church on Gotland, studied with SEM in three different scales (100x, 2500x and 25000x). It is a very lime rich mortar with more lime than sand, where the sand particles are imbedded in the lime. Several micro cracks and a few air pores are visible in the binder. The lime particles have the same sizes and are oriented in an airy structure.

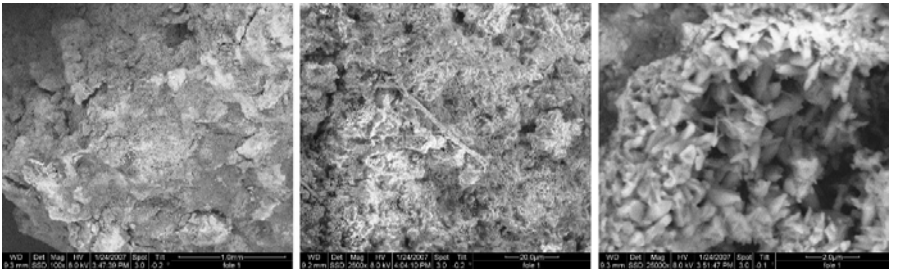

Fig. 8 Medieval lime mortar from Fole church on Gotland, studied with SEM in three different scales (100x, 2500x and 25000x). Another extremely lime rich mortar with a few air pores visible. The lime particles exist in different sizes and shape, oriented in an airy structure.

Investigation of thin section specimens of mortar and plaster by optical microscopy was also found to be very informative in the studies of historic mortar. It can give information about the amount and type of binder and aggregate and of the mixing ratio between them. It also gives a lot of information about the pore structure and the surface working technique [3]. Additives or layers of lime wash can also be seen depending on how each sample was cut out. In the examples below several historic lime mortars from Sweden are shown. All regions are represented by lime rich mortars. A big unwhipped lime lump is visible in the second example from Fole. Additives such as wooden coal and sea shells become visible in the examples from Bara and Lundby. Layers of lime washes are made different at Garda compared to Älvros – fresco technique is followed by secco. The examples from Hassela and Sunne are made by hydraulic lime containing only small amount of aggregate.

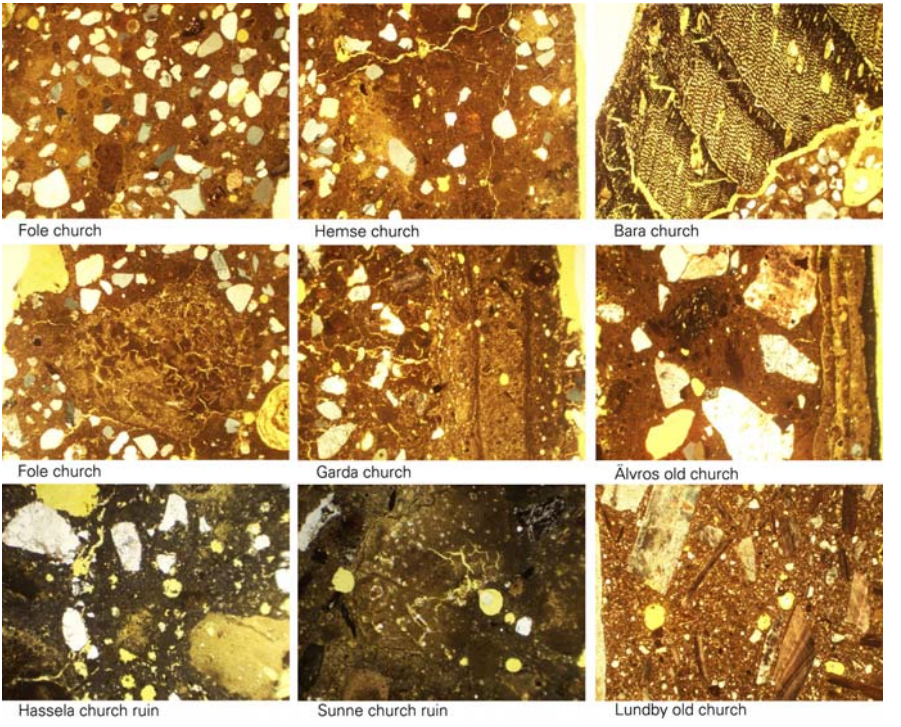

Fig. 9 Examples of thin sections of medieval lime mortar from churches around Sweden. All of them are very lime rich. The first five examples come from the island of Gotland. The first two examples from Fole and Hemse church are typical medieval mortar based of lime and only a small amount of aggregates. They also contain only a small amount of air pores and micro cracks. The mortar from Bara church shows a piece of wooden coal. In the second example from Fole there is a lime lump of unwhipped lime. The examples from Garda (Gotland) and Älvros (Härjedalen) have several layers of lime wash on the surface made in different thickness due to the consistency of the lime wash. The mortar from Hassela and Sunne (from Hälsingland and Jämtland) contain hydraulic lime and only small amounts of aggregates. In the example from Lundby church (from Bohuslän) the aggregates are made of sea shells. The width of each sample is 4.5 mm.

Mineralogical analysis by X-ray powder diffractometer can be used as a complement to the optical methods mentioned above. Thus, the crystalline matter present can be detected and identified, see Fig. 10.

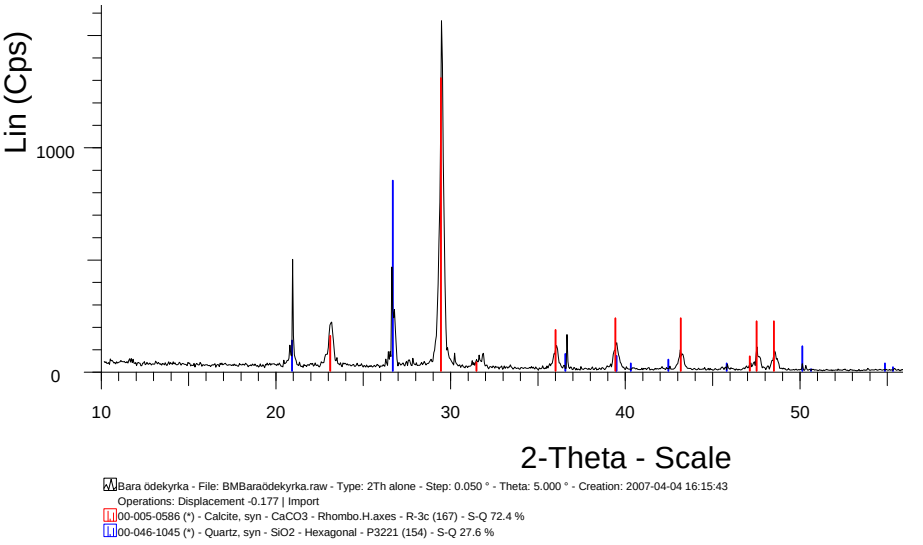

Fig. 10 X-ray diffraction made on a medieval mortar sample from Bara church ruin on Gotland. The sample only contains $CaCO_3$ (kalcit) and SiO_2 (quartz); carbonated lime and quartz sand.

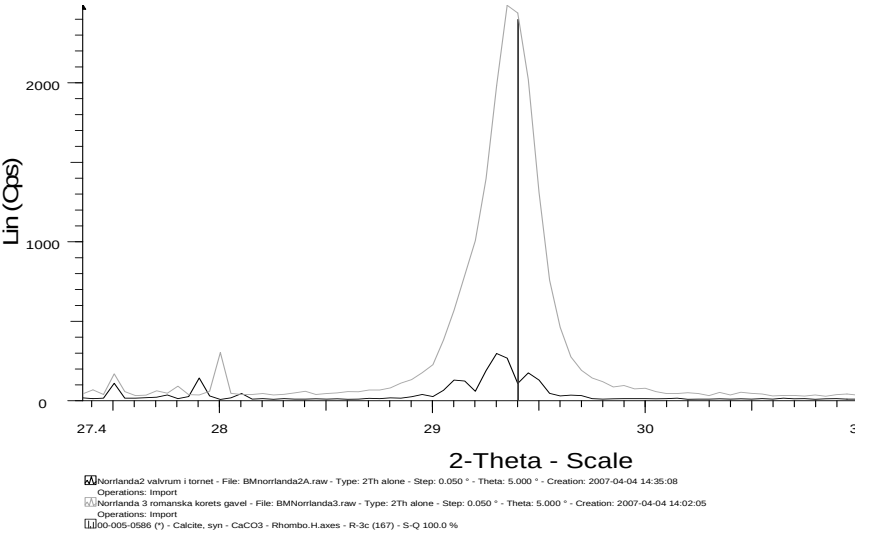

Fig. 11 X-ray diffraction made on two medieval mortar samples from the attic of Norrlanda church on Gotland. The lower black line is from a joint inside the tower while the upper gray line is from a render surface once being an outdoor render on the choir but since the last building phase (around year 1300) it has been indoors on the attic. Because of the low intensity of the sample from the tower, the conclusion can be made that it has transformed and re-crystallized to a less crystalline form.

In some cases it is also possible to follow changes in the samples over time, as in the example in Fig. 11. In this case part of the rendered wall became an indoor wall in the attic during a reconstruction of the church. The plaster on this wall has been exposed to the indoor climate probably alternating between dry and humid and the lime has thus re-crystallized into a less well defined form (lower black curve) than it had on the other wall (upper grey curve).

4 Conclusions

The variation of historic lime mortars are as widely spread as there are sources of aggregates and sources of lime stone suitable to be burned. In a country with great geological variations the specific combinations and variations for each region need to be known. To be able to follow the international charters [9] saying that our architectural heritage should be restored with traditional materials compatible to the original material – we need detailed information about the original material. This paper has shown that one mortar defined as lime mortar is not likely to have the exact same composition and properties as another historic lime mortar. By combining ocular studies with analyses of thin section specimens, SEM and XRD the variations can be known and a proper restoration mortar can be designed to match the historic mortar in all possible ways.

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I.03

Irish Medieval Mortars: Implications for the Formulation of New Replacement Mortars

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Abstract This paper provides an overview of medieval lime mortars in Ireland, based on comparison of the petrography and microstructure of 110 lime mortars from 35 archaeological sites in the Republic of Ireland. These comprise bedding, plastering and rendering mortars from a range of secular and ecclesiastical buildings including castles, churches, round towers and city walls. The paper outlines current gaps in knowledge of Irish historic mortars, and the challenges in using the data gained from analyses to specify repair and replacement mortars.

1 Introduction

The analysis of historic mortars in Ireland is carried out from three distinct, though interlinked, perspectives:

- Conservation: focusing on understanding the characteristics of a mortar, its degradation and interaction with the rest of the building fabric, and most often to obtain specific information to formulate a compatible repair mortar.
- Archaeology: focusing on determining the provenance of raw materials, on production processes (lime burning, mortar mixes, use of additives etc.), and also to provide absolute and/or relative dating evidence for a particular site or structure.
- Historic Materials Research: analyses aim to increase knowledge and understanding of burning, mixing, hydration and carbonation processes, and identifying the different minerals formed.

This paper, focusing on mortars from the medieval period, provides an overview of the key findings from studies of the petrography and micro-structure of 110 bedding, plastering and rendering mortars from 35 archaeological monuments gathered during research and consultancy work from the late 1990s to

2010. The paper also addresses some of the issues encountered in transforming analytical data into useful knowledge to conserve historic structures.

2 Historical architectural context

Lime mortar technology was introduced to Ireland sometime towards the end of the early medieval period (AD 500-1000). Prehistoric (pre-AD 500) Irish building technology is based on the use of dry-stone, earth, timber and other organic building materials. The arrival of mortared masonry building techniques is directly linked with the development of the early Christian church in Ireland, and the technology of lime production and building with lime mortar was almost certainly brought from elsewhere in Europe. Timber churches predominate in the early medieval period, and the first historical references to 'damliac' or 'stone houses' appear from AD 724 onwards. These may have been dry-stone buildings, and it is not until the ninth or tenth centuries that secure evidence for mortared masonry structures appear, such as Clonmacnoise Cathedral, built c. AD 909 [1].

Fig. 1 The north wall of Clonmacnoise Cathedral, Ireland, constructed c. AD 909, with an elaborate perpendicular Gothic doorway inserted at the western end of the wall c. AD 1460. Recent conservation of the cathedral focused on repointing the ruined structure (above right).

Early stone churches in Ireland tend to be simple, single-celled buildings, rectangular in plan and with little (if any) decorative detail. However, the advent of masonry mortar allowed the introduction of new architectural forms within these rectangular churches such as round arches, barrel vaults and stone roofs. Perhaps the most striking new building type made possible by masonry mortar technology were tall, tapering, free-standing 'round towers' which appear from the tenth century onwards at ecclesiastical sites. The twelfth century saw the transformation of the historical built landscape with the introduction of significant new masonry building types including the adoption of Romanesque architectural forms at many sites, the arrival of the formal architecture of European monastic orders such as the Cistercians, and the new towns, fortifications and other buildings which developed following the arrival of the Anglo-Normans c. AD 1170. The vast majority of mortared masonry medieval buildings in Ireland survive as ruined structures, and relatively few form part of a site which is still in

use, for example as a place of worship. The most common conservation intervention is mortar-based (e.g. repointing and/or grouting), and the determination of a compatible repair mortar to preserve both the character and the fabric of the ruined structure is integral to conservation work at medieval sites.

3 Petrography of medieval Irish lime mortars

The usefulness of studies of the petrography and microstructure of historic lime mortars has been widely recognised [2, 3, 4, 5, 6] for both archaeological and conservation work. Surviving mortars from the medieval period in Ireland comprise bedding and pointing mortars, external renders and internal plasterwork, and special purpose mortars (e.g. chimney flue lining, wicker-centred vaulting). In some cases, such as Stradbally Church, Co. Waterford and the 13th century Bishops Palace at Kilteasheen, Co. Roscommon built in 1253 and destroyed in 1258 [7], lime mortars were used to coat the internal and external surfaces of clay-mortared masonry walls. Medieval mortars in Ireland were therefore originally intended to perform a wide range of functions.

3.1 Mixes

Historical Irish lime mortars tend to be binder-rich with an open porous network, often 10-20% by volume [3]. The aggregate:binder ratio can vary significantly from 3:2 to 1:3 among general building and specialist mortars, while internal plastering mortars typically contain very scarce (<2%) aggregate 'floating' in a binder-dominated matrix.

3.2 Aggregate

The aggregate fraction of a mortar may consist of a number of elements, including inert and/or reactive sand aggregate, binder-related particles, and additives intended to improve the workability and durability of a mortar.

3.2.1 Inert aggregate

Historic lime mortars in Ireland normally contain a diverse range of inorganic aggregate due to the exploitation of naturally occurring sources of sand. Depending on the location of the building, the aggregate may have been derived from any of wide range of geological deposits and include sands from rivers, beaches, sand pits or crushed rock, which often poses challenges to sourcing matching aggregate for any new repair mortars. Aggregate tends to be unsorted, ranging in size from >15mm to < 0.004mm, and comprising a range of different

rock types. For example, the bedding mortar of the 14th century Hall-house of Moygara Castle, Co. Sligo contains three different varieties of limestone, two sandstones and quartz [8], while the 12th century priory of St. John in Waterford City contains conglomerate, sandstones, rhyolite, volcanic rocks, slate and some schist[9]. Limestones (fossiliferous, oolitic, dolomitic, micritic and sparry etc.) form a significant part of the aggregate fraction in most Irish medieval mortars, and were found in 86% of the mortars examined. In addition, lime lumps >1mm ø are a common feature of historic mortars; recorded in 77% of samples, where they form part of the aggregate fraction. Shell is also commonly found as part of the aggregate fraction (15% of samples), especially in coastal locations. Other calcareous aggregate such as tufa and carbonate-rich sandstones have also been recorded in Irish lime mortars. The frequent presence of calcareous aggregate in Irish medieval mortars confirm the lack of confidence in the appropriateness of acid digestion-based chemical analytical techniques for the study of historic lime mortars cited by other researchers[4, 5, 6].

3.2.2 Reactive aggregate

Reactive aggregate can contribute to the hydraulicity of a lime mortar, and were recorded in 18% of medieval mortars examined. Reaction rims are commonly found on siliceous aggregate such as chert, but have also been recorded on clay-bearing rock fragments such as shale and greywacke. However, reactive aggregate may only be one of a number of sources of hydraulicity within a mortar.

3.2.3 Pozzolana

Pozzolans are fired clay materials rich in reactive silica/alumina which react with Ca(OH)2 and water to form calcium silica and aluminate hydrates with cementing properties [10]. Fragments of pozzolanic fired ceramic fragments, often referred to as ‘brick dust’ are found in bedding, plastering and rendering mortars, and though occurring in only 18% of the mortars examined, their use is widely distributed throughout the country. In addition, fragments of fossil fuel (e.g. ash, charcoal, coal) are a common occurrence in historic lime mortars, found in 59% of the mortars examined. Their presence is usually interpreted as accidental contamination from the kiln fuel used in the production of lime. However, hydraulic reaction rims are frequently observed surrounding remnants of burnt fossil fuel, and can be considered as contributors to the overall hydraulicity of historic Irish lime mortars.

3.2.4 Other additions

A large variety of organic and inorganic additives were used in the past to enhance workability, act as mechanical reinforcement, accelerate hardening and to improve durability. However, relatively few of these have been observed from medieval Irish material. Evidence for hair is confined to plastering and rendering

mortars during the medieval period, where they appear to have been added as structural reinforcement and to minimise fracturing by retraction. Though the principle of adding hair was well-known, occurring in 24% of samples, its execution is often poor - clumps of hair are frequently observed while well-distributed hair appear to be a rarity in surviving mortars. Fragments of unburnt wood and straw are occasionally found in bedding mortars. However the wide range of additives known in the literature, and detected in later post-medieval mortars in Ireland [3], have not yet been identified from any medieval material.

3.3 Binder

Medieval lime binders are usually completely carbonated to calcite, and while binder-related particles are often present (e.g. lime lumps and under-burnt relict limestone), these form part of the aggregate fraction though can be useful in determining the source of the lime. In contrast to a widely held belief in the 20th century regarding the 'purity' of Irish limestones, many of these rocks contain clay-based and other impurities which impart hydraulic properties – a phenomenon referred to by 19th century authorities on Irish limes [11, 12] and confirmed by analytical research on material from medieval monuments [13].

Fig. 2 Comparison of original in mortar (top right) and new replica mortar (bottom right) used for ongoing conservation work at the remains of Stradbally Church, County Waterford.

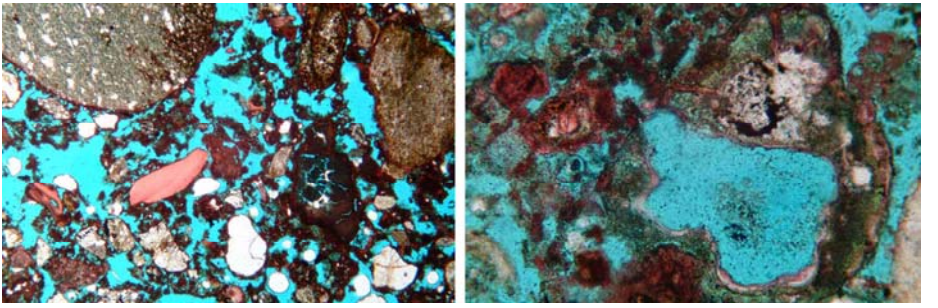

Fig. 3 General texture of bedding mortar from the west wall of the medieval nave of Stradbally Church, County Waterford showing angular aggregate of variable composition and charcoal (left, 2X natural light) with detail showing recrystallisation of carbonated lime and reaction of volcanic silica and glass (right, 10X natural light).

3.4 Weathering of the microstructure

The weathering of medieval mortar and its interaction with surrounding masonry has been a long-standing area of concern [2, 3, 7, 8, 9, 14]. Moisture is the key agent of decay of mortars in Ireland, while salt attack is relatively rare, and where it occurs is normally associated with later inappropriate repairs rather than naturally occurring salts or pollutants [15]. The most common weathering forms observed within the micro-structure of medieval mortars are micro-fracturing (32%), loss of binder:aggregate cohesion (27%), secondary porosity evidenced by pore-lining calcite (27%), and evidence of dissolution and recrystallisation elsewhere in the matrix (32%). Areas of 'original' binder not showing alteration are visible using optical microscopy, and reaffirm the importance of correctly interpreting the textural relationships within a historic mortar

3.5 Relative and absolute dating of historic mortars

Historic lime mortars can provide absolute and/or relative dating evidence for archaeological sites and historic buildings, and are useful in differentiating between different phases of a site which may have been occupied and altered over a long period of time. While it is not yet possible to 'date' medieval or early post-medieval mortars with fine precision, mortars are useful in identifying changes to a wall fabric, as different mortars can be distinguished (through aggregate type(s), mix, character & texture, durability, porosity, and number and type of intentional additions such pozzolana) from one another. This allows mortars to be used as a tool to understand how a masonry wall has been altered or repaired over time, and can thus assist in relative dating a structure or site. In addition, extraction of the charcoal commonly found in historic lime mortars, if uncontaminated and present

in sufficient amounts, is a useful and well-established part of modern archaeological practice, though only occasionally used to date buildings in Ireland [8, 16]. For example, Moygara Castle, Co. Sligo is a complex fortification consisting of an enclosing circuit of towers and defensive walls following the 'trace Italienne', a gatehouse and a rectangular structure with no datable architectural features, but appeared to be earlier that the main defensive circuit [17]. Radiocarbon dating of bedding mortars from the site [8] suggested this rectangular structure may be a 13th or 14th century hall-house or hall-keep. This new information significantly altered perceptions and understanding of the site, and is currently guiding discussions of how the castle should be conserved.

4 Discussion

A wide range of Irish medieval lime mortars survive, and there are many unanswered questions regarding the introduction, adoption, preparation, application and curing of these complex materials. The majority of published work on lime mortars tends to arise from materials research science and conservation work. In comparison, there is relatively little published work on the archaeological significance of historic lime mortars, kilns and lime-clamps etc. [18], and great potential for researchers to discover new perspectives with which to re-evaluate and study historic building materials. Examining the data from different perspectives allows historic lime mortars to become much more powerful contributors to the overall conservation and archaeological processes which determine the preservation of a site, rather than as simply source material from which to formulate a new repair solution.

While analysis and interpretation of historic materials is an engrossing study in its own regard, using the data to formulate repair solutions adds additional layers of complexity. Ensuring compatibility and safeguarding the original material are key issues. Many (but not all) medieval Irish lime mortars show several sources for hydraulicity, including combinations of intentional pozzolanic additives, the use of reactive aggregate, reactivity from the residues of burnt fossil fuel used for lime production, and mineral impurities naturally occurring in limestones. However, it may not be appropriate to exactly replicate the properties of the original material as changes to the formulation may have to be incorporated to safeguard original material, especially in proximity to carved stonework. In addition, the majority of medieval buildings in Ireland survive today as ruined structures and a 'fit-for-purpose' repair mortar must also meet certain aesthetic needs as a poorly-formulated new repair mortar, though materially compatible with the original mortar, can significantly detract from the character of the structure, which also forms an important part of its historic value.

Fig. 4 The Romanesque portal of Clonfert Cathedral, County Galway (AD 1161-1171) showing the original white pointing mortar [19] and the red-coloured lime-based repointing mortar.

5 Acknowledgements

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I.04

Ancient Mortars Under Action of Marine Environment: a Physico-Chemical Characterization

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Abstract Climatic and environmental conditions are often very severe for construction materials, namely in the presence of high humidity or in direct contact with water. However, some historical buildings currently are in very good condition due to careful construction and/or accurate materials selection and probably to a specific construction technology. This article presents the results of historical mortars characterization from two monuments: the Santa Marta Fortress in Cascais, near the Atlantic coast, and the Defence Wall of Lisbon town, in which lime mortars were used under severe environmental conditions. Historical buildings are important fingerprints of the history and culture of a region and its communities. The understanding of old mortar composition, based on integrated physico-chemical techniques, plays a fundamental role in the preservation of cultural heritage, allowing for information about the used materials, their performance in its environment, and the development of adequate and compatible materials for conservation.

1 Introduction

The effect of water on ancient mortars deserves special attention because the simultaneous action of physical and chemical deterioration processes can result in an accentuated degradation of renders in historical buildings. The study of mortars that have been submitted to the action of water for many centuries and survived is particularly important; such studies provide valuable data about the characteristics of durable ancient mortars and on the complex degradation processes involved. These studies hopefully will provide important information about materials and

their performance, contributing to the development of new solutions of conservation and repair of ancient renders.

Historical mortars are normally complex composite systems containing aerial lime binder and aggregates, from either natural or artificial sources, that interact over time to create neoformation compounds from new reactions in situ. In many situations those new compounds have contributed to the good state of conservation of the mortars [1]. The use of physico-chemical-microstructural characterization techniques, including optical and electronic microscopy, X-ray diffractometry, thermal analysis, and chemical analysis, allows the determination of mortar composition and an investigation of their high performance in a particular environment and use.

The main objective of this work is to present the results of the characterization of some historical mortars that have been exposed to severe environmental conditions, namely the presence of water, in order to understand the reasons for their performance in that environment.

2 Case studies

Santa Marta Fortress is an important building from historical and architectonic points of view, located on the Cascais coast, approximately 30km north of Lisbon. According to the military typology, the fortress was probably constructed in the XVII century within the program of construction of the defense line of the coast near Lisbon. According to historical reports [2] the footprint and the size of the fortress remained the same from 1786 until the end of the XIX century, when an interesting lighthouse was constructed in its interior that now marks the landscape of this place (Fig. 1a). In the end of the XX century the fortress underwent conservation and rehabilitation works in order to adapt it to cultural activities. During that occasion several mortar samples were collected from the south-west wall, the building facade more exposed to the salt spray, which appeared to be in a very good state of conservation.

The medieval defensive wall of Lisbon dates to Roman times and had probably several interventions until and after 1147, when troops of the first Portuguese king conquered Lisbon, ending the rule of the Moors. The mortar samples were collected from the Jesus arch (Fig. 1b), which corresponds to the old Furadouro door at the eastern end of the medieval defensive wall in the direction of Tejo River. This section probably had been subjected for many years to the action of the river water, which, due to the proximity of the sea, was possibly salty.

Fig. 1 (a) and Santa Marta Fortress and lighthouse (b) Details of Jesus Arch belonging to Defensive Wall of Lisbon

Table 1 Samples identification and macroscopic description

Samples	Origin		Macroscopic Description
SM1	Santa Marta Fortress	Interior wall of the south-west facade	Mortar render composed of three layers, with similar aspects and without signs of degradation. The aggregates exhibit different colours, sizes and morphological forms. The binder has a light colour, and the presence of well dispersed lime lumps is evident
SM2		Exterior wall of the south-west facade	Mortar render composed of two layers and, as SM1 mortar, containing different aggregates and a light colour binder. Seems to have a higher proportion of aggregate than SM1
M1	Medieval Defensive Wall of Lisbon (Jesus Arch)	Mortar from the basement infrastructure that supports the door	Mortar render composed of a single uniform layer with aggregates of different forms and colours. The binder is homogeneously distributed with aggregates.
M2		Mortar from the door-stone, in a zone that has undergone several repairs.	Light mortar colour, with high proportion of aggregates and with homogeneous aspect.

3 Experimental

3.1 Samples

The samples studied are identified and described in Table 1.

3.2 Characterization methodology

The physico-chemical characterization methodology used comprises a wide range of techniques that complement each other, including x-ray diffraction analysis (XRD), thermogravimetry and differential thermal analysis (TGA-DTA), optical microscopy and petrography, scanning electron microscopy and x-ray microanalysis (SEM-EDS), chemical analysis, and sand grain size analysis.

After collection, all samples were registered and observed in a stereo-zoom microscope and then dried at 40 ºC for at least 12 hours, with exception of the samples for chemical analysis, which were dried at 105 ºC. The mortar samples were carefully disaggregated to avoid breaking the existing aggregates and separated into several fractions to be analysed by the different analytical techniques.

The specific preparation for each analytical technique and the analysis conditions employed are presented in previous works [3-5].

4 Results and discussion

4.1 XRD analysis

The mineralogical compositions of the mortars obtained by XRD analysis are presented in Tables 2 and 3.

Table 2 Mineralogical composition of the mortars from the Santa Marta fortress. Notation: +++ abundant, ++ present, + small amount, T traces, ? doubts in presence, - undetected; OF – Overall fraction ; BR – Binder rich fraction

Crystalline phases	SM1						SM2			
	Interior layer		Middle layer		Exterior Layer		Middle layer		Exterior layer	
	OF	BR	OF	BR	OF	BR	OF	BR	OF	BR
Quartz	+++	+	+++	++	++/+++	+	+++	++	+++	++
Feldspars	+/++	+	+/++	+	+	+/T	+/++	+	+/++	+
Mica	+/T	T	T	?	T	-	T	T	T	T
Kaolinite	T	-	-	-	-	-	T	T	T	T
Calcite	++/+++	+++	+++	+++	+++	+++	++/+++	+++	++/+++	+++
Hematite	T/+	?	T/+	T/+	T	T	-	-	-	-
Magnesite	T	?	-	-	-	-	-	-	-	-
Ettringite	+	+	+	+	+	+	T	T	T	T
Halite	-	-	+	+	+	+	T/+	+	T/+	T/+
Calcium chloro aluminate	+	+	+	+	+	+	T	T	T	T
Vaterite	-	-	-	-	-	-	-	T	-	T
Aragonite	-	T	-	T		T		T		T

Table 3 Mineralogical composition of the mortars from the Medieval Defensive Wall of Lisbon. Notation: +++ abundant, ++ present, + small amount, T traces, ? doubts in presence, - undetected; OF – Overall fraction ; BR – Binder rich fraction

Crystalline phases	M1		M2	
	OF	BR	OF	BR
Quartz	++/+++	+++	+++	+++
Feldspars	++	++	++	++
Mica	T	T	+	+
Calcite	+++	+++	+++/++	+++/++

The XRD results show that the mortars from Santa Marta Fortress exhibit a larger diversity of minerals than the mortars from the medieval defensive wall, specificly in terms of neoformation/alteration compounds. This is consistent with the more aggressive environment where the fortress is located, which has contributed to the formation of calcium chloroaluminate and sulfoluminate compounds.

4.2 Thermal analysis

TG-DTA analysis (Fig. 2) confirms the XRD results, especially in the case of the SM2 mortar, which presented several weight losses in the decarbonation zone that can be attributed to the presence of different carbonate species. Apart from the carbonated lime, these could be due to the inclusion of calcitic aggregates and carbonated pozzolanic compounds formed by reaction between the aggregates and the calcitic binder [6, 7]. The TGA-DTA charts for all other mortars are typical of aerial calcitic lime mortars, showing an intense weight loss in the range 550-900º C that corresponds to the calcite decarbonation.

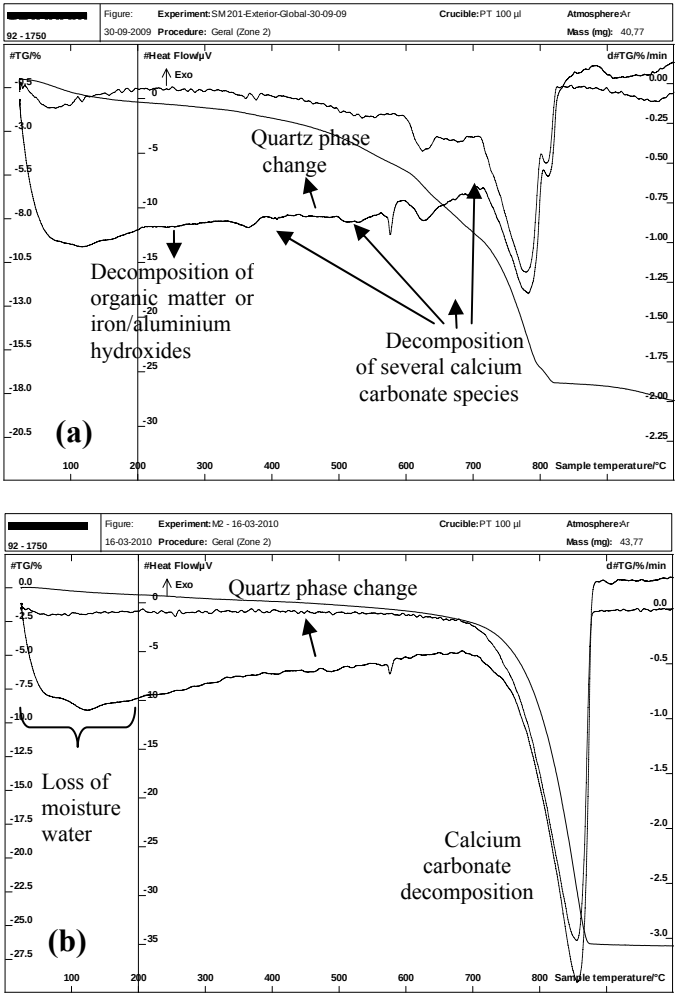

Fig. 2 TG-DTA for the samples SM2 (a) and M2 (b). (___%TG, - - -%DTG, ...Heat Flow)

4.3 Chemical and grain size analysis

Table 4 presents the chemical composition of the analysed mortars. The apparent diversity in soluble salt content correlates well with the mortars' actual environment and is consistent with the neoformation compounds detected by XRD in the SM2 mortar. Excluding the M2 sample, all mortars have a similar siliceous sand content. SM2 mortars have the highest content of chlorides and alkalis, as expected.

Table 4 Chemical composition of the mortars (wt %)

Sample	Insoluble Residue	Na_2O	K_2O	Cl^-	SO_3	Soluble Si
SM1-interior	55	0.08	0.02	0.04	0.22	0.65
SM1-middle	53	0.06	0.04	0.06	0.16	0.19
SM1-exterior	55	0.05	0.04	0.02	0.16	0.22
SM2-middle	53	0.25	0.16	0.99	0.22	0.19
SM2-exterior	55	0.35	1.13	1.02	0.17	0.19
M1	57	0.06	0.14	0.01	0.32	0.57
M2	37	0.04	0.04	< 0.01	0.30	0.37

The simplified compositions of the mortars (Table 5) were calculated using the 'Jedrzejewska' method for old lime mortars [8], combining the calcium carbonate % estimated by TGA/DTA with the insoluble residue obtained by chemical analysis.

Table 5 Simplified mortars compositions (wt %)

Sample	Siliceous aggregate[1]	Carbonates[2]	Soluble Fraction[3]
SM1-interior	55	39	**6**
SM1-middle	53	43	**4**
SM1-exterior	55	39	**6**
SM2-middle	53	33	**14**
SM2-exterior	55	35	**10**
M1	57	36	**7**
M2	37	57	**6**

1 – Silliceous Aggregate = insoluble residue content obtained by hydrochloric attack
2 - Carbonates_= $CaCO_3$ content determined by TGA
3 – Soluble fraction = 100 – Σ (siliceous aggregate + carbonates)

As seen in Table 5, the SM2 sample has the highest values of soluble fraction, which, besides some pozzolanic reaction compounds formed after the reaction between the lime binder and reactive constituents in the sand, can be attributed mainly to the action of the external environmental agents, particularly maritime salt spray.

The grain size distributions of the insoluble residues are presented in Figs. 3 and 4. This information is very important for the production of compatible mortars for restoration works [7]. The grain size distributions revealed that the different layers of mortars SM1 and SM2 have similar distributions and aggregates, mainly with diameters between 0.315 and 1.25mm. As expected, samples M1 and M2 have aggregate size distributions in different ranges, which correlate well with their simplified compositions (Table 5).

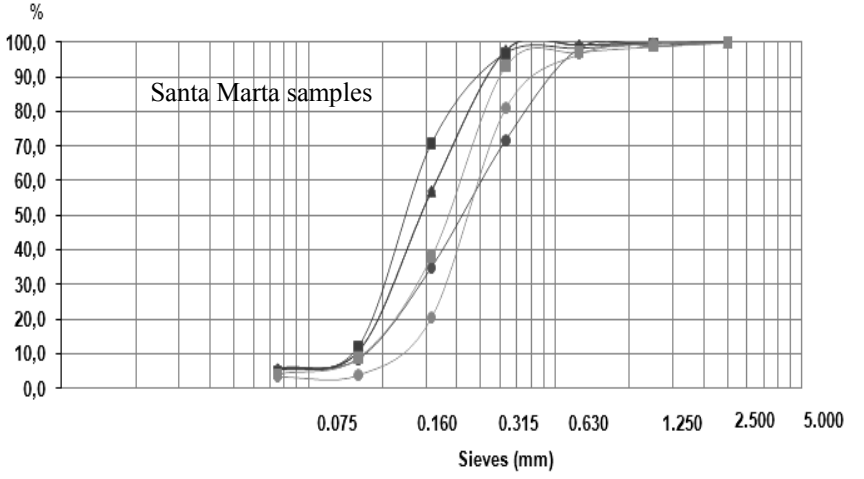

Fig. 3 Grain size distribution for the mortars from Santa Marta Fortress and Medieval Defensive Wall of Lisbon (SM1: ■ internal layer; ▲middle layer; ● external layer; SM2: ■ external layer; ● middle layer

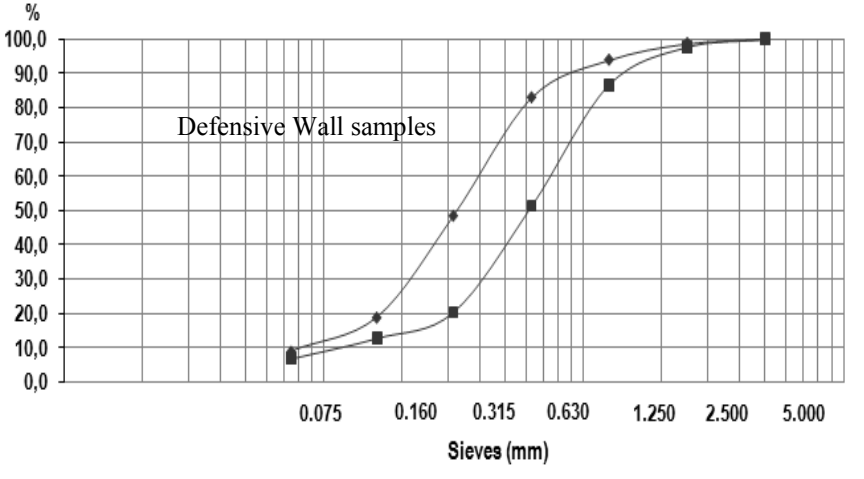

Fig. 4 M1 ■ and M2 ◆

4.4 Optical microscopy

4.4.1 Petrographic observation

The observation of mortar with a petrographic microscope allows the characterization of aggregate morphology and helped to identify some minerals that are not identified with XRD. Particularly important is the ability to distinguish carbonate aggregates from the generally calcitic binder (Figs. 5 and 6).

As visible in the Santa Marta Fortress thin-sections (Fig. 5), the aggregates present a sub-rolled morphology and are mainly composed of siliceous grains, shell, and fossil carbonate grains, suggesting a marine origin. The siliceous aggregates are predominantly monocrystalline quartz with some polycrystalline and alkali feldspars, altered volcanic rocks, and ceramics. The lime paste is well-carbonated with profuse microcracks connecting voids. Some reaction rims are evident around some aggregate grains, suggesting the occurrence of pozzolanic reactions between these aggregates and the calcite lime.

The samples from the Medieval Defensive Wall of Lisbon (Fig. 6) also contain aggregates of predominantly siliceous nature and voids with recrystallized carbonates. It is possible to observe some carbonatic particles, badly calcined lime lumps, and also some degraded metamorphic rocks.

The mortars from Santa Marta Fortress present irregular cavities of variable size and with occasional microcracks filled with precipitation products like ettringite and halite. These infilling products are probably related to the mortars' more severe exposure to salts from the surrounding maritime environment, which have reacted with the calcium and aluminium silicates formed during the reaction between lime and the altered minerals present in the aggregates. These features could be the reason for the mortars' good cohesion due to their capacity of infilling pores and the density increase of the material's structure.

4.4.2 Scanning electron microscopy analysis (SEM/EDS)

The SEM/EDS analyses show that all mortars have a compact calcitic matrix, typical of old lime mortars, with aggregates well-mixed with the binder (Figs. 6 to 9). The samples from Santa Marta Fortress (Figs, 6 and 7) contain formations of ettringite, either as needles occupying pores or in a massive form at the aggregate/binder interfaces. The carbonated lime binder is well-crystallized throughout the paste and is evident inside cracks or voids, corresponding either to secondary recrystallization phenomena or to neoformation products rich in calcium-aluminum silicates. Some formations of calcium phosphates are present in either a gel or botryoidal forms, mainly in the SM1 mortar. Ceramic powder also is visible in small quantities.

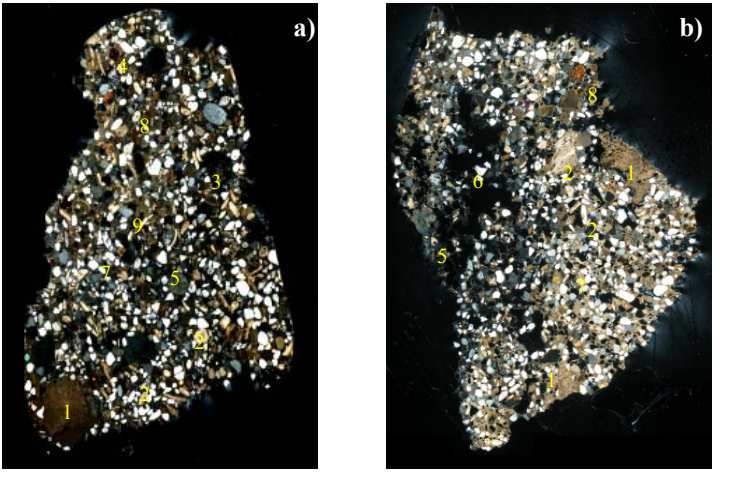

Fig. 5 Thin section observation in crossed polars of (a) SM1 and (b) SM2 mortars: (1) lime lump, (2) fossil or shell fragments, (3) void, (4) volcanic aggregate, (5) feldspar (6) Heterogeneous porosity, (7) Quartz, (8) Weathered aggregate, (9) Fragment of wood

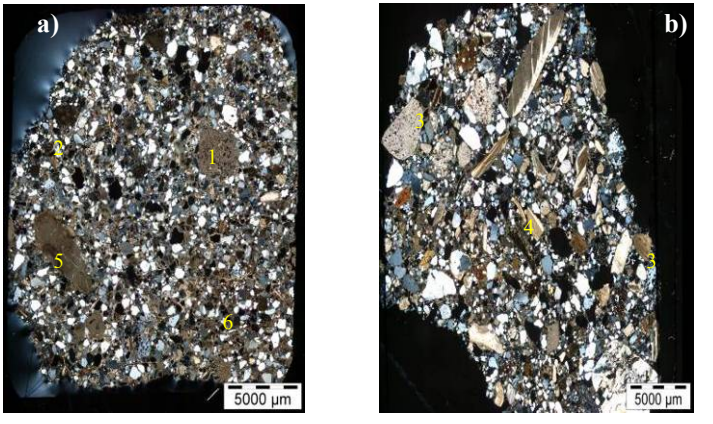

Fig. 6 Thin section observation in crossed polars of (a) M1 and (b) M2 mortars: (1) lime lump, (2) pore, (3) carbonate aggregate, (4) Fragment of wood, (5) basaltic rock, (6) quartz mono and polycrystalline

Halite crystals cover large zones of the paste, mainly in SM2 mortar. In the mortars from SM1 and SM2, the presence of the minerals mentioned above and their frequent occurrence in porous zones could explain the good cohesion and durability of these mortars in the aggressive environment where they are exposed.

The observation with SEM/EDS [9, 10] of the mortars from the M1 and M2 has revealed a much higher microporosity than in the mortars from Santa Marta Fortress, with some of this porosity also covered by secondary calcite recrystallisation. There also is some evidence of microbiological activity due to

the presence of calcium phosphates, which could have originated from the decomposition of muds from the soil.

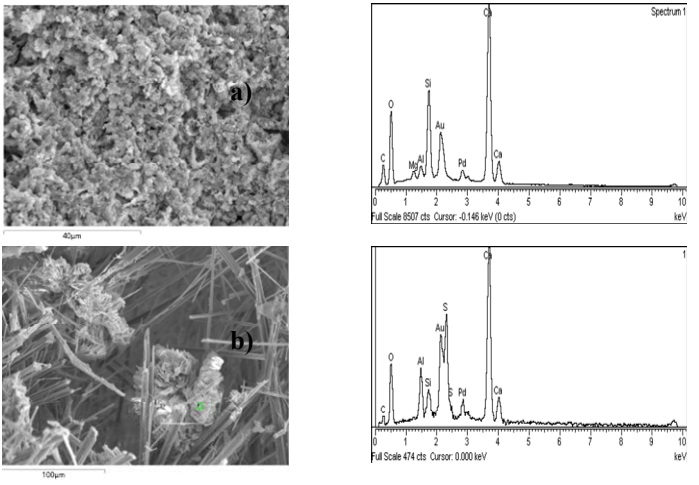

Fig. 7 SEM micrographs of (a) the paste of the SM2 mortar and the corresponding EDS spectrum, and of needles of ettringite (b) in a porous zone of the SM1 paste and the corresponding EDS spectrum.

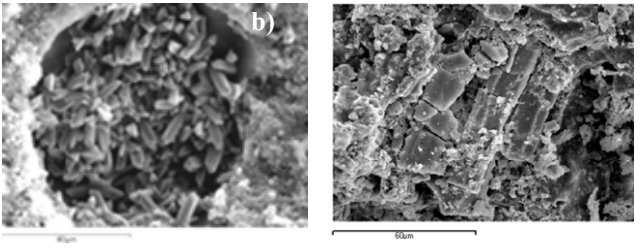

Fig. 8 SEM micrographs of the mortars from Medieval Defensive Wall in Lisbon showing a void (a) completely filled with calcium carbonate crystals and (b) calcium phosphate formation in the paste probably due decomposition of organic compounds.

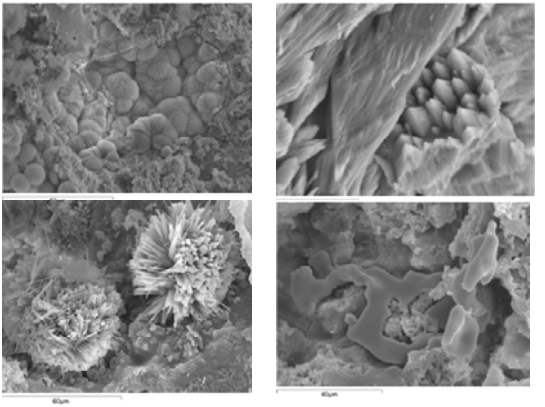

Fig. 9 SEM micrographs on the SM1 mortar showing (a) calcium phosphate with botryoidal form and recrystallized calcite (b) in a pore; c) SEM micrographs on the SM2 mortar showing calcium-aluminium silicates in a porous zone near a feldspar aggregate and (d) halite crystals covering the microporous binder

5 Conclusions

The mortars that have been exposed to a severe maritime environment with huge salt ingress retain a remarkable durability, which could be related to the salt's combination with the calcium-silicates and calcium-aluminum compounds formed in old mortars in the presence of water. The results illustrate the great importance of raw materials and the use of predominantly calcitic lime mortars. No hydraulic binders were found in these mortars, in particular no hydraulic lime or natural cement, confirming the idea that old Portuguese mortars were mainly based on air lime, both calcitic and dolomitic [5]. In some mortars we have detected the presence of ettringite, which seems to have been the product of a reaction between sulphates from the exterior and calcium-aluminates formed during the pozzolanic reactions of the sand and calcitic lime binder. Ettringite is generally expansive, but not in the present case studies. The expansive behavior of the ettringite formation seems to be *diluted* in the porous structure of the lime mortars, avoiding the usual destructive effect and, on the contrary, giving more resistance to this material. Some of the lime paste microporosity also has been covered by secondary calcite, which may have formed from the action of water through slow dissolution/re-precipitation processes. In these two case studies, the pores observed in all samples often were filled with neoformation products and were not connected in the majority of cases. In the authors' opinion, the salts retained from sea spray and salts formed in situ, in conjunction with the presence of water, have contributed to the durability of these lime mortars.

In the further development of this study, experiments will be carried out with lime mortars and aggregates similar to those found in the described case studies. These will be submitted to climatic cycles simulating reality in order to gather information for the development of mortars with satisfactory behavior for the conservation of structures exposed to the sea.

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I.05

Chemical, Mineralogical and Microstructural Characterization of Historical Mortars from the Roman *villa* of Pisões, Beja, Portugal

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Abstract In southern Portugal over one hundred Roman villae have been identified; such villae are examples of typical Roman rural construction and have led to the characterisation of a particular type of territorial occupation of Roman society. This paper presents the results of the physico-chemical characterization of the Roman mortars sourced from the archaeological site of the villa of Pisões (I-IV century A.D.), 6 km south of Beja (Alentejo), approximately 230 km southeast of Lisbon. Several samples were extracted from various locations within the villa, including the residential area, with its well preserved mosaics, and the thermal baths, which are indicative of the importance of this rural structure. Full chemical-mineralogical characterisation was carried out and the investigations led to the conclusion that the mortars were composed of aerial calcitic lime with quartz, schistose and granitoid aggregates (extracted from local quarries) and artificial pozzolanic materials (brick powder and fragments). The survival of these mortars, for more than eighteen centuries, is a testament to the careful selection of the materials that ensured their strength and durability.

1 Introduction

Discovered accidentally in 1967, the *villa* of Pisões, located 6 km south of Beja (Alentejo, Portugal) is a Roman construction of great historical interest

representative of the Roman geographical and agricultural exploration in the Iberian Peninsula.

In the Beja district there are in fact more than one hundred *villae*, which are not yet explored or studied. Such villae are divided into three parts, the owner's house (*pars urbana*), the agricultural sector with the workers' residences and the agricultural warehouse (*pars rustica* and *fructuaria*).

The *villa* of Pisões, built in the I-IV century AD, is only partially excavated and presents more than forty rooms and divisions, including a central portico with several interesting and well preserved mosaics. Near the main building is a thermal structure and a large swimming pool (40x8.5m). Close to the *villa* complex is a small dam and a mill, which were both fundamental for the agricultural production of this 200-400 hectare site [1].

Fig. 1 Photos of the *villa* complex: a) Small-scale model of the *villa*; b) detail of the thermal baths; c) view of the east part, with the external portico and mosaics.

2 Samples and characterization methodology

2.1 Samples

The eleven samples collected represent the diverse nature and appearance of the mortars found within the villa; details of these are shown in Table 1 and Fig. 2.

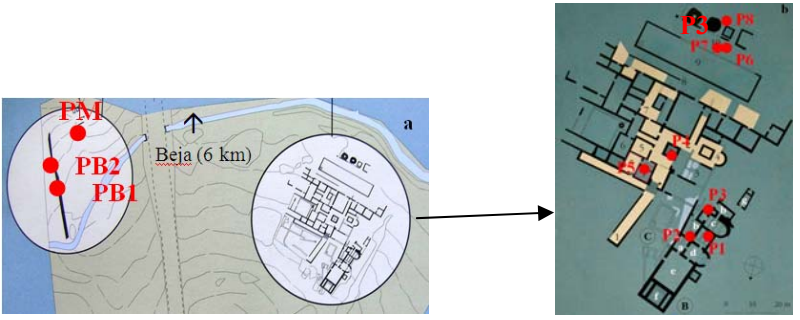

Fig. 2 a) Plan of the Pisões archeological site [1] showing the location of samples from the dam and the mill; b) Detail of the *pars urbana*, showing the location of the extracted samples.

Table 1 The identification and description of the samples and the sampling sites.

Sample identification	Location	General description
P1	Warm bath room (*Caldarium*)	Mortar of red colour, rich in brick and ceramic materials
P2	Furnace (*Praefurnium*)	Cream-colour mortar with green, red and black aggregates
P3	Clothing (*Apodyterium*)	Mortar of brownish colour with brick fragments
P4	Portico (*Peristilio*)	Mortar of brownish colour with brick fragments
P5	Rooms	Mortar of brownish colour with brick fragments
P6	Swimming pool (*Natatio*)	Cream-colour mortar with green, red and black aggregates
P7	Swimming pool (*Natatio*)	Mortar of light colour with grey and dark aggregates
P8	Mausoleum	Mortar of brownish colour with brick fragments
PM	Mill	Cream-colour mortar with brick fragments
PB1	Dam	Mortar of yellow colour with green and light aggregates
PB2	Dam	Mortar of light colour with green aggregates

2.2 Characterization methodology

A great number of physical and chemical techniques can be applied to the characterization of old mortars. The characterization methodology developed by the authors, presented in other studies [2, 3], comprised of a wide range of complimentary techniques, namely XRD, TGA-DTA, , SEM-EDS, optical microscopy, petrography, grain size analysis and chemical analysis.

XRD analysis was performed with a Philips PW3710 X-ray diffractometer with 35 kV and 45 mA, using Fe-filtered Co Kα radiation (λ=1.7903 Å). Diffractograms were recorded in the range 3-74 °2θ, at increments of 0.05 ° with a count time of 1 second for each step.

For thermal analysis a Setaram TGA-DTA analyser was used; samples were analysed in an argon atmosphere, with a uniform heating rate of 10° C/min, from room temperature to 1000 °C.

Thin sections and polished surfaces of the plasters were prepared by vacuum impregnation with an epoxy resin. These were observed with an Olympus SZH stereoscopical microscope and an Olympus PMG3 metallurgical microscope, while petrographical observations were performed on an Olympus BX60 polarized microscope.

For the chemical analysis, small portions of the plasters were carefully disaggregated and all types of impurities and limestone grains were separated. Samples were then attacked with warm diluted hydrochloric acid (1:3) to separate the siliceous aggregates from the binder. For the soluble fraction, chloride ions were determined by potentiometry and sulphate ions were determined by the infra-red analysis of the SO_2 content obtained after the calcination of the sample in a Leco CS244. The insoluble residue was weighed and sieved to determine the particle size distribution of the aggregate fraction i.e. the siliceous sand.

Scanning electron microscopy (SEM) was performed with a Jeol JSM-6400 SEM coupled with an Oxford energy dispersive spectrometer (EDS) x-ray detector.

3 Results and discussion

3.1 XRD analysis

The results show that all the *villa*'s mortars present a calcitic aerial lime binder.Table 2 presents the qualitative mineralogical compositions obtained through XRD analysis of the analysed mortars.

Table 2 Qualitative mineralogical composition of the mortars assessed by XRD.

Crystalline	Samples										
compounds	P1	P2	P3	P4	P5	P6	P7	P8	PM	PB1	PB2
Quartz	++	+/++	+/++	++	+/++	+	++	+++	+/++	+/++	+/++
Feldspars	++/ +++	+/++	T	+/++	T	+/++	+/++	+	++/ +++	+/++	+/++
Mica	T/+	-	T/+	T	T/+	T	-	+	-	?/ T	-

Kaolinite	-	T/+	T	-	T	T	-	+	T /+	T	T
Chlorite	-	+	T	T	T	T	-	T	+	+	T /+
Pyroxenes	-	T	?	T	?	T	-	T	T	T	T
Amphiboles	+	?/T	?/T	T/+	?/ T	T	+	-	+	T	T
Calcite	T	+++	++/ +++	++/ +++	++/ +++	++/ +++	++/ +++	++/ +++	++/ +++	++/ +++	++/ +++
Aragonite	-	-	?	-	?	T	-	-	-	T	T
Hematite	+	T	T	T	T	T	T	T	T	-	-
Halite	-	-	-	-	-	-	-	-	T	-	-
CCH	-	-	-	-	-	-	T	-	-	-	-

+++ abundant, ++ present, + small amount, T traces, ? doubts in presence, - undetected, CCH – Calcium carbo-aluminate hydrate

The main differences between the mortars occur within the binder content and the agregate type. The aggregates, which are of a siliceous composition, contain quartz, alkali feldspars, amphiloboles and phyllosilicates.

Samples P3, P5, PB1 and PB2 show similar mineralogical compositions, while samples P6, P8, PB1 and PB2 contain aragonite, which can be biological in origin. Sample P7 contains hydrated calcium carboaluminates, most likely formed from the reaction of the calcitic lime with some pozolanic compounds (of ceramic origin) in a humid environment or in the presence of water.

3.2 Thermal analysis

The thermograms obtained are typical of calcitic aerial lime mortars (Fig. 3). An important weight loss occurs between 550 and 900º C, corresponding to the de-carbonation of calcium carbonate. Moreover, a weight loss between 200 and 600º C is evident, which may be related to the quantity of clay minerals present [4] and to the neo-formation products, induced by pozzolanic reactions between some of the aggregate minerals and the calcitic lime binder.

The results obtained (table 3) show that mortar P1 has a low binder content, since it is mainly composed of brick powder and ceramic fragments; mortars P3, P6, P8 and PM all have a similar lime content, while mortars P2, P7, PB1 and PB2 are the samples with the greatest binder content (above 40%).

Table 3 Weight losses by TGA and the obtained calcite content (wt in %).

Samples	Temperature ranges (ºC)				Loss of ignition	$CaCO_3$ (1) content
	25→200	200→600	600→900	900→1000		
P1	0.18	0.33	0.17	0.02	0.70	2
P2	2.43	3.66	20.14	0.12	26.35	46
P3	2.65	3.40	12.79	0.07	18.91	29

P4	3.67	3.52	11.39	0.10	18.68	26
P5	1.88	2.88	11.28	0.06	16.10	26
P6	4.21	3.65	11.68	0.15	19.69	27
P7	3.97	3.18	16.54	0.10	23.79	38
P8	3.14	3.92	9.42	0.11	16.59	21
PM	1.38	2.28	10.26	0.07	13.99	23
PB1	3.14	3.67	14.74	0.18	24.87	34
PB2	2.84	4.35	18.63	0.08	25.90	42

(1) $\%CaCO_3 = (P_{CO2} \times MM_{CaCO3})/MM_{CO2}$
P_{CO2} – Content of CO_2 (mass %) = Mass loss in the range 600 →900º C
MM_{CaCO3} – Molar Mass of $CaCO_3$
MM_{CO2} –Molar Mass of CO_2

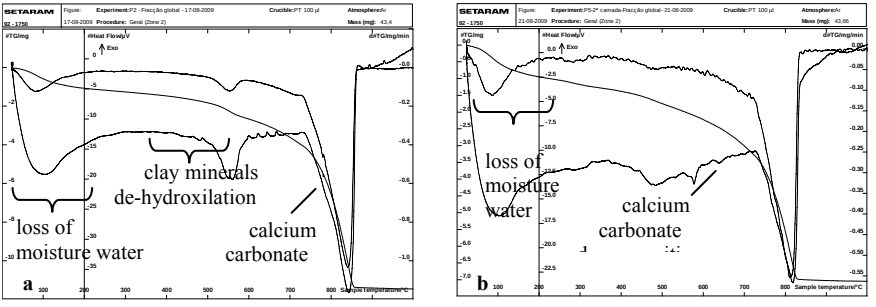

Fig. 3 TGA/DTA curves of mortars a) P2 and b) P5.

3.3 Chemical and grain size analysis

Table 4 shows the results of the analysis of the soluble fraction in nitric acid, which can provide valuable information about the composition of the mortars and its environment. Samples P2, P3, P4 and P8 were selected since they are, according to XRD results, representative of the different mortar samples under study.

Table 4 Insoluble residue, sulphate and chloride contents (wt %) of the analysed mortars

Mortar Identification	Insoluble residue	Sulphates (SO_3)	Chlorides (Cl^-)
P2	43	0.14	< 0.01
P3	61	0.13	< 0.01
P4	57	0.15	0.01
P8	63	0.18	0.02

The data obtained confirms the XRD analysis and highlights the absence of alteration compounds, which have led to the good state of conservation and high mechanical resistance of these mortars.

The grain size distribution of the aggregates (Fig. 4) reveal that samples P2, P3 and P8 are similar, with well sorted aggregates over 1 mm (till 65%); P4 has a distribution quite similar to those but with a larger grain size.

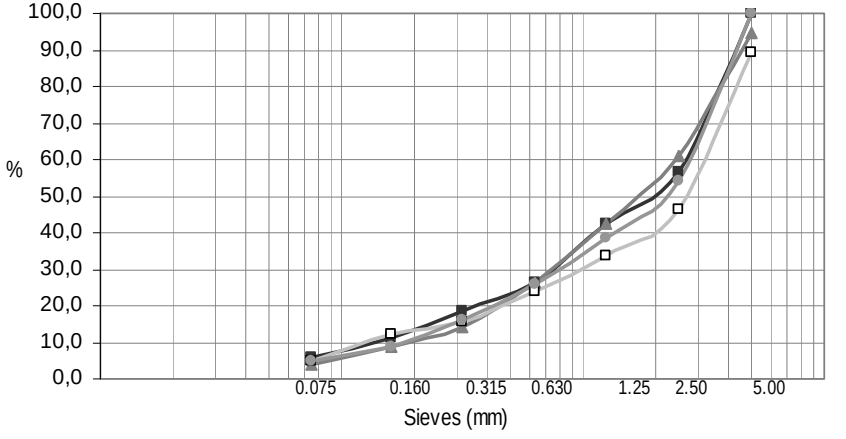

Fig. 4 Grain-size distribution of the aggregates from mortar samples P2 (■), P3 (▲), P4 (□) and P8 (●).

The simplified compositions of the mortars (Table 5) were calculated on the basis of the method designated as 'Jedrzejewska' [5] referring to old lime mortars, where the calcium carbonate percentage, estimated by TGA/DTA, is combined with the insoluble residue amount obtained through chemical analysis.

Table 5 Simplified mortar compositions (wt %).

Mortars identification	Siliceous aggregate (1)	Carbonates (2)	Soluble Fraction (3)
P2	43	46	11
P3	61	29	10
P4	61	29	10
P8	63	21	16

1 – Siliceous aggregate = insoluble residue content obtained by hydrochloric attack;
2 - Carbonates_= $CaCO_3$ content determined by TGA;
3 – Soluble fraction = 100 – Σ (siliceous aggregate + carbonates).

3.4 Optical microscopy

Stereozoom observations

Polished sections observed under a stereozoom microscope showed that the mortars are all very heterogeneous, with aggregates of different colours, mineralogical nature and grain size.

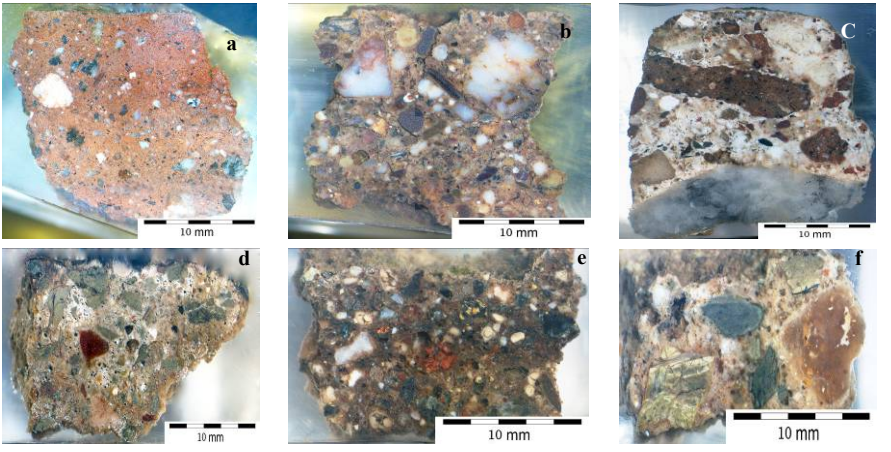

Fig. 5 Observation of polished sections under a stereozoom microscope,samples a) P1, b) P3, c) P7, d) P2, e) PM and f) PB1.

Mortar P1 contains aggregates of a dark, intrusive igneous rock type with siliceous minerals well dispersed in a binder matrix besides large white lime lumps, ceramic fragments and powder. These ceramic materials are typical in Roman mortars, and are normally introduced to increase the impermeability and hydraulicity of the renders.

Mortar P2, like PB1 and PB2, contains an aggregate which is dark in colour and is seen to contain green schist and siliceous material. Samples P3 andP5, are clay rich with siliceous and dark aggregates. Mortar P4, like sample P7, presents a remarkable quantity of ceramic and brick fragments as well as dark, siliceous aggregates.

Finally sample P8, like sample PM, shows a yellowish-brown clay and heterogeneous aspect, with a large variety of aggregates which vary greatly in colour and mineralogy.

Petrographic observations

Petrographic microscopy was employed to confirm the aggregate types used and to recognize neo-formation products within the samples.

All mortars present siliceous minerals and rocks, namely quartz, quartzite, pyroxenes (P1, P2, PB1) and amphibolites (P1, P3, P6, PB1). However, some mortars also present phyllosilicate minerals, like chlorite (Fig. 6c) and mica (P2, P3, PB1), as well as brick/ceramic fragments (P1, P3, P6, P8, PB1). Some of the mortars are characterized by the presence of granitoid (P1, P6) and schistose rocks (P3, P6, P8, PB1) (Fig. 6b) [6, 7].

Observation of the mortars with ceramic materials reveals the occurrence of rims around the brick fragments (Fig. 6d), which result from pozzolanic reactions with the calcitic binder.

The observation of mortars P3 and PB1, which have the highest calcitic binder content of the samples analysed, revealed large calcitic lime lumps and the presence of non-calcined carbonate rock fragments. The high calcite content of these mortars may explain the high quantity of microcracks and the high microporosity which is responsible for the low mechanical resistance of these mortars.

In samples P1, P2 and P6, the presence of altered iron-magnesian minerals in volcanic and plutonic igneous rocks were noted; such minerals are easily alterable in a basic lime environment (Fig. 6e). These samples also showed the lowest paste porosity which, associated with the pozzolanic products formed, could explain the high resistance of these mortars.

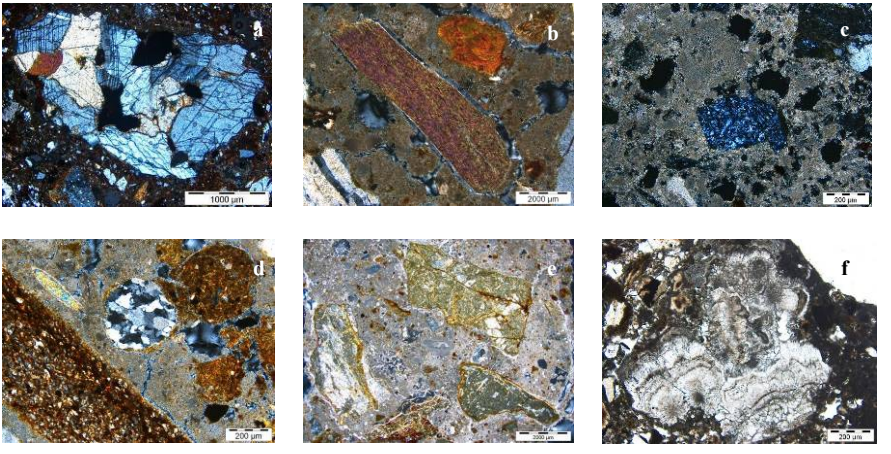

Fig. 6 The main petrographic features of the mortars: a) a granitoid aggregate in mortar P1, b) schist aggregate in mortar P3; c) chlorite in mortar P2; d) brick and ceramic fragments in mortar P3; e) igneous rocks strongly altered in mortar P6; f) carbonate crystals with drusiform texture in mortar PB1.

Scanning electron microscopy (SEM/EDS)

The SEM/EDS analysis confirmed the results of the petrographic and XRD analysis, by showing that the presence of brick and ceramic fragments (in P1, P4 and P7), related to the functionality of the mortar since they were applied within the areas of the thermal baths and the swimming pool. These pozzolanic materials have contributed, together with some of the altered aggregates, to the formation of calcium-aluminosilicate hydrates (Fig. 7a), a pozzolanic reaction product responsible for the improved hydraulic properties and for the impermeability of the mortar. Biological colonization is also evident in some of the samples.

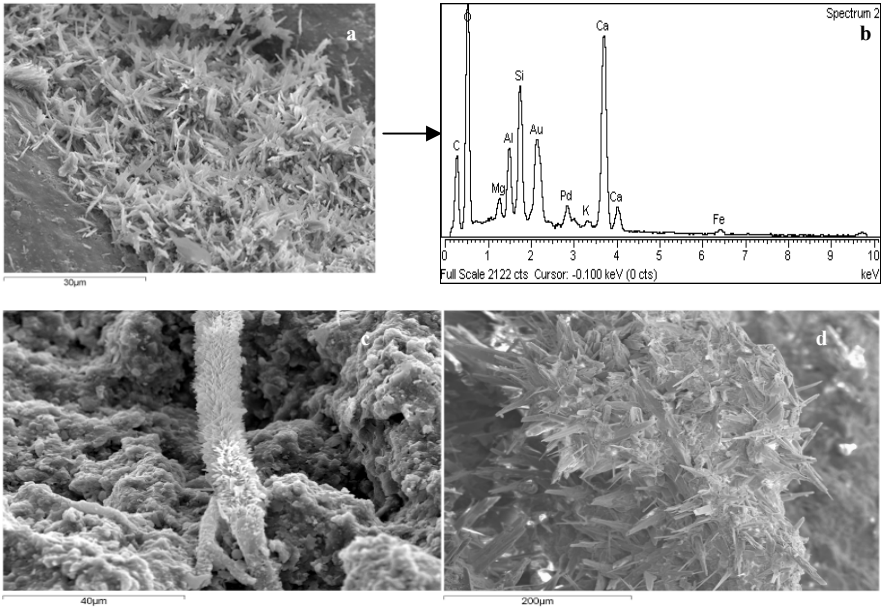

Fig. 7 a) Calcium-aluminosilicates (CAS) formed in an aggregate interface in mortar P3; b) EDS spectra corresponding to CAS products; c) biological colonization in mortar P3; d) carbonate crystals in mortar PB1.

4 Conclusions

The results showed that all mortars present a calcitic aerial lime binder. Mortar P1 is poor in lime but rich in ceramic fragments and clay minerals, with small quantities of granitoid and quartzitic rocks.

Mortar P2, like PB1 and PB2, contains ceramic/brick fragments as well as siliceous rocks as aggregates, and has a binder/aggregate ratio of approximately 1:1 by mass.

Mortars P3, P5 and P8 represent a typical binder/aggregate ratio of 1:3 by mass and are characterized by the presence of large white lime lumps, which indicate the poor mixing of the lime binder or the use of the hot lime mixing method [8-10], which could explain their mechanical behaviour [11]. In these mortars the aggregates are mainly of a siliceous and schistose nature.

Mortar P4 presents a binder/aggregate ratio of 1:3 by mass, and is characterized by a high content of pozzolanic materials, including ceramic and brick fragments, which have induced the formation of calcium alumino-silicates that have led to an improved mechanical strength and a high resistance to deterioration.

Mortars P6 and P7 are both from the swimming pool and, with the exception of siliceous and brick aggregates, are quite different; the mortar P6, recovered in a

external wall, contains schists and large lime lumps, while the mortar P7, recovered from an internal wall, contains fragments of granites and a better aggregate/binder ratio which has resulted in a higher resistance to deterioration.

Mortars P8 and PM both have a binder/aggregate ratio of 1:4 by mass and contain ceramic, siliceous and schistose rock fragments.

The presence of amphibolites, igneous rocks and schist has helped us in the identification of the presumable origin of the aggregates which, according to the geology of the neighbouring Alentejo Region [12, 13], is derived from a local source.

All mortars are characterized by brick fragments (*cocciopesto*) and pozzolanic neoformation products which were responsible for the mechanical properties of the renders and their resistance to chemical detachment or alteration. All the mortars display low contamination by soluble salts such as chlorides and sulphates, which can further explain their good conservation state. This once again, underlines the deep knowledge of a mortar's properties possessed and implemented by the Romans across the Empire.

5 Aknowledgements

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I.06

Petrographical Study of Meroitic Mortars from an Amun Temple (el-Hassa)

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Abstract Mortar samples from various archaeological Meroitic sites located along the Nile (currently Sudan), and dating from the first century AD, have been previously analyzed with X-ray diffraction, X-ray fluorescence and mercury intrusion porosimetry. This work aims to show that the petrographical study of the samples complements these analyses. The petrographical study, carried out for the first time on two facing mortar samples from the Amun temple of el-Hassa enables the structure, the porosity and the mineralogical nature of paste and sand to be characterized separately. The application of a new interpretation methodology based on the crossing of the data obtained by all analytical techniques indicates that the paste was probably made of a mixture of both lime and a material comprising gypsum and limestone grains.

1 Introduction

Identifying the initial structure and composition of Meroitic mortars is difficult, because some current features correspond to the original mortar, while others result from ageing processes that have altered the materials for two thousand years. Therefore, their study often requires the use of multiple analytical techniques and the resulting data must be cross referenced. Moreover, mortars are composed of a paste and of sand, which must be characterized separately while maintaining an overview of the heterogeneous structure of the material. The petrographical study by the observation of thin sections under a polarized optical microscope provides information at an ideal intermediate scale. Such a method had never been applied to Meroitic mortars previously and would complement efficiently the earlier studies [1, 5, 6].

The facing mortar samples considered in this work were collected from the Amun temple (first century AD) of the archaeological Meroitic site of el-Hassa (20 km south of Meroe, between the 6th and the 5th cataract). These samples were

buried a few decimeters deep in a silty soil and exposed to the aggressive climate of the region (average temperatures from 23 to 35°C; 10 months of dryness and 2 months of rainy season) for about two thousand years. Both samples were found near a pylon made of fired brick at the entrance to the temple (Fig. 1). They were recovered with yellow ocher pigment. The first sample (EH01) is a loose piece of a painted wall. The second sample (EH02) is a fragment of a painted low relief which depicts the king.

Fig. 1 Amun temple of el-Hassa, excavated by the French Section of the Sudanese Corporation for Antiquities and Museums since 2000 (source: www.sfdas.com)

2 Observation technique

Mortar samples were first impregnated with an epoxy resin. After hardening, they were cut in half and the sawed surface of each sample was impregnated again. Then, sawed surfaces were ground and glued onto a glass slide, and the excess of each sample was ground down to leave a thin layer of mortar that was abraded down to a thickness of 20 to 25 µm. The petrographical study of these thin sections was carried out on an optical microscope equipped with a rotary turntable. The magnification ranged between 4X and 40X. The observation was performed in transmission under either plane polarized light (PPL) or under cross-polarized light (XPL).

The observation of the samples under the microscope makes possible the identification of the mineralogical nature of sand grains and the measurement of their size and shape. It also gives information about the paste, including composition, crystalline phases, and porosity. It is also possible to evaluate the relative amount of sand and paste [4].

3 Observations

Petrographical observations were carried out on samples EH01 and EH02 (Fig. 2). Each sample has a multilayer structure, typical for a wall painting that consists of two separate mortar layers covered with yellow ocher paint. The study of the pigmented layer will not be covered in this paper.

- The internal mortar layer (Fig. 2,B) was originally applied to level and protect the wall. It is a coarse-grained layer of grey-brown colour, a few centimeters thick, and it includes a large amount of sand grains with a wide size distribution (see Tab.1).
- The external mortar layer (Fig. 2,A) assured the smoothing of the surface on which the paint was applied. This 2 to 3 mm thick layer has a very light colour, and its sand grains are quite fine (see Table 1).

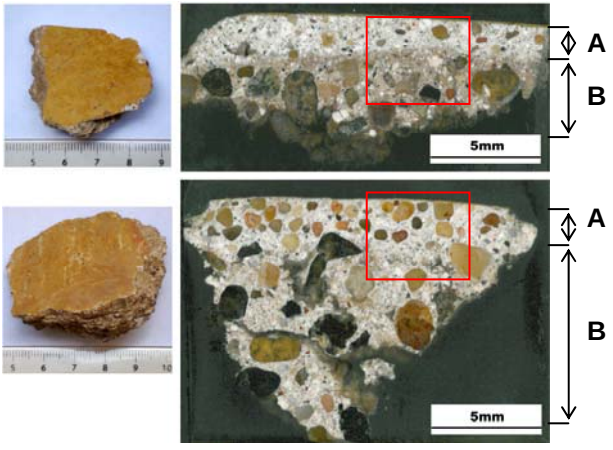

Fig. 2 The samples and their cross sections – **top**: EH01; **bottom**: EH02 (A: external layer; B: internal layer; red rectangles indicate the location of the snapshots of Fig.3a-b)

Petrographical observations reveal that the two mortar layers do not have the same microstructure. The data extracted from the petrographical observations of the external layers of EH01 and EH02 are summarized in Table 1. These two samples are quite similar. Therefore, when not otherwise specified, the data and the remarks presented in this paper apply to both. Visual charts based on 2D representations of the microscope field give an estimate of the volume composition of each layer (see Table 1), assuming that the observed material is homogeneous and isotropic.

Table 1 Data extracted from petrographical observation of the mortar samples.

Mortar layer			External layer (A)			Internal layer (B)		
Thickness			2-3mm			a few cm (>2cm)		
Volume composition (visual charts)			paste 30%	sand 40%	porosity 30%	paste 30%	sand 50%	porosity 20%
Paste	Nature		calcium carbonate (calcite); some underburnt limestone fragments					
	Density		low			high		
Porosity			air-induced voids with smoothed outlines; cracks due to the shrinkage					
Sand grains	Shape		rounded					
	Size	<1mm	quartz and mica grains (Fig. 3d)			quartz grains; iron oxides (Fig. 3c); other grains in minority		
		2-4mm	-			quartz grains; cryptocristalline calcareous grains (Fig.3f), sometimes with small quartz inclusions and/or brown organic deposits on the surface; iron oxides		

- *Observation of the paste* (see Table 1): The paste of the internal layer is dark-coloured and is neither transparent under PPL nor under XPL (Fig. 3a-b-c). This feature is due to the very small size of calcite crystals (mineralogy corroborated by XRD), which do not exceed a micrometer. The high density of the calcitic paste suggests that the craftsmen had not used much water to prepare the mortar. In sample EH02, the paste of the external layer is similar to that of the internal layer (Fig. 3b). By contrast, it is lighter-coloured and less dense in sample EH01 (Table 1, Fig. 3a-d) and therefore almost transparent under PPL. The lower density of the external layer indicates the craftsmen probably added additional mixing water to make smoothing the surface easier. The difference in density between the two layers is more significant for sample EH01, which comes from a wall painting, the surface of which needed to be flat. Under XPL, brown cracked limestone fragments are visible in both layers, particularly the internal layer (Fig. 3e). The observed cracking results from the incomplete burning of the lime, so these grains correspond undoubtedly to underburnt limestone fragments.

- *Observation of the porosity* (see Table 1): The voids with smoothed outlines certainly have several origins. Some of them are typical of porosity due to the consistency of the paste, while others are caused by the excess of mixing water or by dissolving phenomena (Fig.3c-d). The cracks with angular outlines are probably due either to the shrinkage of the paste because of rapid drying or to mechanical constraints that can appear during ageing processes [4].

- *Observation of the sand grains* (see Table 1): The sand grains of the mortar samples have a rounded shape, so we can expect that they have been carried by the Nile over long distances. In the internal layer, the grain size distribution ranges up to 1mm for both samples, but the average size is higher for EH02. In

the internal layer of both samples, the sand grains have a bimodal size distribution (Fig. 3a-b). Perhaps the craftsmen blended two different types of sands. Moreover, the sands in the external and in the internal mortar layers do not have the same mineralogical composition. They do not seem to be of the same origin. Iron oxides and organic residues in the internal layer could explain its colour.

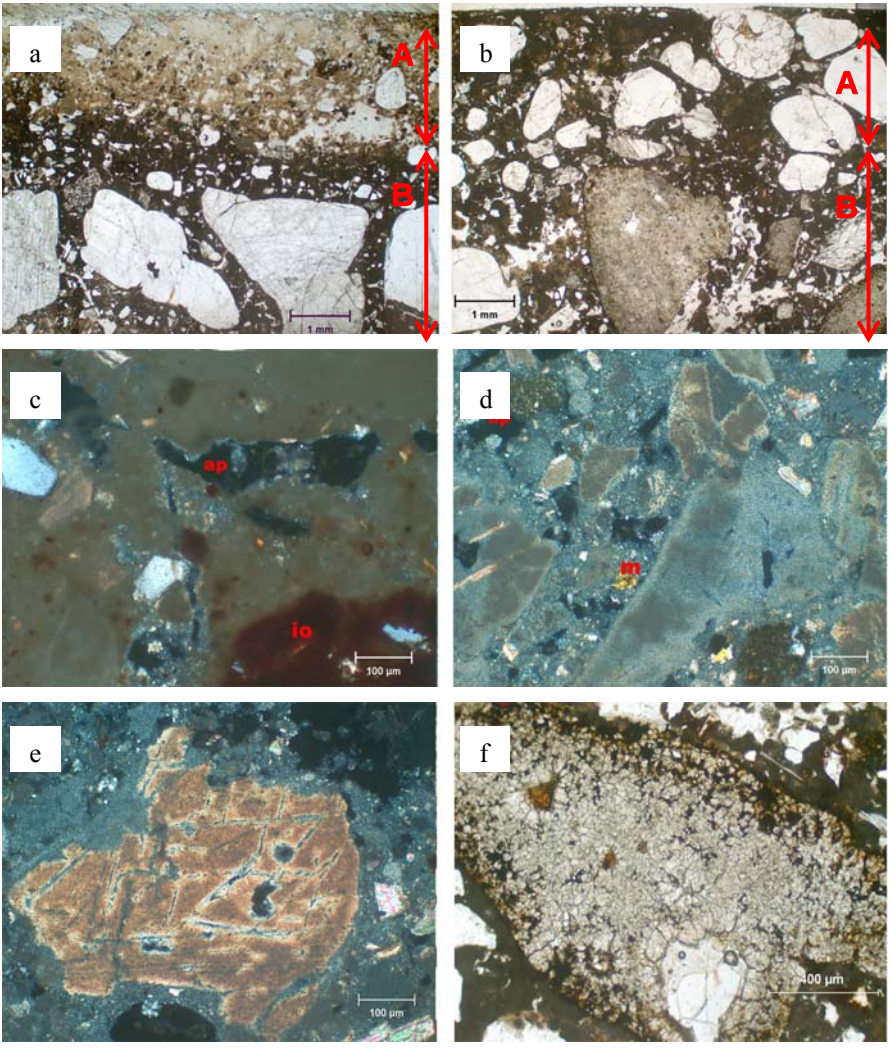

Fig. 3 a-b: Samples EH01 (a) and EH02 (b) under PPL: *the external layers (A) and the internal layers (B) appear clearly for EH01 and can be discerned thanks to the size of the grains for EH02)*. c-d: Internal mortar layer (c) and external mortar layer (d) of EH01 under XPL *(ap: porosity, io: zone containing iron oxides, m: mica grain)*. e: Underburnt limestone grain in the external mortar layer of EH01, XPL. f: Cryptocristalline limestone grain in the internal mortar layer of EH02, XPL.

4 Interpretations

4.1 General interpretation methodology

The petrographical observations are intended to complement the analyses of various Meroitic mortar samples from the Amun temple of el-Hassa as well as Sudanese raw material samples. These analyses have been performed using X-ray diffraction (XRD), X-ray fluorescence (XRF) and mercury intrusion porosimetry, and the results have been presented in other complementary papers for HMC08 [5] and HMC10 [1]. According to these results, the paste of all Meroitic mortar samples from el-Hassa is today made of calcite, and its porosity is about 20 to 30% [1, 5, 6]. However, the facing mortar samples (like EH01 and EH02) are quite different from a sample of setting mortar. The latter presents a low porosity (about 4% in volume) and contains only 0.07% SrO, whereas the content of our facing mortars reaches 0.12 to 0.15% SrO.

If we assume that the setting mortar has been made with lime and sand comparable to those of our facing mortars, the significant SrO content in the facing mortar certainly must come neither from the sand grains nor from the calcium carbonates. Comparing the SrO content and the porosity of our samples with those of the setting mortar sample, we can surmise that the paste of the facing mortars originally could have contained an additional material. Given that the climate in the region of el-Hassa has remained nearly constant since Antiquity, the mortars have been subjected to seasonal hygrometric variations that have amplified dissolution and leaching phenomena for about two thousand years. Therefore, the total disappearance of one component of the paste seems possible. *A priori*, several hypotheses could have been considered concerning the initial composition of the paste (see Table 2).

Table 2 Composition hypotheses for the paste of Meroitic facing mortars from el-Hassa.

Origin of the calcium carbonates of the paste		**Other components of the paste**	
Hypothesis 1	Lime	**1a**	Gypsum plaster [1, 5, 6]
		1b	Clay impurities [1]
		1c	Organic materials (egg white, blood, resin…)
Hypothesis 2	Lime	**2a**	Gypsum plaster [1, 5, 6]
	+ unburnt powdered	**2b**	Clay impurities [1]
	limestone	**2c**	Organic materials (egg white, blood, resin…)
Hypothesis 3	Unburnt powdered	**3a**	Gypsum plaster [1, 5, 6]
	limestone	**3b**	Clay impurities [1]
		3c	Organic materials (egg white, blood, resin…)

However, by crossing petrographical observations with the data obtained by XRF, XRD and mercury intrusion porosimetry, it has been possible to eliminate many of these hypotheses and to determine which is most likely to describe the initial composition of the paste.

4.2 Application of the methodology to EH01 and EH02

The samples EH01 and EH02 are composed of siliceous silty sand and calcium carbonate. They also present a relatively highly porous paste. Because ageing processes could have altered the initial materials [5, 6], the current composition is likely quite different than the original.

Considering the presence of underburnt limestone fragments in samples EH01 and EH02, the calcium carbonate could not come only from unburnt powdered limestone, so the paste must have contained lime. Hypothesis 3 can be rejected.

Hypotheses 1c and 2c seem unlikely but can not be rejected. However, the presence of deteriorated organic materials, such as proteins, is very difficult to identify.

Hypotheses 1b and 2b are impossible for several reasons. Firstly, no trace of remaining clay was detected in the paste of our samples, whereas clays are very resistant to ageing processes. Secondly, a paste made in part of clay would certainly be coloured by impurities like iron oxides and therefore would be darker than the paste of our samples. Finally, some Meroitic mortars of the same period, the paste of which contains clays, have been analyzed by XRF (results presented in a complementary paper for HMC10 [1]) and do not contain significant SrO contents.

At this stage of the study, hypotheses 1a and 2a are most probable. The mixing of lime and gypsum plaster could explain both the high porosity of the paste and the significant SrO content in our facing mortar samples relative to the setting mortar sample from el-Hassa. According to the previous study presented for HMC08 [5], XRF analyses show that samples with a relatively high SrO content also present a slightly higher SO_3 content than that in other samples. Strontium sulphate could have been associated with the gypsum of the paste and would have been left behind as the gypsum gradually leached out with time. The presence of strontium in the samples could be explained by the very low solubility of strontium sulphate in comparison to gypsum [5, 6]. Unfortunately, $SrSO_4$ content lower than 1% is below the detection limits for XRD.

The following comparison between hypotheses 1a and 2a is based on our first analyses of Sudanese raw materials [1, 2]. Hypothesis 1a suggests that the Meroits had access to a source of gypsum, the SrO content of which is compatible with XRF measures on facing mortar samples from el-Hassa like EH01 and EH02 [5, 6]. The nearest source of pure gypsum was along the side of the Red Sea. The SrO content of this gypsum reaches 0.9%. However, the use of this gypsum supposes that the Meroits had transported it through the desert, which would have been

quite difficult. We found no other available source of gypsum, but we have started analyzing a material from Omdurman, near Khartoum, which is apparently a mixture of gypsum and limestone [2]. This material contains about 0.2% SrO, which is an acceptable rate, and it easily could have been transported on the Nile. We could imagine that the craftsmen heated it, obtained hemi-hydrated gypsum blended with limestone grains, and then used it to make a lime-and-gypsum paste. At this stage, hypothesis 2a seems to be the most plausible.

5 Conclusion

The petrographical study, applied to Meroitic mortar samples for the first time, complements the data obtained by global analyses in previous studies. In particular, it enables the mineralogical composition and the structures of the internal and external layers to be characterized separately. Petrographical observations show that the paste derived from a lime-based binder and that the Meroits used different types of sands for the internal and external mortar layers. We considered several hypotheses concerning the initial composition of the paste. By crossing the results obtained by overall analytical techniques and the petrographical observations, we gathered clues that enable us to determine the plausibility of each hypothesis. The hypothesis of a paste derived from a binder made of a mixture of lime and a material comprising gypsum plaster and limestone grains is quite credible, though it cannot be fully proved at this point. Other analyses of new Meroitic mortar samples and of Sudanese raw materials are planned to help progress in this study.

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I.07

Famous Men Busts Decorating a Parisian Façade: Characterization and Decay Process of a Cast Artificial Stone from the XIXth Century

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Abstract After cleaning, four 19th century cast busts of illustrious men decorating a Parisian façade revealed severe deterioration. A network of large cracks 0.5 cm wide gave the appearance of a broken up puzzle, although each individual piece maintained good general cohesion. In order to determine the cause of the intense decay and to propose an adequate conservation protocol, the composition of this artificial stone was thoroughly investigated. Sample analyses showed that the material was composed mainly of crushed and probably sieved limestone aggregate bonded with hydrocerussite and an amorphous silica gel containing a small amount of potassium. The binder surrounded and linked calcite aggregates together. Analytical results were consistent with artificial stone recipes from the 19th century. In this paper, we report the results of analyses performed on those strange objects. We also will discuss two hypotheses of composition based on potassium silicate and propose an explanation for the peculiar degradation patterns.

1 Introduction

During the first decade of the 19th century, precisely between 1825 and 1828, *René Bony*, a rich speculator, commissioned *Jules de Joly* to build a pair of stone buildings in Paris: the *Hôtel Boni* in the 9th district, and a commercial building, *4, rue d'Aboukir*, in the 2nd district. Each shows a similar decoration, including busts of famous men placed on the upper floor, as an attic level, and statues on the noble floor just below. The statues have disappeared from the lower façade of the *Aboukir*, though they are still in place at the *Hôtel Boni*. The four busts placed on the *Aboukir's* upper façade represent illustrious men from Greek Antiquity:

Demosthenes, Socrates, Homer and Euripides (Fig. 1). Both architectural and decorative programs are very coherent and show how often those decorative elements were present on façades in the 19th century, illustrating the romantic taste for antique art. Hundreds of busts were cast using moulds made from original museum pieces. Antiques from the *Louvre* museum were often used to create replicas.

The 19th century was a period of technological progress, especially in the chemical industry, and diverse recipes of artificial stones were conceived, tested, applied, and finally modified or adapted by the moulding studios. Even though initial recipes are mentioned in the literature, the on-site material may have been modified in the workshops and over time. Therefore, it is sometimes difficult to establish a link between literature recipes and material observed in present day. The main source of information on innovative materials used in the 19th century in France is the book from Théodore Chateau published in 1880 [1]. He made a long list of chemical recipes for technological applications in the building industry. A specific chapter is dedicated to artificial stones and the different ways to make them. They are of three different types. The first one, based on chalk, cement or concrete, is mainly used in building construction. The second one is based on alkali silicates and the third one on plaster. The author specifies that these two methods can be used to mould architectural elements and cast figures.

Within the framework of the general conservation project, it was necessary to characterize the material used for the creation of these cast busts and to define the decay observed.

Fig. 1 On the left side, the Aboukir façade, showing the four busts before cleaning, and on the left the Hotel Boni conceived by the same architect and presenting the same iconography. (Photos after Sébastien Cord and François Brugel, architects)

2 State of conservation

The busts were cleaned in 2008 by micro-sand blasting after the elimination of bird droppings that partially covered them (Fig. 2). After cleaning, a network of large cracks about 0.5 cm wide and 1 cm deep was revealed and gave the heads the appearance of a broken up puzzle (Figs. 2 and 3). The cracks were blunt, did not penetrate the depth of the busts, and apparently had been present before cleaning, as they were filled with a mending mortar. The large cracks exposed the iron cord grids present inside the busts. The surface of the busts appeared very irregular because of differential erosion. Nevertheless, the busts kept a good general cohesion but, because the sealing mortar had been lost, were at risk of falling off the façade.

3 Materials and methods

As the busts have a hollow core, samples could be collected at their inner and external surfaces. Observations and analysis were conducted on polished cross sections and fresh broken pieces. The study included macroscopic observations to evaluate material texture, X-Ray diffraction to determine crystalline phases (Bruker AXS D8 ADVANCE), back scattered and secondary electron observations coupled with EDS analyses on scanning electron microscope to determine elemental composition and microstructure (Jeol JSM-5600LV).

Fig. 2 Cast busts of the four famous men before and after micro-sanding cleaning.

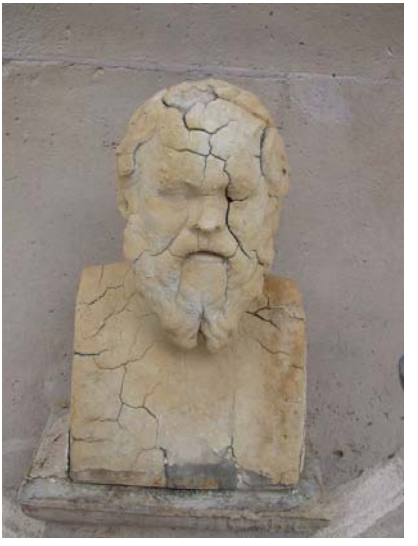

Fig. 3 Cast bust of Socrates, one of the four famous men after micro-sand blasting cleaning.

4 Results

Observation of the interior samples under binocular microscope reveals the presence of grains from 10-50 μm bound with finer grains below 10 μm. The grains seem to be covered by a shiny veil. Some white grains are distributed throughout the material. External samples of the castings present similar grains as well as additional white grains, but no binder could be found.

The identified crystallized phases are calcite ($CaCO_3$) and lead carbonate hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) in both interior and external parts of the casting. The interior sample appears to be composed of large grains rich in calcium and carbon (calcite grains) bound with finer grains of calcite mixed with a lead carbonate charge (white spots on Figs. 4 and 5). In the external sample, the lead carbonate remains around the aggregates but the fine calcite grains are not present. The interior sample appears to have retained its calcite binder, which seems absent from the environmentally exposed external surface of the bust.

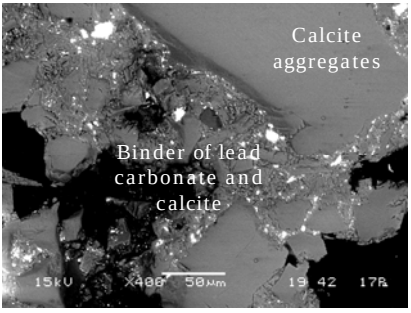

Fig. 4 Backscattered image of inner part of the casting NUM20090055

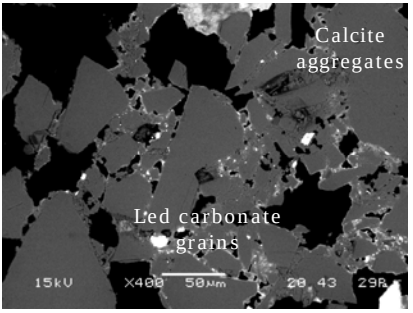

Fig. 5 Backscattered image of external part of the casting NUM20090056

A broken surface of a sample taken from inner part of the bust was observed under secondary electron and revealed two morphological characteristics:

The presence of fungal hyphae and spores indicating biological colonization (Fig. 4).

The presence of an amorphous gel covering and linking the grains (Fig. 7). This gel can be crackled in the same way as a broken glass (Fig. 6) and is composed of silicon (Si) and potassium (K). This composition and microstructure are consistent with "water glass" gel, which was in use during the XIXth century for stone consolidation.

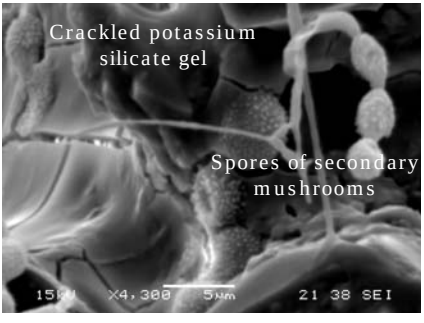

Fig. 6 Secondary electrons image of the inner part of the bust NUM20090058

Fig. 7 Secondary electrons image of the inner part of the bust NUM20090057

On the basis of our analytical results, the hypothesis of a silicatisation treatment can be expressed. Sodium and potassium silicates were utilized in the 19th century in two different ways. The most common was the so-called "dry way," which was initiated by the German chemist Fuchs in Munich in 1825 and then by the English chemists Wern and Siemens in 1848. The dry way was further developed by Ransome [1] or Kuhlman [2] and finally largely applied by 19th century architects such as Viollet le Duc. The silicate solution had the ability to penetrate and

combine with stone components during drying and to form a hard and resistant substrate. Viollet le Duc applied it to consolidate and prevent stones from further weathering on several medieval monuments [3]. Brand new sculptures could also be treated with silicate solutions as a preventive protection measure. The statues decorating the Napoleon courtyard in Louvre Palace were treated in this way [4].

Another way to use potassium silica solution consisted of mixing it directly with stone powder, moulding the mixture as a mortar and drying it in an air oven between 50 and 100°C for a period dependant on the size of the moulded object.

This method also has been used for producing artificial stones for construction or architectural elements. Metallic oxides could have been added to simulate the colour of natural stones.

This process was most probably the one used to create the busts we have studied. If potassium silicate had been applied after casting, it would not have penetrated to the inner core of the material (the gel was found deep in the material, at 5 cm depth). Our assumption is that potassium silicate has been mixed with stone powder, moulded, and probably dried in an air oven, rather than applied to the bust surfaces. Lead carbonate may have been added to obtain a colour close to that of natural stone.

This last process may have initiated cracks, as important thermal variations or shrinkage may take place following air oven drying. Indeed, the cracks we observed cannot be due to oxidation of the cord grids or dilatation, as they are not in star or chipping shape. Instead they form a polygonal network typical of swelling patterns. The external surface of the casting was in direct contact with the mould and may have been exposed to the strongest temperature variations. When temperature gradient varies from the surface to the depth, cracks are likely to be located in the stressed area rather than penetrating the depth of the object, which, here, is the first few centimetres of the castings. Too high a temperature or too rapid cooling of the castings may be the source of the final observed degradation pattern.

5 Discussion and conservation plan

Cast and cord grid busts of the famous men placed on the façade of the *Aboukir* are made of limestone powder and lead carbonate grains bound with potassium silica gel. References to those recipes exist in the literature, but as far as we know, no existing proofs of their existence for decorative elements had been previously described. The only proof we have are ancient moulds still existing in moulding studios. They are called "*moules à pièce*" or "pieces mould," and their pieces were connected with a sealing mortar. The mortar needed to be broken to open the moulds and take the casting out. However, it was impossible to find any further information on the way the cast busts were finally prepared. Casters have probably

tried new recipes or made mistakes in artificial stone preparation that involved strong cracking.

The conservation initiative has been to relocate the busts to the entrance of the building and to install on the façade new busts similar to the original, but cast in resin. They were made by the *Louvre* moulding studio and recently placed in January 2010 (Fig. 8).

Probably the same sponsor and surely the same architect are at the origin of the *Hotel Boni* and *Aboukir* street façades. Their similar iconography suggests that other similarly decorated façades may exist. A starting study and research have been initiated with the *Aboukir* façade and may lead to new research on historical buildings of the 19th century.

Fig. 8 New cast busts made in resin by the moulding studios of *L'Atelier des Moulages de la R.M.N.*, and replaced in January 2010 on the façade, *rue d'Aboukir N°4th*.

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I.08

How Did the Romans form Concrete Underwater?

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Abstract The Roman's ability to cast hydraulic concrete underwater relied on their skill in being able to construct temporary or permanent formwork in the open sea that could withstand the force of currents and survive being buffeted by waves. The design of the forms frequently followed the description provided by Vitruvius in *De Architectura* (5.12.3); however, there was a technique that he did not refer to, that being the use of prefabricated floating caissons. It is surprising that Vitruvius made no mention of them as they were widely used. Based on archaeological evidence a new categorisation of Roman formwork designs used in underwater or submerged concrete construction addresses this omission. Three categories are proposed; 1, for in-situ constructed inundated forms for use with hydraulic concrete; 2, in-situ constructed drained forms for use with non-hydraulic concrete; and 3, prefabricated floating forms for use with hydraulic and non-hydraulic concrete.

1 Introduction

The discovery of hydraulic concrete sometime in the 2nd century BC or possibly earlier was one of the most extraordinary inventions of the Roman era. It allowed the Romans to build structures in the open sea with greater freedom either as the substructures to breakwaters, moles and lighthouses, or as elaborate geometric designed fishponds.

As with modern concrete it has to be shaped or formed within a mould whilst it hardens. The key to the success in working with concrete is in the design and construction of the formwork, especially when working in the sea. Vitruvius's text is the only contemporary source that describes how the material was sourced, mixed and laid. He also included a description of the construction of formwork. In *De Architectura* (5.12.2-6) which he wrote sometime around 25 BC he outlined three techniques of which two are supported by archaeological evidence. The

author is proposing an alternative third category based on extant remains that includes techniques not referred to in *De Architectura*.

2 Categories of Formwork

2.1 Category 1 – an in-situ constructed inundated form that includes the type described by Vitruvius (5.12.3)

Used in the hydraulic concrete construction of either extensions to harbour moles, jetties, isolated blocks (*pilae*) and walls to fishponds. The formwork was usually constructed in timber. Piles were driven into the sea bed and framed with

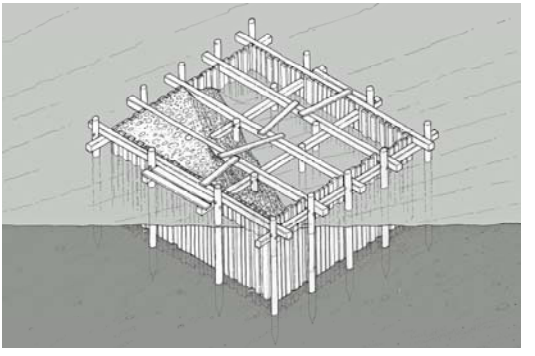

Fig. 1 Category 1 formwork - C Brandon

horizontal beams against which vertical boards were set whilst being pounded in, see Fig. 1. The boards, which ranged in size from 9.5 cm to 50 cm wide with the majority being between 25 to 30 cm and 3 to 8 cm thick, were set reasonably closely together with gaps of not much more than 2 cm.

Evidence of this type of formwork can be found at Anzio (*Antium*) where the impressions of horizontal cross beams set at approximately 1m above sea level can be seen on the outer mole with evidence of vertical piles at 2.5 m centres [14], and also the remains of the ends of vertical planks 0.23 – 0.5 m wide by 0.07 – 0.08 m thick have been found imbedded in the seafloor adjacent to the inner quay structure [16]. At Astura there is evidence for vertical planking with horizontal tie beams secured to vertical piles on the harbour mole [14, 15]. At Baiae (*Baianus Lacus*) on the upper surface of the entrance channel jetties can be seen the impressions of horizontal cross beams, 60 – 70 cm in diameter set at 2 - 2.5 m centres , and 20 – 25 cm diameter vertical piles set at alternating sides of the horizontal tie beams and stiffened with 20 cm diameter raking braces. The continuous run of concrete was laid in sections with the end bulkhead of the

formwork removed after each casting [31]. In the harbour at Caesarea Maritima in Israel there are blocks of concrete on CAHEP survey line number 3 that have horizontal tie beam impressions, some with single beam and some with cross tie beams [27]. At Cosa (*Portus Cosanus*) there are vertical impressions 0.10-0.15 m wide and 0.15-0.20 m deep on the western face of pier 1, and two square beam holes 4 m apart approximately 0.26 x 0.25 m in pier 2 [17]. At Egnazia there is clear evidence of beam, pile and tie impressions on the concrete harbour mole [1]. At Marseille in the South of France random width horizontal planks have survived in situ fixed to vertical piles that formed the concrete foundation to quay F.120 [21, 22]. At Misenum there are beam and post impressions in several of the concrete *pilae* [18] and one shows evidence of a repair to the formwork [4]. At Paola (*Circeii*) there is evidence for a complex shaped formwork with impressions of vertical piles, planking and horizontal beam holes [14]. In the Claudian harbour of Portus on the northern concrete mole there is extensive evidence of vertical planking with horizontal tie beams and external collar beams [14, 33, 25]. At S. Marco di Castellabate there is evidence for forms that were 6 to 8 m long by 4.5 m wide used to caste concrete in a continuous pier. Each bulkhead section of shuttering was removed (for re-use?) to allow concrete to be cast up against concrete. Horizontal cross beams were set at 1.5 m centres with 15 cm diameter diagonal braces fixed at 22°. The vertical piles were 15cm in diameter and some of which were in-bedded between 45 and 60cm into the rocky seabed [3]. At the fishpond at Santa Severa there is evidence for vertical planking formwork 0.10 to 0.40 m wide and 0.03 to 0.045 m thick [29]. At Sapri, on the Roman harbour pier, there are 16-18 cm diameter horizontal and vertical post and beam impressions, and in one case a 10 cm diameter vertical pile hole and two 20 cm wide horizontal beams [32]. On the sides of the concrete mole at Side in Turkey there is, apparently, the impressions of horizontal planking fixed to vertical piles 0.3 x 0.15m at 0.8m intervals, although the author could find no evidence of the horizontal boarding that may have been mistaken for courses of aggregate [23]. The concrete harbour mole at Thapsus in Tunisia is now completely buried under a modern rubble mole. However, Dallas and Yorke made a record of it in their survey along the coast of North Africa and noted the marks of circular horizontal beams in the upper surface at 1.3 m centres that would have tied the side walls of the form together [12].

At a number of these sites surviving timber planking suggest that the formwork was left in place and not removed after the concrete had set. It is apparent that permanent or semi permanent cladding was often part of the finished structure. It is known that Roman concrete gains strength very slowly, over a matter of years [28]. The builders may have opted to leave the timber formwork in place to protect the concrete from potential erosion. In cases where a mole or pier was cast in a continuous line then the bulkhead sections of formwork appear to have been removed, and even possibly re-used.

Stone blocks were used as a permanent facing in addition to being used to form the enclosure within which the concrete was cast. At Pompeiopolis [35] and Kyme

in Turkey [13] and S. Cataldo near Lecce [2] ashlar marginal walls were built out into the sea to form inundated cells that were in filled with hydraulic concrete in a similar manner to the timber variant. The blocks were heavily clamped to bind the stones together particularly at the time when they were most vulnerable to damage from the sea, before the concrete core had been placed.

2.2 Category 2 – an in-situ constructed, de-watered, cofferdam formwork described by Vitruvius (12.5.5-6)

Vitruvius (12.5.5–6) describes the construction of a double walled cofferdam form that was pumped dry for casting non-hydraulic concrete. This category includes formwork with watertight enclosures that were constructed with single and double walls. In addition to being used for casting non-hydraulic concretes they were used also for revetments, bridge footings and other applications where an underwater dry working environment was required.

The simplest type of cofferdam was that described by Vitruvius; piles were driven vertically into the seabed (or lake or riverbed) at regular spaces around the area to be enclosed and drained, either as a single line or double row. Horizontal

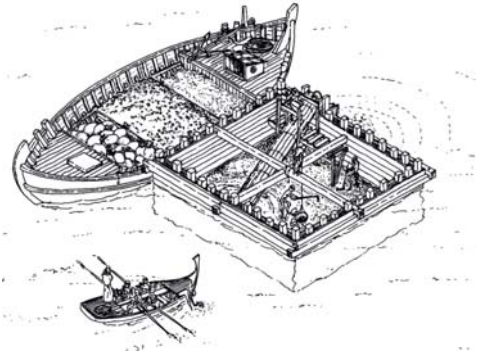

Fig. 2 Category 2 Cofferdam – C Brandon

timber planks were then secured to the piles on both faces, internal and external, see Fig. 2. The void in-between the boarding and the piles was packed with puddled clay. The Romans developed rebated or grooved piles into which boards could be slotted making it considerably easier to set them underwater. Elaborate interlocking piles were also developed, some with continuous dovetails where additional strength was required, as found at Lake Nemi [34].

Evidence for Category 2 formwork construction can be seen at Marseille in France where a permanent double walled cofferdam to quay F.28 was built with 149 pine piles 12-14 cm in diameter and between 5.5 and 6 m long. Parts of 5 different vessels were also used in the sides of the cofferdam [21]. A cofferdam was also used as temporary works associated with the construction of quay F. 120

[22], at Minturnae on the river embankment are the remains of a revetment structure comprising vertical oak posts onto which horizontal planks edge fixed with mortice and tenon joints were fitted [30]. Around the lakeside at Nemi were found the remains of cofferdams formed with a double wall spaced 0.75 m apart built with 30 x 20 cm interlocking piles and the void filled with clay. Also a double wall set 0.75 m apart formed with 5 cm thick planks fitted to close piled timbers 52 x 25 cm in section with the second wall built with 40 x 20 cm piles at 90 cm centres fitted with oak panels in between [34]. In Rome the bridge piers of Pons Cestius [5] and Ponte Elio [8] and at Tier in Germany [11] were constructed behind cofferdams and as was also the case for quayside structures along the River Tiber in Rome [24, 10].

Category 2 forms might well have been used to build *opus reticulatum* or brick faced structures deep underwater. At Ponza there appears to be evidence of a second line of timber sheet piles set off from the face of the wall, but inside the modern over-cladding, to provide the dry working space needed to lay the quasi *opus reticulatum* faced concrete [19]. How the Roman engineers resolved the practical problems associated with creating watertight enclosures and manually pumping out large deep water cofferdams, such as the one needed to construct the outer *pila* at Nisida (circa 15 m x 9 m by 9 m deep) with its *reticulatum* faced sides, are difficult to comprehend [18].

2.3 Category 3 – Prefabricated Forms

Vitruvius failed to include in his *De Architectura* (5.12. 2-6) any mention of the use of prefabricated forms. However, he does describe how pre-cast blocks could be constructed above sea level and only when they had cured and set solid were they tipped into the sea by a method that sounds particularly impractical and for which there is no archaeological evidence. Vitruvius suggests that this technique was intended for sites where the seas were too rough for in-situ construction of formwork (Vitruvius 5.12.3-4). One could question whether what he was actually describing was a prefabricated form that could be launched from the shore rather than a pre-cast block and somehow over time it has been lost in translation or it was simply misunderstood by Vitruvius in the first place.

Driving piles into a seabed in an exposed site offshore and keeping the pile driving barge on station without the benefit of modern powered winches and anchors must sometimes have been challenging. Also fixing beams and planks underwater in situations with strong currents or rough seas would have been very difficult. It would have been impossible to pump dry a category 2 evacuated cofferdam enclosure where the sea or river bed consisted of gravel or had an equally porous substratum.

The remains of a series of rectangular wooden forms, 14m x 7m on plan and 4m high were found in Area K to the west of the entrance to the harbour Sebastos at Caesarea Maritima in Israel [7]. Comprising carefully built watertight floating

box caissons, fabricated along the shoreline and towed out to the site of the northern end of the main southern mole, see Fig. 3. When they reached their final position they were filled with a mixture of hydraulic and non-hydraulic concrete and sunk in a line to form the foundations to the mole and warehouses described by Josephus. These caissons built using ship construction techniques; were in fact rectangular barges that had a single mission. Edge jointed boards set with mortice and tenon joints formed a watertight enclosure. Floor timbers or frames were let into chine beams that also took side-wall frames. The side-wall and floor planking were attached to the floor and wall frames by treenails and to the chine beam with tenons, in addition the joint was stiffened with knees. Internal bracing provided additional strength when it was subjected to hydraulic loads as it settled onto the seabed with a part fill of concrete and held it together while the concrete set.

A similar caisson design was discovered in the harbour of Alexandria [20]. The forms were originally about 10 to 15m long, 5 to 8m wide and 1 to 3m high. Watertight and constructed with a floor they were used to cast blocks of hydraulic concrete as part of foundations to the harbour esplanade. The caissons were made of 3 to 4 cm thick boards edge fixed with mortice and tenon joints and strengthened with frames and transversal beams. Unfortunately, at present, there is very little information available about these important structures. Although dated by carbon 14 tests to around 250 BC the concrete material and the formwork design studied by ROMACONS in 2007 suggest a much later date and one contemporary with the Caesarea forms, between the 1st century BC and 1st century AD.

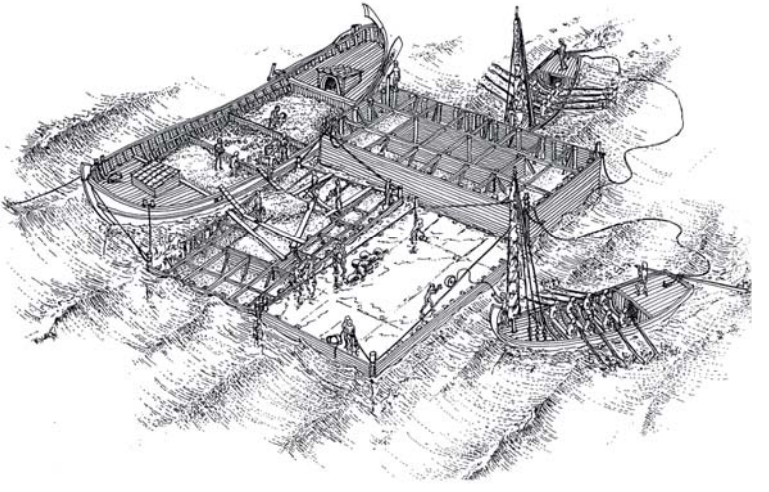

Fig. 3 Caesarea Area K Category 3 Caisson – C Brandon

The remains of a wooden caisson, 22.9m long by 2.2m wide was found on the northern edge of the Roman harbour of Laurons in the South of France [36]. This rectangular structure had a floor made up of wide planks fitted to a frame or chine

beam from below. The upper surface of the chine beams had deep grooves that originally held the ends of vertical boards making up the sides of the caisson. Vertical elements were also let into the floor frames and chine beams. Unlike the caissons at Alexandria and Caesarea the method of construction used appears not to bear any relationship with ship building techniques. The jointing details were similar to those used in terrestrial based structures rather than ship construction, however, the unit was watertight and floated. It was constructed on the edge of the shore and then towed or pulled into place with ropes and the sunk with rubble to form the jetty.

An unusual cofferdam was used to build the Roman Bridge footings at Chalon-sur-Saône in France dated to the beginning of the 3rd century [6]. Unlike the design described by Vitruvius, the piers for the bridge at Chalon were constructed within watertight caissons each with a floor. They were built using ship construction techniques and the boards were secured with mortice and tenon joints fixed to frames. The caisson or bridge barge pier was at least 12m long by 6m wide and was built on the riverbank; this is evident from the fixings in the chine that were fitted from below.

One of the most innovative designs used by the Romans was the type of form used in the construction of the East side of the harbour entrance at Caesarea. Built as a floating open bottomed enclosure with a double walled perimeter that acted as the flotation collar, and allowed it to be positioned and sunk in a controlled manner by gradually infilling the void between the two walls. By not having a floor it could cope with an uneven seabed although it would be liable to raking and might only have been used in relatively sheltered waters [26]. These forms seem to be unique to Caesarea and may have proved too difficult to manoeuvre to have been used elsewhere.

Redundant ship hulls also fall into this category; although not purpose built they achieved the same objective. The most renowned example was the hull of a very large ship that was used to transport an obelisk to Rome and subsequently used in the construction of the outer breakwater of the Claudian harbour of Portus (Pliny, *Natural History,* 16.201-2, Suetonius, *Claudius,* 20.3). Rubble filled abandoned hulks were used to form part of the harbour mole at Toulon [9].

Vitruvius made no mention of these floating caissons maybe because they were not commonly used or that he simply was not aware of them. If it was necessary to build moles or breakwaters in deep or rough water then a more usual approach would be to dump large stone blocks from barges to form rubble breakwaters as witnessed by Pliny the Younger at Civitavecchia (*Centum Cellae*).

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I.09

Mortars from Historical Buildings in Switzerland: Petrographic Examination

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Abstract Twelve samples of mortars from historical buildings dating between the 1st century B.C. and the 20th century A.D., located along the Swiss Alpine Arch, have been examined with optical and fluorescence microscopy to ascertain some common features possibly responsible of their good behaviours. The majority of the samples are lime-based mortars, though a few samples show the characteristic features of magnesium lime mixed with siliceous and carbonatic sands; the composition reflects the local availability of raw materials. The microstructure does not show defects or particular features that could significantly influence the behaviour of the mortars. The results confirm that the high durability of the analyzed samples probably is not dependant on the composition or proportions of the mixes but must be due to other influencing factors, such as the preparation of the substrate, waiting the appropriate amount of time between the application of the different layers, and the careful preparation, processing and application of the binder and mixes.

1 Introduction

The research reported here is part of a larger project in which the properties and behaviours of traditional lime-based mortars are compared with dry, ready-mixed mortars used today in restoration works. In this study, historic mortars are analyzed to ascertain whether or not the composition of the mix influences the durability of the studied samples within a framework that maintains manual skill, builders' experience, and conditions of the worksite as invaluable aspects of historic concrete science and technology. The aim of the research is the analysis of historical mortars to extract useful information for the preparation of adequate mixes for restoration works.

2 Material and methods

Twelve samples of mortars from historical buildings along the Swiss Alpine Arch (Fig. 1), dating between the 1st century B.C. and the 20th century A.D., have been examined. The mortars differ in terms of building type (private houses, churches, chapels), typology (renders, plasters generally painted, decorative elements), and age (Table 1).

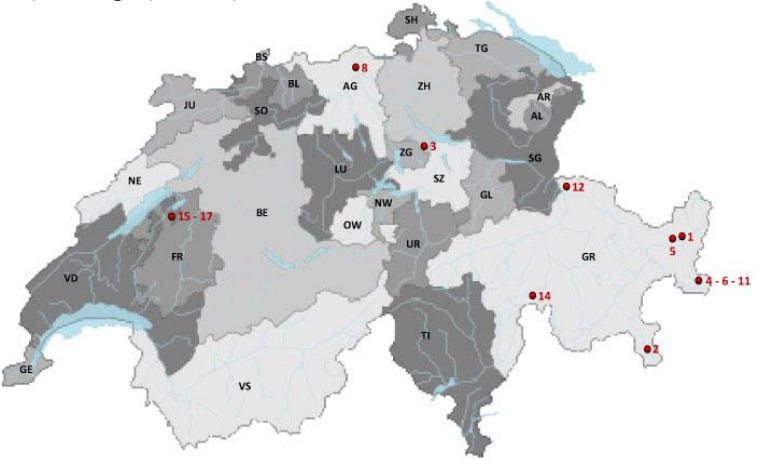

Fig. 1 Swiss map: general view of sample locations

Table 1 List of the samples

No.	Place of origin	Building	Typology	Age
1	Scuol (Grison Canton)	Private house	Unknown	XVI-XVII A.D.
2	Poschiavo (Grison Canton)	Town Hall	Cornice	1712
3	Hütten (Zurich Canton)	Countryman house	Render	1770
4	Müstair (Grison Canton)	Church	Wall painting	Unknown
5	Tarasp (Grison Canton)	Chapel at the castle	Unknown	XII
6	Müstair (Grison Canton)	Pitsch house	Unknown	Early XX A.D.
8	Vindonissa (Argovia Canton)	Unknown	Painted plaster	I B.C.
11	Müstair (Grison Canton)	St. Giovanni monastery	Plater, Ulderico Chapel	XI A.D.
12	Malans (Grison Canton)	von Salis Palace	Unknown	Late XVI A.D.
14	Splügen (Grison Canton)	Red House	Unknown	1750
15	Avenches (Vaud Canton)	Unknown	Painted plaster	I A.D.
17	Avenches (Vaud Canton)	Unknown	Painted plaster	I A.D.

The methodology used for the characterization of the samples includes polarizing light microscopy (PLM) and fluorescence microscopy (FM), which are suitable for studying porous building materials [1, 2]. Each sample has been studied according to the regulation UNI 11176:2000 [3] and recommendations supplied by the Applied Petrography Group [4].

3 Experimental

3.1 Polarizing light microscopy (PLM)

3.1.1 Binder

The analysis of thin sections allows the characterization of the binder; it is generally calcitic lime. The binder of samples 2, 5, 8, 17 exhibits the typical rounded lumps characteristic of magnesian lime [5]. Rounded lumps derive from the non-hydration of MgO. This phenomenon is rather common in this type of binder when the firing temperature of the dolomitic raw material was high and the slaking was not prolonged for sufficient time [6]. Hydrous magnesium phases have been observed in sample 5 at the interface between layers 1 and 2, due to the hydration of MgO in presence of water or in a humid environment [7]. Hydraulic lime has been detected in sample 3 and in the first layer of sample 12. Cement mixed with lime has been detected in sample 6.

3.1.2 Aggregates

The composition of the aggregates is reported in Table 2. A general homogeneity in terms of mineralogical and petrographic composition of the aggregates has been observed, reflecting the geological sources of the used sands. The main composition is represented by siliceous sands, including metamorphic quartz from gneiss and micaschists and subordinately from plutonic rocks, sometimes associated with carbonatic sedimentary rocks. Accessory minerals are biotite, muscovite and chlorite. Fragments of metamorphic rocks (amphibolites and serpentinites) also have been detected.

The grain size distribution is variable among the studied samples and within the layers of a single sample, ranging from 40 μm (lower value) up to 4 mm (higher value); medium values range between 100-400 μm and 2.0-2.5 mm. This estimation is based on thin section analysis. Larger grains (maximum grain size 10 mm) can be seen in macro-samples. The variability of the grain size distribution probably indicates that a grading curve was not deliberately chosen.

Table 2 Mineralogical and petrographic composition of the aggregates

Aggregates composition	Samples											
	1	2	3	4	5	6	8	11	12	14	15	17
Quartz	++	+++	-	+++	+	++	++	++	++	++	++	+++
Limestones	+	tr	++	-	+++	++	++	-	+++	-	++	++
Calcite	+	-	tr	++	-	-	-	tr	+	-	tr	+
Dolomite	-	-	-	+++	+++	+	+++	-	-	-	-	-
Muscovite	-	+++	-	++	-	+++	+	tr	+	+++	-	-
Feldspars	+++	+++	-	-	-	-	-	-	-	-	tr	+++
Biotite	-	+++	-	+	-	+++	-	tr	-	tr	tr	-
Qtz-sandstones	++	-	-	-	-	-	-	-	-	-	+	++
Plagioclases	-	tr	tr	++	-	-	++	-	-	-	tr	++
Marbles	-	-	++	-	-	+	-	tr	+++	+++	-	-
Micaschists	+	+++	-	+++	-	++	-	tr	-	+	-	-
Opaque minerals	-	tr	-	+	-	-	-	-	-	tr	-	tr
Metamorphic rocks	-	-	-	-	-	++	+	-	-	-	-	-
Semipelitic rocks	+	-	-	-	-	-	-	+++	-	-	-	-
Marl limestone	-	-	++	-	-	-	++	-	-	-	-	-
Serpentinite	-	-	-	-	-	-	++	-	++	-	-	-
Chlorite	-	tr	-	-	-	+++	tr	-	-	-	-	-
Sedimentary rocks with quartz	-	-	+++	-	-	-	-	-	-	-	-	-
Chert	-	-	-	-	+	-	-	-	-	-	+	-
Schists	-	-	-	-	-	-	-	tr	tr	+	-	-
Glauconite	-	-	tr	-	-	-	-	-	-	-	tr	tr
Granates	-	-	-	-	-	-	-	-	-	tr	-	-
Fe-oxides	-	-	-	-	-	-	tr	-	-	-	-	-
Amphibolites	-	tr	-	-	+	-	-	-	-	-	-	-
Amphiboles	-	-	-	-	-	-	-	-	-	-	tr	-
Sandstones	-	-	-	-	-	-	-	-	-	-	tr	-
Stilpnomelane	-	-	-	-	-	-	-	-	tr	-	-	-
Talcoschists	-	-	-	-	-	-	-	-	-	tr	-	-

Legend

+++ main component; ++ subordinate component; + accessory component; tr traces; - absent

3.1.3 Additions

Angular ceramic fragments and brick powder have been observed in discrete amount in samples 1, 4 and 17, imparting hydraulic characteristic to the mortars. Trace amounts have been found in samples 3, 8 and 15. Vegetal fibres (mainly in

sample 14) are present, having been added to improve the tensile strength. Impurities of charcoal are present in trace amounts in samples 1 and 17.

Table 3 reports the additions used for the mortars.

Table 3 Additions

Additions	Samples											
	1	2	3	4	5	6	8	11	12	14	15	17
Ceramic fragments	++	-	tr	++	-	-	tr	-	-	-	tr	++
Vegetal fibres	-	tr	-	-	+	-	-	-	-	++	-	-
Charcoal	tr	-	-	-	-	-	-	-	-	-	-	tr

Legend

+++ main component; ++ subordinate component; + accessory component; tr traces; - absent

3.1.4 Relationships between binder and aggregate

The estimated binder/aggregates ratio [3] is variable, even though it corresponds to 1/3 in volume in most of the samples. Some factors such as the binder cohesion, the good binder-aggregate bond (Fig. 2), suggest high reactivity of the lime [8].

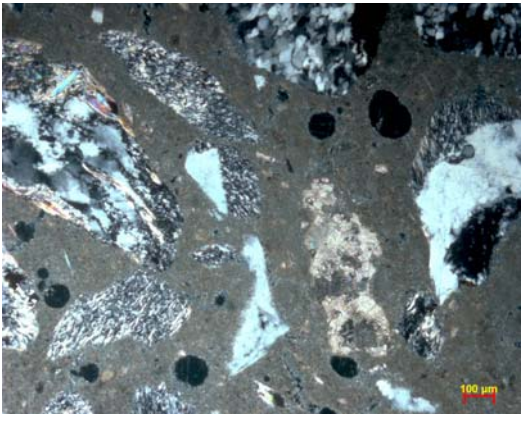

Fig. 2 Sample 4: photomicrograph showing the good bond between siliceous aggregates and lime (XPL)

Reaction rims between calcareous aggregates and lime have been observed in a few samples (Fig. 3). The presence of microcrystalline calcite at the aggregate-binder interface, the result of $CaCO_3$ dissolution and re-precipitation, is due to the non-linearity of the carbonation process corresponding to cycles of carbonation, dissolution, and re-crystallization [9].

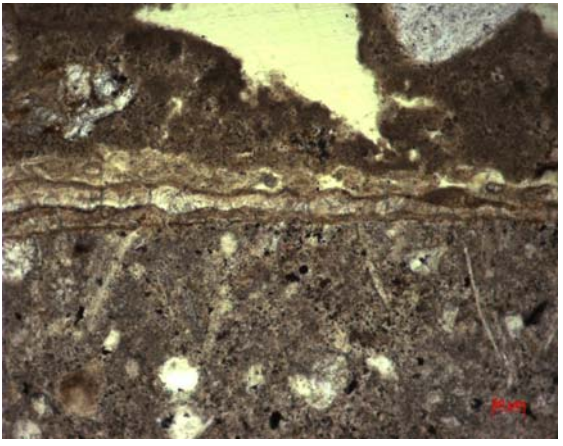

Fig. 3 Sample 15: photomicrograph showing the reaction rim (in the middle of the picture) between lime and a calcareous coarse size aggregate (PPL)

3.2 Fluorescence microscopy (FM)

3.2.1 Microstructure

The macro-porosity is due to cavities and pores of variable size and shape. Generally, the shape is irregular and seldom the pores are rounded. Frequently (samples 4, 5, 8, 14, 15, 17) shrinkage cracks have been observed, mainly in the upper layers, due to rapid volume reduction from the loss of water and to the high percentage of binder in the mix. Aggregate-binder porosity has been observed for a few samples and is limited to angular grains of very coarse size.

The different layers of each sample maintain the same degree of adhesion and thus remain in direct contact. The state of conservation is satisfactory; the macro-porosity (air-voids) is 2-5% in volume. Because the macro-porosity generally is linked with compressive strength, porosity values suggest these mortars have good mechanical properties.

4 Discussion and conclusions

The number of the layers in the samples, as well as grain size distributions, appear to differ on a macroscale from those observed under the microscope. The mineralogical paragenesis of the samples coming from several Cantons in Switzerland reflects the mineralogical and petrographic composition of the raw material sources: alluvial fluvial-glacial and glacial-lake deposits (Avenches, Vaud Canton); sands deriving from the physical and mechanical disgregation of

metamorphic (sometimes granitoids) and volcanic rocks (Grison Canton); and fluvial-glacial deposits (Hütten, Zurich Canton and Vindonissa, Argovia Canton) [10].

The binder derives from the burning of limestones and dolomitic rocks. Only two samples have been set with natural hydraulic lime obtained by burning impure limestones. Cement has been detected in sample 6, which suggests the sample can be dated to the XX century A.D. Lime-based mortars with the addition of ceramic fragments and ground brick powder are used as plaster for wall paintings (samples 4 and 17); the correct mortar typology is unknown for sample 1, which contains this type of addition. The trace addition in the remaining samples is not noteworthy regarding the hydraulic properties of the mix.

The grain size distribution is variable, and it does not indicate the adoption of a precise grading scale. The microstructural analysis carried out by FM does not reveal particular defects inside the matrix or between binder and aggregates. The state of conservation is very good except for some damage related to hydrous magnesium crystallization phases and with pores between large aggregates and binder.

In our study, no relationship between aggregate composition and the durability of the mixes can be established by PLM. We can state that in this specific case study siliceous and calcareous sands do not influence the behaviour of the mortar. Instead, the analysis of the binder gives interesting results: the density and the cohesion of the matrix, the good bond between aggregates and binder, and the absence of cracks suggest an accurate procedure for the preparation of the mixes and their application. Factors such as the adequate preparation of the substrate, the protection of the render from the direct action of incident solar radiation, and the final treatments of the render may significantly influence the durability of the system [11].

5 Acknowledgments

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I.10

Proteomic Identification of Milk Proteins in Historical Mortars

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Abstract Since ancient times organic additives such as milk, curd, whey, blood, oils, fruit juices, etc. have been added to mortars. The majority of technological procedures were forgotten by the end of 19th century. Rediscovery of the old technologies could help in the restoration of historical buildings. Model samples of mortars containing common milk additives were prepared for testing by the peptide mass mapping method that is used for protein identification. The model samples were analyzed fresh and naturally aged to assess the effect of ageing on the identification of the additives. In case of the aged mortars it was necessary to multiply the amount of samples ten times in order to obtain good-quality spectra. The effect of different values of pH on the identification of protein additives were also studied on mixtures of silica sand and protein additives (without lime).

1 Introduction

The first occurrences of plasters are recorder at 6,000 to 7,000 BCE [1]. Since this time various natural additives (e.g. milk proteins - caseins, fruit juices, fats) were added into mortars and plasters. Although the organic materials were added in small amounts (less than 5 %), they greatly influenced and modified the mechanical properties of the mortars (see Table 1). Some of the materials exhibit more than one effect depending on whether they were added into the fresh or the partly solidified mortar [1-4].

Recipes for preparation of mortar with the organic additives were inherited from father to sons and from master to his trainee only verbally, therefore, only a few documents pass on now. Once synthetic additives, which have been industrially produced since the 19th century, were knows to have similar effects as

the natural organic additives, the natural materials disappeared. Therefore, the organic analysis of historical mortars is important, because it could help to rediscover these lost recipes, which can be used for the restoration of historical buildings.

Table 1 List of organic additives and their effects on the mortar's properties. [1-4]

Attribution	Effects	Natural materials
Accelerators	Accelerate setting and increase initial solidity of mortars	Curd, egg white, blood, sugar, fat, starch
Retarders	Elongate time of mortar's workability	Sugar, molasses, fruit juices, blood, egg white, gluten
Plasticizers	Improve workability, compress fresh mortar	Milk, egg white, fat, oil, sugar, resin
Aerators	Improve durability and frost proofness of plasters	Malt, beer, urine
Sealing and hydrophobic additives	Provide impenetrability for water	Fat, oil, wax, asphalt, sugar materials
Adhesives	Increase mortar's adhesion on under layer	Casein, resin, gelatine, animal glue
Compactors	Raise mortar's solidity	Molasses, fruit juices, fat, oil
Reinforcers	Adjust mortar's consistency	Soured milk, casein, cheese, rye dough, gluten, plant gums, blood, collagen, gelatine

Determination of organic compounds in mortars still presents an analytical challenge. Concentration of the natural additives usually does not exceed more than a few percent and their content decreases during ageing. Natural compounds are affected by alkaline conditions in mortars, oxidation processes and they are also degraded by ubiquitous microorganisms.

Historical frescoes and artificial marbles contain much more protein additives than other types of historical mortars [5]. Therefore they can be analyzed by the common analytical methods such as gas chromatography with mass spectrometry detection (GC/MS) and high performance-liquid chromatography (HPLC) with fluorescence detection [6, 7]. These methods are based on comparing the ratios of individual amino acids that are obtained after complete hydrolysis of protein materials. Currently, more sensitive approaches like immunochemical methods and peptide mass mapping method employing mass spectrometry are used [8, 9].

In this work, peptide mass mapping method followed by mass spectrometry was used for the analysis of mortars containing milk protein materials. Fortunately, this method exhibits sufficiently low detection limits that enable the identification of the additives. In our laboratory, this method was at first applied

on the identification of protein binders in paintings, where the whole egg or casein could be used as a part of temperas [10]. Model mortar samples with an addition of various milk materials (curd, bovine milk and whey) were prepared to evaluate the applicability of this method on the historical mortars [11].

The peptide mass mapping method is based on comparison of *m/z* (mass/charge of molecule) values of peptides contained in an analyzed sample with *m/z* values of peptides originating from reference protein materials (curd, milk, eggs, animal glues, etc.). The values of *m/z* are characteristic for every protein additive and can be regarded as its fingerprint. The mass spectra with the characteristic *m/z* values of reference protein materials were inserted in the reference library. However, for the broader application of the developed method the results should be evaluated on a statistical basis.

Identification of protein additives is complicated by ageing processes and the effects of the high pH that occurs in the wet mortar. To study these effects, siliceous sand, as an inert solid phase, was mixed with solution of protein additives (animal glue, egg, yolk, egg white, bovine milk, curd, and whey) with different pH (7, 9, 11 and 13). Sands with protein additive were analyzed after 1 day, 1, 7, and 8 weeks, find out in order to assess the effect of ageing on identification of protein additives.

2 Experimental

2.1 Reagents and materials

Trypsin (TPCK) from Promega Corporation, trifluoroacetic acid and 2,5-dihydroxybenzoic acid (DHB) both from Sigma, acetonitrile (p.a.), ammonium hydrogen carbonate and calcium hydroxide from Lachema Brno were used.

Protein additive standards: bovine milk, curd, egg, yolk, egg white - all from Delvita production, whey (Magador s.r.o.) and animal glue (Kremer 2406) were used.

2.2 Preparation of model samples

The protein additives (Table 2) were added to the basic mixture that was prepared from sand, lime and water in a ratio of 4: 1: 1. The samples were shaped into the plates (20x10x2-3 cm) and were then left for three weeks to fully dry in outdoor conditions (Prague, Czech Republic, average temperature = 10°C, average relative humidity = 77%). After this, they were analyzed at first. Model mortars were kept in outside condition, but under the roof, next nine months and they were analyzed again.

Table 2 Composition of model mortar samples.

Proteinaceous binder	Binders weight [g]	Binders percentage [%]	Basic mixture of mortar [kg]
Whey*	50	2.50	2
Curd	40	2.00	2
Milk	75	3.75	2
Blank	-	-	2

* The whey solution was prepared by mixing 40 g of whey powder in 500 ml of water.

To prepare model samples, siliceous sand was mixed with a solution of protein additive in different pH (7, 9, 11, 13). Alkaline pH was reached by addition of calcium hydroxide - 30 ml of $Ca(OH)_2$ solution with protein was mixed with 50 g of sand so that the final content of protein additive was approximately 3%. Sand with the protein additive was kept at laboratory temperature and humidity (20°C, 50%).

2.3 Experimental conditions

A few tens of milligrams of the powdered solid material was digested in 80-100 µl 50 mM ammonium hydrogen carbonate (pH 7-8) containing approximately 10 µg/ml of trypsin at room temperature for two hours. The resulting solution with peptides was purified and concentrated on reversed phase. Purified solution (2 µl) was mixed with 4 µl of 2,5-dihydroxybenzoic acid solution (17 mg of DHB in 1 ml of mixture of acetonitrile/0.1% trifluoracetic acid (1/2, v/v)). This mixture (2 µl) was spotted on stainless steel. Analyses were performed using a Bruker-Daltonics Biflex IV MALDI-TOF mass spectrometer equipped with standard nitrogen laser (337 nm) in positive reflector mode. Before each measurement the instrument was externally calibrated. At least 200 laser shots were collected for each spectrum. Resulting spectrum was processed with XMASS software (Bruker) and compared with our reference database of protein additives.

3 Results and discussion

Various natural protein materials were added to mortars over many centuries for modification of their mechanical properties. The analyses of these additives still represent a serious analytical problem. The solid form of the analyzed samples, low concentration of proteins, oxidation processes taking place during ageing, alkaline pH, contamination by microorganisms, these are a few examples of different effects that complicate analyses of proteins in mortars. Identification of protein additives is based on comparison of mass spectra of unknown samples with spectra of reference materials that are saved in our reference library.

3.1 Study of ageing processes on model mortar samples

The prepared model samples were used for determination of the influence of ageing on identification of protein components in historical mortars. The comparison of mass spectra of the same amounts of fresh (three weeks old) and aged mortars (nine months) with the addition of curd are shown on Fig. 1. A large decrease of number of peaks and their intensity is observed. Hence, ten times larger amount of the aged sample (approx. 55 mg) was used to obtain spectrum of the same quality as the spectrum of the fresh mortar.

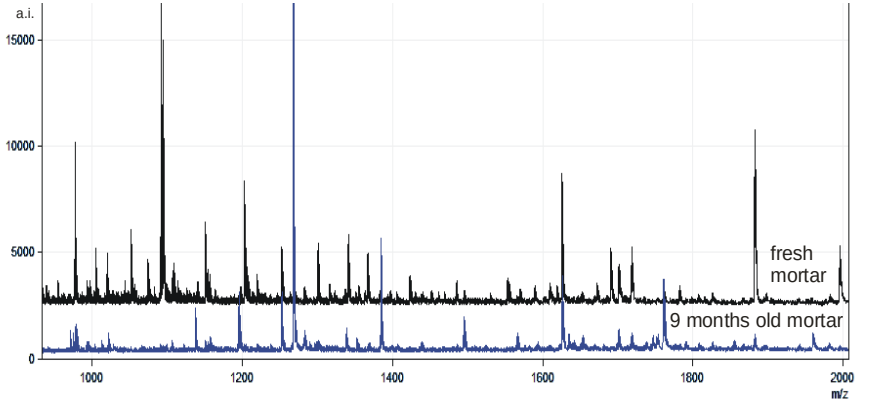

Fig. 1 Comparison of spectra of the same amounts of fresh and aged mortar with the addition of curd.

The requirement of the larger amount of aged samples could be explained by recrystallization that is caused by carbonation process that decreases the amount of protein mainly on the surface of the mortars.

Degradation by microorganisms is another potential reason for the decrease of protein concentration in mortars. This hypothesis could be supported by the presence of non-identified peaks in the spectra of model samples after the nine-months ageing.

3.2 Study of ageing processes on sand mixtures

Ageing tests were performed on the mixtures of sand and protein additives. Siliceous sand was used in place of the mortar mixture (sand and lime) for elimination of chemical reactions of proteins with the lime. Influence of temperature and air humidity changes were eliminated too, because the mixtures were kept at steady laboratory conditions (temperature 20°C, humidity 50%).

The sand-bearing samples were at first analyzed one day after their drying up, than after one, seven and eight weeks. The spectra obtained were compared (with

each other); the decreases of peak intensities were observed in all of studied protein additives (Fig. 2). A significant decrease of peak intensities in the spectra of samples at the same pH was observed after eight weeks of ageing. This decrease is assigned to degradation of protein additive.

Lists of peaks (their *m/z* values) obtained from the analysis of model samples were submitted to our identification program, which matched them to corresponding *m/z* values obtained from the analysis of protein reference materials. The number of *m/z* values in the sample spectra matching with milk proteins did not exhibit any significant change. Most probably eight weeks of natural ageing was too short a time to observe some effects on identification of milk proteins.

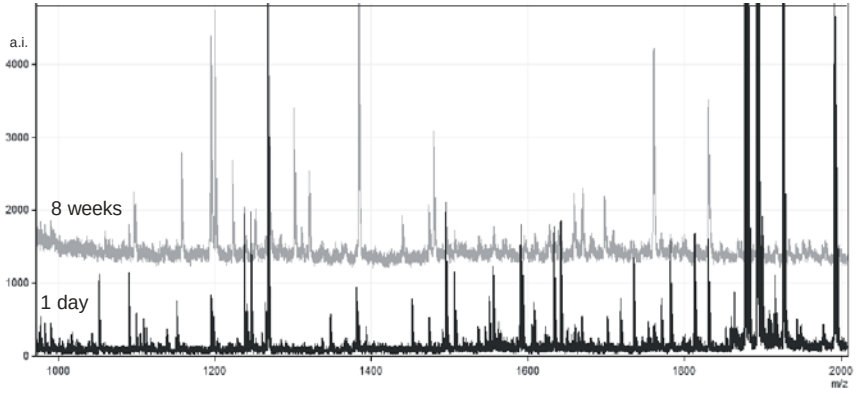

Fig. 2 The decrease of peaks number and different peaks in spectra of the sand with whey solution at pH 13 during its ageing.

3.3 Study of the effect of alkaline pH on the protein identification

Value of pH in fresh mortar mixture is alkaline due to the presence of lime and this alkaline pH could influence the identification of protein additives. The effect of the pH was tested on samples as at ageing (mixtures of siliceous sand and solutions of protein additives in different pH (7, 9, 11, and 13)). The effect of pH on the identification of the protein additive was evaluated as a change in number of *m/z* values matching the database. From the changes of the numbers of identical *m/z* values it was deduced that the effect of pH on identification of protein additives is insignificant.

4 Conclusion

The knowledge of protein additive use in mortars could be helpful in the reconstruction and conservation of historical buildings. However, determination of protein compounds in mortars is very complicated and only a few analytical methods can be applied. Peptide mass mapping is one of the most promising. This method was successfully applied on the model samples of historical mortars.

Ageing processes are one of the factors that significantly influence the protein identification in mortars. This effect was studied on a model mortar samples and samples prepared from sand and protein solution. Decrease of numbers of peaks in mass spectra was found in both cases. The influence of ageing was mostly evident on the amount of analyzed samples, when ten times larger amount of aged mortar have to be taken for obtaining the same good-quality spectra.

The influence of alkaline pH in the fresh mortar on identification of protein additives was also studied. The expected negative effect of pH increase on identification was not proved.

The results of studying of the influence of ageing and pH increase on the identification of protein additives in historical mortars are in conformity with the experience of the analyses of historical mortars.

5 Acknowledgement

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I.11

Development of a Methodology for Characterization of Historical Mortars in the Walloon Region (Belgium)

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Abstract A wide-scale program on the suitability of mortar formulation for heritage buildings in the Walloon Region has been undertaken to improve restoration habits in order to guarantee the permanence of patrimonial monuments. A global methodology has been established for the collection, registration, and macroscopic description of mortar specimens sampled in the field and the experimental physico-mechanical characterizations performed in laboratory.

1 To improve the restorations habits

Today Wallonia, the southern region of Belgium, has 2,840 listed monuments (Fig. 1). Each year, our region sees nearly 150 work sites undertaking restoration on these listed monuments. Resurfacing, re-pointing, coating, and whitewashing work are among the most frequent repairs. The use of lime in these operations is of fundamental importance. Our research [1-3], launched in 2006, is focused on the characterization of the mechanical properties of mortars, properties which still are not well-known.

Our main objective is to improve contemporary interventions in terms of compatibility with the ancient environment. The importance of compatibility is fundamental in ensuring the structure maintains the physical and chemical characteristics that have enabled it to reach the present almost unscathed [4]. One of the steps of this research is to collect and study mortars used in the old buildings, considering both the cultural heritage and archaeological context. The

collected samples are then submitted for the characterization of their mechanical properties at University of Mons. We are presenting here a global methodology for the collection, registration and macroscopic description of the mechanical characterization of the mortar samples and an example of an application of the method.

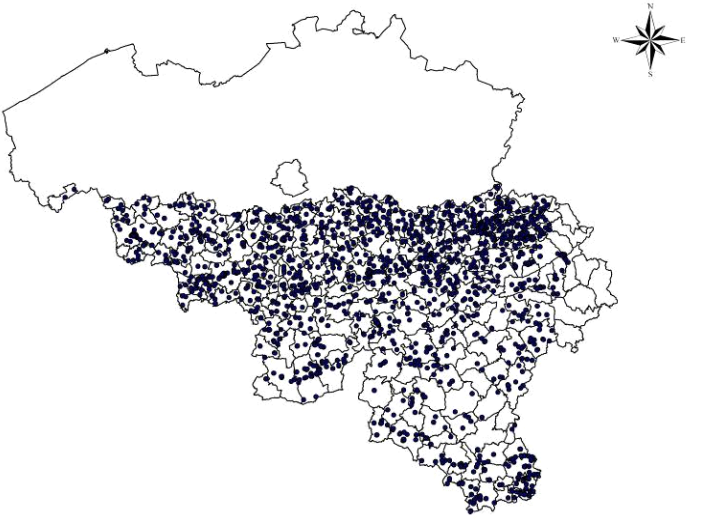

Fig. 1 Listed monuments in Wallonia.

2 Collect on the heritage

Every selected site of collection must be listed. Preferably, the monument or site should be under excavation or study before the restoration. The site must be accessible for sample collection during the archaeological work. In this way, the collection is set up using an accurate protocol employed at all sites. Following these criteria, about twenty sites have been chosen.

2.1 Selection of the monuments

In order to establish the problems and specificities of ancient constructions in the territory of the Walloon region, the collection of samples must satisfy a number of criteria covering a balanced geographic distribution, a chronological distribution, and a distribution according to types of use (Table 1). Following these criteria, 23 sites have been selected. Taken together, these sites are representative of the region's architectural history. More than 60 percent of sample collection has already been carried out.

2.1.1 Geographic distribution

At this point in the study, every province has been represented (Fig. 3). The most important province in surface area, the Hainaut, counts nine sites. Liège, a province that accounts for half of the listed monuments in the region, is represented by seven sites. Some locations contain two or more sites selected for sample collection, including the cities of Liège, Tournai or Nivelles, which are very important. This balanced distribution in the region will also allow a good representation of several geological environments (Fig. 2). Various aggregates and limes were used since Roman period, following geological resources and historic local customs.

Table 1 Data base of ancient mortars in the Walloon Region: list of sites.

Ref.	Province	Town	Site	Type of structure	Civ./ Rel.	Time	Sampled
1	Hainaut	Ath	Rue de la sucrerie	Outer walls	C	post-medieval	✓
2	Hainaut	Ath	Tour Burbant	Outer walls	C	medieval	
3	Liège	Amay	Amay	Church	R	medieval	
4	Liège	Amay	Thiers d'Olne	Fortress	C	medieval	
5	Namur	Doische	Matagne	Sanctuary	R	roman	✓
6	Hainaut	Erquelinnes	Merbes	*Villa*	C	roman	✓
7	Liège	Huy	Ben-Ahin	Castle	C	medieval	✓
8	Liège	Liège	Place E. Dupont	Urban Settlement	C/R	medieval/ post-medieval	
9	Liège	Liège	Seigneur D'Amay	Urban settlement	C	post-medieval l	
10	Lux.	Marche	Hollogne-Waha	*Villa*	C	roman	✓
11	Liège	Modave	Pt-de-Bonne	Fortress	C	medieval	✓
12	Hainaut	Morlanwelz	Mariemont	Castle	C	post-medieval	
13	Namur	Namur	Namur	Castle	C	medieval	✓
14	Namur	Namur	Place M. Servais	Urban settlement	C	roman	✓
15	Brabant	Nivelles	Grand-Place	Churches	R	medieval	
16	Hainaut	Quaregnon	Grand-Place	Church	R	medieval/ post-medieval	✓

17	Namur	Rochefort	Malagne	*Villa*	C	roman	✓
18	Hainaut	Soignies	Soignies	Church	R	medieval	✓
19	Liège	Stavelot	Stavelot	Abbey	R	medieval	✓
20	Hainaut	Thuin	Aulne	Abbey	R	medieval	✓
21	Hainaut	Tournai	Notre-Dame	Cathedral	R	medieval	✓
22	Hainaut	Tournai	Tour H.VIII	Outer walls	C	post-medieval	✓
23	Brabant	Villers-la-V	Villers-la-Ville	Abbey	R	medieval	

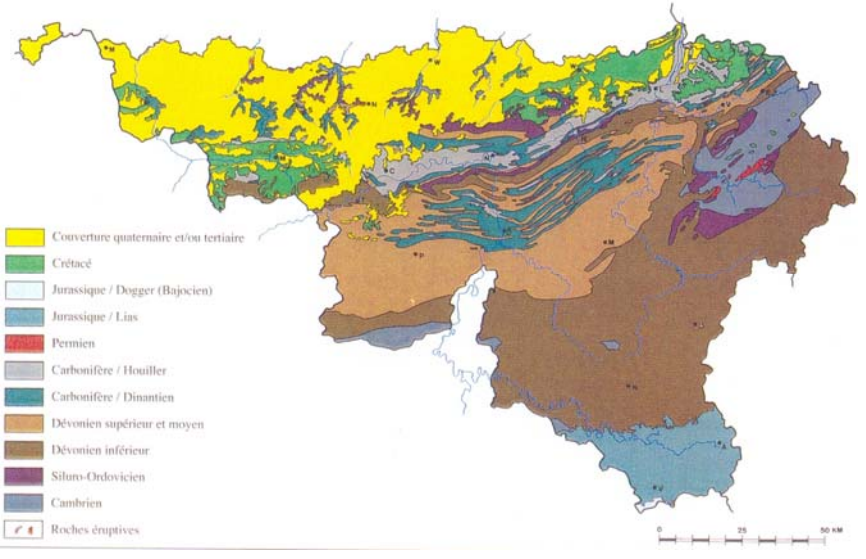

Fig. 2 The Walloon Region's geological subsoil [5].

2.1.2 Chronological distribution

Only five sites in the database date from the Roman period. The limited number is due to the needs of conservation-restoration professionals for specific information. Thus, the most represented period within this study (17th) will be proportionately better covered than others, although our ambition is to cover all periods from Antiquity to the 19th century. Our purpose here is to understand the behavior of all materials and their ageing, even if the restoration concerns essentially medieval and post-medieval buildings.

2.1.3 Types of use

Collected samples also represent the range of distribution according to type of use, both technological (vault, foundation, elevation, coatings) and functional (purpose of the construction: thermal baths, buried chamber, subject to fire, etc.).

Fig. 3 Database of ancient mortars in the Walloon Region: site locations.

2.2 Collection on site

Our project is part of the archeological and heritage program of research in the region. We are working hand in glove with the archaeologists, historians, and architects who study the buildings. Every building in the database counts on several scientists working on the site. The research into ancient mortars must contribute to a better knowledge of the building concerned. This contribution is formalized in a convention that describes how we work and who can use the results.

2.2.1 Choice of questions

If we want to collaborate on a research project, we must define, together, the useful questions for archaeologists and architects. Every site includes its own

series of hypotheses, which can be chronological, functional, or technological. For example, at Grand-place of Nivelles, where medieval remains of an abbey and several churches were found, we can compare the mortars and coatings from every structure and propose a catalogue of the material properties. Moreover, three Roman *villae* at the rural settlements of Merbes, Hollogne and Malagne, and the private thermal baths represented at each site, also will be compared. The materials found in different parts of these buildings, with their cool and heated rooms, probably present specific physical and mechanical properties. Likewise, at Tournai and Ath, two different cities in the same province, two outer walls reworked in the 19th c. can be compared to assess the properties of the mortars from this period.

2.2.2 Sample collection

After defining our questions, we take samples in each representative structure. If possible, we base our sampling on the archaeological interpretation. For example, we take samples from each stratigraphic unit (US). Samples are always taken from the heart of the wall (Fig. 4). If possible, we also take samples from joints and coatings to compare the property of each material on the same structure. In a single site, a church for example, we can take 50 samples. The minimum size is 5 cm^3.

Fig. 4 Sampling in the heart of the wall- Tour Henry VIII- Tournai.

2.2.3 Registration during sample collection

During sample collection, we produce photographs, descriptions, and sketches to describe exactly the location of the samples taken. Each specimen is marked on the structure with a nail, which is reported on a plan (x,y,z).

2.2.4 Packaging

We try to split each sample and reserve one part for potential later chemical analysis. Each part is packed in a bag with its complete references (site, date of sampling, structure, US, orientation, level, type of sample), and all bags are stored in a plastic box. The cover is pierced to reduce humidity within the box.

2.2.5 Description in the database

The database includes 26 criteria. The chief criteria are exact localization, macroscopic description (color, state of preservation, presence of lime, of stones, etc.), tactile estimation of the resistance, and results of analytical tests.

2.3 Physico-mechanical characterization of mortars

The physico-mechanical characterization of historical and contemporary mortars is based on the measurement of their density, their porosity, their sonic wave propagation velocity, and their strength. The methodology for the characterization tests has been described in a previous contribution [2]. We further propose a presentation of the first results.

3 Application: Henry VIII Tower in Tournai

3.1 Site description

The Henry VIII tower was built in the early 16th century by King Henry VIII Tudor (Fig. 5). This tower is the only vestige that survives from the English fortress in Tournai, a city in the South-West of Belgium [6, 7]. This tower was the first military structure built after the appearance of powder artillery. Its diameter is 27.5 meters, and its height is 20 meters. In 1562, the structure was used as a prison, and in the XIXth century it became a military museum. The tower was restored in 1852. In 1963, the tower was listed as a monument by the authorities. In 2007 and 2008, preliminary investigations were begun to prepare for restoration.

In this context, we wanted to collect, in collaboration with the archaeologists, some ancient samples of mortars and study them according to our wide-scale program.

Fig. 5 Henry VIII Tower, Tournai, Belgium (Guy FOCANT © SPW).

3.2 Description of the samples

In November 2008 we collected eleven samples, which are described in Table 2.

Table 2 Tour Henry VIII, Tournai: localisation of the main samples. (*) US: stratigraphic unit.

Ref.	Date	US (*)	Material location
35	XIXth c.	US 029	Stair-shape masonry on the top of the structure
36	XIXth c.	US 029	Mortar under the gutter (from 19th c.) on the top of the structure
37	No date	US 080	Brick-wall in the staircase
38	No date	US 026	external surface of the wall, ground floor
39	XVIth c.	US 004	Middle of the wall of the casemate in the 1st floor
40	No date	US 092	Brick-wall in the end of staircase
41	No date	US 004	Filling of the wall, ground floor
42	XIXth c.	US 029	Stair-shape masonry on the top of the structure

43	XVIth c.	US 097	Stone –wall in the end of staircase
44	XIXth c.	US 094	Filling of the wall
45	XIXth c.	US 029	Wall in the end of staircase

3.3 Tests results

The mortar specimens sampled from the Henry VIII Tower have been studied with the mechanical characterization methodology noted above [2]. Results are presented in Table 3.

Table 3 Physico-mechanical properties measured on mortars specimens sampled in the Henry VIII Tower.

#	Age	Sonic test		Density - Porosity tests			Scratching test	Micro-drilling test	
		Sonic velocity	Dynamic Young Modulus	Porosity	Apparent Density	Absolute Density	Intrinsic specific energy	Weight on bit	Drilling strength
		[m/s]	[MPa]				MPa	N	MPa
35	**XIX**	1977	5748	27.2%	1.9802	2.7188	25.84	17.0	0.868
36	**XIX**	917	874	41.5%	1.3990	2.3913	20.48	6.8	0.346
37		1996	5101	17.4%	1.7227	2.0860	43.74	12.8	0.654
38		1704	3473	23.4%	1.6102	2.1027	17.06	11.3	0.575
39	**XVI**	1735	3249	43.3%	1.4530	2.5639	10.72	4.2	0.214
40		1335	2071	33.7%	1.5651	2.3598		7.3	0.373
41		1175	1429	47.2%	1.3942	2.6393	10.10	1.3	0.066
42	**XIX**	2239	6623	26.4%	1.7777	2.4166	43.59	10.9	0.555
43	**XVI**	1936	4637	25.0%	1.6652	2.2194	29.80	14.4	0.734
44	**XIX**	2182	7055	17.3%	1.9946	2.4127	29.70	11.8	0.601
45	**XIX**	1354	2546	9.2%	1.8702	2.0607	32.58	16.1	0.819

3.4 Discussion

3.4.1 Strength measurement

We can observe high strengths for very old mortars. Strength values are generally under 10 MPa for historic lime mortars. The lowest values (ca. 10 MPa), have been observed for the older samples from the heart of the original building (16th c.). These samples are from the middle swiping of the wall (7m. depth) on the first floor (ref. 39) and the filling of the wall on the ground floor (ref. 41). An important exception is ref. 43, from 16th c., with a strength value near 30 MPa. This sample contains lime (typical white trace in macroscopic observation). The

highest values are related to structures from the 19th c. Macroscopic observation shows a grey colour, typical for the cement used at that period of time.

3.4.2 Density and porosity measurements

More porous samples are related to older structures (ref. 39 and 41). In spite of this, they both present very high values of absolute density. Some tests (DRX, for example) are projected on both samples, to attribute this value to composition (inorganic materials?). Middle range values of porosity (23-33%) are associated with samples from the 19th c. (ref. 39 and 42). These samples have high density measurements. Mortar from under the gutter on the top of the structure (ref. 43), which exhibit interesting strength measurement (near 30 MPa), shows a low porosity even though it dates to an earlier period in the building's history (16th c.). The density of this sample is in the middle range. The samples with lowest values of porosity (ref. 37, 44 and 45) all date to the 16th c.

3.4.3 Sonic velocity measurement

The highest values of Young's Modulus are found in samples from recent structures (19th c., ref. 35, 37, 42 and 44). They are probably all made of cement, a very common material at this time and one known for its high Young's Modulus values. The oldest samples, dating from the 16th c. (ref. 39 and 43), exhibit middle range values. Other samples are difficult to interpret following the chronology of the building. They are dated just as well from the 16th c. (ref. 36 and 45) as the 19th c. (ref. 41).

3.4.4 Tendencies

Some interesting tendencies already have been observed based on the physico-mechanical characterization. Strength properties appear to correlate to porosity and density measurements. Lowest strength and highest porosity seem to be linked. These properties also are connected with the age of materials: the older the material, the higher the porosity and the lower the strength. This is true except for the ref.43, dating from the 16th c., which shows low porosity and proportionally high strength.

4 Conclusion and perspectives

The preliminary results of the analysis of mortar from the Henry VIII tower are widening perspectives for the characterization of historical mortars. Of course, it is too early to use these first results to recommend formulations in restoration. With a rigorous collection methodology based on archaeological principles and a database that is representative of the main research questions, we hope to increase

knowledge of the materials. Our main objective is to improve restoration habits and contribute to chronological, structural, and functional applications in archaeology.

5 Acknowledgements

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I.12

Lime Mortar with Natural Hydraulic Components – Characterization of Reaction Rims with FTIR-Imaging in ATR-Mode

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Abstract Reaction rims of natural hydraulic relicts in historic mortars were investigated using a novel technology, a FTIR-spectrometer equipped with a focal plane array detector enabling in ATR-mode IR-imaging with a spatial resolution of 1.0µm. IR spectra show two regions with main absorption bands at 1280–1580cm^{-1} and 900–1120cm^{-1}. Bands at 1450cm^{-1} and 1396cm^{-1} correspond to the asymmetric stretching of CO_3^{2-}, indicating two different forms of $CaCO_3$; the 900–1120cm^{-1} group of bands is assigned to Si-O stretching vibrations indicating C–S–H phases. The ratio of the integral absorbance of these two main regions of absorption bands shows an inhomogeneous spatial distribution in the reaction rim. Our investigation shows that the reaction rims consist of $CaCO_3$, C–S–H phases and SiO_2 gel in variable proportions. In areas with low carbonate-to-C–S–H phase ratios, carbonate is mainly present as metastable aragonite. The associated C–S–H phases show a comparatively low Ca/Si ratio and a high degree of polymerization. In areas with high carbonate-to-C–S–H phase ratios, both, aragonite and calcite are present. The C–S–H phases show a comparatively higher Ca/Si ratio combined with a lower degree of polymerization. The presence of SiO_2 gel and aragonite indicate carbonation of C–S–H phases. The matrix outside of the cloudy reaction rim consists mainly of calcite. FTIR imaging measured in ATR-mode is a promising method to gain information on the hydraulicity of natural hydraulic mortars in its spatial distribution on a micrometer scale and to characterize the hydration and carbonation products as well.

1 Introduction

The major mineral phase of limestone that is used for the production of lime mortar is calcite [$CaCO_3$]. If silicate phases, in particular clay minerals and quartz, are present in addition, then hydraulic components may form during firing of the limestone, provided that the firing temperatures are sufficiently high. In contact with water these hydraulic components (activated by calcium hydroxide) will hydrate to form calcium silicate hydrate [C–S–H] phases.

The degree of hydraulicity of the binder has an important effect on the properties of the mortar. C–S–H phases are the main hydration products in Portland cement and are mainly responsible for its physical, chemical, and mechanical properties. Although the amount of hydraulic components may be very small in natural hydraulic lime binder (so-called sub-hydraulic binders), their effect on final strength and porosity cannot be excluded [1].

In Portland cement C–S–H appear as extremely variable, poorly crystalline or amorphous phases [2]. The detection of hydraulicity of a natural hydraulic lime binder, especially in sub-hydraulic binders, with common methods such as wet chemical analyses, differential thermal analysis (DTA) or X-ray diffraction (XRD) is difficult. Virtually nothing is known about the nature of the hydration products in sub-hydraulic lime binders.

The degree of hydraulicity of any binder can be quantified with wet chemical methods by determination of the amount of acid-soluble silica [3, 4]. This is considered a proxy for the hydraulic components. Nevertheless, there are limitations imposed on the determination of the exact amount of the acid-soluble silica-content and its interpretation. This is the case (1) when carbonate-bound aggregate is used [4], (2) when very fine grain size fractions of the aggregates (e.g. quartz sand) act as pozzolanic components [5] or (3) dolomitic lime is part of the binder [6].

Alternatively the degree of hydraulicity can be evaluated by differential thermal analysis (DTA), where the weight loss of the binder fraction in the temperature range 200–600°C (loss of water chemically bound to C–S–H or calcium aluminate hydrates) is set in relation to the weight loss at temperatures > 600°C (loss of CO_2 due to decarbonation) [7, 8]. However, to make use of this method, the presence of organic substances, clay minerals, hydrated salts, hydrous magnesium phases (e.g. in dolomitic lime mortars [9]) and relicts of carbonate-bound aggregates whose decomposition would interfere with the release pattern of H_2O or CO_2 must be excluded.

In many cases XRD is not an option for the determination of hydraulicity due to the low modal amount and/or poorly crystalline character of the hydraulic phases.

Even more difficult is the characterization of hydraulic products in their spatial context. SEM investigations on fracture surfaces only reveal the textures along an internal zone of weakness. In polished thin sections C–S–H phases are not

detectable by microscopy. Nevertheless, diffuse cloudy structures [5, 10] and reaction rims around hydraulic particles [6, 11] are taken as indication for the presence of hydraulic phases. While elemental mapping of Si with electron microprobe (EMPA) is able to detect the spatial distribution of C–S–H phases in reaction rims, the detection of C–S–H phases in binder areas is very difficult or even impossible because of the additional presence of very fine grained siliceous aggregates [12].

An alternative method to observe the spatial distribution and the structural character of solids is high resolution Fourier transform infrared (FTIR) microspectroscopy mapping or raster scanning [13].

In this study we characterized the distribution and nature of C–S–H phases in reaction rims with FTIR imaging using the attenuated total reflection (ATR) mode combined with a focal plane array (FPA) detector consisting of 64 x 64 elements. This combination enables a spatial pixel resolution of less than 1 µm.

2 Analytical methods

2.1 Microscopy and electron microprobe analysis

The mineralogy and textures of a representative selection of historic mortar and plaster samples from Western Austria (Tyrol) and Northern Italy (South Tyrol) were studied using polished thin sections.

Identification and quantitative analysis of the mineral phases were carried out by electron microprobe analysis (EMPA, JEOL JXA 8100) in both energy and wave length dispersive analytical modes. Analytical conditions of 15 kV accelerating voltage and 10 or 5 nA beam current were used with spot sizes between 3 and 50 µm to minimize beam damage of the analyzed phases. To study element distributions wavelength dispersive X-ray mapping was performed. In addition to quantitative and mapping analysis, the backscattered electron (BSE) imaging mode was used to study textures and assemblages on a micrometer scale.

2.2 FTIR spectroscopy

IR absorption spectra were recorded at room temperature using a Bruker Vertex 70 FTIR spectrometer combined with a Hyperion 3000 microscope equipped with a Ge-ATR-objective, a focal plane array (FPA) detector, a globar light source and a KBr beamsplitter. The FPA detector consists of 64 x 64 mercury-cadmium-telluride (MCT) detectors, enabling in combination with the ATR-objective FTIR imaging of an area measuring 32 x 32 µm with a spatial pixel resolution of 0.5 µm. Using a FPA-detector, the locus of the measured point is determined by

the position of the detector itself and no optical aperture is necessary. Thus, the spatial resolution of the mid-IR-signal is only limited by the wavelength of the IR-radiation (i.e., approximately 1 µm at 2000 cm^{-1} when an ATR-crystal with an index of refraction of 5 is applied). For each spectrum, 64 scans in the 850 – 3950 cm^{-1} range were performed with a spectral resolution of 8 cm^{-1}. Thus, an area of 32 x 32 µm could be imaged within less than one minute, and by sequential analysis larger areas could be mapped in a few minutes.

Data reduction was performed by defining the high and low wave number margin of an absorption band. In between these two points a linear background was subtracted and the area of the absorption band was calculated. The values of the most characteristic absorption bands were set into relation, colour-coded and graphically displayed as map.

3 Results and discussion

3.1 Microscopy and electron microprobe analyses

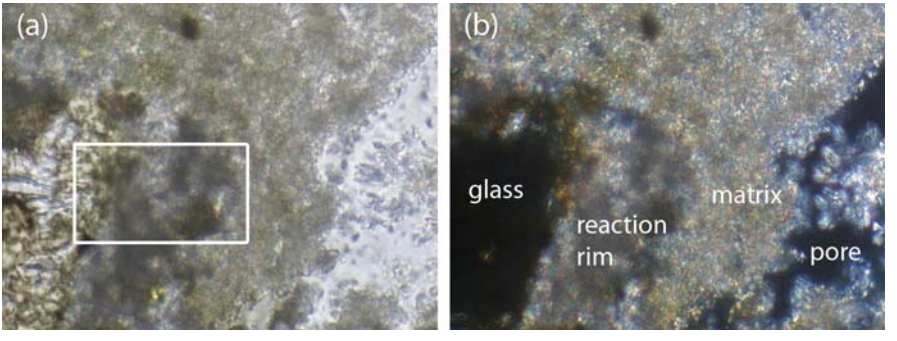

Fig. 1 Thin section photomicrograph with (a) plane polars, (b) crossed polars of an area in a lime lump (Gothic plaster from Finstermünz-Fortress/Austria). A glassy, hydraulic relict (located at the left image edge) is in contact with a cloudy reaction rim and surrounded by a fine grained matrix. Parts of a pore structure are visible on the right hand side. (Field of view 0.18 mm, the frame in Fig. 1 (a) marks the region for the FTIR-imaging).

Optical microscopic images of the investigated mortars often show diffuse cloudy structures in the binder and in binder related particles (lime lumps *sensu stricto* [10]). In some instances transparent glass patches of up to several hundred µm in size (Fig. 1) surrounded by these cloudy structures may also be present.

In a Gothic plaster (~1500 AD) from the Finstermünz-Fortress in the upper Inn-Valley, Austria, the glasses are rich in K and Si (average composition: 67.3 wt% SiO_2; 15.1 wt% K_2O; 7.4 wt% CaO; 6.7 wt% Na_2O; 1.1 wt% MgO and 0.9 wt% Al_2O_3) and frequently contain idiomorphic needles of wollastonite [$CaSiO_3$].

They formed during partial melting of silicates in the firing process of impure limestone. The most likely source of K is mica (biotite or muscovite), which is a very common constituent of siliceous carbonates (marls).

Even though individual phases within the cloudy rims cannot be identified due to their extremely small grain size, BSE-imaging clearly shows a mixture of phases. Elemental mapping reveals that these cloudy rims are Ca- and Si-rich. Large area EMPA with a rastered beam of the Ca- and Si- rich reaction rims yield a wide range in Ca/Si-ratios [12].

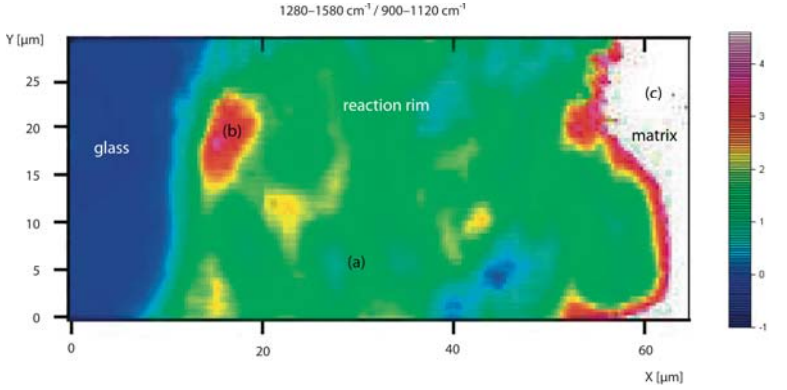

Fig. 2 FTIR-ATR image of the reaction rim (marked area in Fig. 1 (a)): colours (scale bar on the right hand side) represent the ratio of the integral absorbances of the absorption bands in the region 1280–1580 cm^{-1} to the absorption bands in the region 900–1120 cm^{-1}.

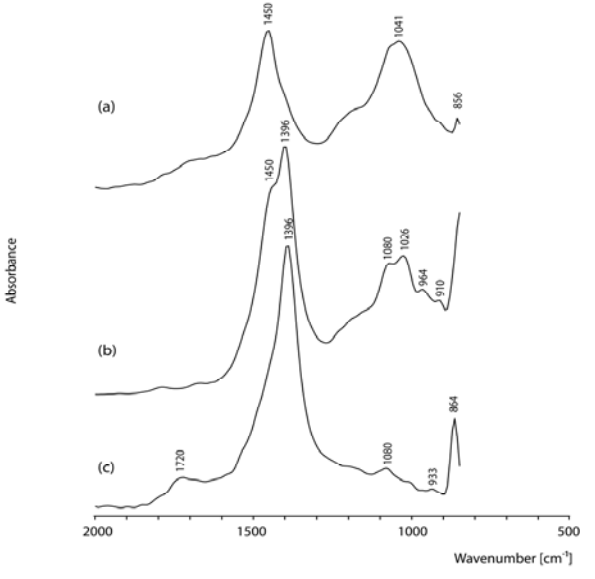

Fig. 3 ATR spectra obtained from areas (a), (b) and (c) in Fig. 2: *(a)* area consisting of aragonite, C–S–H phases and SiO_2 gel; *(b)* area consisting of calcite, aragonite, C–S–H phases and SiO_2 gel; *(c)* area next to the reaction rim (within the white area in Fig.2), dominated by calcite.

3.2 FTIR spectroscopy

For FTIR analyses two groups of bands were selected: group I in the range of 1280–1580 cm^{-1} is assigned to carbonate phases, group II in the range of 900–1120 cm^{-1} is assigned to C–S–H phases. To detect the relative proportion of carbonates and C–S–H phases in the cloudy reaction rim (marked area in Fig. 1), the modal amount of these phases is then deduced from the area ratios of these groups of bands and are graphically displayed as map in Fig. 2. The map shows an inhomogeneous spatial distribution of the areas intensity ratios, whereby cold colours represent high II/I-ratios and warm colours (including pink and white) represent high I/II-ratios, respectively. Representative ATR spectra from the reaction rim and from the surrounding matrix were extracted and are shown in Fig. 3 (a), (b) and (c).

All ATR spectra show bands at 1450 cm^{-1} and/or 1396 cm^{-1}. These bands can be attributed to the asymmetric stretching (ν^3) of CO_3^{2-} in carbonates: the band at 1396 cm^{-1} to calcite; the bands at 1450 cm^{-1} and 1080 cm^{-1} to aragonite. This assignment is consistent with results from X-ray diffraction, where both polymorphs of $CaCO_3$ were detected in corresponding powder probes. The main bands at 1450 cm^{-1} and 1396 cm^{-1} are shifted towards lower wave numbers compared to literature data obtained by KBr-technique [14, 15], but compare well to ATR spectra from the RRUFF database [16].

Both spectra Fig. 3 (a) and (b) in the cloudy reaction rim show bands in the region of 950–1100 cm^{-1} and a shoulder at ~1200 cm^{-1}. These bands are related to the presence of silica compounds. The bands at 950–1100 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of Si–O bonds. C–S–H phases contain a characteristic set of bands centered at ~970 cm^{-1} which are assigned to Si–O stretching vibrations of the Q^2 tetrahedra [15]. Yu et al. [15] show that this group of bands is shifted systematically towards higher wave numbers with decreasing Ca/Si ratios. They further show that in a mixture of C–S–H phases and SiO_2 gel the Si–O band broadens, and the main position is shifted towards higher wave numbers. The shift of the Si-O band reflects a higher Si content and a higher degree of polymerization due to the presence of Q^3 and Q^4 sites in the SiO_2 gel. The occurrence of Q^3 sites is also specifically related to a broad shoulder at 1200 cm^{-1} [15]. Based to BSE imaging and elemental mapping [12], which reveal that the rim consists of newly formed Ca- and Si-phases, the 1041 cm^{-1} band in spectrum (a) and the bands at 964 cm^{-1} and 1026 cm^{-1}, respectively, in spectrum (b) are attributed to C–S–H phases. This interpretation is in agreement with Yu et al. (*op. cit.*).

In spectrum Fig. 3 (a) the main band in the 950–1100 cm^{-1} region is centered at 1041 cm^{-1} and is very broad. This indicates a high Si content of the C–S–H phases and, in addition, the occurrence of polymerized SiO_2 gel. The presence of SiO_2 gel is also consistent with the broad shoulder at 1200 cm^{-1}.

In spectrum Fig. 3 (b) bands at 910, 964, and 1026 cm^{-1} are assigned to Si–O stretching vibrations at Q^2 sites of the C–S–H phase. The band at 1080 cm^{-1} is

attributed to aragonite. Again, the shoulder at 1200 cm^{-1} is assigned to Si–O stretching vibrations in Q^3 sites of SiO_2 gel. The group of bands at 964–1026 cm^{-1} is shifted towards lower wave numbers, which might be due to a lower Si content of the C–S–H phases and a lower degree of polymerisation. In both areas (a) and (b) of the reaction rim, the presence of SiO_2 gel and aragonite indicate carbonation of C–S–H phases as observed in carbonated cement pastes [17].

Spectrum Fig. 3 (c) obtained from matrix (Fig. 1 (b)) is largely dominated by calcite.

4 Summary and conclusion

K- and Si- rich glasses are present in the binder of ~500 year old mortars and plasters. The glasses formed during partial melting of silicates in the firing process of impure limestone. The reaction rims around the glass patches indicate that they act as hydraulic components, forming C–S–H phases.

With FTIR-ATR imaging the spatial distribution of different phases in a reaction rim was determined on a micrometer scale.

Our investigation shows that the reaction rims consist of $CaCO_3$, C–S–H phases and SiO_2 gel in variable proportions. In areas with low carbonate-to-C–S–H phase ratios, carbonate is mainly present as metastable aragonite. The associated C–S–H phases show a comparatively low Ca/Si ratio and a high degree of polymerization. In areas with high carbonate-to-C–S–H phase ratios, both, aragonite and calcite are present. The C–S–H phases show a comparatively higher Ca/Si ratio combined with a lower degree of polymerization. The presence of SiO_2 gel and aragonite indicate carbonation of C–S–H phases. The matrix outside of the cloudy reaction rim consists mainly of calcite.

FTIR imaging measured in ATR-mode is a promising new method to gain information on the hydraulicity of natural hydraulic mortars in its spatial distribution on a micrometer scale and to characterize the hydration and carbonation products as well.

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I.13

Ancient Wall Plasters Found in Archaeological Excavations in Marseilles (France): Evolution of Techniques and Materials

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Abstract A multidisciplinary research project has been initiated to study wall plaster fragments found in recent archaeological excavations in Marseilles. The chemical, petrographical and physico-chemical characterization of these mortars allows the determination of their evolution and their processing techniques from the ancient Greek city of the 6th century BC until its Romanization in the 3rd century AD. Several important steps are apparent within the plaster fragments; these show a gradual development from the earth plasters associated with earthen architecture, to the gradual introduction of lime, crushed tiles or bricks as a pozzolanic material and the use of various aggregates, to the use of pure lime plasters with siliceous sand and pozzolanic material.

1 Introduction

The Archaeological Department of the City of Marseilles and the Inter-regional Centre for Conservation and Restoration of Cultural Heritage, in collaboration with the National Institute of Preventive Archaeological Research, have initiated a research program to study the wall plasters from Marseilles (painted wall plaster and mortar) which date from after its Greek foundation until its Romanization.

Since 2005, the materials discovered in up to ten archaeological sites throughout the city have been systematically studied. Mineralogical and physio-chemical analysis has been performed on selected samples in order to describe their materials, technical design, implementation and evolution. Three major phases of mortar design are apparent; these relate to the following temporal

periods present during the development of the city between the 6th century BC to the 3rd century AD:

- throughout the period of Greek Marseilles, first Archaic then Hellenistic
- the Late-Hellenistic and Augustan period
- during Roman times

A synthesis of results will be presented for each of these three phases and a conclusion providing information regarding specific techniques found in several sites, will also be provided.

2 Methodology

Pluricentimetric fragments of wall plasters found in secondary position demolition layers or filling layers have been dated by the ceramic objects contained within these layers or in the level of origin. The chronological processing was of course more difficult on these fragments than it would have been for coatings still in place, but at the same time, there was a reluctance to use some of these scattered remains for the investigations.

Each fragment was described under a stereo microscope. Chemical elemental analyses were carried out by micro-fluorescence (μXRF, ARTAX/BRUKER, source Rhodium, 50Kv-800μA with a collimator diameter of 600μm under helium flow (magnesium being the lightest detected element)) directly on the mortars and paintings to determine their bulk composition. Some sample fractions were ground for X-ray diffraction analysis (BRUKER D8 Focus, Co, 40mA-35Kv, Lynxeye detector). Samples were cut by sawing in order to make cross and thin sections that were observed under a petrographic microscope. Micro-Raman analyses were both performed on these preparations or on grains, mainly for the identification of pigments. Samples were also observed under a scanning electronic microscope (SEM/LV, FEI Philips XL30, LaB_6) fitted with a microanalysis probe (Energy Dispersive Spectrometry EDAX 4). The size distribution of aggregates was made by sieving after the dissolution of the carbonates using dilute Hydro-Chloric acid, HCl (15%).

3 Earth-based plasters in Greek Marseilles

3.1 Archaic Greek Marseilles

The only ancient text referring to the construction techniques of ancient Marseilles is that of Vitruvius [1] detailing the specific use of mud, for both the design of roof daub and adobe for the walls. Analyses were performed on the earth

plaster of two sites of the Archaic Period: *Place de la Madeleine* and *College Vieux-Port* (Fig. 1), where the building is probably connected to worship.

In the site *Place de la Madeleine* [2], some fragments of earth plaster have been found in the filling of an archaic structure dated to 575-550 BC. They consisted of fragments of daub showing superficial traces of a red colouring. The mortar, which contained some vegetal fibres, was a mixture of an orange clayey and sandy earth and a brown calcareous earth. This coating was spread in two layers each 6mm thick. The mineralogical analysis showed the predominance of calcite associated with quartz, and a muscovite/illite mineral. Chemically, traces of titanium, zinc and sulphur were systematically detected.

At the site of *College Vieux-Port* [3], dated from the early 5th century BC, the wall plaster material was a mixture of slightly dolomitic, gypseous clayey earths of different colours with a rather similar elemental composition. The presence of kaolinite and the extreme brittleness of the earthy matrix confirmed that it was not fired. The analysis of the brown earth revealed mainly calcite associated with quartz, dolomite, clay minerals (smectites, kaolinite, muscovite/illite), traces of gypsum and feldspar. The grey portions of earth also included organic components and looked like a marine mud deposit. The enrichment in calcium and the mixture of different earths play a stabilizing role for the material and serve to reduce cracks which are due to shrinkage [4].

This mix of brown and dark grey earth was found within the adobe and joints of the masonry. These plasters contained fine sand or silt (added or naturally present in the soil), and rounded quartz sand with many mollusc shell fragments, which serve to indicate a marine origin.

Fig. 1 The archaic painted plaster on the site of *College Vieux-Port* (Photography S Mathie, INRAP)

These archaic plasters had received a fine grey earth finishing layer which contained less sand, or a white lime-based layer, prior to the application of the blue (Egyptian Blue, cuprorivaite mineral) or red (red ochre) paint. The elemental composition of the grey finishing layer and the plaster were close, with calcite as the main phase associated with quartz, dolomite, mica/illite, smectite and kaolinite clay minerals. The materials were probably of a local origin. They had the same composition as the Stampian marls collected on the site. Both contained calcite,

quartz, dolomite, traces of gypsum, mica and kaolinite minerals. These mixed earth based materials were still used throughout the Hellenistic period.

3.2 Hellenistic Greek Marseilles

Earth plasters were also found in the domestic habitations of the Hellenistic period. Plasters from two close sites, *Tunnel de la Major* and *Esplanade de la Major*, were studied.

The layer of demolition of the house J, *Tunnel de la Major* [5], following the last occupation of the 3rd century BC, included some rather compact fragments of painted earth plaster. The blue, red or white paint layer was applied upon a thin white layer of lime showing a slight relief.

The fragments of earth plaster painted in blue (Egyptian blue) from the site of *Esplanade de la Major* [6], have been found in the filling materials of the Augustan levels; however these were found to have come from an earlier occupation. The plasters made of clay, lime and sand, were 5mm thick and very brittle. They were covered with a white lime-based layer. Above them, decorative reliefs made with the same earth as the bottom layer, were painted in black and blue.

4 Plasters made of earth, lime and crushed tile and brick in the Late-Hellenistic – Augustan period

At the last quarter of the 2nd century BC, which corresponds to the creation of the Roman Province of *Narbonensis* after the Roman conquest of the region, two new elements appeared in the composition of earth plasters: lime and crushed tile or brick. The addition of these compounds makes them harder and more resistant than simple earth plasters. These coatings have been observed at several archaeological excavations from Marseilles: *Bourse, Pistoles*, *Tunnel de la Major*, *Esplanade de la Major*, and *Place de la Madeleine*.

In *Esplanade de la Major*, very hard earth–based coatings painted in red were discovered in the fillings of the end of the Hellenistic / Augustan period. The matrix had a pinkish colour and was a mixture of lime and earth. The coating contained approximately three volumes of lime and about one volume of insoluble residue. This residue consisted of a very thin clayey earth with particles less than 0.15mm. The aggregates were composed of thin quartz sand with a few crushed tiles or brick (particle size less than 4mm). The analysis confirmed that the earth was unfired and indicated calcite as a main compound, associated with quartz, mica, dolomite and feldspar. The pigments were applied *al fresco* on a very thin layer of lime.

Excavations within the habitations of *Place de la Madeleine* provided a few fragments of painted plaster which were made of earth and lime. The observation

of polished cross sections showed a mixture of lime, unfired clay, some rounded crushed tile or brick and angular quartz sand of 0.2mm in average diameter, with a few rounded coarser grains (1mm in diameter).

The habitations of the late Hellenistic period (end of the 2nd century AD), at the site of *College Vieux-Port*, had also provided fragments of a pink wall plaster covered by red or black painting. This coating was relatively hard, resistant and compact. The pinkish matrix seemed to be a marly earth extracted locally from the Stampian marl formation, and mixed with lime; it was seen to contain quartz, calcite, muscovite/illite, a low proportion of kaolinite clay minerals, feldspar and traces of gypsum. The analysis, which did not show any dolomite, indicated a source of marl different from that used during the Archaic period. The aggregate was composed of an angular quartz sand of a very fine particle size (50% was less than 0.18mm in diameter) with a few coarser grains. The amount of lime was relatively large: two volumes of lime for one volume of sand. The material also included a few crushed tiles or brick with a grain size between 2mm and 0.25mm, mica, charcoal, nummulite microfossils (also present in Stampian marls), and a few grains of red ochre pigment.

5 Roman plasters based on lime, sand and crushed tile or brick

The Roman plasters have been studied from two major sites, *Ilot 9* [7] and *Rue François Moisson* [8], where coatings were found as fallen fragments on the ground. They were made of two layers, each 10mm thick, of lime mortar with quartz sand and sometimes a few crushed tiles or brick inclusions. The grain size was coarser than in the Hellenistic period. The sand was very clean and rounded, which implied a fluvial or marine origin. Vitruvius [1] advised the use of crushed tile: "*If one wished to add to the river and sea sand a third part of crushed and sieved tile, this would produce a mixture of an even better use*."

Fragments of painted plaster, collapsed on the floor of a *domus* on the site of *Ilot 9* (first half of the 1st century AD) showed a mortar made of lime and sand. The mortar was spread in two layers of different compositions. The lower layer, 10mm thick, was a white lime mortar with a 1 to 1.5 volume of lime for 1 volume of rounded quartz sand, with a few fragments of crushed tile or brick with a grain size of 0.25 to 4mm. The average diameter of the aggregate was 0.85mm, with less than 3% under 0.15mm. The upper layer was a pinkish mortar, 10mm thick; its matrix was composed of lime (2 to 3 volumes for 1 volume of sand) and powdered tile or brick with the addition of rounded quartz sand.

On the site of *Rue François Moisson*, the painted plaster collapsed on the floor of another *domus*, of the late 1st century AD - 2nd century AD, was made of two layers each 10mm thick. The mortar matrix was white, lime-based (from 1.5 to 2 volumes for 1 volume of sand), with fine to coarse rounded sand, a few crushed

tiles or brick and many echinoderm spicules suggesting a marine sand. About 40% of the aggregate were grains larger than 2 mm.

6 Specific techniques

6.1 The struggle against humidity

Humidity affects both the comfort and the durability of a building; construction techniques against humidity appeared as early as the Hellenistic period through the use of insulating materials such as ash or crushed pozzolanic material. Such material was found within several of the sites in Marseille.

At *Ilot 9,* under the decorative painting of the median part of the wall of a *domus* , (first half of the 1st century AD), was an upper pinkish layer of plaster which was seen to contain about 8% of broken tile dust. Such addition of pozzolanic material (crushed tile or brick), might have been done with the intention of providing the coating with hydraulic properties in order to prevent its degradation. The installation of terraced housing within a damp environment in this sector of the town probably required such protection.

The plinths were subjected to more specific treatment. In the *domus* of *Rue François Moisson*, dated from the second half of the 1st century AD, ash was added to the lower layer at the bottom of the walls in order to prevent moisture; such a technique has been referred to within Vitruvius [1] and had already been used in the Hellenistic house G of *Tunnel de la Major*, 135 BC.

Fig. 2 Place de la Madeleine. Floor and walls in *opus signinum* (Photography LF Gantès)

Plinths covered with a Roman concrete *(opus signinum*) were a common feature within many of the excavated sites. This kind of mortar was recommended by Vitruvius [1] for the bottom of the walls up to a height of three foot, for rooms located on the ground floor, in order to reduce damage caused by moisture. The

opus signinum was also used as a flooring material within the late Hellenistic (2nd Century BC) houses of *Tunnel de la Major* and *Place de la Madeleine* (Fig. 2).

Analyses were performed on the wall plaster of one such house in *Place de la Madeleine*. It was a very fine, dense and extremely hard (resistant) pozzolanic mortar. Lime (2 volumes of lime for 1 of aggregate) and pozzolanic material (60-75% of residue had a particle size less than 0.06mm) was mixed with a small portion of sand and a few coarser fragments of crushed tile or brick (less than 4mm in diameter). This coarse mortar was made from 2 volumes of lime, with an aggregate consisting of 1/3 volume of sand and 2/3 volume of pozzolanic material. It was applied in two layers; the bottom layer, containing mica minerals (muscovite, illite) and a smaller amount of sand, was weaker than the upper layer. The latter contained twice the amount of sand and traces of kaolinite clay minerals, but no mica or illite. Kaolin fired clay is known to react better with lime than illite, the use of which may have lead to disintegration [9, 10].

The hardness of the upper layer may be due to a superficial strengthening treatment like beating. Since the firing temperature did not completely destroy the clay, one could assume that the tiles or bricks were fired at a low temperature (below 700°C). Such clays, when fired at low temperatures, prove to be more reactive as pozzolanic materials [10].

6.2 Improvement of adhesion

Traces corresponding to surface patterning on the wall or on a lower layer have been preserved on the back of the Hellenistic earth or lime plasters from the site of *Esplanade de la Major*. Such a surface treatment could have been used to improve the adhesion of the plaster prior to application. An alternative system, with fragments of amphora embedded in the earth masonry and in the plaster, has been identified at the sites of *Tunnel of Major*, (Hellenistic period), *Rue Trinquet* [11] (second half of the 1st century AD), and in the *domus of, Rue François Moisson* (late 1st century AD - 2nd century AD).

6.3 The treatment of the finishing layer

In some cases, the finishing layer received a specific treatment according to the colour of the paint layer: for example, the blue paint layer (Egyptian blue) of the earth plaster at *Esplanade de la Major* was applied over a grey earth layer in order to darken the blue pigment. White marble grains were also seen to be introduced within some of the mortars to make their surface glitter. Vitruvius [1] made reference to how such marble was prepared for use: *"We crush the chips with iron hammer, we sift them into three kinds of powder"*.

At *Rue François Moisson*, the blue paint layer of the wall plaster of the *domus* (late 1st century AD - 2nd century AD) was applied to a grey earth-based layer that contained fine marble grains. The marble served to highlight the blue and brought

a shimmering glow to the paint. The same technique was applied at *Esplanade de la Major* and *Ilot 9* where yellow paint was applied over a finishing layer containing crushed marble. Occasionally, the yellow paint layer was applied on a pink upper layer to provide a colour enhancement. Micro-analysis on fragments of the pink coat from *Rue de la République Nord* [12], showed that the pinkish colour was the result of the presence of iron, most probably pure hematite or red ochre.

7 Conclusions

This study allowed for the distinction between the three major developmental phases of plastering in Marseilles, to be made. Throughout the Greek period, the city continued the tradition of earth-based architecture and plastering. The use of lime was limited to elements of decorative stucco work only and the material used was of a local origin.

At the end of the Greek period, which corresponds to the creation of the *Narbonensis*, crushed tile or brick and lime were added to improve the durability of earth-based plaster. Finally, with the Roman phase of the city, coatings based on lime, sand and a few crushed tiles or brick became usual; as is seen throughout Roman Gaul. Specific techniques to enhance the comfort or durability of the construction, were also seen to appear throughout this period

These studies served to both trace and understand the techniques of building, and served to provide an aid in dating such material. The analytical data collected on wall plasters can also to be taken into account in terms of compatibility, when modern materials are going to be used for the consolidation and the restoration of ancient buildings.

It must be pointed out that the study of earth plaster is still rare because of the very bad state of conservation of such brittle and fragile coatings. Careful excavation methods and sampling techniques are crucial to their preservation and study. Complementary studies are suitable for this kind of material, especially for clay quarries.

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I.14

Hydraulicity in Historic Lime Mortars: a Review

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Abstract Natural hydraulic limes were used in ancient times and are still produced nowadays. A comparison of the chemistry and mineralogy of currently available NHL2 and NHL5 limes indicate that there are no clear differences except for the amount of 'undefined material', mainly consisting of an amorphous phase. The chemical composition of these different limes is nearly identical. However, the classification of ancient hydraulic limes is mainly based on their chemistry, obtained from the analysis of ancient mortar binders. Moreover, it is shown that the phase composition of these limes evolves with time. This makes their classification uncertain and difficult.

1 Introduction

A variety of binders have been used in the past (Fig. 1). The oldest types; clays and bitumen, were readily available. Materials needing heating and subsequent mixing with water before application were used subsequently. The use of plaster (hemi-hydrate: $CaSO_4 \cdot 0.5H_2O$) probably dates back earlier than the use of lime since its production from gypsum requires lower temperatures compared to the production of lime from limestone and was therefore easier to obtain. Both binders harden in air.

A next step in the development was the manufacture of `hydraulic' binders obtained by mixing lime with pozzolans. `Hydraulic' refers to the ability of the binder to harden under water [1]. More recently, other types of hydraulic binders are obtained; either by burning an impure limestone or by mixing Si- and Al-bearing materials with a pure limestone and burning them together.

Although the hydraulicity of ancient mortars provides us with technological information or with indications for their restoration, it appears very difficult to

measure. This article starts with a tentative definition of hydraulicity and then discusses the chemistry and mineralogy of some commercial hydraulic limes that are presently available on the market. Afterwards, a survey will be provided on the current knowledge about ancient hydraulic mortar technology and finally an overview of the methods that have been used to identify and measure this hydraulicity in ancient mortars will be given. The last part of the paper shows, with an example, that the hydraulicity of ancient mortars cannot always be determined unambiguously. Less attention will be paid to the addition of pozzolanic materials to lime. This subject was treated by for instance Charola and Henriques [2].

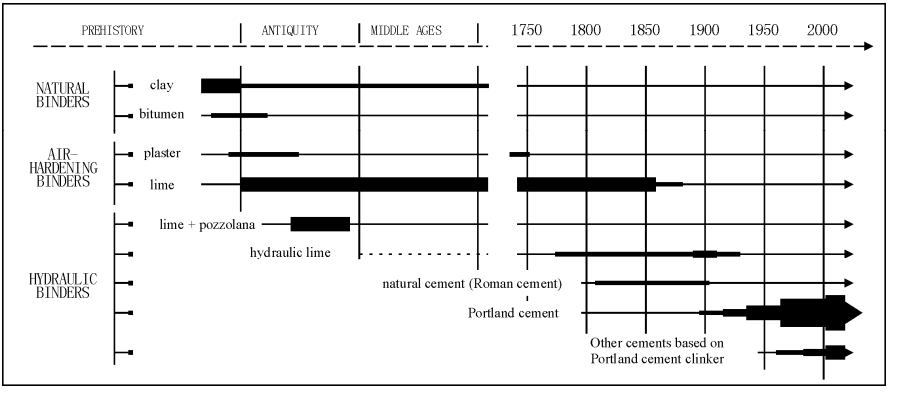

Fig. 1 Use of binders during history (Adapted from [3])

2 Definitions

Hydraulic limes are limes containing enough free CaO to be slaked with water and capable of setting under water. A minimum amount of free CaO must be present in the calcined product to reduce the entire mass to a powder when it is slaked [4]. The combination of the free CaO with water induces an expansion that leads to the disintegration of the freshly burnt limestone. The maximum amount of free CaO is determined by the second condition. If too much free CaO is present, the product will not be able to harden under water. There is a large range of products complying with this definition. They are most commonly classified according their chemical composition and more specifically to their Cementation Index 'CI' (Equation 1) or Hydraulicity Index 'HI' (Equation 2). Boynton [5] proposed a classification into 'feebly', 'moderately' and 'eminently hydraulic' limes based on their Cementation Index. In the actual European norm (EN459-1:2001), the following classes of natural hydraulic limes with pozzolanic additives are defined; NHL2, NHL3.5 and NHL5. However, they do not correspond to

Boynton's classes and tend to neglect the 'feebly hydraulic limes'. As the strength of the binders is tested at 28 days, according to the norm, 'feebly hydraulic' limes tend to be omitted because their final strength is only attained at longer curing times. The main reason is that carbonation plays a major role in their hardening. Carbonation is generally a much slower process than the hydration reactions that are dominant in the more hydraulic binders. This has important implications for the restoration of constructions where 'feebly' or even more feebly hydraulic binders have been used. Lindqvist [6] therefore defined the class of sub-hydraulic mortars, having a hydraulic character between that of the pure air limes and the 'feebly hydraulic limes' defined by Boynton [5].

$$CI = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{CaO + 1.4MgO} \quad (1)$$

$$HI = \frac{SiO_2 + Al_2O_3}{CaO} \quad (2)$$

The term `hydraulic lime' was first suggested by Vicat. `Lean lime' and `water lime' were terms used previously.

Hydraulic limes can also be produced by adding pozzolans to non-hydraulic limes. This technique was known since ancient times and was revalued during the Renaissance. However, only since the 18th and mainly during the 19th century, the use of pozzolans in lime for water-related structures or foundations became common practice. Pozzolans react with the $Ca(OH)_2$ in the lime to form reaction products similar to those formed in the previously defined natural hydraulic limes (NHL2, NHL3.5 and NHL5).

3 Present-day Natural Hydraulic Limes

Currently, natural hydraulic limes (NHL's) are only produced in a few places in Western Europe. Actual production is for instance done by Otterbein and Hessler-Kalkwerke in Germany, by CIMPOR in Portugal, by Singleton Birch and Roundtower in the UK, by the SOCLI-group, Lafarge, Boehm and St. Astier in France and by Tassullo in Italy. Some of these, as well as some other companies as Unilit, sell pre-mixed mortars and concretes based on natural hydraulic lime. The mineralogical composition of some of these limes has been plotted in Fig. 2. Part of the data in this figure were obtained from the Rietveld refinement of the X-Ray Powder Diffraction (XRPD) patterns of the natural hydraulic limes after mixing them with an appropriate crystalline standard (10wt.% ZnO). The other part of the data, marked with an asterisk, was obtained from Kraus et al. [7]. Their quantitative phase analyses were obtained from the chemical and XRPD data.

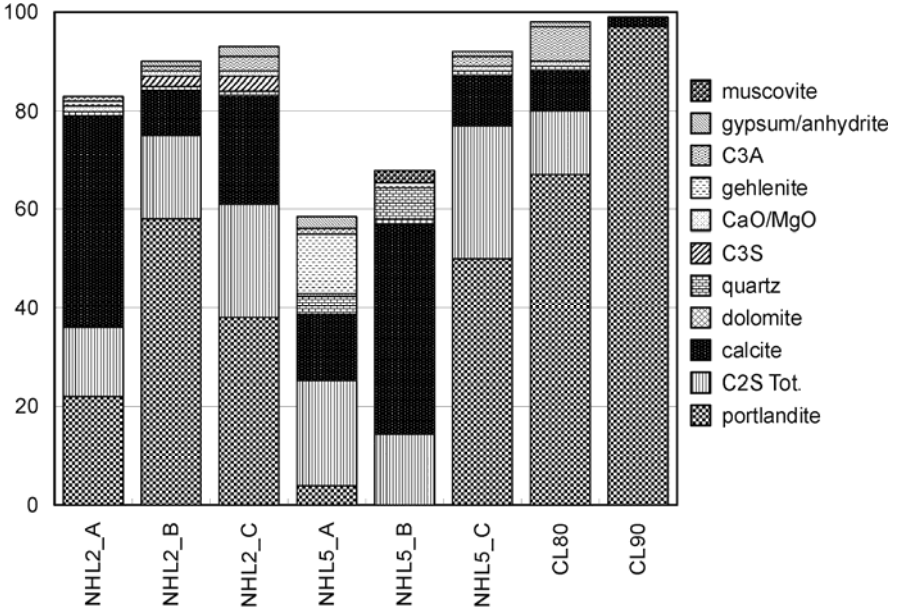

Fig. 2 Mineralogical composition of the studied limes: NHL2 and NHL5 samples are classified as hydraulic, CL80 and CL90 as non-hydraulic.

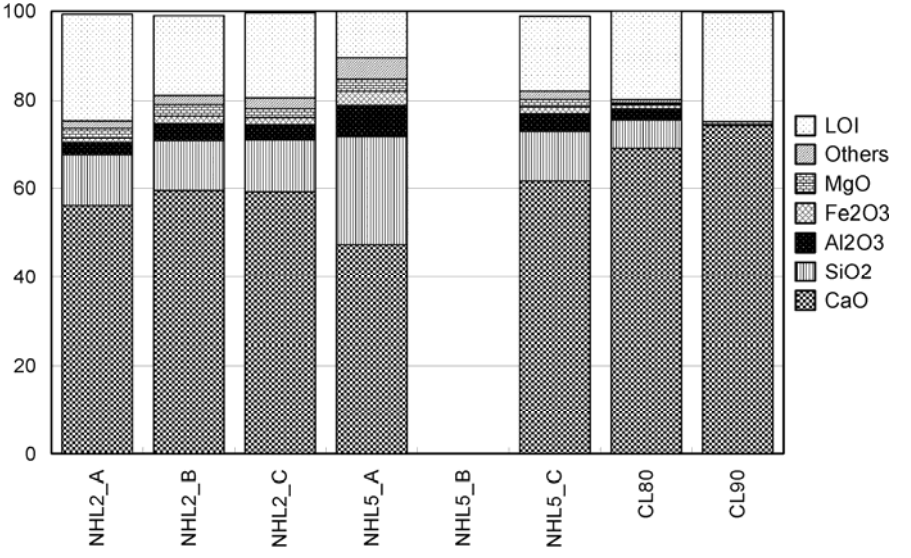

Fig. 3 Chemical composition of the studied limes: NHL2 and NHL5 samples are classified as hydraulic, CL80 and CL90 as non-hydraulic.

The chemical composition of the NHL's can be found in Fig. 3. For comparison, the composition of two non-hydraulic limes ('CL80' and 'CL90') is plotted in the same figure.

From these data it appears that there is no clear correlation between the mineralogy and the type of lime. However, the portlandite content in the non-hydraulic limes is higher than that in the hydraulic limes. Although 'CL80' is classified as non-hydraulic, Kraus et al. [7] identified considerable amounts of C_2S and C_3A. These minerals are mostly characteristic for hydraulic binders. Nevertheless, the concentration of C_2S and C_3S in the non-hydraulic limes is lower than in the hydraulic ones. In accordance with this, higher SiO_2 contents are observed in the hydraulic limes compared to the non-hydraulic limes.

The only clear difference between the NHL2 and the NHL5 samples lies in the amount of 'undefined material'. Most of it consists of amorphous material, although it possibly includes a small amount of undefined minerals that could be overlooked in the XRD spectra. Nevertheless, the amount of 'undefined material' appears to be generally higher in the more hydraulic NHL5 samples compared to the NHL2 samples. No clear difference could be observed between the chemistry of the NHL2 and NHL5 samples. The content of the main elements in NHL5_C for instance is similar to that in NHL2_B and NHL2_C. This is an indication that the chemistry alone is probably insufficient to give a clear indication about the hydraulicity of the sample.

4 Historical use of hydraulic lime mortars

4.1 Pre-Middle Ages

The Greek knowledge of the use of highly siliceous, volcanic Santorin Earth (pozzolans) goes back to 500-300BC [8]. The use of pozzolanic materials in mortars used in the construction of draining canals dated 400BC, has also been noticed in Olynthos, on the continent more to the north of island of Santorin [9]. In Eastern civilizations, rice husk ash was used as a pozzolan [10]. Other Greek mortars, in which no pozzolans were used, were found to be extremely hard. This is perhaps due to the quality of the limestone, which was of lower purity compared to that used by the Romans [11]. To the Romans, the best lime was that produced from pure limestone.

Around the 3rd century BC, Roman builders discovered how to make hydraulic mortars [12]. A natural deposit of reactive 'sand', similar to that found by the Greek on the Island of Santorin, was discovered near the Mount Vesuvius. This 'pulvis puteolanus' ('earthy material from Puteoli') survived in many languages as 'pozzolana'.

Hydraulic mortar and concrete was used on land by the later 3rd century BC [13]. Whenever pozzolanic materials were not available and a mortar insoluble in water was needed, the Romans used a mixture of hydrated lime and crushed ceramics. Many names have been used to designate these crushed ceramics over the world; Horasan in Turkey, Surkhi in India, Homra in arabic countries and cocciopesto in Italy [14, 15]. The most common name for this type of mortar is `opus testaceum' [16, 17].

In a few areas, `sands' resembling those found near the Mount Vesuvius, such as for example Trass, were used to produce hydraulic mortars. During Roman dominion, little seems to have changed to preparation techniques and mortar composition [18]. After Roman times, a clear uniform mortar and lime composition is lacking.

Even though studies about medieval mortars are scarcer than those treating of mortars and mortar technology from classical antiquity, it appears that great differences exist in their composition. Whereas medieval mortars from Pamplona (Spain) appear to be non-hydraulic [19], others from Crete (Greece), for instance, show a clear hydraulic character [20]. Even in the same area, such as for example in the city of Pisa, both mortars with a marked hydraulic character as mortars prepared from non-hydraulic lime have been used alternatively without any apparent reason [21].

However, studies from a 16th century dockyard in Venice (Italy) indicate the deliberate use of hydraulic lime for foundations and air-lime for indoor masonry [22]. Mortars made with hydraulic lime also seem to be used deliberately in Ottoman baths in Budapest during the same period [23]. Whereas the only hydraulic mortars known from the Roman era are those made from pure lime mixed with pozzolans, medieval hydraulic mortars appear to be prepared either from the addition of pozzolans or from burnt and slaked clay-bearing limestone [24]. Moreover, there are indications of the use of a variety of pozzolanic additions, ranging from the classical crushed ceramics [22, 25] over volcanic ashes [25, 26] or metamorphosed soils (agghiara; see [27]) to the addition of fine opal-A ($SiO_2 \cdot nH_2O$) from unclear origin [28]. The use of specific deposits with pozzolanic properties, known from Roman times, such as for instance Trass - knows a certain revival during the Middle Ages [29, 30].

Blezard [31] identifies a gradual decline in the quality of the mortar after Roman times, throughout the Middle Ages and notes that mortars in Saxon and Norman buildings often show evidence of bad mixing and the use of imperfectly burnt lime. By contrast, some authors [26] claim that the use of particular sands, rich in volcanic ashes, in south-Italian mortars from the 10th-11th century testify a deep knowledge of the raw materials and a deliberate selection of building materials.

During the Renaissance, the ancient techniques are revalued [17, 31]. Moreover, contemporaneous writings testify of the deliberate use of hydraulic limes prepared from impure limestone. Beside the `white lime' (pure lime), `dark lime' (hydraulic lime) was obtained from the calcination of grey and dark

limestones as substitutions of pozzolans (Palladio, 1570 and Scamozzi, 1615 in [32]).

From this, it appears that conflicting ideas and perceptions about the technological knowledge and practices in the Middle Ages exist.

4.2 Post-Middle Ages

The first detailed investigations carried out in the field of hydraulic limes made from impure limestone were those of John Smeaton. His investigations in 1756 led to the discovery that mortars with limes made from impure limestone gave the best results. By dissolving the limestones in nitric acid he obtained an insoluble residue of quartz SiO_2 and clayey material to which he attributed the hydraulicity. At about the same time in Sweden, Bergmann (1735-1784) attempted to discover why some limes harden when immersed in water [33]. The hydraulic limes he analysed, all contained manganese. Therefore he attributed their hydraulicity to the presence of this element. In France, at the beginning of the 19th century, Guyton de Morveau analysed the properties of an artificial mixture with the same composition as the natural limes studied by Bergmann. He calcined it and found that the lime obtained was an excellent `water lime'. He also attributed this property to the manganese (4%) and not to the clay, which had been added in a proportion of 6% to the lime carbonate [34]. In Switzerland, Saussure (1740-1799) also dissolved `meagre limes' in acid and found that the residue was composed of quartz and clay. However, he adds that "the manganese would appear to have greater influence than the siliceous content". Vitalis (in 1807), among others, found that some good quality hydraulic limes contained no manganese, and stated that "clay was the chief source of their water setting properties" [34].

The French engineer Collet Descotils (in 1813) was the first to relate clearly the properties of the meagre limes to the presence of silica. He stated that an intimate combination of silica with lime is produced when these limes are slaked. He found that the silica in the used limestones was insoluble in acid, whereas it became soluble in the lime derived from it. His conclusions were correct in that a high quality meagre lime must contain a high quantity of finely disseminated siliceous matter.

The hydraulicity of binders is highly variable. The first attempt to classify hydraulic binders was made by Louis Vicat [35], who introduced the Hydraulicity Index (see Equation 2)

In this formula, Vicat compiled all knowledge then available and directly related the hydraulicity to the SiO_2 and Al_2O_3 contents. However, equal importance was incorrectly attributed to the two constituents. Gradually it was found that Fe_2O_3 and MgO also had an influence on the hydraulicity. An adapted formula was therefore developed about a century later by E.C. Eckel [4]. The formulation of this Cementation Index is shown in Equation 1.

It was conceived to be a direct expression of the quantity of CaO combined with the other constituents to form hydraulic minerals. The use of this cementation index is based on a number of assumptions. Firstly, it is assumed that all available SiO_2 combines with CaO to form C_3S (Ca_3SiO_5) and that all Al_2O_3 combines to form C_3A ($Ca_3Al_2O_6$). MgO is considered equivalent to CaO and Fe_2O_3 to Al_2O_3. This is clearly an oversimplification, since the mineralogy of hydraulic binders is more complex than assumed here. Eckel emphasized that the properties of hydraulic binders not only depend on their composition ('CI'), but also on the conditions of their manufacture. The hydraulic properties are indeed indirectly related to the burning temperature and time, since these influence the mineralogy of the final product [36].

A more detailed discussion on the origin of modern hydraulic binders and their classification can be found in [37].

5 Determining the hydraulicity of ancient mortars

5.1 Remaining hydraulicity in ancient mortars

A characteristic property of ancient calcareous binders is their hydraulicity. To determine this hydraulicity, which can be deduced from microscopic observations only in some rare cases, a chemical analysis is useful. However, the main difficulty resides in separating the binder from the other mortar constituents. Generally, this is achieved by dissolving a part of the mortar, or a previously disaggregated fraction of the mortar, in a dilute acid [20, 26, 38-42]. Other studies [16, 43, 44] mention the analyses of the entire mortar or a smaller grain size fraction after disaggregation and sieving. However, the results of such analyses are not helpful to obtain any information on the binder, because a significant contribution of the aggregate can never be ruled out.

A wide range of analyses methods to determine the chemistry of mortars or the binder fraction more in particular have been used. Difficulties arise when trying to compare the results of these analyses. In an attempt to obtain uniformity in the procedure for the chemical analysis of binders, Middendorf et al. [45] introduced a standardised methodology.

However, difficulties were previously observed during the implementation of the method [46]. Hofkens [46] made an evaluation of different analysis procedures and concluded that the treatment of the sample with HCl (10%) appears most straightforward. Many other authors [19, 39, 47-49] have adopted for the determination of the soluble silicic acid content. Specifically, 1g of sample is dissolved in 50ml HCl (10%) and the suspension is filtered after 5 minutes of reaction. The filtrate is used for the determination of Si by ICP-OES or AAS.

From the amounts of the main elements, the hydraulicity (Equation 1) and cementation indices (Equation 2) can be calculated. However, high acid-soluble silicic acid contents, resulting in a high 'HI' and 'CI', might not provide clear evidence for the use of hydraulic lime as binder material [45]. The silica might as well originate from pozzolanic additives that reacted with a more or less pure lime binder.

In general, the contribution of acid soluble SiO_2 from the aggregates is considered to be limited [50]. However, the use of hot HCl in mortar analyses revealed that part of the aggregate fraction may dissolve, especially clays such as smectites and kaolinites [40].

If the previously described methodology is considered to be suitable to assess the bulk chemistry of the binder, microprobe analyses are useful to provide more detailed information of points or areas in the polished (thin) sections. Moreover, information about individual mineral phases can be obtained. However, the main restriction is that no volatile components like CO_2 and H_2O can be measured. In spite of this limitation, microprobe has previously proven to be useful for the analyses of ancient mortars [21, 25, 39].

Additional information on the mineralogy of the mortars can be obtained by X-ray diffraction. The data complement the results of the petrographical and chemical analyses. The identification of the nature of the binder is easily made with X-ray diffraction. Hydrated calcium silicates or -aluminates can point towards the use of hydraulic binders. Some authors [47] state that a mineralogical analysis can make a distinction between different types of hydraulic binders possible. X-ray diffraction also enables to identify possible pozzolanic admixtures, which are sometimes too fine to be recognisable in thin sections.

The Thermo-gravimetrical (TG) patterns of ancient mortars are often subdivided in temperature ranges that allow making a more or less accurate delineation of characteristic transformations. For calcareous binders, most authors [14, 18, 20, 52-54] make a distinction between hygroscopic water (temperature range from 30°C to 120°C), water from hydrated salts (temperature range from 120°C to 200°C), the loss of water bound to hydraulic compounds (temperature range from 200°C to 600°C) and the loss of CO_2 (>600°C).

More in particular, TG reveals to be useful for the differentiation between hydraulic and non-hydraulic mortars [52]. Most often [20, 25, 52-56] a plot is made of the weight loss >600°C and of the ratio of the weight losses >600°C and from 200°C to 600°C. Samples with high amounts of water bound to hydraulic compounds and proportionally low amounts of CO_2 are considered to be hydraulic.

Many studies reveal the presence of crushed ceramics in Roman mortars [44, 57-60] but also in younger mortar samples [14, 61, 62]. In addition to these fired clayey materials, other types of pozzolans have been found in ancient mortar samples, being either natural or artificial. Some authors make mention of slag fragments [63], charcoal [57] and flint [8, 64] particles. However, in many cases it

is difficult to distinguish between the deliberate use of these mineral admixtures and their accidental addition.

It is however difficult to determine whether the hydraulicity of a mortar is induced by the addition of the supplementary materials or by the use of natural hydraulic lime. An analysis of the Binder Related Particles can be therefore be useful [65, 66]. The chemistry of the binder related particles is expected to be identical to that of the limestone used to prepare the lime.

5.2 Vanishing hydraulicity of ancient mortars

It was previously indicated that making a chemical analysis of the binder alone and as a whole is probably impossible, because it is closely intermixed with the aggregate. Moreover, different dissolution techniques are likely to yield distinct results. Therefore, the authors [67] analysed the binder fraction in a selected set of thin sections from mortars excavated at the Cathedral of Tournai [39] with the microprobe (CAMECA SX 50 at 15kV and 6nA). Small areas of approximately 15µm x 12µm (depth of a few µm) were quantitatively analysed (Table 1).

A first important observation is that the binder can be very heterogeneous within one mortar sample. If some analysis reveals compositions near to that of pure C-S-H, other analyses within the same mortar reveal areas that are much poorer in SiO_2 and with a Cementation Index (Equation 2) of only 0.09.

Secondly the results reveal that the Cementation Indices of the binder calculated from the microprobe results are systematically higher (with one exception out of 12 samples) than those calculated from the chemical analyses obtained by acid dissolution used for the determination of the bulk chemistry.

By looking on a smaller scale, it appears that the binder in many samples does not consists of a single phase, but appears to be composed of at least two distinct components that are intimately intermixed (Fig. 4). In several samples, a lightly coloured zone (in BSE mode) with a composition close to that of pure Ca-carbonate is intermixed with darker material rich in Si and having an average composition of 8 wt.% CaO, 16 wt.% SiO_2 and 2 wt.% Al_2O_3 at this specific location. The composition of the latter phase is however variable and ranges between CaO contents of 0-10 wt.% and SiO_2 contents of 15-70 wt.%. These specific point analyses (volume of approximately 5-10 μm^3) reveal the heterogeneous nature of the binder that has an average composition of 18 wt.% CaO, 14 wt.% SiO_2, 2 wt.% Al_2O_3 as determined by the analyses of larger areas (15 µm x 12 µm and a depth of a few µm). Because of the porous nature of the binder, these analyses are only suitable to establish the concentration ratios between different oxides. The ratios of Ca/Si=1.3 and Si/Al=7.5 are similar to those found in C-S-H [67]. It is therefore suggested that segregation has occurred in the C-S-H phase, whereby Ca and Si are moving into separate phases. The lightly coloured zones correspond to that of nearly pure Ca-carbonate and are an indication that a carbonation reaction of the C-S-H has occurred. The spatial

distribution of the two phases confirms these results as the lightly coloured material in Fig. 3 is consistently located on the outside, adjacent to the pores and enclosing the darker zones that are richer in silica.

Table 1 Microprobe analyses of the binder for a selection of mortar samples from Tournai. Analyses inside one zone (z) are made at a distance of less than approximately 1mm from each other. The distance between two zones in one thin section is at least 1cm.

sample name	numbre of analyses		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	CI
D03B	4	average	4,2	0,6	0,0	0,1	47,6	0,26
		stdev.	1,3	0,3	0,0	0,1	2,8	0,09
D06B (z1)	3	average	16,6	3,0	0,1	0,2	24,6	2,03
		stdev.	2,3	0,3	0,1	0,0	1,2	0,38
D06B (z2)	4	average	8,6	1,3	0,3	1,4	39,1	0,63
		stdev.	1,7	0,3	0,2	0,7	2,4	0,15
D07B (z1)	2	average	12,3	1,4	0,7	0,2	39,5	0,92
		stdev.	0,2	0,4	0,7	0,2	0,7	0,02
D07B (z2)	3	average	0,1	0,1	0,1	0,1	0,1	0,11
		stdev.	0,1	0,1	0,1	0,1	0,1	0,05
D08B	3	average	3,1	0,4	0,4	0,2	50,6	0,18
		stdev.	0,8	0,1	0,0	0,1	1,2	0,05
D09B	4	average	5,7	0,7	0,1	0,1	47,2	0,36
		stdev.	0,9	0,2	0,1	0,0	1,1	0,07
D19B	6	average	5,4	1,3	0,6	0,3	41,9	0,40
		stdev.	2,1	0,7	0,8	0,3	2,9	0,16
D20B	5	average	6,7	1,0	0,5	0,2	44,3	0,46
		stdev.	1,5	0,2	0,3	0,0	1,7	0,12
D22B	3	average	3,4	0,3	0,1	0,1	45,0	0,22
		stdev.	0,5	0,1	0,2	0,0	1,7	0,03
D23B	5	average	5,7	0,8	0,6	0,3	47,4	0,36
		stdev.	2,4	0,4	0,4	0,2	2,1	0,15
D36B (z1)	5	average	23,4	3,7	1,0	0,7	19,0	3,57
		stdev.	1,7	1,1	0,8	0,3	3,1	0,46
D36B (z2)	2	average	1,6	0,3	0,0	0,4	53,7	0,09
		stdev.	0,0	0,1	0,0	0,1	0,5	0,00
D41B	6	average	2,9	0,4	0,4	0,2	50,5	0,18
		stdev.	1,6	0,2	0,2	0,3	4,0	0,11
D48B	6	average	6,0	0,8	0,4	0,2	40,3	0,47
		stdev.	2,1	0,4	0,2	0,0	5,9	0,20

Microprobe analyses can only reflect the chemical composition at specific locations in the binder, but does not necessarily reveal the exact mineralogy of the different components. Ca-carbonates are observed in each X-ray diffraction pattern of the binder-enriched fraction (<63 µm fraction of the gently disaggregated mortar sample). Calcite, one of the Ca-carbonate polymorphs, is indeed present in each sample. However, vaterite ($CaCO_3$) and aragonite ($CaCO_3$), other Ca-carbonate polymorphs, are also present in many samples. Remarkably, their occurrence and abundance appears to be related to the hydraulicity (read CI) of the samples determined from their chemical analyses by acid dissolution. Vaterite and aragonite are generally considered to be less stable compared to calcite at atmospheric pressures and near-room temperatures. Therefore, they do not occur upon carbonation of pure lime (portlandite). However, these two polymorphs were proven to form upon carbonation of C-S-H.

This phase evolution might have consequences for the bulk chemical analyses, since the dissolution of these neo-formed phases might differ significantly from that of the phases initially present.

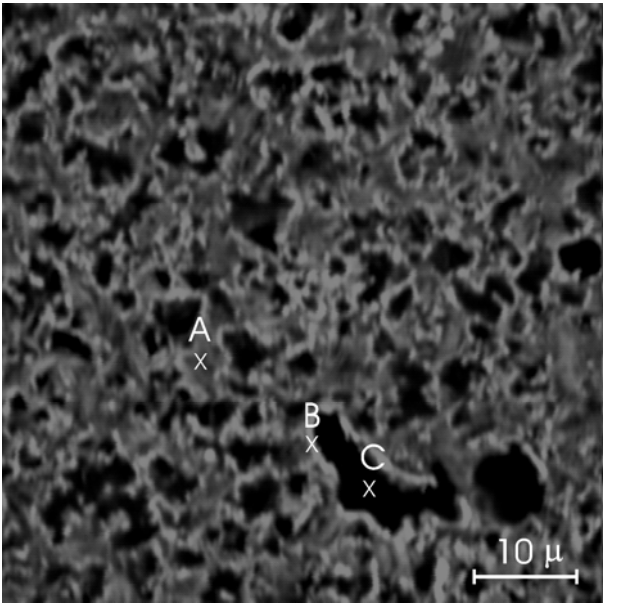

Fig 4 BSE micrograph of the hydraulic binder in a mortar sample from Tournai with a lightly coloured zone (B) rich in Ca (CaO: 49.3 wt.%; SiO_2: 1.4 wt.%; Al_2O_3: 0.2 wt.%), a darker zone rich in Si (A) (CaO: 8.3 wt.%; SiO_2: 15.5 wt. %; Al_2O_3: 1.6 wt.%) and a black zone (C) corresponding to the porosity. These are average analyses results of points (volume of approximately 5-10 μm^3) obtained at 15kV and 6nA.

6 Conclusions

From a chemical and mineralogical viewpoint, the composition of the currently available natural hydraulic limes is different from that of the non-hydraulic limes. However, the differences between samples of NHL2 and NHL5 limes are less obvious and mainly based on the amount of amorphous material. In ancient times, hydraulic limes were used in mortars. Although hydraulic binders made from the addition of pozzolans to lime are identified in many mortar samples since Antiquity, the natural hydraulic limes made from impure limestone seem to be used less frequently. Many questions remain about their deliberate use, because the theoretical knowledge of hydraulicity only dates from the end of the eighteenth century. Moreover, the analysis of ancient lime binders is not straightforward because it is difficult to separate from aggregate in ancient mortars. In addition, the identification and classification of hydraulic binders is complicated by their physico-chemical evolution through time.

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I.15

Characteristics of Mortars from Ancient Bridges

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Abstract Mortars from two medieval bridges (Charles Bridge in Prague and bridge in Roudnice) and two Roman bridges (Ponte di Augusto in Narni and bridge in Sardinia) were analyzed using various techniques to obtain their chemical and physical characteristics. The analysis of binder quality was based on thermogravimetric analysis, using an appropriate methodology which enables the hydraulicity of the mortar to be expressed by the CO_2/H_2O ratio. The mechanical tests were performed on non-standard mortar specimens. The ratio binder/aggregate was determined dissolving the binder by an acid, and a sieving analysis was applied to the separated aggregate. The material characteristics of mortars from historic bridges were compared with each other, taking into account the requirements for mortar strength according to construction position and degree of exposure.

1 Introduction

Bridges are fascinating engineering works which in many places have survived in service for thousands of years not only due to their excellent structural concepts and features but also owing to the quality of the materials and the excellent technological skills of their builders. The mortars of ancient bridges were analyzed in the past from the point of view of the aggregate and binder characteristics, but there are few references concerning the relation between chemical composition and the mechanical characteristics.

This paper presents data from a more complex analytical approach applied to a study of the mortars from four ancient bridges - two Roman and two medieval built in different environments. The medieval bridges did not introduce remarkable innovations into bridge engineering and were based on the proven Roman design and construction. However, some material development is apparent.

The scope of the paper does not allow for a very detailed analysis and description of the results, or for repetition of data already published elsewhere. Therefore, the methodology for non-standard testing is not included, and reference is made to other papers [1, 2, 3].

2 Experimental

2.1 Sampling

2.1.1 Charles Bridge in Prague

During the preparations for recent repairs to Charles Bridge in Prague, a probe was dug and several samples of the medieval mortar and stone were extracted for testing in the ITAM laboratories.

2.1.2 Gothic bridge in Roudnice

One of the oldest bridges in Bohemia (in the Czech Republic) did not survive the Thirty Years War in the 17th century, when it was blasted and almost totally destroyed. Some remains of the bridge were recently taken from the river bed and they were made available for testing the mortar characteristics.

2.1.3 Roman bridge in Narni

A core drilled into a pier of a Roman bridge at Narni delivered samples of a lime concrete of varying composition and with varying chemical and physical characteristics [4]. The question was raised whether the varying composition, which corresponds with various levels of the pier, might have been intentionally designed to take into account the variable loading or other functional conditions. The mechanical characteristics of the lime concrete from the Roman bridge at Narni were therefore tested on non-standard specimens, using the ITAM methodology for tests of this kind.

2.1.4 Roman bridge in Sardinia

A small sample of lime mortar extracted from a Roman bridge in Sardinia was tested in bending and compression.

A list of the sampling sites and a description of the mortars samples are given in Table 1.

Table 1 Sampling sites

Site	Century of construction	Symbol of sample	Functional type of mortar
Charles Bridge, Prague, CR	14 th	KM 1A, KM 1B	Joint mortar of an inner hammer- dressed stone arch
		KM 1C	Mortar in filling stone masonry above the arch
Gothic bridge, Roudnice, CR	14 th	R 3	Fine-grained joint mortar of ashlar stone arch
		R 4	Coarse-grained joint mortar of ashlar stone arch
		R 8	Cast mortar (lime concrete) on the ashlar stone arch top
Ponte di Augusto, Narni, IT	1st BC	N 1	Cast mortar in pier core
		N 2	Cast mortar in pier core
		N 3	Mortar in footings
		N 4	Mortar from the foundations
Roman bridge , Sardinia	3rd BC	Sa 1	Bridge rail mortar

2.2 Analytical methods

The following analytical methods were applied to the mortar samples:

- *Optical microscopy* - polished thin sections of the mortar samples were examined under an optical polarising
- *Wet chemical analysis* – about 10 g of powdered sample was dissolved in 2 M HCl according to the RILEM methodology [5]. Dissolving binder by acid attack enabled its separation from aggregate and so allowed estimation of binder/aggregate ratio. Subsequent element analysis of dissolved binder by gravimetric and volumetric methods was performed and cementation index *CI* of mortar binder was calculated as

$$CI = \frac{2.8xSiO_2 + 1.1xAl_2O_3 + 0.7xFe_2O_3}{CaO + 1.4xMgO} \quad ;$$

- *Granulometry of the aggregate* – aggregate was after separation from the binder sieved through ISO 3310-1 series sieves and the granulometric distribution was expressed as the fineness modulus $F.M. = \frac{\Sigma x_i}{100}$

where x_i is cumulative percentage retained on sieves 0.125 mm, 0.25 mm, 0.5 mm, 1 mm, 2 mm, 4 mm from ISO 3310-1 sieves series;

- *Thermal analyses (thermogravimetry/ differential scanning calorimetry)* – TG/DSC analysis was performed in order to determine the quality of the binder.

The experiments were carried out over a temperature range of 30 – 1000°C with a heating rate of 10°C/min in a nitrogen atmosphere on a fraction <0,063 mm;
- *Porosity accessible to water* – according to RILEM I.1;
- *Bulk density* – determined by means of hydrostatic balance weighing;
- *Water uptake coefficient* – according to DIN EN ISO 15148;
- *Mechanical tests* - a three-point bending flexural and compression test was performed on a non-standard mortar specimen according to ITAM methodology [1, 2].

3 Results and discussion

3.1 Microscopic observations

The results from a microscopic analysis of the samples from Charles Bridge indicate that the dominant component of mortars aggregate is river quartz sand. K-feldspar, plagioclase and mica can be determined among the other lithic grains.

The aggregate in the bridge at Roudnice is very similar to the aggregate used for Charles Bridge, where the main component is quartz. Orthoclase, plagioclase and mica are present in smaller amounts.

The mortars from Narni Bridge have a rather different macroscopic appearance: there are grains of various colours and shapes, some of them were 2-3 cm in size. The binder colour of N1 and N2 is whitish, while for samples N3 and N4 the colour is light grey and dark grey. Microscopic analysis determined that the aggregate is mainly made up of rounded fragments of micritic limestone and secondarily of chert and travertine fragments, quartz, feldspars and pyroxene. Samples N3 and N4 contain tuff fragments, which make the material strongly porous [4].

3.2 Chemical composition

Thermal analysis and wet chemical analysis were carried out in order to characterize the quality of the binder. The comparative hydraulic character of the lime was expressed as the CO_2/H_2O ratio, which is the ratio between the mass loss above 600°C due to the CO_2 released by decomposition of the carbonates, and the mass loss in the range 200-600°C, due to the loss of the water bound to the hydraulic compounds [6, 7]. By comparing the loss due to CO2 release and the CO_2/H_2O ratio we can sort the mortars into 2 groups, as follows:

- hydraulic lime mortars have 3-6 % of bound water and 18-34% of CO_2, CO_2/H_2O ratio reaches values between 4.5 and 9.5

- natural pozzolanic mortars have more than 5% of hydraulic water and less than 20% of CO_2, while CO_2/H_2O ratio is less than 3.

Results of wet chemical analysis provided data for characterization of aggregate, expressed as fineness modulus, and for classification of binder hydraulicity according to its cementation index [8].

The data obtained from the thermal and wet analysis are reported in Table 2. In the case of the Narni Bridge samples, the wet analysis described above could not be applied, because the aggregate consists mainly of carbonates so it dissolves during an acid attack together with the binder.

Table 2 Chemical analysis of mortars

Sample	TG analysis				Wet analysis				
	Struct. bound water % w	CO_2 % w	CO_2/H_2O ratio	Binder nature	B/A weight ratio	Aggr. nature	Fineness modulus aggregate	Binder cement. index CI	Hydraul. grade
KM 1A	5.9	8.7	1.4	Natur.pozz.	1:2.7	silic.	3	1.3	Eminently
KM 1B	8.5	7.8	0.9	Natur.pozz.	1:3	silic.	3.1	1.1	Eminently
KM 1C	10	9.2	0.9	Natur.pozz.	1:2.4	silic.	3.5	0.9	Eminently
R 3	4.6	23.2	5	Hydr.lime	1:0.8	silic.	4.3	0.6	Moderately
R 4	4.1	18.3	4.4	Hydr. lime	1:2.4	silic.	3.4	0.3	Feebly
R 8	4.1	12.3	3	Hydr. lime	1:3.3	silic.	2.1	+	+
N 1	4.2	22.2	5.3	Hydr. lime	1:3 *	carb.	+	+	+
N 2	6.2	19.4	3.1	Hydr. lime	1:2 *	carb.	+	+	+
N 3	6.1	11.7	1.9	Natur.pozz.	1:2 *	carb.	+	+	+
N 4	6.5	12.9	1.9	Natur.pozz.	1:2 *	carb.	+	+	+
Sa 1	4.5	35.9	7.9	Hydr. lime	1:1	silic.	+	+	+

* weight ratio was obtained by recalculation of the volume ratio determined by optical microscopy analyzing a thin section of mortar

+ not analyzed

From the both analyses results it is obvious that all tested samples were of hydraulic nature. According to the recommended thermogram interpretation [6, 7], the samples from Charles Bridge and N3 and N4 from Narni Bridge were classified as natural pozzolanic mortars because their content of $CaCO_3$ is lower

than 20 %, while the content of structurally bound water is higher than 5%. In the case of Charles Bridge fine-grained clayey-calcareous silicite is present [9], and it probably played the role of pozzolanic material. Cantasani et al. [8] made a detailed analysis of sample N2 of Narni Bridge and they suppose that the high hydraulicity of the mortar may be due to lime produced from local sources of cherty limestone. This might explain the high Si content, and consequently the weight loss higher than 5% (6.2%) in the range of 200-600°C. In samples N3 and N4 the presence of pozzolanic material - tuff - was microscopically confirmed.

The mortars from Roudnice Bridge were probably prepared using moderately hydraulic lime as a binder. The values for the structurally bound water released during heating of the samples did not exceed 5%, which indicates the use of natural hydraulic lime without the addition of pozzolana.

3.3 Physical properties

Table 2 Physical properties of the mortars

Sample	Bulk density kg/m3	Porosity % vol.	Compressive strength MPa	Bending strength MPa	Water upt. coef. $kg/m^2h^{-0.5}$
KM 1A	1690	39.1	5.2	1.4	5.2
KM 1B	1564	39.6	2.8	2.4	1.5
KM 1C	1599	38.2	8.9	2.3	6.3
R 3	1500	38.6	5.1	2.6	6.7
R 4	1711	32.7	3.7	3.2	3.5
R8	1855	28.7	5.4	2.4	+
N 1	1690	36	1.9	0.9	+
N 2	1790	31	14.5	0.4	+
N 3	1300	50	1.6	1.2	+
N 4	1160	54	1.0	0.3	+
Sa 1	1486	43.2	1.5	1.2	+

\+ not analysed

The compression strength values of the Charles Bridge mortars are quite high (except the sample 1B) and correspond with determined chemical composition of the binder (lime with natural pozzolanic material). The compression strength values in the Roudnice Bridge mortars which consist of river sand and hydraulic lime are slightly lower (from 3.7 to 5.4 MPa) but the bending strength of this type of mortar is higher.

The attained values of bending (flexural tension) strength of mortars from the Ponte di Augusto Bridge at Narni and the mostly significantly plastic behaviour correspond with typical lime mortar characteristics. It can be concluded that the

concrete bending strength (modulus of rupture) reaches values from 0.3 MPa to 1.3 (1.5) MPa. The measured values are influenced by quite gross aggregate grains. This is specially apparent when small specimens are tested. We can therefore expect the tension strength measured on standard specimens to exhibit higher figures.

The compression strengths measured on non-standard mortar specimens of slenderness inferior to 1 exhibit higher values than those from the standard tests. These were estimated using empirical correction coefficients dependent on the slenderness, the strength of the mortar and the length of the base. The compression strength values in the Narni Bridge mortar types 1, 3 and 4 are quite low in the ranges between 1 MPa and 2 MPa, corresponding to a high ratio of gross aggregate grains. In the investigated Roman mortar, the aggregates and their packing and compacting play an important role. The strength measured on type 2 mortar was strongly influenced by the very large size of the aggregate grains in the test specimens. A pessimistic value of the strength may be estimated from the stress/displacement diagram around the moment when the material started to stiffen significantly. This happened at about one fourth or one fifth of the total force. Under such an assumption the strength of the type 2 mortar would be about 2.8 – 3.5 MPa, which would be in better accordance with the rather low bending strength.

The measured mechanical characteristics (strength and stiffness) vary in a rather large range of values, which may indicate that the cast lime concrete parts did not attract a high level of technological care.

It does not seem likely that the different composition of the Narni pier lime concrete was designed intentionally and for the purposes of changing load carrying capacity from the point of view of the statistics of the structure. However, it might be interesting to evaluate the dynamic characteristics of a structure made of such a material and its earthquake resistance.

The results of tests of mortar from Sardinia were 1.53 MPa for compression and 1.22 MPa for bending. These test results correspond very well with the Narni Bridge results.

4 Conclusions

The production technology and especially the raw material composition of mortars differ from locality to locality and also from culture to culture. In the past, the Romans were able to create mortars of relatively low porosity, with strong mechanical characteristics and high hydraulicity. The analyzed samples show similar characteristics, which were probably achieved in different ways. While the mortars from the bridge at Roudnice (R3, R4, R8) and from Narni Bridge (N1, N2) seem to be made from hydraulic lime obtained from local impure limestone, the mortars from Charles Bridge and from the footings of Narni Bridge (N3, N4)

appear to be pozzolanic. In historic mortars, pozzolanic materials were commonly added. These contain high amounts of hydraulic oxides, which can react with lime and form water-resistant hydrated calcium and aluminium silicates. Such manufacturing technologies were often kept secret, so that no kind of documentation is left.

The nature of the pozzolana and aggregate mixed in the mortar was dependent on local resources. In the Czech lands, for example, quartz sand with feldspar and mica admixtures (as observed in the Charles Bridge and Roudnice samples) is typically used as aggregate in historic mortars, in contrast to the analysed ancient mortars from areas where various limestone and other lithotypes were available for aggregate.

The results of the thermal analysis indicate that samples of mortars used as cast or joint mortars from filling, hammer-dressed stone and foundation masonry (KM 1A, KM 1B, KM 1C, R8, N3, N4) have the highest hydraulicity values. Samples of joint mortars (R3, R4) are richer in calcium carbonate, which means that the workability of original mortars was better, and the workable times were longer than in mortars with higher hydraulicity.

Earlier research indicated that there are apparent tendencies toward simple and direct interdependencies among some parameters [2]. Naturally, there is a strong linearly reciprocal relation between density and porosity, and therefore also other apparently dependent parameters, e.g., water absorption. That is, a reduction in porosity implies a rise in density. Further a rise in density correlates with an increase in both compressive strength and bending strength, and consequently a rise in porosity correlates with a decrease in strength. When assessing the results, we should have in mind how heterogeneous our sample of historic mortars is.

The other parameters influence the mechanical characteristics in a more complex way and cannot be simply revealed from a limited number of samples. It seems that a rise in the binder-to-sand ratio does not simply cause a corresponding rise in the strength parameters.

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I.16

Characterization of Gypsum-Selenite Plasters from Historic Buildings in the Emilia-Romagna Region (Italy)

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Abstract The use of whole gypsum plasters, i.e. made of gypsum binder and coarse selenite aggregate, still can be found in several historic buildings in Italy (both monumental and rural), but it is absent in historical architectural treatises and totally neglected in current restoration works. The main features of these plasters include good mechanical properties and good resistance, even to outdoor environments, despite their gypsum-based composition; thus, they appear worthy of conservation. In this paper, several specimens of such plasters collected from historical buildings are characterized for the assessment of their formulation, microstructure and state of conservation, as a contribution to the preservation of this interesting technological legacy.

1 Introduction

Materials for architectural restoration must be compatible with the pre-existing ones, not only from an aesthetic point of view, but also in terms of chemical-physical-mechanical properties, since the architectural surface materials actually transmit the building image, as noted by Cesare Brandi [1]. Moreover, the conservation of architectural surface materials (not only structural materials, but also finishing ones, such as plasters) helps to preserve the city's image and place identity (*genius loci*) [2]. As a consequence, the characterisation of ancient plasters is fundamental to compatible restoration work, e.g. in order to identify suitable repair materials without disfiguring the building's image.

In this paper, several plasters, composed of gypsum binder and coarse selenite aggregate (as determined through visual assessment), were taken from different Italian historic buildings in the Emilia-Romagna Region and were investigated. These "whole gypsum" plasters were collected from both indoor and outdoor

walls, as opposed to gypsum stuccoes, which, due to gypsum's well-known solubility, were traditionally limited to indoor applications. The investigated plasters exhibited a good resistance to outdoor environment and a fair hardness.

It is noteworthy that the formulation of mortars made of gypsum binder and selenite aggregate is totally absent in historical architectural treatises (by Vitruvius, Milizia, Palladio, etc.) and may be connected with the local availability of gypsum quarries. As a matter of fact, local selenite stone was used in Bologna as structural building material since the Middle Ages and as a raw material for the production of gypsum binder. In the 17th century, the gypsum binder from Bologna was known as the hardest in Italy [3].

The plaster samples were characterized to determine their composition and microstructure, as a contribution to the conservation and consistent restoration of such scarcely known material and technology.

2 Experimental

2.1 Samples

The samples of whole gypsum plasters were taken from different historical buildings:

- *Santissimo Sacramento* [Holy Sacrament] church at Castel Guelfo di Bologna, XVI-XVII century: samples "CG1" and "CG2" are mouldings from the altar in northern side, "CG3" is plaster from a niche in the eastern wall, "CG4" is plaster from a pillar in the western wall, "CG5" is plain plaster from the eastern wall. All samples were originally located in the interior, but the church lost its roof due to bomb damage in the Second World War, so the indoor plasters and mouldings have been exposed to environmental aggression since then.
- *San Pietro* [St Peter] cathedral in Bologna, XVII century: samples "SP1" and "SP2" are indoor plasters from the bell-tower.
- *Malvezzi* villa, at Budrio, near Bologna, XVII century: sample "VM" is an outdoor plaster from one of the buildings over the courtyard.
- Homestead and rural building at Torriana (near Rimini), 19th century: samples "T1", "T2", "T3" and "T4" are all plain outdoor plasters.
- *S. Giacomo* [St James] palace at Russi (near Ravenna), 16th century: sample "R1" is plain plaster from the rear portico.
- Selenite is a stone specimen, here named "Se", from a quarry near Bologna and has been used for comparison.

2.2 Procedure and methods

Freshly chisel-broken plaster samples (about 0.7 g) were dried at 70°C up to constant weight and then analyzed by mercury intrusion porosimetry (Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba, equipped with Milestone 200 software) under the following operating conditions: maximum pressure 2000 bar; cylindrical calculation model; contact angle mercury/material=141.3°. The plaster samples were then characterized by means of X-ray diffraction (XRD, Philips Diffractometer PW1840 operating at 40 kV/20 mA, Cu Kα radiation; the samples were powdered to pass through a 0.075 mm sieve); thermogravimetric analysis (TGA, TA Instruments Thermogravimetric Analyzer Q50, under the following conditions: temperature increase 20 °C/min up to 850°C in nitrogen atmosphere); and by the Dietrich–Frühling method for the determination of carbonate content.

In order to identify the mortars' components and formulation, with the objective to ultimately reproduce new plasters compatible with the previous one, the samples were manually disaggregated for further tests. Manual disaggregation, required for a reliable separation of binder from aggregate [4], was impossible in dry conditions due to the great hardness of these plasters; therefore, the process was enhanced by a preliminary immersion in distilled water for at least 48 hours (depending on the sample hardness). To confirm the complete dissolution of gypsum binder and the absence of binder residue on the surface of the aggregate grains, the aggregates were observed by a stereo-optical microscope (SOM, Wild M3 Heerbrugg). Then, the aggregates were dried at 50°C for 5 minutes and sieved with standard UNI sieves (6.7–5.6–4–3.35–2–1–0.5–0.25–0.075 mm) under mechanical vibration (10′). After sieving, the single fractions were observed again by SOM and separately investigated through the methods reported above.

3 Results and discussion

The composition and carbonate content of the samples (expressed as $CaCO_3$, wt%) are reported in Table 1. Most of the samples exhibit a complete or almost complete bi-hydrated calcium sulphate nature, thus confirming that the aggregates are made of selenite. XRD also detected the presence of calcium carbonate (calcite) in some samples; in particular, the samples from Castel Guelfo (CG-series) showed significant amounts of calcite, as well as traces of quartz. The presence of calcite and the good hardness of these samples suggest that the CG plasters were made with a lime-gypsum binder in order to improve their strength and fresh-state workability, as evidenced in [5-6]. The fresh-state workability and hardening time were very important for these plasters, as they were used for ornamental mouldings. No significant abundance of calcite was detected in samples from Torriana and Malvezzi Villa, probably because these plain wall

plasters had no particular workability requirement. SP samples did not contain calcite (and in fact they are not moulded, but plain plasters), while some quartz was present in the SP1 sample aggregate. The traces of feldspars (orthoclase group) detected in CG4 and R1 samples may be attributable to the addition of quartz/feldspar aggregates to the plasters.

Table 1 Results of XRD analysis and carbonate content of the plasters.

Sample	G	C	Q	F	$CaCO_3$, wt%
CG1	+++	-	-	-	-
CG2	++	+++	+	-	55.8
CG3	+++	+	+	-	17.6
CG4	+++	++	+	+	15.0
CG5	+++	+	+	-	7.8
SP1	+++	-	++	-	-
SP2	+++	-	-	-	-
T1	+++	-	-	-	-
T2	+++	-	-	-	-
T3	+++	-	-	-	-
T4	+++	-	-	-	-
R1	+++	+	-	+	9.2
VM	+++	+	-	-	0.7

+++=dominantly present, ++=present, +=traces, −=not present,

G=gypsum, di-hydrated calcium sulphate (PDF number 33-311), C=calcite (PDF number 5-586), Q=quartz (PDF number 33-1161), F=feldspar (orthoclase group, PDF number 41-1480).

TGA was performed on powdered samples to determine gypsum content (binder and aggregate) and to highlight differences between the samples and/or the presence of organic admixtures, common in ancient gypsum stuccoes [7]. The TGA-DTG curves of some significant samples are shown in Fig. 1. No organic admixtures were detected in the samples, while gypsum content, calculated on the basis of the weight loss in the range 130-180°C [8], spans from 41% (CG2 sample, lime-gypsum bound) to 96% (T3 sample, whole gypsum plasters). After water immersion and dissolution of the gypsum binder, the aggregates were sieved. The resulting grain size distributions are reported in Fig. 2.

Selenite aggregates were easily detectable by SOM in the sieved fractions (Fig. 3). The selenite aggregate in the Malvezzi Villa plaster was quite coarse, and its low porosity, might improve the plaster's resistance to environmental decay. The CG3 sample, a quite strong plaster, also exhibited coarse aggregate. On the other hand, the samples from the rural buildings in Torriana, showing a small grain size, appeared quite weak, as the selenite aggregate seemed too fine to provide significant toughness. The use of gypsum in the rural buildings at Torriana seems

linked not to the achieving of particular performances, such as strength or workability, but to its cheapness (due to low firing temperature) and wide availability in the area [9].

After sieving, the aggregate fraction 0.5-3.35 mm was tested for carbonate content, in order to assess whether calcite was present in the aggregate. Results substantially confirmed all findings reported above.

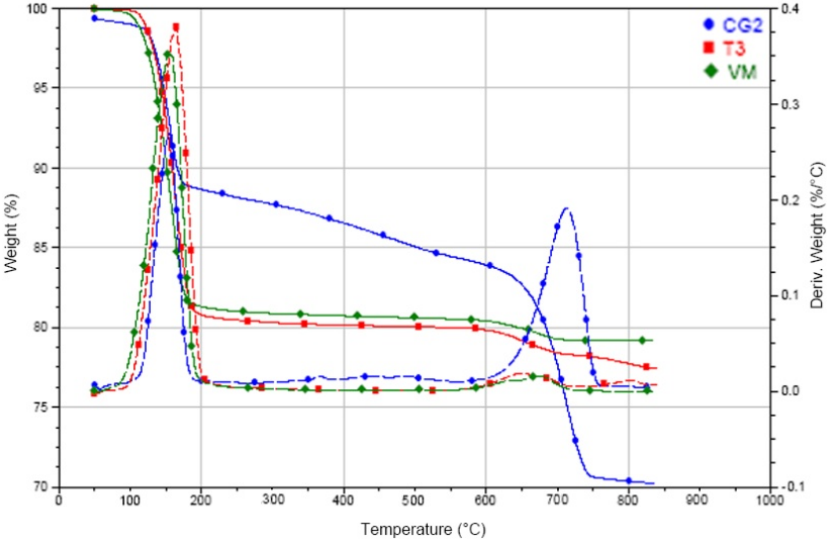


Fig. 1 TGA results for some significant samples (continuum lines: TG; dotted lines: DTG)

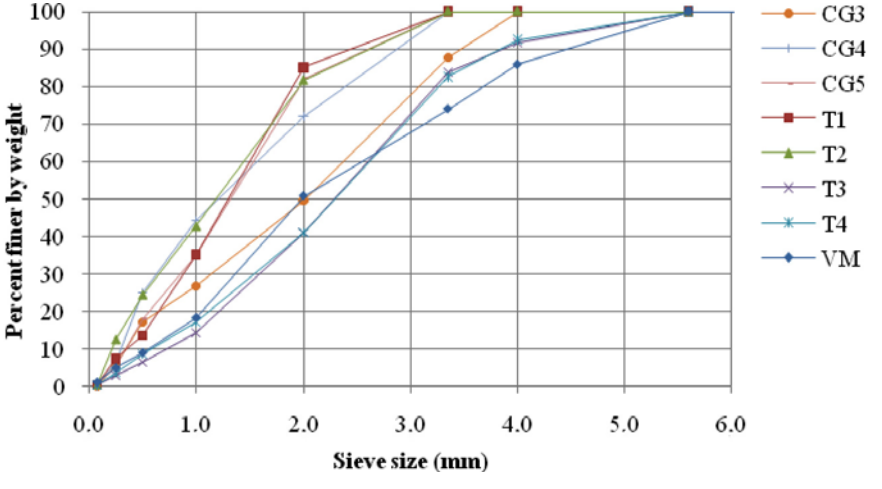
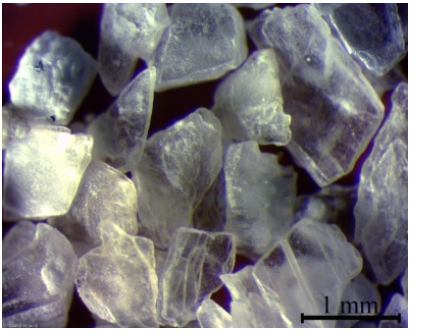


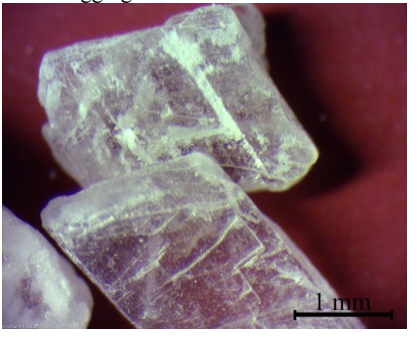
Fig. 2 Plasters' grain size distribution curves

The pore size distributions of the samples are reported in Fig. 4. The low porosity of selenite confirms the improvement of strength and durability connected with the use of such aggregate. The wide variability of the curves in Fig. 4 illustrates the different microstructures of the gypsum plasters, surely affecting their hardness.

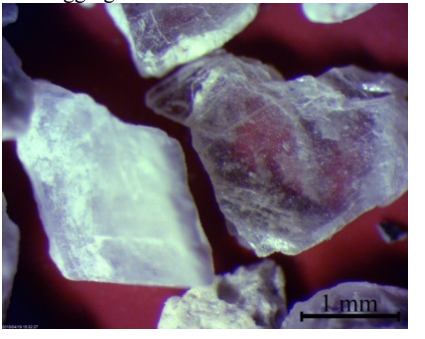
"CG5" aggregates retained at 1 mm sieve.



"T2" aggregates retained at 0.5 mm sieve.



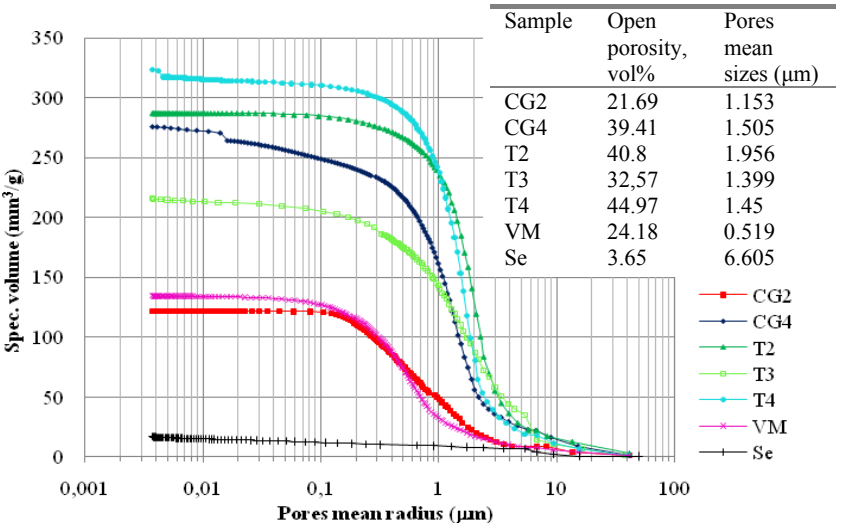
"T4" aggregates retained at 1 mm sieve.



"VM" aggregates retained at 1 mm sieve.

Fig. 3 Stereo-optical microscope pictures of some significant samples

The softer samples (such as T4, T2 and CG4) are highly porous plasters with a large mean of pore radius, while the harder samples, difficult to disaggregate, exhibit lower open porosity (as seen in sample CG2). Hence, porosity and hardness are influenced by both selenite aggregate (abundant and coarse aggregates give harder mortars) and the addition of slaked lime to gypsum binder (apparently the most significant factor). Plasters exhibiting high carbonate content from lime carbonation also are characterised by low porosity.



Sample	Open porosity, vol%	Pores mean sizes (µm)
CG2	21.69	1.153
CG4	39.41	1.505
T2	40.8	1.956
T3	32,57	1.399
T4	44.97	1.45
VM	24.18	0.519
Se	3.65	6.605

Fig. 4 Pore size distribution of some significant samples

4 Conclusions

The characterisation of the gypsum plasters accomplished in this paper confirms that selenite aggregates were used together with gypsum binder. Moreover, this study has demonstrated the role of mixed gypsum-lime binder and coarse aggregate size in improving the mortars strength and durability. The results contributed to an understanding of the microstructure and formulation of gypsum plasters in order to design new compatible plasters for restoration, especially where it is necessary to fully replace older plasters or fill gaps. Moreover, this study is intended to contribute to the rediscovery of an ancient building technique that today is totally neglected.

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I.17

Characterization of Decorative Portuguese Gypsum Plasters from the XIX-XX Centuries: the Case of the *Bolsa Palace* in Oporto

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Abstract In order to achieve the issues of compatibility for the design of new repair products a complete characterization of the original materials is of extreme importance. Gypsum plaster materials are not an exception to that rule. The characterization work of the Portuguese historical gypsum plasters has never been done as well as the study of efficient solutions for their preservation. In this paper the results of the characterization of gypsum plaster samples from the second half of the 19th century belonging to the Arabian Room of the Bolsa Palace, located in Oporto, North of Portugal, are presented and discussed. XRD, TGA-DTA, optical microscopy and FESEM-EDS observations were used for the chemical and microstructural characterization. Some physical properties, such as dynamic modulus of elasticity and capillary absorption were also determined. A relationship between the results obtained, namely composition and characteristics observed in the samples, and the technology associated to their use and application on site is established.

1 Introduction

The use of gypsum plasters in Portuguese architecture is thought to have been likely since the Roman period [1, 2]. However, their presence was particularly expressive in the period between the 18th century and the first half of the 20th century. The quality and variety of gypsum plaster decorations in Portuguese monumental and domestic architecture contrast with the lack of information on the materials and the techniques of application used to produce them.

The studies on this subject are one of the main issues for the restoration and conservation of this important heritage and can provide a decisive contribution to the reduction of its rapid loss.

The present research occurs in this context, where the microstructural, chemical and physical characterization of the decorative historical gypsum plasters from the 19th and 20th centuries is the first step to reach the final purpose: the development of new compatible gypsum products for the repair of the ancient plasters.

Besides the lack of knowledge on the materials used there are usually no records about their techniques of preparation and application, even from subsequent interventions when they have already occurred. The case study presented in this paper follows that trend. The aims of this research work are to study the materials used and also the methodology adopted by the plasterers for their application.

2 Experimental Programme

2.1 Case Study - The Arabian Room of the Bolsa Palace

The samples studied in this paper belong to the *Arabian Room* of the *Bolsa Palace,* a building located in the city of Oporto, North of Portugal. Considered an architectural icon of the 19th century and also one of the greatest examples of the neoclassical style, it is classified as a national monument.

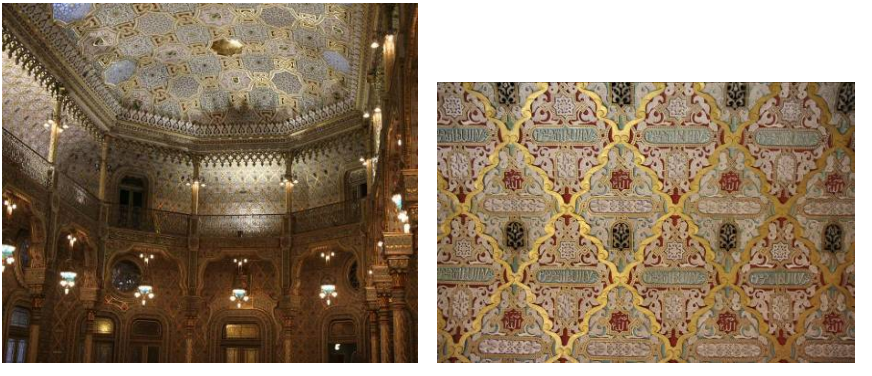

Fig. 1 General view of the *Arabian Room* (left) and detail of some stucco decorations (right)

The *Arabian Room* (Fig. 1) is the most emblematic of all the palace's rooms and the only one of its kind in the country as it embodies the clearest expression of the neo-Moorish art in Portugal. Its construction began in 1862 and was finished only in 1880. The coloured stucco decorations were inspired by the Palace of

Alhambra, in Granada, Spain, and cover practically the whole ceilings and walls, constituting one of the richest and most original decorative Portuguese gypsum plasters of this period [3].

2.2 Sampling

The samples were collected by the authors in two different ways: indirectly, meaning they had been previously detached due to some anomaly in the building (five samples), and directly on site, one sample of a total of six samples. They all belong to elements of the decorative program. The identification and description of the samples is summarized in Table 1; Fig. 2 shows two of the studied samples.

Table 1 Identification and description of samples

Identification	Sample description
PB1	Frame from the ceiling (gilded) (Fig. 2)
PB2	Ornaments from the breathing holes of the ceiling (gilded) (Fig. 2)
PB3	Octagonal base of PB2 (gilded) (Fig. 2)
PB4	White ornaments from the ceiling
PB5*	White ornaments from the coronation of the cove that limits the ceiling (partially gilded)
PB6	Preparation layers and ornament of a wall of the gallery (with polychromes)

* Rejected due to strong evidence of not being original: golden layer is painted, interior structuring metal frame is not rusted like the others and shows a superficial blue colour (possibly copper frame reacting to copper sulphate).

Fig. 2 Sample PB1 (left) and PB2 plus PB3 (right)

2.3 Analytical methods

The mineralogical and chemical properties of the samples were determined using the analytical methodology developed by Santos Silva *et al.* [4]. After a

detailed visual observation of the samples and photographic registration, they were dried at 40ºC for about 12 hours. To enable the detection of the possible presence of hygroscopic compounds or soluble salts that can lose their crystallinity, the samples were not dried to mass constancy. Each specimen was split into several fractions to be used for different techniques.

Polished surfaces of the gypsum samples were prepared by impregnation under vacuum with an epoxy resin. They were observed with an Olympus stereo-zoom microscope and images were recorded digitally. The stereo-zoom microscope was used to study the textural properties of the existent layers in the samples (stratigraphy) and to also identify the mineralogy and morphology of the aggregates and possible pigments.

X-ray diffraction was performed to allow a further insight on the mineralogy of the binder and other constituents such as the aggregates. A Philips X'Pert diffractometer with cobalt Kα radiation, step of 0.05º/s, between 2θ 3º and 74º, was used.

The thermo analytical techniques provided additional data on the quantitative composition of the samples, namely the relationship between the gypsum and calcite content. A Setaram TG-DTA analyser was operated in an argon atmosphere and with a uniform heating rate of 10ºC/min from room temperature to 1000ºC.

Scanning electron microscopy observations on polished surfaces were performed in backscattered electron image mode (BSE) on a field emission scanning electron microscope (FESEM) JEOL JSM7001F coupled with an OXFORD energy dispersive spectrometer x-ray detector (EDS). The polished surfaces were sputtered with a gold palladium film in a BALTEC sputter coater.

Some physical properties were also determined using a methodology developed by Veiga *et al.* [5]. The samples collected were irregular; they were cleaned of any powder and biological colonisation before being maintained within a controlled environment (23ºC and 50% RH). Water absorption tests were performed using the capillary absorption by contact technique [5]. The dynamic modulus of elasticity was determined using ultrasound, based on the emission of high frequency sound waves and the measurement of their velocity through building materials, allowing the calculation of elastic parameters (BS 1881-Part 203).

3 Results and Discussion

The data obtained by visual observation of the samples, both directly and with the stereo-zoom microscope, is summarized in Table 2. It was difficult to determine how many layers composed samples PB1 and PB6 and only after observation under the stereo-zoom microscope was it decided which of them would be able to be separated and analysed by XRD and TGA-DTA.

Table 2 Visual observation of the samples

Sample	No. of layers	Identification	Description
PB1	Min.10	PB1/1+PB1/2	White plaster layers from within the moulded frame*
		PB1/3	Very thin yellowish plaster layer, immediately above PB1/1+PB1/2 that seemed to display some flexibility
		PB1/4...	Very thin layers (at least 7), consisting of the preparation for the 1st leaf gold application and subsequent restoration operations, till the 2nd leaf gold (the last layer, already decayed)
PB2	1	PB2	Fragments from a breathing hole ornament of the ceiling. This ornament showed traces of Armenian bole, leaf gold and restoration plaster(s)
PB3	1	PB3	Octagonal base of PB2. It presented restoration plaster(s) and traces of Armenian bole and gold leaf.
PB4	1	PB4	Fragments of white ornaments from the ceiling. These fragments had traces of a blue paint in the base of the side faces that had a different colour in one of them
PB6	3	PB6/1	White preparation layer of a wall of the gallery (Fig. 3, left)
		PB6/2	Thin layer that is the finishing layer in the surfaces where there are no ornaments applied (with polychromes) and works as "glue mortar" between the preparation layer (PB6/1) and the ornaments (PB6/3)
		PB6/3	Ornaments moulded directly on the wall, applied with the PB6/2 layer still fresh (with polychromes) (Fig. 3)

* Analysed together by XRD and TGA-DTA as is was very difficult to have a physical separation with 100% certainty.

Fig. 3 Sample PB6: preparation layer, PB6/1 (left) and ornament, PB6/3 (right)

In the case of PB1 a polished surface was prepared for stratigraphic analyses (Fig. 4).

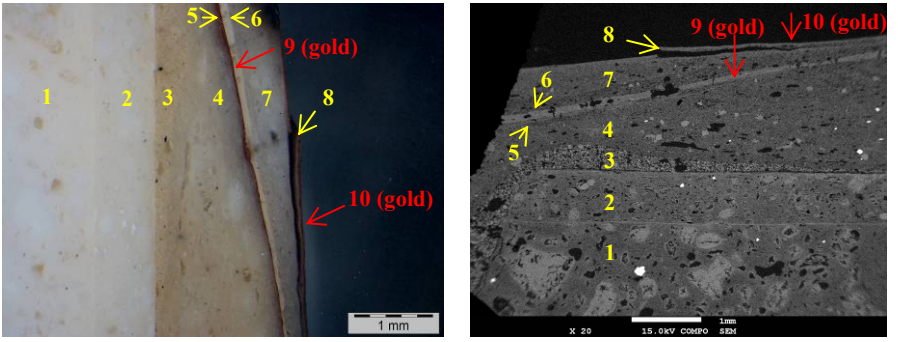

Fig. 4 Polished surface of PB1: stereo-zoom microscope (left) and FESEM (right)

Due to the large number of layers and low thickness of most of them, their composition was first determined by FESEM-EDS (Table 3, Fig. 5).

Table 3 FESEM-EDS results for sample PB1 stratigraphic analysis

Sample	Layers				
PB1	1+2	3, 6	4, 7	5, 8	9, 10
EDS	Gypsum, Calcite	Calcite	Gypsum	Si, Al, Mg, Ca, Fe (Armenian bole)	Au, traces of Ag

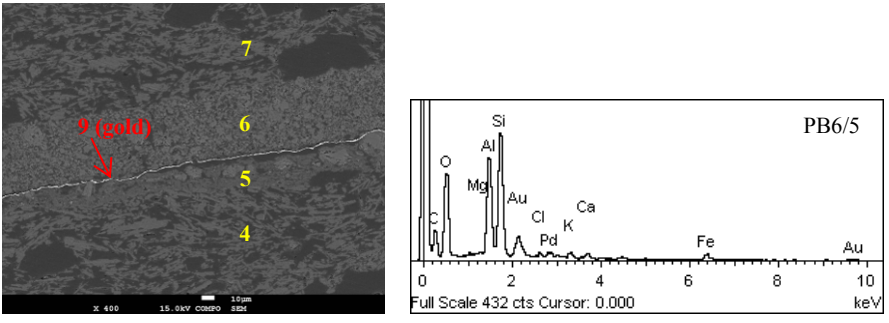

Fig. 5 Polished surface of PB1: FESEM image (left) and EDS of layer 5 (right)

The first restoration layer is the 6th. Its morphology and composition is similar to the 3rd layer and differs from all the others. In fact, calcite is the main constituent of these two layers which also have a common function: to promote good binding with the precedent layer in order to be strongly attached to it.

This pattern in similarity of composition / morphology / function can also be observed between the other entire original *versus* restoration layers (3, 4, 5 and 9 similar to 6, 7, 8 and 10, respectively).

XRD and TGA-DTA analyses were then applied to the first two layers together (it was not possible to separate them) and to the third layer (Table 4).

Table 4 XRD results and calculated gypsum/calcite content through TGA results

Sample	Identified crystalline compounds					Calculated gypsum and calcite contents (%)	
	Gypsum	Calcite	Quartz	Celestine	Halite	$CaSO_4.2H_2O$	$CaCO_3$
PB1/1 PB1/2	+++/++++	++	?	-	-	63	32
PB1/3	++	+++/++++	trc	-	trc	26	69
PB2	++++	-	trc	-	-	97	3
PB3	++++	+	?	-	-	90	6
PB4	+++	++/+++	?	-	-	51	45
PB6/1	+++/++++	+/++	trc	trc	-	77	18
PB6/2	+++/++++	+	trc	trc	-	83	9
PB6/3	++++	trc	trc	trc	-	93	1

Notation used in XRD:

++++ - very high proportion (predominant compound)
+++ - high proportion
++ - medium proportion
\+ - weak proportion
trc - traces
\- - not detected

For the mix of the first two layers, XRD and TGA-DTA results are in agreement with those obtained by FESEM-EDS, indicating that they are mainly composed of gypsum, with calcite being the second constituent. However, for the third layer EDS analyses detected only calcite, while XRD and TGA-DTA clearly indicated the presence of gypsum, probably due to sample contamination during its separation.

Another feature that was noticed in the observation of the polished surface of PB1 is the change in the design of the frame due to the restoration; the lines of the original piece have been slightly straightened as a result of this procedure.

Sample PB6 was also observed under the stereo-zoom microscope in order to clarify some uncertainties: (a) PB6/1 seemed to have 2 distinct layers, as it showed a preferential fracture pattern and (b) the way the PB6/3 had been moulded (directly on site or precast) was an enigma. These observations gave the answers to the previous questions: (a) a very discrete interface exists in part of the polished surface of PB6/1, which means that the plaster was in fact applied in two parts; however each part must have been applied immediately after the other, as the intergrowth of the crystals between them seems to be very high indicating the lack of two distinct layers; (b) the interface between PB6/2 and PB6/3 has small empty holes that are present in both (Fig. 6, left) which means they were applied one after the other or, in other words, the ornament PB6/3 has been moulded directly on site, when PB6/2 was still fresh. In fact, an accurate observation of other areas of this interface confirms this information, like the evidence that PB6/3 was pressed against PB6/2 (Fig. 6, right).

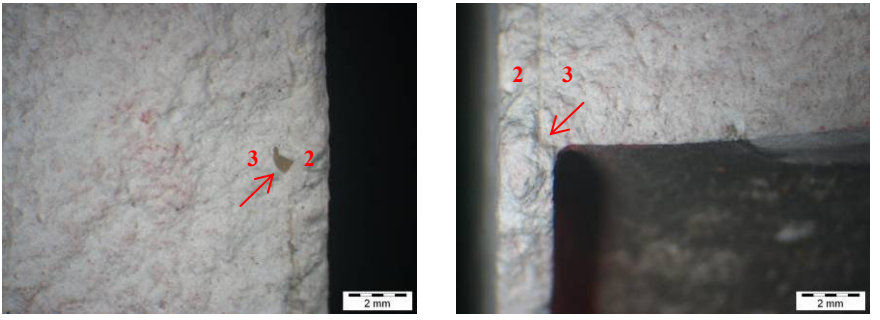

Fig. 6 Interface between layers 2 and 3 on sample PB6

Physical properties were only determined in the samples where the quantity and shape were appropriate to perform the corresponding experimental techniques. The dynamic modulus of elasticity (DME) was determined in samples PB4 and PB6/3 and the coefficient of capillary absorption by contact (Ccc) only in sample PB4 (Table 5).

Table 5 Results of the physical properties determined and comparison with the calculated chemical content

Sample	DME (MPa)	Ccc - 5min ($kg/m^2/h^{1/2}$)	Bulk density(*) (kg/m^3)	Calculated gypsum and calcite content (%)	
				$CaSO_4.2H_2O$	$CaCO_3$
PB4	970	24.38	995	51	45
PB6/3	2590	-	1045	93	1

(*) Calculated: weight / (area of the base x height)

The low DME of sample PB4 is in agreement with its high Ccc after 5 minutes and follows the usual inverse relationship between these two parameters; however, it is lower than usually found in samples with the same gypsum/calcite composition and density [6]. The use of air entraining admixtures is a possible explanation but is very difficult to prove.

On the contrary, for sample PB6/3 the DME result is in total agreement with those already found in previous studies for samples of precast elements with a high gypsum content [6].

4 Conclusions

All the samples analysed showed evidence of having already undergone some restoration which, in the case of PB1, introduced a slight change in the design of the respective element.

The samples belonging to decorative gypsum plasters can be divided into two groups: (1) those prepared with a mixture of gypsum and hydrated lime that has

carbonated and appears now as calcite (PB1/1+PB1/2 and PB4); (2) those prepared mainly with gypsum (PB2 and PB3 were precast and PB6/2 and PB6/3 were applied directly on site, one immediately after the other).

The use of a mixture of gypsum and lime in PB1/1 and PB1/2 can be explained by the fact that they form the inner structure of a frame and were probably moulded on a bench. In fact, to improve the workability of gypsum it is a common practice to add hydrated lime to it [6, 7]. However, in the case of sample PB4 the reason must be different as one can clearly see that the constituent elements were precast before being applied to the ceiling.

The preparation layer PB6/1 was applied directly on the mortar as is usual in these situations. It has an average thickness of 6 mm and presents a relieved pattern in the outer face, in order to improve adhesion of the subsequent layer PB6/2. The volumetric proportion of gypsum and hydrated lime used to prepare it is above 2:1 i.e. is much higher than the 1:1 proportion usually used in similar cases [6, 7]. Maybe the experimental data from other case studies of the north of Portugal will help to find out whether this was due to a regional influence or just a coincidence.

The materials used in the manufacture of the gypsum decorative plasters of the *Arabian Room* of the *Bolsa Palace*, in Oporto, were carefully chosen according to the purpose and techniques of application, even in some of the later interventions (the case of the frame from the ceiling, corresponding to sample PB1). The stucco decoration of this room's walls and ceilings is undoubtedly one of the most precious works of art of its kind in Portugal.

5 Acknowledgments

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I.18

Petrographic Examination of Gothic Mortars of the House of Lords of Kunštát in Brno, Czech Republic

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Abstract The paper aims at characterising Gothic mortars of The House of Lords of Kunštát in Brno, Czech Republic. The House of Lords of Kunštát in Brno was built in Gothic style in the middle of the 13th century and rebuilt in Renaissance style in 1585-99. Light and electron microscopy, microanalysis, and X-ray diffraction were used to characterize the mortars. Provenances of lime and aggregate were identified. The age of the examined mortars was estimated based on micrite recrystallization in the binder and comparison of the recrystallization level with archaeologically dated samples exposed to identical conditions.

1 Introduction

Until 1970-1980 the characterisation of historic mortars was based mostly on traditional wet chemical analyses [1]. The examination of historical mortars from a petrographic point of view, especially by light microscopy, has come to a focus in the last decades. The petrographic approach may provide archaeologists and conservators basic characteristics of the material, such as: the source of limestone used for lime production, identification of the used lime character, the source of aggregate, estimation of lime burning degree, and examination of deterioration processes [1, 2].

The hydraulic character of historically used lime can be determined through the identification of unhydrated clinker minerals by microscopic or X-ray diffraction (XRD) techniques [1, 3, 4]. An excellent paper on mineralogical analysis of hydraulic limes by XRD was published by Mertens et al. [5]. The hydraulic phases of hydraulic lime correspond to some minerals present in cement clinker, so-called

clinker minerals. Also, hydration and later carbonation processes of these hydraulic phases are similar to those in cement pastes. The hydraulic character of historical mortars may also be identified based on the presence of calcium hydrosilicates (C-S-H) or calcium hydroaluminates (C-A-H). However, identifying these mineral species in historical mortars using just XRD data is more than complicated. First, it is not possible to completely separate all of the aggregate from the binder during the sample preparation, which results in complexity of the XRD pattern. Some of the C-S-H products are amorphous and are prone to carbonation [6-8].

The identification of C-S-H products based on XRD also may be misleading in some cases. For instance, numerous C-S-H and C-A-H products in historical mortars from Charles Bridge in Prague have been identified using XRD [9, 10]. Moropoulou et al. have identified significant content of tobermorite in historical mortars from Greece [11]. Miriello et al. [12] report the presence of hillebrandite, tobermorite, and xonotlite in Pompeiian mortars. It should be mentioned that the stability field of various tobermorite forms lies between 55 and 650°C at atmospheric pressure [13-15]. Most of the C-S-H species listed by the authors [9, 12] (C_2SH, C_2SH_3, hillebrandite, xonotlite) are, according to Lea et al. [15] and numerous other authors [e.g. 13, 16], formed at the temperature range 140-350°C, truscottite at 200-300°C and foshagite at 300-500°C. The possibility that historic mortars reached such high temperatures during the hydration process is unrealistic. The mentioned mineral species usually form under hydrothermal conditions. The only C-S-H products that form at ambient conditions are C-S-H I and C-S-H II [13, 15, 17]. Thus, the identification of historical lime hydraulic character is a complex problem. Other methods such as differential thermal analysis or scanning electron microscopy (SEM) may be needed to complement historic mortar characterisation. The durability of historical mortars supports the theory that at least some of them were made of hydraulic lime. It may be assumed that most historically produced limes were hydraulic due to the burning of limestones together with impurities, such as clay minerals.

As mortar ages, submicroscopic crystalline carbonates (micrite) dissolve from the lime binder, followed by a gradual growth of larger carbonate crystals (sparite). The recrystallization of carbonates contributes to the loss of strength of mortar due to crystallization pressure and the formation of cleavage cracks in sparite [18].

2 Materials and Methods

Polished thin sections, about 30μm thick, were prepared by grinding and polishing. The thin sections were examined by light microscopy using an Olympus BX51 polarization microscope. Polished sections etched with acetic acid fumes were used for the identification of unhydrated clinker minerals. Structural

examination of mortar fragment surfaces was carried out on carbon-coated samples using scanning electron microscopy (SEM). Mineral species were identified using energy dispersive spectroscopy (EDS). Both the SEM/EDS analyses were conducted on a JEOL JSM – 6490 LV, under 10kV and 0.5nA. The samples were softly ground using a mortar and pestle and then sieved with 0.063mm mesh to separate most of the aggregate from the binder. The undersize fraction was pulverised again and analysed by X-ray diffraction (XRD) using the Bruker D8 system with CuKα radiation (λ= 0.15418nm) and variable divergence slits at convention reflection geometry in the 6 – 80°2Θ angle range.

The age of historical mortars may be estimated by examining the secondary sparitic carbonates. The use of a calibration set of historical mortars of known age exposed to the same conditions is crucial for the estimation of the age [6].

3 Examination of the Gothic Mortars

3.1 Sampling

The House of Lords of Kunštát in Brno, Czech Republic, was built in Gothic style in the middle of the 14th century and rebuilt in Renaissance style in 1585-99. The building has been a part of The Brno House of Arts since 1958.

Twelve samples of Gothic mortars taken from various parts of the building (see Table 1) were examined with petrographic methods.

Table 1 List of examined samples, their age and position

sample	wall no.	estimated age	position
1	903	late Gothic*	ground floor, 1 – 1.8m above floor; pointing material
2	901	14th – 15th c.	ground floor, pointing material
3	905	14th – 15th c.	ground floor, 1 – 1.8m above floor; pointing material
4	919	14th –15th c.?	ground floor, 1 – 1.8m above floor; pointing material
5	900	late Gothic*	courtyard; rendering
6	1913	2nd half of the 13th c.	basement, ceiling just below ground level; masonry
7	1927 = 933	2nd half of the 13th c.	basement, 1.2 – 1.8 m above floor; pointing material
8	1928=933	2nd half of the 13th c.	basement, 2.4 m over floor; masonry of window seat
9	924	14th –15th c.	ground floor, 1 – 1.8m above floor;

			pointing material
10	1924	14th –15th c.	ground floor level; masonry
11	1912=919	14th –15th c.?	ground floor, 1 – 1.8m above floor; pointing material
12	1934	2nd half of the 13th c.	basement, 1.6 – 1.8 m above floor; masonry

*late Gothic = 2nd half of the 15th – beginning of the 16th century.

3.2 Basic characteristics of the samples

The basic characteristics of the samples are given in Table 2.

Table 2 Basic characteristics of the examined samples

sample	colour	character of binder*	binder [vol.%]	porosity [vol.%]	granulometry of aggregate	gravel [vol.%]	sand [vol.%]	estimated speed of recrystallization [mm/100years]
1	light pinkish surface, grey-white core	het	36	6-8	very coarse grained	32	25	0.00030
2	light pinkish	het	58	6-8	medium grained	10	25	0.00030
3	light brownish	het	16	8	coarse grained	58	26	0.00030
4	light brownish	het	51	7-9	very coarse grained	18	23	0.00020
5	light brownish	het	17	8	very coarse grained	48	35	-
6	light brownish	het	53	5	coarse grained	19	20	0.00033
7	light brownish	hom	38	8	coarse grained	19	35	0.00037
8	light brownish	het	44	5	very coarse grained	41	10	0.00030-0.00037
9	light grey-white to grey-brown	hom	10	7	coarse grained	53	37	0.0002-0.0025
10	light grey-white to grey-brown	fgs	31	10	coarse grained	16	38	-
11	light brown	het	21	8	very coarse grained	27	43	-
12	light brown	het	44	5	very coarse grained	41	10	0.0030-0.0033

*hom=homogeneous, het=heterogeneous, fgs=fine grained sparitic

3.3 Characterisation of the aggregates

The mineralogical and petrographic compositions of aggregates are shown in Tables 3 and 4.

Table 3 Semiquantitative mineralogical composition of aggregates

sample	quartz	alkaline feldspar	plagioclase	muscovite	biotite	amphibole	pyroxene	epidote	tourmaline	kyanite	staurolite	garnet	ore minerals
1	+++	++	++	++	-	+	+	+	+	+	-	-	-
2	+++	++	++	++	+	+	-	+	+	+	-	-	+
3	+++	++	++	++	+	+	-	+	+	+	-	+	+
4	+++	++	++	++	+	+	-	+	-	-	-	-	-
5	+++	++	++	++	+	+	-	+	-	-	+	+	-
6	+++	++	++	++	+	+	-	-	-	-	+	-	-
7	+++	++	++	++	+	-	-	+	-	-	-	-	-
8	+++	++	++	++	+	+	-	-	-	-	-	-	-
9	+++	++	++	++	+	+	-	-	-	-	-	-	-
10	+++	++	++	++	+	+	-	+	-	-	+	-	-
11	+++	++	++	++	+	+	-	+	-	-	-	-	-
12	+++	++	++	++	+	+	-	-	-	-	-	-	-

Table 4 Semiquantitative mineralogical composition of aggregates (follow up)

sample	granitic rocks	aplite	diorite, metadiorite	metabasalts	mylonite	mica schist	chlorite schist	garnet schist	chlorite schist	garnet schist	sillimenate gneiss	quartzite	metaquartzites	silicite	sandstone	„old red“ conglomerate	limestone	pottery fragments	slag	biomass	lime lumps
1	+	-	+	+	-	+	+	+	+	+	-	+	-	+	-	-	-	+	-	-	+
2	+	-	+	+	+	+	+	+	+	+	-	+	-	+	-	+	+	-	-	-	+
3	+	-	-	+	+	-	-	-	-	-	+	+	-	-	+	-	+	-	-	-	+
4	+	+	+	+	+	-	-	-	-	-	-	+	-	-	+	-	-	-	-	-	+
5	+	+	-	+	+	-	-	-	-	-	-	+	-	+	-	-	-	-	-	-	+
6	+	+	-	+	+	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	+
7	+	+	+	+	-	-	-	-	-	-	-	+	-	-	+	-	-	+	+	+	+
8	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+

9	+	+	-	+	+	-	-	-	-	-	-	+	-	-	+	-	-	+	-	-	+
10	+	+	+	+	+	-	-	-	-	-	-	+	+	-	+	-	-	+	-	-	+
11	+	-	-	+	+	-	-	-	-	-	+	+	-	-	+	-	-	-	-	-	+
12	+	+	-	+	+	-	-	-	--	-	-	+	-	+	-	-	-	-	-	-	+

In all examined mortars quartz, alkaline feldspars, and plagioclases are more abundant than micas (muscovite and biotite) and amphiboles (see Table 3).

Among rock fragments, granitic rocks generally outnumber metabasalts and mylonites. Quartzites, sandstones, aplites, and fine-grained diorites are less abundant. Sillimanite gneiss was identified in one of the samples.

The sand and gravel fractions are coarser in the light brown mortars from the 2nd half of the 13th century than in the younger samples. The aggregate is relatively diverse in the pinkish and light brown pointing mortars from the 14-15th century and from the late Gothic period (2nd half of the 15th – beginning of the 16th century). They are composed of a variety of mineral and rock clasts of variable shape and rounding. In the older mortars, granitic rocks are more abundant than metabasalts. Aplites, quartzites, silicites, and mylonites are less abundant. In addition to quartz, alkaline feldspars, and plagioclases, muscovite, chloritised biotite, garnets, amphiboles, pyroxenes, epidote, and seldom kyanite, tourmaline, and ore minerals are present among the mineral fragments (see Table 3). The aggregate mainly consists of sand grains (1–2 mm), with less abundant gravel (2–20 mm fraction).

The sand fraction of the 13th and 14-15th century mortars is composed only of eroded bedrock fragments. The late Gothic mortars also contain river sand. Most likely, the sand comes from the terraces of the Svitava or Svratka river. Pottery fragments and slag were identified in some samples (see Table 4, Fig. 1).

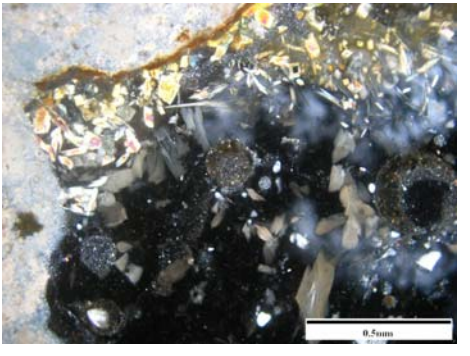

Fig. 1 Sample no. 7 - photomicrograph of slag fragments; crossed polars

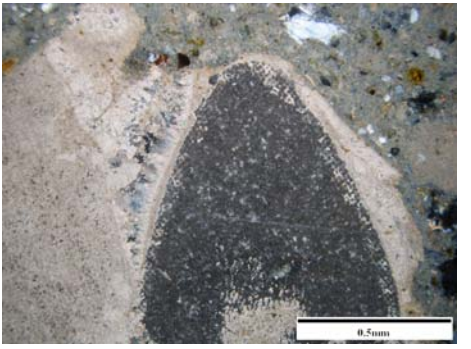

Fig. 2 Sample no. 2 - photomicrograph of unburned crinoide limestone corresponding to samples from Stránská Skála; crossed polars

3.4 Binder

All examined mortars were lime-based. The lime for their production was burned at low temperatures. Lime lumps can be identified in all the examined samples (Fig. 3), and the origin of the limestone may be tracked. The source of limestone for lime burning was the Oxfordian limestones of the Stránská Skála historical quarry. The Stránská Skála Oxfordian limestones are formed of relatively pure calcite with low contents of clay, quartz and other constituents [19, 20].

No relics of unhydrated hydraulic phases were found in thin sections or acetic acid fume-etched polished sections. The presence of very low amounts of unhydrated clinker minerals cannot be excluded based on XRD measurements (Fig 5); however, it also cannot be verified due to overlaps of the most intense belite peaks with diffraction lines of the other minerals present in the samples. No crystalline calcium hydrosilicates or calcium hydroaluminates were identified in the X-ray diffraction patterns. Due to their durability, it can be assumed that most of the examined mortars were slightly hydraulic lime-based, although no clear evidence supporting this theory was found.

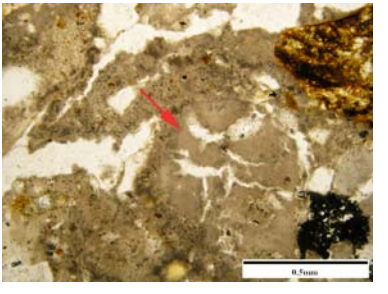

Fig. 3 Sample no. 11 - photomicrograph of a lime lump; plane polars

Gypsum was identified in samples 4 and 8, possibly of secondary origin. Sample 4 has low carbonate and very high illite content (Fig. 5), which corresponds to high clay content in the mortar. Secondary halite was identified with SEM/EDS in sample no. 4 (Fig. 4).

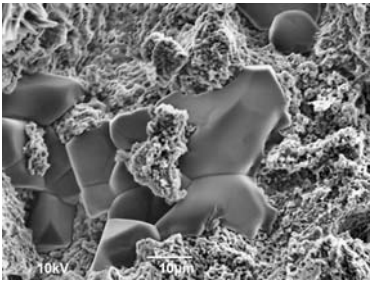

Fig. 4 Sample 4 - SEM image of halite crystals in recrystallized carbonate binder

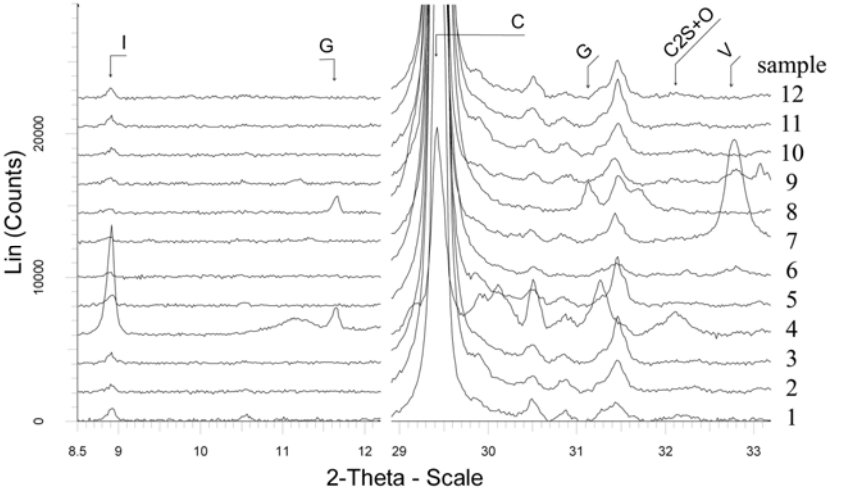

Fig. 5 Sections of diffractograms of the examined samples evaluated with respect to binder composition; I = illite, G = gypsum, C = calcite, C2S = belite, O = orthoclase (overlapping with belite doublet), V = vaterite

Vaterite was identified in samples 6, 7, and 9. Despite the fact that vaterite is considered to be a metastable mineral that tends to transform to calcite [21, 22], it represents quite a common constituent of mediaeval mortars. Conditions of vaterite formation and stability are still not clearly explained.

The composition of the examined mortars does not vary considerably, but the mortars display different degrees of micrite recrystallization (Fig. 6). Based on the evaluation of the carbonated lime-based binder recrystallization degree and by comparison with archaeologically dated samples, it was concluded that the mortars belong to three separate periods. Samples 1, 2, 4, 9, and 11 display low micrite recrystallization degree and, thus they are the youngest in the set. A higher recrystallization degree was identified in samples 5 and 6. Samples 7, 8, and 12 are the most recrystallized and, thus the oldest in the set. The estimated speed of recrystallization is given in Table 2.

The degree of recrystallization strongly depends on the age and also on the position of the sample within the structure. The samples of mortars from the walls 1 – 1.8m above the ground have a much lower degree of recrystallization than samples from the courtyard and basement from the same period. Therefore, comparative archaeologically dated samples are necessary for age estimation.

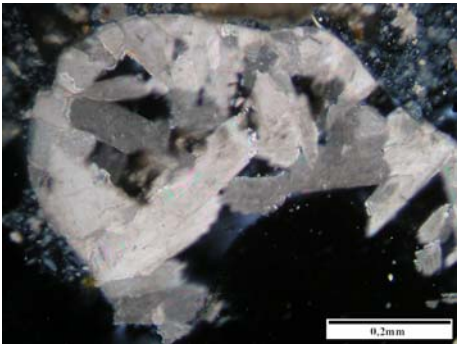

Fig. 6 Sample 8 - photomicrograph of calcite crystals filling a pore

4 Conclusion

By studying the sampled mortars, it was possible to identify three building periods: 2nd half of the 13th century, 14th-15th century, and 2nd half of the 15th – beginning of the 16th century. The limestone used to produce the lime came from the Stránská Skála historical quarry, where the lime was also burned. This site is located about 4km from the House of Lords of Kunštát in Brno. The aggregates of

the oldest mortars came from the eroded bedrock, while the younger samples displayed an addition of river sand. The nearest river terraces are about 2km away from the structure of interest. The technology of mediaeval mortar production is also documented by presence of pottery fragments and slags in some of the samples.

5 Acknowledgements

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I.19

On the Relevance of Earthen Supports Material Characterisation: Case Study Nako in Western Himalayas, India

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Abstract Since 2004 the Conservation Department of the University of Applied Arts Vienna has been active in saving Tibetan cultural heritage of Nako in Western Himalayas, North India. Main goals are the conservation, study, and long-term preservation of the Buddhist temple complex interior decorations dating back to the 12th century. The research project *Scientific Study of the Artwork at Nako, India,* addresses the polychrome surfaces of the significant decorative elements that are executed on earthen supports. First of all, the research on adobe, earthen joint and rendering mortars, clay from sculptures, and local soils used for traditional building practice considerably contributes to the conservation of the mural paintings and sculptures of the temples. Furthermore, the analyses on material characterisations of the earthen supports represent an attempt to contribute to the material culture of earthen building practice, its past and tradition until present.

1 Introduction

Situated at 3.600 m above sea level in the Western Himalayas, North India, the small village of Nako houses a rare example of an early Tibetan Buddhist temple originating from the 11th to 12th centuries (See Fig. 1). The four earthen temple buildings are built as a windowless single-storey construction capped with a flat roof. The building foundations are made of stones onto which are built walls composed of adobe, joined, rendered, and plastered with earthen mortars; the roofs are constructed over wooden beams and columns which are insulated with earth. Nondescript from the outside, the temples' 12th century and later interior decorations, today partly overworked and over painted, bear witness to the outstanding art and cultural history of Western Tibet: including valuable mural

paintings executed on earthen supports, polychrome wooden elements and ceilings, and clay sculptures.

Due to natural disasters, climate change, and centuries of inconsistent maintenance, the earthen buildings have shown alarming signs of damage and deterioration. Thus, in 2002 the multinational and interdisciplinary *Nako Research and Preservation Project (NRPP*) [1] funded by the World Monuments Fund (WMF), was initiated to save and preserve the endangered ensemble. Evolving from its participation within the NRPP, the Conservation Department of the University of Applied Arts, Vienna, together with its Indian project partners, has been active in the research and preservation of the rich cultural village heritage from 2004 to date [2]. The main tasks have been the conservation of the temple interiors and their scientific examination, the establishment of a village museum, the preservation of the local Thangka collection and the establishment of workshops for the village and lama community.

Fig. 1 Nako temples © Conservation Department, University of Applied Arts, Vienna.

A comprehensive three-year programme on the temples´ interior decorated surfaces, the *Scientific Study of the Artwork at Nako, India* funded by the Austrian Science Fund (FWF project no. L335-N19) has focused on the basic research of the materiality and technology of the earthen supports and paintings as well as their decay and deterioration. A key goal of the study was to develop appropriate conservation treatments for the interior decorations which could be gradually implemented into a conservation programme.

Research on the earthen supports leading to the reproduction of support specimens addressed the four temples' architectural structures which consisted of adobe, joint and rendering mortars, clay from the sculptures and local soils [3-9]. The work was based on previous studies related to the temples´ earthen structures including architectural surveys [10, 11], the examination of mural paintings [12]

and ceiling panels [13] and the study of plasters and earthen conservation materials [14]. Since the architecture of the Western Himalayan earthen temples has rarely been studied from the material point of view, the study of clay for conservation purposes in the Ladakh region is particularly noteworthy [15].

2 Materials and Methods

2.1 Research Scope

Conservation, preservation, and long-term maintenance of the temples' interiors pose a wide scope for study of the earthen supports. Material composition, structure, mechanical and physical properties were investigated to characterise the supports and soils. Field work and analytical examinations, including standard and non-standardized tests, have been applied.

Besides its priority to conservation, this research has strongly contributed to the understanding of earthen material culture and its traditions for this particular region. Earthen architecture often, as in Nako, presents anonymous architecture that usually lacks written records regarding building dates, architects, craftsmen or building practices; the earthen temples themselves are the only historical and material sources to address simple questions such as "Who built the temples? When? and How?". Well aware that these questions could not be answered unambiguously through materials characterisation, this paper attempts to interpret and discuss the study results in regards to the following key questions: how were the earthen supports of the four temples made? What was the technology of their preparation? And, is the building know-how from the past still relevant in recent *traditional* earthen building practice?

2.1.1 Field work

Field work consisted of a historic structure survey of the supports, the documentation of the different building materials used and technologies applied and an assessment of the structural damages, deterioration processes and their possible causes and environmental monitoring. On-site survey was documented with photographs, descriptions, and digital mapping [16]. On-site measurements were applied to assess the supports' surface resistance, conductivity, temperature and moisture content [17]. Sampling was performed not on intact wall surfaces but on areas with damage to the architectural fabric that required conservation treatment.

Local soils used as raw materials for still-existing traditional earthen building practices were identified and sampled. Recent building techniques known and applied by craftsmen in Nako were studied and documented [18].

2.1.2 Analytical work

Selected samples of adobe, joint mortars, plasters, local soils used for traditional building practice, and reproduced support specimens were investigated. Thin sections were studied using optical microscopy in normal and polarized light. Particle size distributions were examined using the standard sieving method. Mineralogical compositions and clay mineralogical compositions on fractions < 2 μm were analysed with X-ray diffraction, supported by differential thermal analyses and carbonate determination according to Scheibler; these were quantified through X-ray fluorescence analysis. Loss of moisture and loss of ignition were assessed, as well as the total carbon content through combustion in oxygen and by using infrared detection. Contents of vegetal fibres were determined with the standard sieving method. The salt content of the soils was analysed through ion-chromatography. Soil-mechanical parameters of local soils such as Atterberg and shrinkage limits were investigated as well as critical shear strengths which were determined through direct shear tests. Analyses on bulk and true density, water vapour adsorption isotherms, water vapour permeability, water uptake, porosity through Hg-porosimetry and optical microscopy combined with digital image analyses and compressive and bending strength analysis are in process.

3 Results and Discussion

3.1 How were the earthen supports of the temples made?

3.1.1 Local soils

Local soils used as raw earthen materials for application in recent building practices are called Thawa, Tua and Sassa and differ in source, texture, material composition, quality, and resultant use. These materials are also seen to be used in the earthen temples of Western Tibet. The abundant Thawa is a commonly-used, rather coarse aggregate, brown in colour, poor in clay and consisting of around 30% quartz, 50% feldspar, and 11% sheet silicates. Tua is found on one site at Nako, the fine-grained soil is of a whitish brown colour and is utilized as a binder for mortars; 25% of the minerals are of quartz, around 30% sheet silicates, and nearly 40% calcite. The clay minerals of Thawa and Tua are similar, in the main consisting of mica/illite and chlorite. Sassa is an inhomogeneous material; it is fine grained and the clay-rich components are of a greenish white colour and are especially used for waterproofing applications. Sassa comprises of around 50% quartz and feldspars, 35% sheet silicates, and almost 20% calcite and dolomite,

and is seen to contain mostly swelling clay minerals of mixed-layer types (all given in mass %).

3.1.2 The manufacture of adobe

Adobes from all four temples show a very similar material composition, structure and block measures. Unlike joint and rendering mortars, the materiality and technology of adobe manufacturing was not altered during the construction of the temple complex. As the temples feature 60 to 110 cm thick walls, a high amount of pre-fabricated adobe blocks was needed; manufacturing of adobe demanded a quick and efficient, mass-production method. From analyses of particle size and mineralogical composition, simple unsieved Thawa, without any vegetal fibres, mixed with Tua was considered the best material to use. Thawa could be easily taken from the construction site and used immediately without any preparation. The adobes were cast into wooden moulds, compressed by hand, turned out and then left to be sun-dried. Adobe blocks of all the four temples measure c. 10 x 21 x 42 cm, which is in accordance with the typical block size for the early building period in Western Tibet until the 15th century [19]. Due to the mainly Thawa composition, plasticity indices of adobes are low at 7 mass %, critical shear strengths are at a high friction angle of 36°, and there are no salts present due to the raw materials used.

3.1.3 The manufacturing of joint and rendering mortars

Joint mortars can be easily distinguished from those used in renders since the former contain no vegetal fibres, are of a special reddish colour, and are rather coarse in texture. Mineralogical compositions of the joint mortars vary, containing different rations of Tua and Thawa, from 1:4 to 1:5; occasionally they can contain pure Thawa.

The first decoration phase of all four temples used two different mortars for the plastering: a coarser and a finer one. These two mortars do not differ in mineralogical composition, but in grain size distribution and by the addition of vegetal fibres (See Fig. 2). All coarse plasters are made of Tua and sieved Thawa mixtures in varying ratios of 1:4 and 1:5 and contain vegetal fibres; often thick barley straw cut into 3-7 cm long pieces. This mortar preparation technique corresponds to that used in traditional Tibetan architecture [20]. Fine mortars of three of the temples again show the use of the Tua and sieved Thawa mixtures in ratios of 1:4 to 1:5, with rather thin barley straw in 1 cm lengths added to the mix. In the fourth temple no vegetal fibres were added into the fine plaster which contained a higher admixture of Tua. The modification of mortars with organic substances such as animal dung and animal glue needs further investigation.

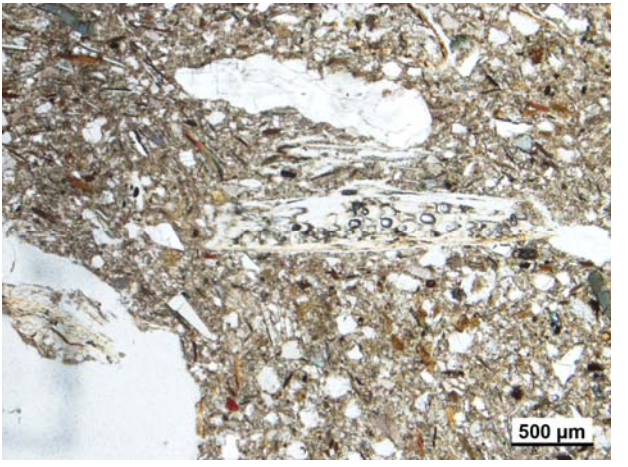

Fig. 2 Coarse plaster in thin-section seen under polarized light (area of 3.5 x 2 mm) © IATCS, University of Applied Arts, Vienna

3.1.4 Application of adobe, joint and rendering mortars

All the temple walls are constructed only of adobe over a foundation of stone, with the exception of one of the buildings that is built up to half the walls' height with stone. The stone and adobe are joined with mortars; joint mortars are laid horizontally between the single rows of adobe, each joint measures c.2 cm. Flat stones have been found inserted into the joints, possibly to serve as anchors for the adjacent renderings.

Fig. 3 Translator's temple, South wall, 8 m in length © Conservation Department, University of Applied Arts Vienna

The plasters of the first decoration phase in all the temples were applied in a two-layer system to level the walls and provide support for the paintings which consist of glue-bound paint layers over a ground gypsum support layer. In secondary decoration phases, only one plaster layer was applied to support the paintings. For the first phase's two-layer system, a coarse mortar was applied as a lower plaster, with its thickness (from 1-7cm) being dependent upon the evenness of the adobe walls to which it was applied. The upper plaster layer, without any further anchoring, consists of a finer mortar applied in a much thinner layer from 0.2 to 1 cm thick. The lower plaster layer had a rough surface and was presumably planed with wood whereas the surface of the upper plaster layer was finely smoothed, probably with stone, to prepare a truly perfect ground for the elaborate murals (See Fig. 3).

3.2 Are the temple-building skills from the past relevant in recent building traditions?

Growing tourism in Nako has caused an increase in prosperity for the villagers and a rising need for new hotels, shops and restaurants. Many of these buildings are built with cement-based materials and bricks, which are considered *modern*. However, there are village authorities and private house builders whose concern for village authenticity results in the continuation of the use of *traditional* earthen building techniques. Local masons still know how to use local soils, Thawa, Tua and Sassa, for different building applications. Earthen rendering and roofing techniques are applied today, but instead of adobe, stones are used for the building of structures. Also the vernacular architecture in the nucleus of this historical village is mainly composed of stone built-houses with wood, plaster and earthen roofs.

Surprisingly the mixture of Tua and Thawa (1:4) that was found to be used for the temples' earthen supports continues to be used in Nako for making plasters; proving that the traditional knowledge of the past is still being used today.

4 Conclusion

This research programme, focussed on the Nako temple interior decorations, opened up the tremendous possibility to study the earthen supports that are usually neglected, or at least not very extensively studied. Similarly, the earthen building materials and techniques used in Nako would probably have never been under investigation if they had not served to support the highly significant polychrome mural paintings and sculptural decorations that the site is famed for.

Through studying the earthen supports and local soils it was possible to define their main components and to characterise their main material parameters; such parameters led to an understanding of the supports´ materiality, technology, and

susceptibility to decay and deterioration and has therefore contributed to the field of earthen material culture studies in the Western Himalayas.

5 Acknowledgements

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I.20

Ancient Gypsum Mortars from Sta. María Magdalena Church (Zaragoza, Spain): Advances in Technological Manufacture

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Abstract Gypsum mortars were very commonly used during the Mudejar artistic period in Spain from the 12th to 16th century. The region of Aragon is one of the most important centres of Mudejar architecture in the country, and the church of Sta. Maria Magdalena sited in Zaragoza, is a particularly authentic example of this artistic style of construction. The research has been carried out by selecting a group of representative and unaltered samples from original joint mortars. The characterization of different mortars was made using Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Differential thermal-thermogravimetric analysis (DTA-TGA). In this paper, the results reveal that all mortars analysed display homogeneous composition in the different sampling areas from the monument. The main component of the samples is gypsum. In addition, different hypotheses are established about technological procedure and the type of raw materials used.

1 Introduction

The Church of Sta. María Magdalena is located in the historic quarter of Zaragoza (Spain) and was built in the 14th century (Fig. 1A). The Monument is a representative temple belonging to Aragonese Gothic Mudejar architecture and was erected upon the ruins of a primitive Romanesque Church dated from the 12th century [1]. It was declared a National Monument in 1982 and has been part of World Heritage since 2001 together with other remains of the Aragonese Mudejar Heritage.

The Monument has undergone a considerable number of transformations between the 17th-18th centuries during the Baroque period, but the structure and tower still preserve their original appearance. The research carried out in this paper was begun in 2007 during restoration works on the Monument, especially on its main façade.

The Monument is built of brick masonry with gypsum mortar-filled joints. There is very scarce previous information about the characteristics (composition, texture or manufacture) of these kinds of mortars [2].

The main objective of the paper was to characterize the ancient gypsum mortars by mineralogical and chemistry techniques. The study will help to better our understanding of the technology of mortar production used in this artistic style of construction. The knowledge obtained from the mortars studied will allow us to prepare restoration mortars with compatible characteristics.

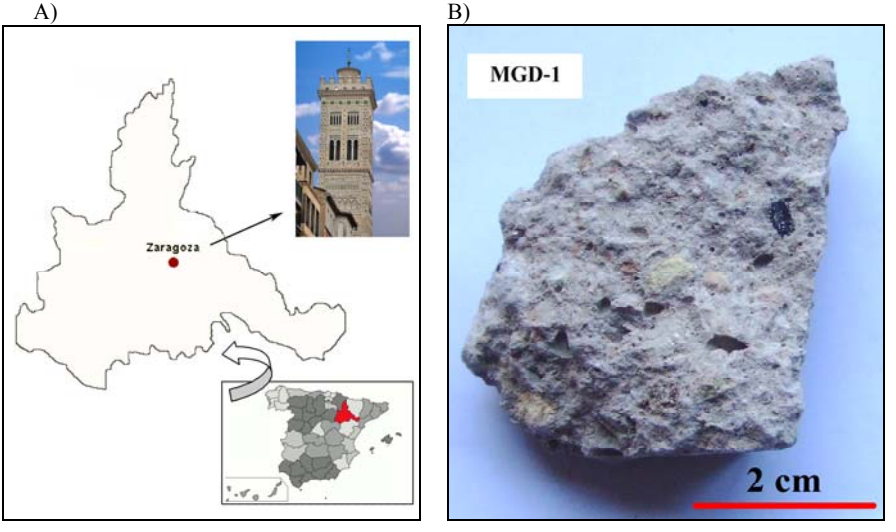


Fig. 1 A) Geographic location of the Monument studied. B) Representative sample in hand specimen. Different kind of aggregates can be observed.

2 Materials and methods

In the preliminary phase, an analysis was made of different architectonic areas of the Monument to guarantee genuine representative samples of the original joint mortars. Samples were taken in different heights of five zones of the building.

A group of 17 representative unaltered samples were collected from both external and internal parts of the original joint mortars. Previously, samples were examined macroscopically using a binocular microscope (Fig. 1B). Next, the whole mortars were analysed by different analytical techniques.

Fourier-Transform Infrared Spectroscopy (FTIR) was used for the qualitative identification of the main mineralogical components and the hypothetical reaction products which can form in the mixtures. A Nicolet 6700 infrared spectroscope equipped with double haze, double diffraction net and a 4 cm^{-1} spectral resolution was employed and FTIR spectra were collected in the range 4000–400 cm^{-1}.

The qualitative mineralogical and chemical characterization of different crystalline phases in mortars was completed with X-ray diffraction (XRD) using a powder crystalline method in bulk samples. These were previously milled in an agate mortar down to < 63μm particle size, mixing fragments from the inner and outer parts of specimens. Powder samples were analyzed with a Philips XPert MPD Pro diffractometer with Cu Kα radiation, working 40 kV and 30 mA in an X-ray tube and step size 0.02º/seg. A 2θ angle range from 5 to 60º was registered. A semi-quantitative analysis was made using reference intensity ratios from mineralogical detected phases, accepting 5-10% of relative error.

Thermal methods employed in this work were thermogravimetric (TG) and differential thermal analysis (DTA) in order to make quantitative determinations of different components in the total sample. Analysis was recorded in nitrogen atmosphere with a TA SDT Q600 mixed-analyser. The heating was programmed with an initial temperature rise from ambient to 250ºC, at a rate of 4ºC/min; a second rise was applied at 10ºC/min until the end of experiment (1000ºC).

3 Results and Discussion

3.1 Visual description of the samples

In Table 1, the samples are presented by different areas and orientation (North to South) from the church. The main data obtained by visual observation of the samples are also summarized in Table 1.

From a macroscopic point of view, all joint mortars displayed a high cohesion and consistency and no evidence of alteration was observed. Samples consisted chiefly of a mixture of gypsum and aggregates with an inhomogeneous grain-size distribution and white-greyish colour. Different kinds of materials could be recognized among the aggregates such as black charcoal particles or orange angular shaped ceramic fragments, but coarse-grain carbonated and gypsum rock fragments are the main component of the aggregates. Relatively abundant porosity was also identified (Fig. 1B).

3.2 Mineralogical characterization

The results obtained by means of FTIR and XRD indicate that the mineralogical composition of the five sampling areas is very similar in terms of the main constituents.

Table 1 Sample locations and main aggregates identified by visual observation.

Sample	Sampling area	Height (m)	Colour	Presence of Aggregates
MGD-2, 15, 16, 17, 18	*Buttress 3. South*	*5*	white-greyish	Gypsum rock fragments + Carbonate rock fragments ± Charcoal particles ± Ceramic fragments
MGD-6, 8	*Façade. North*	*2*		
MGD-10, 11, 13, 14	*Buttress 2. South*	*5*		
MGD-19, 21, 24	*Buttress 2. North*	*5*		
MGD-25, 26, 27	*Buttress 3. North*	*5*		

3.2.1 Fourier-Transformed Infrared Spectroscopy (FTIR)

Fig. 2A shows a qualitative analysis of the mineralogical phases identified by means of FTIR. The corresponding absorption bands and their assignation are also given.

Gypsum is the main component of mortars. It displays strong absorption bands in different regions of spectra (3500-3400, 1700-1600, 1150-1120 cm^{-1}). In all spectra, a strong band shown at 1440 cm^{-1} is attributed to the presence of carbonates. Calcite and dolomite can be distinguished through two diagnostic absorption bands; a weak absorption at 729 cm^{-1} reveals the presence of dolomite while the weak band at 713 cm^{-1} can be attributed to calcite. Different absorption bands related to quartz were also detected in all samples (798-778, 462 cm^{-1}). Finally, potassium nitrate can be displayed as an impurity in the mortars. In several spectra, a sharp band at 1384 cm^{-1} was registered which is correlated to the $(NO_3)^-$ vibration zone.

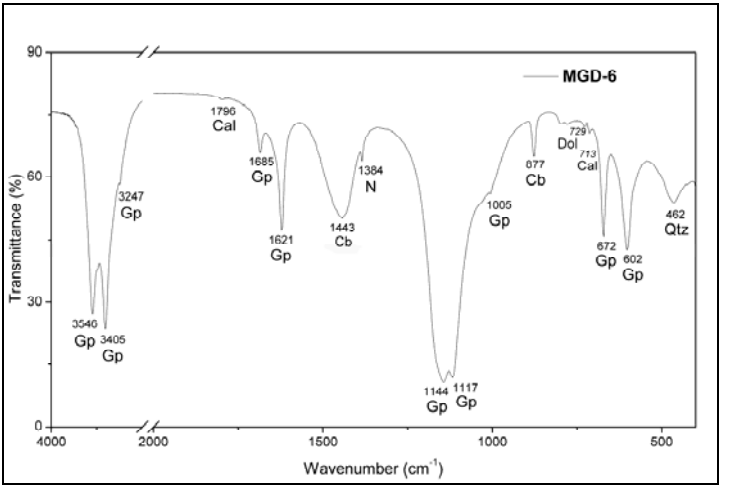
3.2.2 X-Ray Diffraction (XRD)

In the Fig. 2B a representative diffractogram of samples is presented. Results agree with the FTIR data. The XRD patterns indicate the following mineralogical association:

Gypsum + Calcite + Quartz + Feldspar + Anhydrite ± Phyllosilicates

Gypsum is the main mineralogical phase in all mortars. With the exception of sample MGD-15, abundant amounts of calcite have been identified. Quartz, anhydrite and feldspars (anorthite) have also been detected in very low proportions. Phyllosilicates (illite-moscovite), pure lime and dolomite can be distinguished in several samples. The identification of pure lime and dolomite became complicated as it may well have been masked by the gypsum. Furthermore the absence of dolomite may be due to a relatively minor proportion in the mortars with respect to calcite.

A)



B)

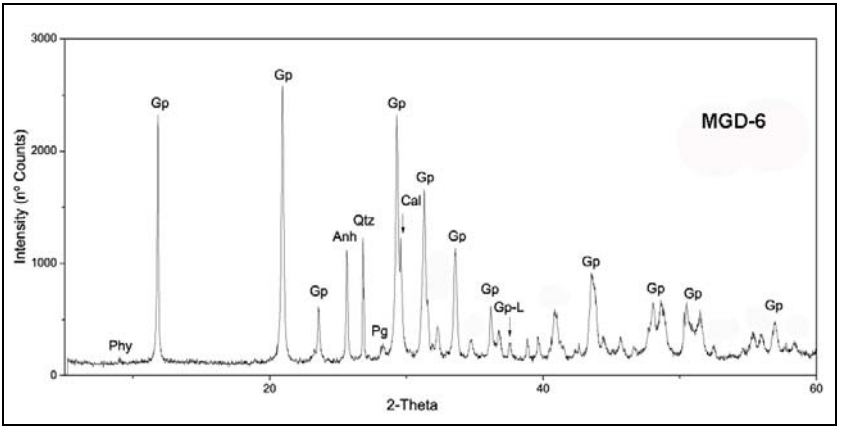


Fig. 2 A) FTIR spectra of the sample MGD-6. B) Diffractogram of the sample MGD-6. Notation used in both Figures. Gp: Gypsum, Cb: Carbonates (calcite-dolomite), Cal: Calcite, Dol: Dolomite, Phy: Phyllosilicates, Anh: Anhydrite, Qtz: Quartz, Pg: Plagioclase, N: Potassium Nitrate, L: Lime.

3.3 Thermal Analysis (DTA-TG)

The results derived from the DTA-TG analysis are shown in both Table 2 and Fig. 3. In Table 2, the weight loss percentage at each estimated temperature range, as well as the quantification of gypsum and carbonate are detailed.

All mortars display similar thermal behaviour with curves in which at least four endothermic effects can be observed (Fig. 3).

In Table 2, the first temperature ranges correspond to the weight loss due to the release of hygroscopic water (20-100ºC). An important reference point in the analysis of these results is the weight loss in the range between 100-180ºC corresponding to the dehydration of gypsum due to it transforming into anhydrite (III). Weight loss within the range 180-635ºC is attributed to the loss of bound water either the dehydroxilation of clay compounds or the presence of organic matter in the mortars [3]. The loss of CO_2 due to the decomposition of carbonates is produced between 550ºC and 800ºC and corresponds to the last endothermic effect observed in all samples.

The total weight loss ranges from 21 to 24%, indicating the homogeneity of the mortar composition. Gypsum is the main component in all sampling areas studied according to the approximate contents (69-83%) obtained (Table 2). These data are in accordance with those obtained by FTIR and XRD.

Carbonate compounds are found in mortars in very low proportions (4-13%). Calcite has been identified in all mortars, whereas dolomite has only been differentiated in the samples corresponding to the *North Façade* sampling area (Fig. 3B). Both carbonates can be distinguished by means of two characteristics endothermic peaks [4]; the weight loss within the range of 550–700ºC is due to the decarbonation of magnesium carbonate, while the weight loss between 700-800ºC is associated with the decarbonation of calcium carbonate (Fig. 3B).

Thermal transformations can also be observed in Fig. 3 from DTA analysis. The samples show at least two exothermic events; a sharp exothermic peak at about 260ºC could correspond to the beginning of anhydrite III to anhydrite II transition. On the other hand, exothermic reactions produced in mortars in the range 300-500ºC attributed to the presence of organic matter, are situated between 440-460ºC (Fig. 3B).

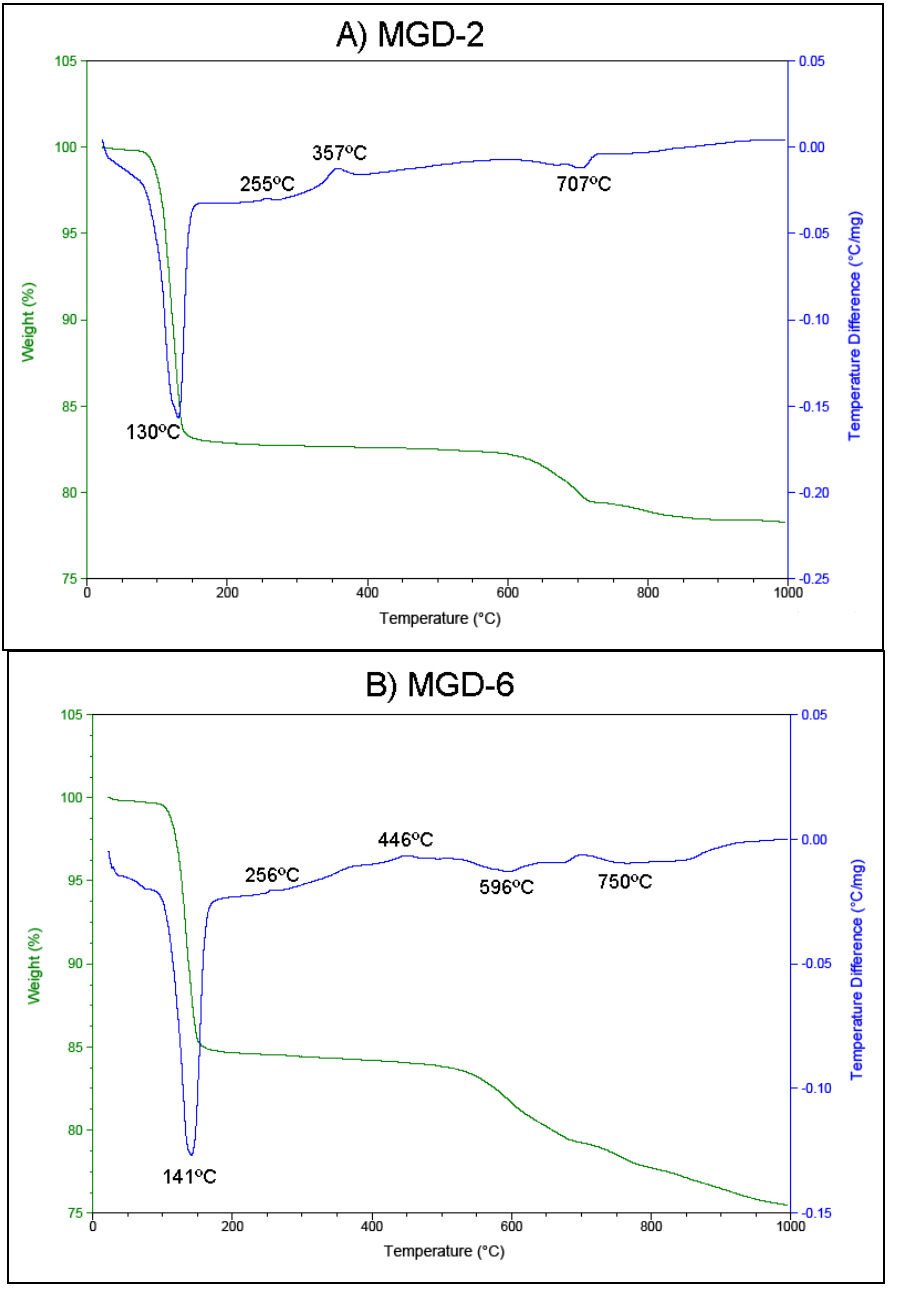


Fig. 3 DTA-TG curves of the samples MGD-2 and MGD-6 with the characteristics peaks of gypsum dehydration and calcium or magnesium carbonate decomposition.

Table 2 Weight loss (%) per temperature range and gypsum ($CaSO_4 \cdot 2H_2O$), calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] quantification in the samples analyzed.

Sampling Area	Samples	Weight loss (%) per temperature range (ºC)						%	%	%
		20-100	*100-180*	*180-635*	*635-755*	*755-1000*	*Total*	Gyp.	Cal.	Dol.
Buttress 3. South	MGD2	0.24	16.69	0.97	2.68	1.13	21.71	79.74	6.09	-
	MGD15	0.55	16.76	0.5	2.2	0.96	20.97	80.08	5.00	-
	MGD16	0.51	17.06	1.84	2.12	0.66	22.19	81.51	4.82	-
	MGD17	0.79	16.46	1.97	2.0	0.98	22.2	78.64	4.55	-
	MGD18	0.25	17.01	1.18	2.58	0.89	21.91	81.27	5.86	-
Buttress 2. South	MGD10	0.27	16.91	0.99	2.78	0.62	21.57	80.79	6.32	-
	MGD11	0.26	17.25	0.93	2.6	0.6	21.64	82.42	5.91	-
	MGD13	0.25	17.11	0.97	2.79	0.9	22.02	81.75	6.34	-
	MGD14	0.27	17.33	1.17	2.19	1.1	22.06	82.80	4.98	-
Buttress 2. North	MGD19	0.24	16.84	1.29	2.19	1.46	22.02	80.46	4.98	-
	MGD21	0.66	16.26	1.48	2.98	0.54	21.92	77.69	6.77	-
	MGD24	0.49	16.56	1.51	2.61	0.87	22.04	79.12	5.93	-
Buttress 3. North	MGD25	0.29	17.25	1.1	2.81	0.92	22.37	82.42	6.39	-
	MGD26	0.61	16.42	1.35	2.92	0.85	22.15	78.45	6.64	-
	MGD27	0.74	15.91	1.66	2.86	0.57	21.74	76.01	6.50	-

Sampling Area	Samples	Weight loss (%) per temperature range (ºC)							%	%	%
		20-100	*100-180*	*180-550*	*550-800*		*800-1000*	*Total*	Gyp.	Cal.	Dol.
					550-700	*700-800*					
Façade North	MGD6	0.51	14.42	1.53	4.18	1.27	2.58	24.49	68.90	2.89	8.76
	MGD8	0.27	15.17	1.37	4.28	1.67	1.4	24.16	72.48	3.79	8.97

4 Conclusions

The characterization of selected samples has revealed that all mortars analysed display homogeneous composition in the different sampling areas from the monument. The proportion and type of carbonates identified are the main differences found between the *North Façade* and the others sampling areas.

The results obtained confirm gypsum as the main component of these ancient mortars displaying an estimated proportion higher than 69% in weight. Calcite and dolomite are subordinate compounds, with relative amounts lower than 13%. Quartz and feldspar are also accessory components in the mortars. Furthermore,

the presence in very low proportions of phyllosilicates as well as organic matter has been corroborated by means of the different analytical techniques used. Nitrates identified by means of FTIR could be attributed to degradation products found on monuments located in polluted areas [5].

Coarse-grain gypsum and carbonated aggregates have been distinguished by visual observation as the main components of the aggregate. Furthermore, a relatively low proportion of anhydrite was detected in the samples by means of XRD. The presence of these compounds shows that the mortars analysed were the result of a multi-phase structure of the gypsum, obtained by craft production methods [6]. Coarse-grain aggregates could have been a by-product from the grinding process. Their addition improves the quality of mortars. With the exception of ceramic and charcoal fragments, the remainder of the components are normally derived from sedimentary deposits used as raw materials. The very low proportions of charcoal particles detected could be attributed to impurities from the kiln fuel.

The use of complementary techniques such as the optical microscopy observations will proceed in order to complete characterization of the samples collected.

5 Acknowledgements

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I.21

Micromorphological Textures and Pozzolanic Cements in Imperial Age Roman Mortars

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Abstract The highly durable pozzolanic mortars of wall concretes from the Theater of Marcellus and Great Hall of Trajan's Markets preserve traces of micromorphological textures in altered Pozzolane Rosse volcanic ash. Reaction of hydrated lime with potassic scoriaeceous ash, and halloysite, phillipsite, and chabazite surface coatings, as well as Tufo Lionato tuff particles, produced distinct, alkali- and alumina-calcium-silica hydrate cement microstructures, including strätlingite. The assemblage of diverse pozzolanic components in the Trajanic mortar was remarkably effective in combining hydrated lime.

1 Introduction

The volcanic ash-hydrated lime mortars of the extraordinarily durable, composite concretes of Imperial age monuments in Rome contain altered granular, scoriaceous ash aggregate (*harenae fossiciae*) from the Pozzolane Rosse pyroclastic-flow, erupted at 456±3 ka from Alban Hills volcano (Fig. 1) [1]. The lime is ~95 wt% CaO calcined from the limestone bedrock of the Appennines [2]. The high quality mortars of the walls of the Great Hall of Trajan's Markets (~96-115 CE), have Pozzolane Rosse from various alteration facies, finely ground Tufo Lionato zeolitic tuff, amorphous alkali- and alumina-rich cement hydrates, and strätlingite (gehlinite hydrate, C_2ASH_8), which gives modern cements good durability and compressive strength [3]. The mortars of the Theater of Marcellus (~23-11 BCE), constructed 120 years earlier, also have strätlingite cement (Fig. 2), Pozzolane Rosse with mainly argillic alteration, and slightly more coarsely ground Tufo Lionato. The pozzolanic components of Pozzolane Rosse ash are the alkali-rich groundmass of altered scoriae; opal and limpid halloysite surface coatings from a transitional Bt to Bw soil horizon (Fig. 3a); and phillipsite and

chabazite surface coatings from the lowermost C horizon of the deposit, altered in ground water (Fig. 3b,c) [1]. Here, we address questions about the diverse compositions of the altered Pozzolane Rosse ash, their relict, authigenic clay and zeolite textures in the mortars, and the compositions and microstructures of associated pozzolanic cements. We emphasize the importance of micromorphological context [4] in describing the stratigraphic distribution and composition of pozzolanic components of the Pozzolane Rosse pyroclastic-flow deposit: the opaline silica, poorly crystalline clay minerals, and zeolites that activate pozzolanic reactions [5]. Petrographic and backscattered scanning electron microscope images (BSE-SEM) and energy dispersive spectrographic (EDS) analyses provide a foundation for gaining insights into the Pozzolane Rosse and Tufo Lionato ashes, describing the mortar microstructures, and developing durable alkali-rich calcium-aluminum-silica cement gels and strätlingite cements for modern repair mortars.

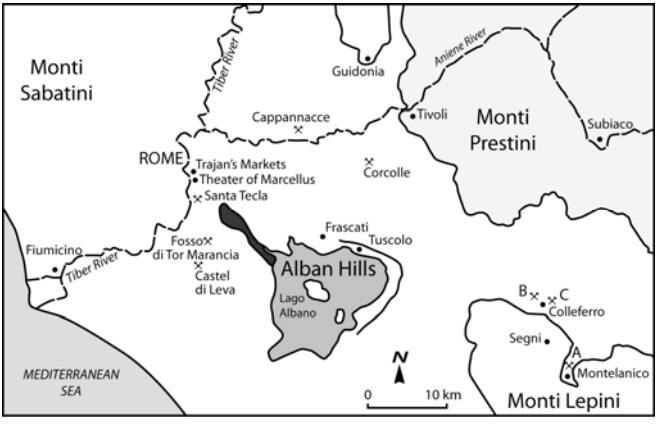

Fig. 1 Map showing the Roman region and specimen sites

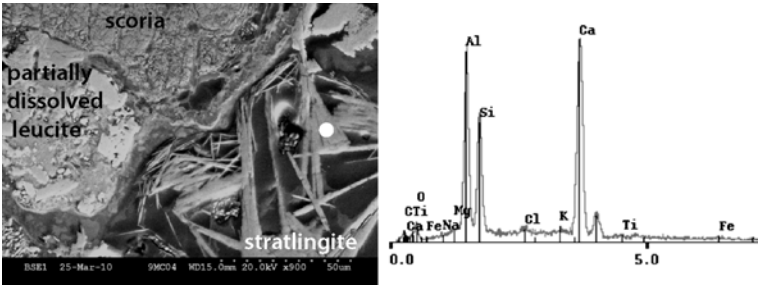

Fig. 2 Theater of Marcellus substructure, SEM-EDS analysis of strätlingite cement

2 Alteration facies of the Pozzolane Rosse pyroclastic-flow

Pozzolane Rosse is the lowermost of the three Alban Hills mid-Pleistocene granular volcanic ash pyroclastic-flow deposits, which are locally interlayered with epiclastic ash and Monti Sabatini airfall and pyroclastic-flow deposits, as shown for the Cappannacce quarry northeast of Rome (Figs. 1, 3). Recent work [1] identifies three main alteration facies, characterized by different pozzolanic components within the Pozzolane Rosse pyroclastic-flow deposit. Several experimental programs [5, 6] have investigated the characteristics of the ash excavated from modern quarries near Colleferro and Segni, ~50 km east of Rome. The samples come from a loose, incoherent reddened facies of Pozzolane Rosse (**A**, Figs.1, 3a) or a lithified, coherent dark gray facies [7] (**B**, **C**, Figs. 1, 3b, c). The studies report conflicting compositions of primary volcanic crystals and authigenic alteration components [7]. Results range from leucite, pyroxene, and brown mica and clusters of dark gray scoriae cemented with chabazite; primary leucite and diopside crystals, authigenic analcime crystals, and chabazite cements; to analcime crystals, only, with clay mineral cements. Furthermore, SEM images of the Colleferro pozzolan show well-developed phillipsite cements [5]. The chemical and mineralogic compositions of [5, 6] correspond to the least altered facies of [1].

Petrographic studies of Pozzolane Rosse collected near Segni, from Montelanico to Colleferro (Fig. 1), give insights into the stratigraphic distribution of micromorphological texures developed during mid-Pleistocene alteration of the pyroclastic-flow deposit. For example, a well-lithified deeper specimen collected at ~210 msl (**C**, Figs. 1, 3c, **c**), has dark gray scoriae and occasional palagonite fragments, and pervasive chabazite cements that have consumed the fine volcanic ash fraction. This resembles the specimen described by Sersale [7] and the least altered facies, altered in ground water at Santa Tecla catacomb in Rome (Fig. 1) [1]. A less lithified specimen collected at ≥210 msl (**B**, Fig. 1, 3b, **b**), has dark gray scoriae with euhedral philipsite surface coatings, and resembles that described by Massazza [5]. Leucite may be intact or replaced by analcime, similar to the higher levels of the least altered facies, altered in ground water at Santa Tecla [1]. However, the void space and phillipsite crystals in the Colleferro ash are partially filled or coated with thin, pale yellow clay, previously shown to be translocated halloysite that developed during hydrolytic weathering and illuviation during mid-Pleistocene pedogenesis [1]. Similar textures occur in dark gray Pozzolane Rosse at the Corcolle quarries northeast of Rome [1]. Higher in the section, outcrops between ~270–260 msl on the Montelanico Road reveal reddened Pozzolane Rosse with leucite replaced by analcime or wholly dissolved (**A**, Figs. 1, 3a, **a**) and thick, birefringent, illuvial halloysite coatings, corresponding to the greatest alteration facies of the mid-Pleistocene paleosol [1], as well as a lower, intermediate alteration facies (**a'**) with partially intact leucite, and opal and pale yellow translocated halloysite coatings coresponding to a Bt to

Bw soil horizon. The approximate stratigraphic locations of the specimens are shown in the context of the Cappannacce quarry, although there is only minimal zeolite in the deeper horizons there. The pronounced zeolite of the lower Segni horizons (**c**) may reflect interstitial water compositions related to closed hydrologic systems [8], probably where the pyroclastic-flow filled deep valleys, and interstitial groundwater with higher alkalinity favored precipitation of chabazite [9]. Imperial age builders selected only the intermediate and least altered facies (**a'**, **b**, **c**) [1] for monumental concrete constructions.

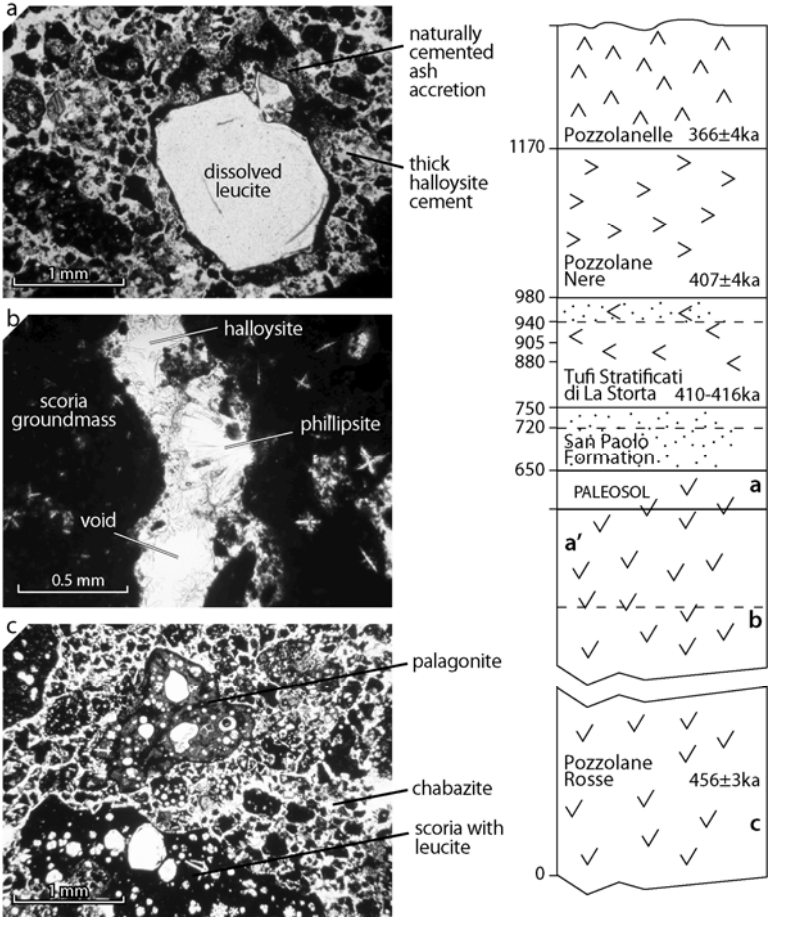

Fig. 3 Micromorphological textures of Segni ash situated within the stratigraphic context of the mid-Pleistocene paleosol and lower horizons of Pozzolane Rosse at Capannacce quarry.

Authigenic components and pozzolanic cements

The Pozzolane Rosse of the Theater of Marcellus mortars is mainly the intermediate alteration facies from the middle horizons of the pyroclastic-flow (**a',** Figs. 3, 4). The opal and halloysite occur as surface coatings, and in naturally

cemented ash accretions on the perimeters of larger scoriae, as at Castel di Leva quarry south of Rome [1]. Leucite (**lc**) is intact, dissolved, or replaced by analcime. Mortar cements in ash accretions (Fig. 4a) occur as lamina of petrographically isotopic cement gel (**Cl**) and acicular strätlingite (**str**). Strätlingite also occurs in the cementitious matrix and in irregular voids (Fig. 2). The palagonitic glass and authigenic phillipsite (**ph**) of Tufo Lionato particles ≥1 mm remain somewhat intact (Fig. 4b). Relict spherical voids, perhaps due to free water in the wet mortar mix, have birefringent, fibrous cement (**Cf**) fillings. Although the mortars are somewhat poorly compacted, they are highly coherent. The Colosseum foundation mortars, ~70–80 CE, also have strätlingite [10].

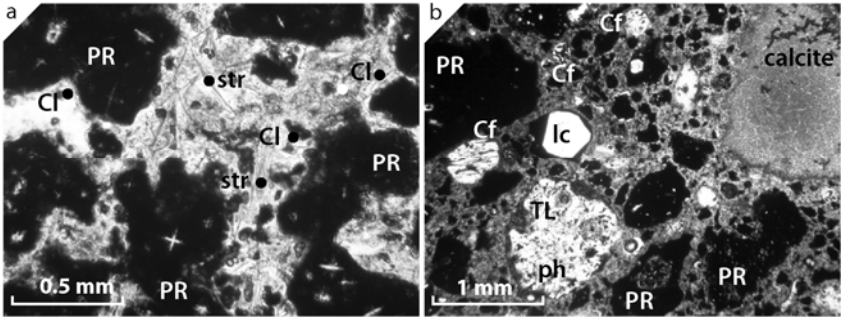

Fig. 4 Theater of Marcellus mortar, a) pozzolanic cements in ash accretion, b) binding matrix

Pozzolane Rosse scoriae in the Great Hall mortars (Fig. 5) preserve traces of halloysite, phillipsite, and chabazite. Builders evidently created an aggregate mix from the full range of alteration horizons (Fig. 3), most likely excavated from different quarries. Tufo Lionato particles are mainly 0.1-1 mm (11). Distinct cement microstructures are associated with the diverse reactive components. For example, an ash accretion on a reddened scoria (Fig. 5a) reveals *in situ* dissolution of microscoriae (**ms**), diopside (**di**), and leucite (**lc**), with coatings of bright, petrographically isotropic, cement lamina (**Cl**). Pale yellow, illuvial halloysite (**hal**) coatings on a dusky yellowish brown scoria (Fig. 5b) contain localized, radiating spherulites of acicular crystals (**Cs**), yet also have incipient alteration to gypsum. Vesicles in a dark gray scoria have apparent phillipsite (**ph**) (Fig. 5c) in contact with a very fine ~10µm equigranular cement with low first order birefringence (**C**). Relict chabazite selvages in the vesicles of another dark gray scoria (Fig. 5d) have intergrown, first order birefringent, acicular crystals in radial spherulites (**Cs**). The palagonitic glass and zeolite of Tufo Lionato particles are strongly dissolved. There are few relict lime clasts.

SEM-BSE images and EDS analyses further illustrate the diverse cement microstructures (Fig. 6). For example, a petrographically isotropic cement in a scoria vesicle that once contained a thin halloysite coating (Fig. 6a), has a potassic silica-calcium-alumina hydrate composition (**a-1**) and fine, fibrous microstructures with a silica-calcium-alumina hydrate composition (**a-2**). The vesicles of a large, gray scoria (Fig. 6b), with a potassic groundmass (**b-1**), have potassic silica-

alumina-calcium hydrate coatings (**b-2**), with an unusual colorless (PPL), first order gray, rod-and-block microstructure that has begun to dissolve. A Tufo Lionato particle (Fig. 6c) has a calcium-silica-alumina-ferric rind (**c-1**) that may reflect dissolution of iron-rich palagonitic glass; diopside is finely etched and phillipsite cement is dissolved (12). The calcium-alumina silica fibrous cement (**d-1**) with second order birefringence, in a spherical void (Fig. 6d), is similar to that in the Theater of Marcellus mortar (Fig. 4b, **Cf**).

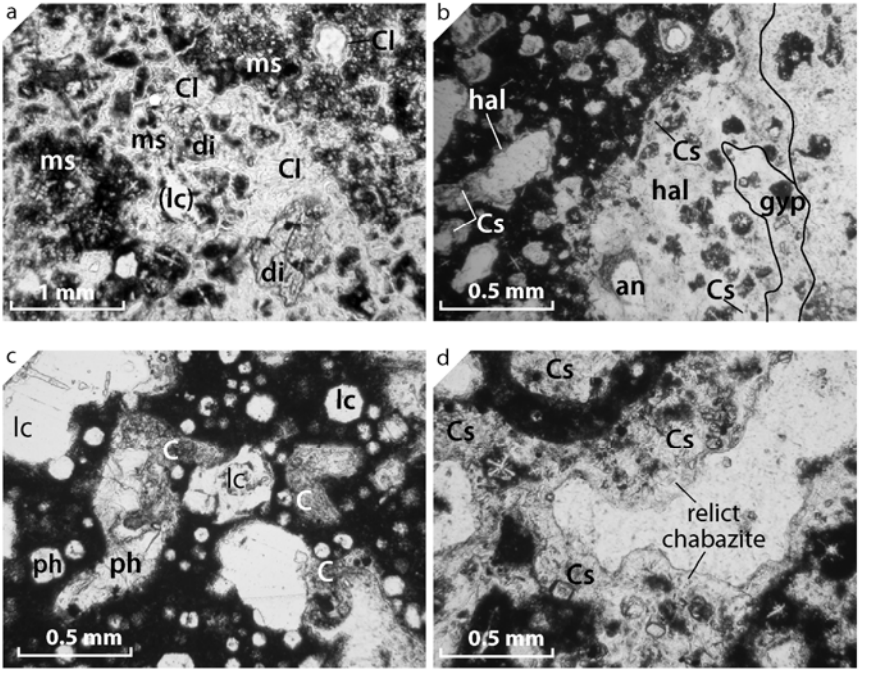

Fig. 5 Great Hall, Trajan's Markets, micromorphological textures and pozzolanic cements, a) *in situ* dissolution of microscoria (**ms**), diopside (**di**), and leucite (**lc**), and bright lamina of cement (**Cl**), b) halloysite (**hal**) and radial spherulite cement (**Cs**), c) phillipsite (**ph**) and cement (**C**) in scoria vesicles, d) relict chabazite selvage and cement (**Cs**) in scoria vesicles.

3 Pozzolanic processes in the Imperial age mortars

The Theater of Marcellus mortars (Figs. 2, 4) have Pozzolane Rosse with predominantly opal (SiO_2) and halloysite ($Al_2Si_2O_5(OH)_4$) coatings. The alkalis released from dissolution of scoriae groundmass and the palagonitic glass and zeolite of Tufo Lionato particles may have lowered lime concentrations and increased silica concentrations in pore fluids, favoring the formation of strätlingite cement [8, 5]. Even so, calcite (relict lime) clasts are common and Tufo Lionato

particles may retain zeolite and glassy matrix (Fig. 4b) suggesting that the volcanic pozzolans could not combine all the lime present; this would have been a 3:1 volumetric proportion if the Vitruvian formulation were followed [2]. In contrast, the Great Hall wall mortar has few relict calcite clasts; Tufo Lionato particles have glass and zeolite nearly wholly dissolved; and distinct cement microstructures and compositions are associated with host pozzolans. Here, pozzolanic reaction apparently proceeded more effectively, more fully consuming free lime and pozzolanic components of the volcanic ash.

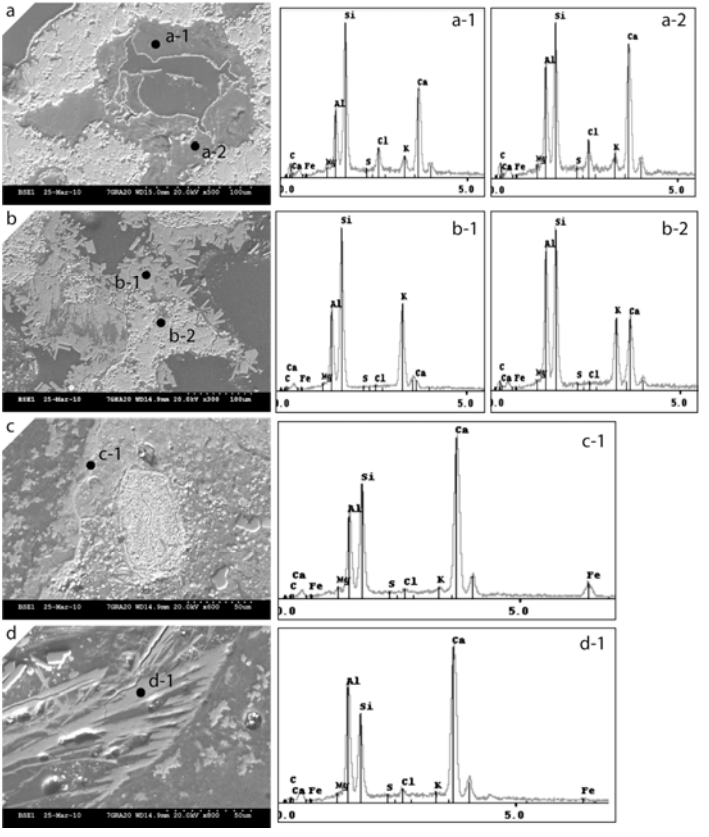

Fig. 6 Great Hall, Trajan's Markets, SEM images and EDS analyses of cement microstructures

The reaction of lime in acqueous suspension and in pastes with a variety of natural pozzolans confirms that a strong relation exists between the compositions of reactants and their pozzolanic products [6, 12, 5]. For example, reaction of chabazite-bearing Pozzolane Rosse from the Segni area with hydrated lime in suspension produced CSH, $C_3A{\cdot}CaCO_3{\cdot}12H_2O$, and C_3AS_3–C_3AH_6 crystalline phases. Significantly, reaction in pastes after five years curing produced CSH, C_2ASH_8 (gehlinite hydrate), and $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ (6). Further investigations of

the ancient cement compositions and microstructures, and pozzolanicity tests of Tufo Lionato and Pozzolane Rosse will provide new insights into the chemical processes that activate the durable Imperial Roman cement systems, as well as the evolving expertise of the engineers who developed the mortars over several centuries of experimentation.

4 Conclusions

Pozzolanic reaction of volcanic ash with lime and water to produce enduring calcium silicate and aluminate hydrates is remarkably effective when mortar systems contain activating phases such as volcanic glass, zeolites, amorphous silica, and poorly crystalline clay minerals (5). Pozzolane Rosse volcanic ash has the extraordinary distinction of possessing all these reactive components, in distinct stratigraphic horizons associated alteration in ground and surface water. Trajanic era builders formulated a highly reactive aggregate design mix with these alteration facies and finely ground Tufo Lionato. Diverse pozzolanic cement phases reflect the compositions of specific micromorphological textures.

5 Acknowledgements

We thank B. Black, M.L. Buonfiglio, P. Ciancio Rossetto, T. Hoisch, M. Klimkiewicz, C. Rosa, L. Ungaro and M. Vitti for research assistance.

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I.22

Cement Compositions and Durability in Ancient Roman Seawater Concretes

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Abstract Roman hydraulic maritime concretes of the central Italian coast have Flegrean vitric tuff as coarse aggregate and mortar pozzolan. Pozzolanic reaction at high pH produced silica-rich CASH and calcium carbonate cements; tobermorite in the residual cores of lime and vitric tuff clasts; and ettringite and calcium-chloroaluminate in bead-like microstructures and voids. Phillipsite may reflect dissolution of residual alkali-rich volcanic glass at lower pH. The cement systems seem to have remained relatively stable during partial to full immersion in seawater for 2000 years. Further analytical investigations will determine the diverse chemical processes that produced specific cement microstructures.

1 Introduction

Between 2002 and 2004 the ROMACONS group drilled several Roman concrete maritime constructions along the central Italian coast (Fig. 1) [1]. The fundamental binding material of the concretes is a hydraulic pozzolanic mortar, prepared from lime hydrated with sea water and pumiceous volcanic ash presumably from the Bay of Naples, the *pulvis puteolanus* of Vitruvius [1, 2], which was sometimes augmented with local sands. The coarse aggregate, or *caementa*, is mainly decimeter-sized volcanic tuff, presumably from Campi Flegrei volcano, quarried near Baia, for the Santa Liberata and Anzio structures [1, 2], and Tufo Lionato tuff from Alban Hills volcano for the Portus structures

[3]. The concretes have remained remarkably free of features indicative of expansion, leaching, and erosion despite 2000 years of complete to partial immersion in sea water [1]. Here, we describe some characteristic microstructures of the mortars to provide a basis for further investigations into their extraordinary durability of the concretes, and the expertise of the builders who carried out the underwater constructions [4].

In November 2004, the ROMACONS group constructed a Roman concrete block in Brindisi harbor, using nearly pure CaO slaked lime putty and the alkali-rich, Bacoli Tuff as coarse aggregate and mortar pozzolan [5, 6, 7]. Comparison of these mortars with those from Portus Cosanus, ~60 BCE, and Santa Liberata, ~50 BCE, in Tuscany, Portus Claudius, ~50 CE, and Portus Traianus, ~115 CE, near Rome, and Portus Neronis, ~60 CE, at Anzio, (fig. 1) gives insights into the initiation of pozzolanic seawater cement system. Chemical processes in the concretes may have analogies to those in natural rock-forming cement systems in pyroclastic deposits immersed in the ocean and in saline lake brines [8, 9, 10].

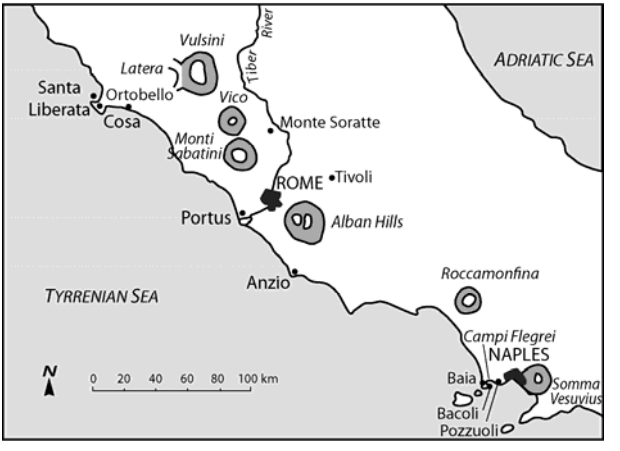

Fig. 1 Ancient Roman harbors and volcanic districts of the central Italian coast

2 Materials and methods

The mortar specimens come mainly from discs sliced from 1–6 meter long, 9 cm diameter drill cores. Polished thin sections were prepared from part of the disc; powders for XRD and chemical analysis were commonly prepared from the rest of the disc. The cementitious binding matrix was lightly crushed or scratched out from the mortar, and sieved to pass the #100 sieve, <0. 0159 mm. Pumices, other aggregates, and white inclusions were carefully scratched out or hand-picked. X-Ray diffraction analyses were performed with a Bruker D8-Advance X-ray powder diffractometerat CTG Italcementi labs. A JEOL 6700F Field Emission scanning electron microscope (SEM) (6/7/Hosler) in the backscatter electron

mode (BSE) was used with Energy Dispersive X-ray Spectrometer (EDS) spot or area analyses on polished thin sections at Pennsylvania State University, to describe the pozzolanic clasts and cement phases of mortar fabrics. Petrographic microstructures were drawn on digital photomicrographs taken with a 2x objective on an Olympus BX51 microscope. Descriptions of vitric tuff fabrics follow [3].

3 Characteristic cement microstructures, Portus Claudius

The seawater mortar fabrics have four predominant components: volcanic pozzolan composed of grayish orange (10YR 7/8–8/5) vitric tuff, pumice, palagonite, and crystal fragments; occasional sedimentary or volcaniclastic sands; a cementitious binding matrix with clasts <1 mm and a fine fraction <0.0159 mm; and dull white (N9) opaque inclusions, 0.1–1 cm. Photomicrographs of the Portus Claudius POR.2002.PO2a (1) mortar illustrate informative microstructures.

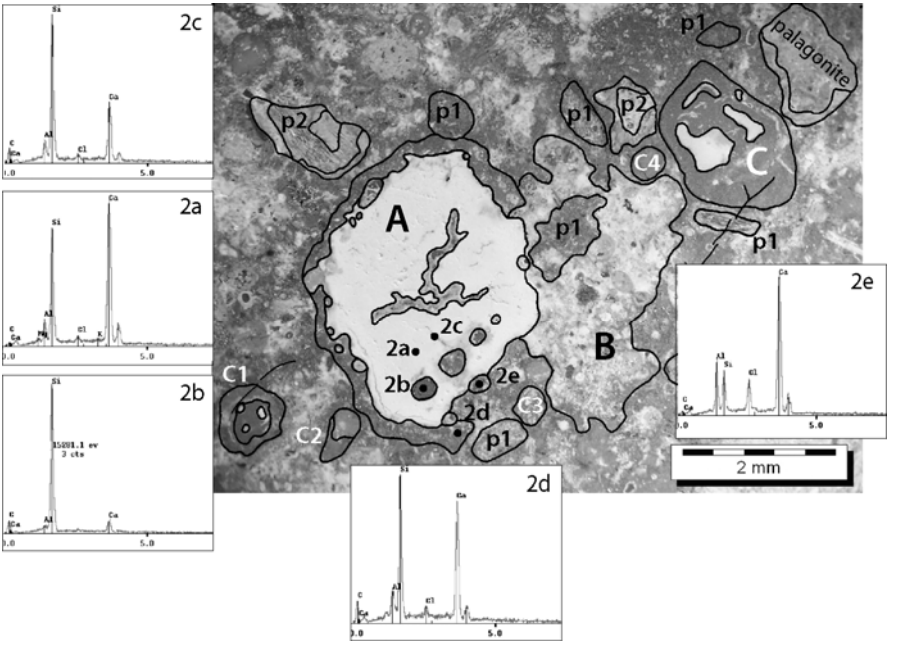

Fig. 2 Microstructures of lime clasts in the Portus Claudius mortar and SEM-EDS analyses

Fig. 2 shows a dull white, relict lime clast (**A**) that is directly in contact with a tuff fragment (**B**), whose altered vitric matrix has mottled zones of white opacity, and a relict lime clast with isolated opaque areas (**C**). Smaller lime clasts (**C1, C2, C3, C4**) are partially to wholly dissolved. Smaller pumices (**p1**) are largely dissolved; larger pumices (**p2**) have partially dissolved perimeters and opaque cores. The opaque mass (**A**) has an amorphous microstructure, dark gray (5Y 4/2

in plane polarized light (PPL)), with a composition compatible with tobermorite (Fig. 2a). Four sub-spherical openings have silica-rich points (Fig. 2b), perhaps the remains of dissolved *tintinnides* macrofossils, preserved in adjacent lime clasts. A dissolution fissure (Fig. 2c) and a perimetral rind (Fig. 2d), which makes a distinct boundary with the cementious matrix and contains quartz microcrystals shattered during calcining of the host limestone, have a silica-calcium-aluminum composition (Fig. 2c, d). The cementitious matrix has microcrystalline calcite, vaterite, aragonite (and hydrocalumnite) (Table 1), also present in the perimetral rinds. A bead-like microstructure (Figs. 2e, 4a) has a calcium-silica-chloroaluminate core with drying shrinkage. Overall, figure 2 suggests a "shrinking core" process [11] where dissolution of lime at pH >12 proceeded inward from clast perimeters, and silica-rich CASH rinds precipitated. The dissolution process at (**A**) terminated before the entire clast was consumed; the opaque nucleus records the eventual precipitation of CSH and possible tobermorite [11]. Neighboring lime clasts record gradational stages in this process.

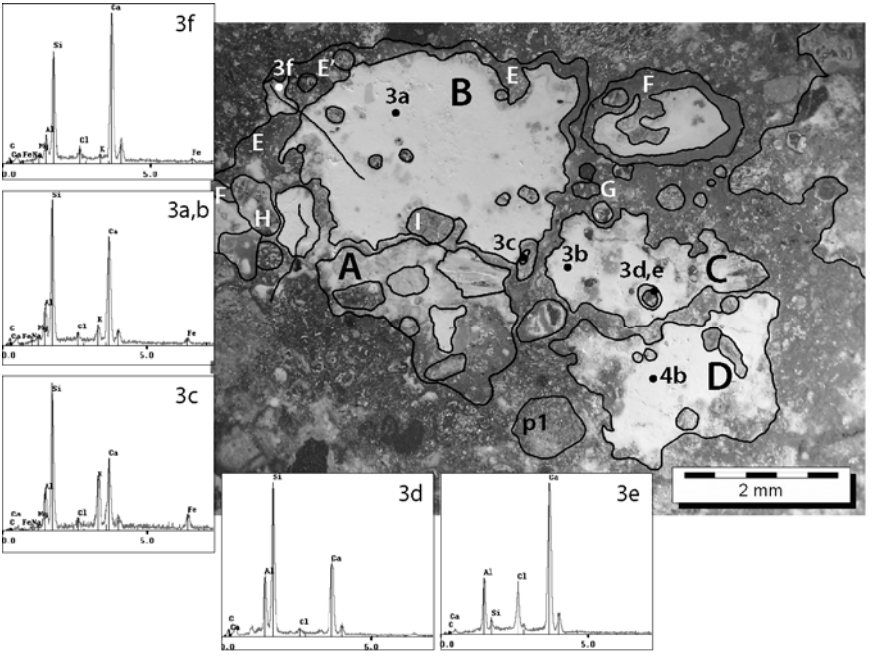

Fig. 3 Microstructures of vitric tuff clasts in the Portus Claudius mortar and SEM-EDS analyses

Fig. 3 shows a cluster of dull white, vitric tuff clasts. Pumice and glass fragments are preserved in a patchy yellowish orange (10YR 7/6) and opaque gray (N4) (PPL) volcaniclastic texture (**A**), similar to fig. 2**B**, and traces of these occur within deeply opaque, dark gray (5Y 4/2) (PPL) masses at **B**, **C**, and **D**. Potassic, silica-rich KMFCASH compositions reflect altered volcanic ash (Figs. 3a, b), as does the opaque core of a pumice with a partially dissolved perimeter (Fig. 3c).

Tobermorite microstructures occur in the most densely opaque mass (**D)** (Fig. 4b). The rind around tuff clast (**B**) varies from lightly opaque (**E'**) to translucent (**E**), similar to the rims of nearby partially dissolved lime clasts (**F**; Fig. 2d); there are also opaque calcium-silica-aluminum patches (Fig. 3f). An annular microstructure has an opaque calcium-chloroaluminate inner zone (Figs. 3d, e, 4c). Bead-like microstructures 0.1–0.8 mm may contain this muddy opacity (**G**), or needle-like ettringite crystals with second order birefringence, and low (-) relief (**H**), or a complex combination of both materials (**I**). Overall, Fig. 3 records perimetral dissolution of vitric tuff clasts (**E, E'**); a gradational alteration to white opacity in their residual cores (**A**, **B**, **C**, **D**), and precipitation of tobermorite (**D**) (Fig. 4b); and discrete microstructures with chlorine and sulphate concentrations (**G**, **H**, **I**)

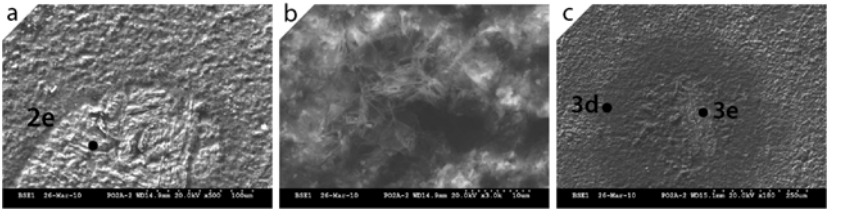

Fig. 4 SEM-BSE images of cement hydrates, a) calcium-silica-chloroaluminate, Fig. 2e, b) tobermorite, Fig 3D, c) silica-calcium-alumina ring and calcium-chloroaluminate core, Fig. 3d, 3e

4 Comparisons with Brindisi experimental mortars

The cementitious binding matrix of the young Brindisi mortar has a rather consistent assemblage of microcrystalline calcite, vaterite, and hydrocalumnite, and little or no portlandite [7]; portlandite does, however, occur in coarse lime clasts (Table 1). Similarly, the cementitious matrix of the Portus Cosa, Claudius and Traianus mortars also has a predominantly calcite, vaterite, and/or aragonite, and hydrocalumnite assemblage, with subordinate cement phases having close associations with lime and volcanic clasts (Figs. 2, 3). Although tobermorite is associated with relict lime clasts in all the ancient mortars (Fig. 2, Table 1), and with certain altered vitric tuff clasts, as well (Fig. 3, 4b), it is not detected in the experimental mortar. However, ettringite occurs in association with portlandite in Brindisi lime clasts, and ettringite is associated with lime and volcanic clasts in the ancient mortars, and occurs in voids as well [2]. Subordinate phillipsite and chabazite occur in the 2008 mortar, associated with vitric tuff clasts. Phillipsite in the ancient mortars may occur as discrete void fillings [2, 7]. In the Portus Traianus concrete, the zeolitized palagonitic fabric of Tufo Lionato *caementa* has altered *in situ*, and the fine vitric fraction consumed to produce dense phillipsite cements that are intergrown with the natural, authigenic phillipsite of the tuff.

5 Inferences from cement microstructures

The ancient seawater mortars have an assemblage of cement phases that represent temperature fields ordinarily considered incompatible in modern cement pastes [2]. For example, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$) is typically stable to about 70ºC at atmospheric pressures; tobermorite ($Ca_5Si_6O_{16}$ $(OH)_2 \cdot 4H_2O$) or Al-tobermorite ($Ca_5Al_{0.7}Si_{5.3}O_{16}(OH)_{1.3} \cdot 4H_2O$), a hydrothermal mineral sometimes associated with ettringite, typically is synthesized above 120ºC (12); and wollastonite ($CaSiO_3$) results from the reaction $CaCO_3+SiO_2$ above 1000ºC (13). Historic mortars in Italy also show occasional tobermorite (2).

The predominance of alkali-rich vitric tuff in the ancient concretes suggests that geological perspectives can be useful in understanding their puzzling but pervasive cement assemblages. Hydrothermal alteration of basaltic glass tephra at 24ºC–149ºC during the 12 years following the 1963-1967 eruption of Surtsey volcano, Iceland, for example, released elements that migrated and combined to form a range secondary minerals, mainly analcite, phillipsite, and tobermorite. The tobermorite formed below sea level at 70ºC–169ºC and above sea level at 55ºC–90ºC (10). Phillipsite crystallized in basalt glass vesicles in variable amounts. Locally elevated pH, above the typical 8.2–8.4 of seawater, developed when hydrolysis of basalt glass formed smectite [8, 9, 10]. In saline lakes, silica-rich rhyolite and silica-poor trachytic volcanic ash sediments alter over a few hundred to a few thousand years, to form phillipsite at pH ~9.1–10 [8]. The Na/K of the phillipsites vary widely; these reflect the compositions of dissolving volcanic glass and saline lake brines, and their silica and alumina activities [8, 9].

Table 1 X-ray diffraction analyses of mortar components. Mineral abbreviations follow [14]

Specimen	Dominant Cements	Subordinate Cements	Pozzolan
PORTUS COSA, mid-first century BCE, center of Pier 1 on modern beach [1]			
PCO.03 cm	Cal Vat	Etr Str Phi	Sa Qtz,Anl
PCO.03 wi	Tbm Cal	Str Wo Etr Vat	/
PCO.03 p	Phi Vat	Tbm Cbz Cal	Sa, Anl
SANTA LIBERATA, mid-first century BCE; center of *pila* off northwest *piscina* [1]			
SLI.04 mor [2]	Cal	Cbz Clc Vat	Ill Sa An Anl
SLI.03 wi	Etr Tbm	Vat Hyc Cal	/
PORTUS NERONIS, ca. 65 CE; center of pila of southeast breakwater [1]			
ANZ.02 mor	Phi Vat	Tbm Cbz Cal	Sa Anl Mus
ANZ.02 wi	Tbm Cal	Wo Etr Vat Brc Hyc Arg	/
PORTUS CLAUDIUS, ca. 50 CE; western mass of north mole [1]			
POR.02 cm	Cal Vat Arg	Hyc	/
POR.02 rlc	Tbm Cal	Wo Etr Hyc Gp	/
POR.02 pum	Cal Vat	Arg Phi Tbm	Sa
PORTUS TRAIANUS, ca. 115 CE; mole and quay at entrance to hexagonal basin [1]			
PTR.02 cm	Cal Vat	Etr Hyc Phi	Anl Di Sa Ill
PTR.02 wi	Tbm Cal	Wo Etr Nor Vat Flr Hyc	/
BRINDISI HARBOR, November 2004, 8m^3 concrete *pila* [5, 6, 7]			
05-BRI cm 6 mo	Cal Vat	Hyc	Anl Sa
05.BRI cm 12 mo	Cal Vat	Cbz, Phi	Anl Sa
06.BRI cm 24 mo	Cal Vat	Phi	Anl Sa
08.BRI cm 42 mo	Cal Vat Hyc	Cbz Phi	Sa Anl Ill
08.BRI wi	Cal Por	Vat Hyc Sjg	/
09.BRI cm 60 mo	Cal Vat	Hyc	Anl Di
09.BRI wi	Cal Por	Ett Hyc	/

cm: cementious matrix; wi: white inclusion; p: pumice; mor: mortar; rlc: relict lime clast

Pozzolanic reaction is the sum of dissolution and topochemical reactions at particle surfaces at high pH, ≥12.7, and the subsequent precipitation of cements [15]. The perimetral dissolution of the lime and vitric tuff clasts (Figs. 2, 3), and their gel-like, silica-rich CASH and microcrystalline calcium carbonate rinds, record this process. The maximal amount of $Ca(OH)_2$ that the volcanic pozzolan could combine was evidently not as great as the total lime in the ancient system, a 2:1 ratio if the Vitruvian proportion were followed [5]. Indeed, the ancient hydrated lime clasts were only partially dissolved, and residual portlandite persists in coarse lime clasts in the young Brindisi mortar (Figs. 2, 3, Table 1). In the ancient mortars, the release of SiO_2 and Al_2O_3+ Fe_2O_3 by pozzolanic reaction into

solution [15] apparently resulted in reaction with the residual portlandite at elevated pH to precipitate tobermorite in the opaque nuclei of the lime clasts (Fig. 2a) [11]. Similar reactions in the cores of vitric tuff clasts evidently produced amorphous KMFCASH, from which tobermorite precipitated, perhaps similar to the Surtsey microstructures [9]. The tobermorites have a small amount of aluminum substitution, common in most cement hydration systems [12].

The strong bonding of lime and the lack of free $Ca(OH)_2$, as in the young Brindisi mortar, would have had a favorable effect on concrete durability [15, 16]. The lime leaching rate would have been low, so there was little increase in porosity, which facilitates penetration of aggressive ions and erosion in modern portland cement concretes [16]. Because there was little $Ca(OH)_2$ to react with seawater salts, CO_3^{2-}, SO_4^{2-}, Mg^{2+}, gypsum and ettringrite did not apparently form quantities large enough to produce dangerous expansions [15]. Instead, ettringite seems to occur in bead-like microstructures and voids around relict lime clasts, as in the ancient Santa Liberata and young Brindisi mortars [2], or near vitric tuff clasts (Fig. 3). If, at pH>12, high solubility of aluminum caused it to preferentially migrate to voids farther from pozzolan grains [16, 11], precipitation of chloroaluminate, and sulphoaluminate [2] would have been favored in these discrete microstructures [16]. Phillipsite may be associated with dissolution of alkali-rich volcanic glass at lower pH, ~9.1–10 [8], similar to the Surtsey and saline lake processes [8, 9, 10], and eventual precipitation in voids [2, 7].

Wollastonite may refect lime that was over-calcined at >848ºC. Indeed, pseudo-calcite indicative of dead-burned lime occurs in the Portus Claudius mortar. If the lime comes from Appennine limestones near Rome, then it is ~95 wt% CaO [17]. However, limestones at Cosa and Santa Liberata might have been calcined onsite [1]. The elevated temperatures often associated with tobermorite remain enigmatic. Significantly, Bacoli tuff-lime pastes hydrated in distilled water formed crinkly foil tobermorite after 5 years curing at ambient temperatures [18].

6 Conclusions

Mortars of Roman maritime concretes from the central Italian coast have remarkably consistent cement compositions and microstructures, apparently associated with dissolution of lime and vitric tuff clasts at high pH, and precipitation of silica-rich CASH and calcium carbonate in perimetral rinds; tobermorite in clast nuclei; and calcium-chloroaluminate and ettringite in voids and bead-like microstructures. Phillipsite may have precipitated at lower pH, from dissolution of volcanic glass. The mortar cements have analogies to the natural rock cements that develop in volcanic ash submerged in seawater and saline lakes. They display a striking resistance to chemical dissolution and attack.

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I.23

Medieval Gypsum Mortars Used for Architectural Details in the Castle of the Teutonic Order in Toruń, Poland

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Abstract This study is focused on Gothic architectonic gypsum mortar decoration from the Castle of the Teutonic Order in Toruń. The aim of the research was to complete a condition assessment of the architectonic details, determine the production techniques of these details and establish the composition of mortars.

1 Introduction

The fragments of architectonic decoration of the Teutonic Order castle in Toruń, were found during archaeological research in 1958-66 [1]. Relics surviving the demolition in 1454, represent a rich variety of technical solutions that were used to decorate the castle. The materials applied were stone, ceramics and gypsum mortars. The collection was secured, preliminarily classified and dated to the period around the 1250's-1350's by art historians [2, 3, 4, 5], and part of it was restored and presented at the exhibition in 1966 [6] – but was not the subject of scientific material research. It is currently under the care of The District Museum in Toruń.

The subjects of the research undertaken at the Department for Conservation of Architectonic Details are the exhibits from this collection, made of mortar (the so-called "artificial stone"). Mortars based on high-fired gypsum were a popular material for the production of architectonic elements in the State of Teutonic Order in Prussia and became regionally specific to this area of insufficient natural stone deposits [5, 7, 8, 9]. Many such details are preserved in churches and castles

(Chełmno, Malbork, Toruń, Gdańsk and others). There is a need for integrated research into this medieval gypsum material, as understanding is required both for conservation practice (to establish and develop suitable treatments), and for art-historical analysis (medieval sculpting and building workshops and dating) [10].

Fig. 1 Window tracery fragment, both sides; ca.:56x20x17,5cm; grey-coloured gypsum mortar, Muzeum Okręgowe w Toruniu, object No. MT/ZK-355

Fig. 2 Balustrade of the gallery, fragment, both sides; ca. 52,5x72,5x19cm; rose-coloured gypsum mortar, central part reconstructed in cement mortar in 1960's, Muzeum Okręgowe w Toruniu, object No. MT/ZK-20

Fig. 3 Ceiling boss fragment, both sides; ca.:19x13x10cm; white-coloured gypsum mortar, originally polychromed; Muzeum Okręgowe w Toruniu, object No. MT/ZK-395

2 Material under investigation

An inventory undertaken in cooperation with the Archeological Department of The District Museum in Toruń showed that the collection of mortar fragments includes over 150 mortar pieces (7 to 58 cm length) which differ in appearance and condition. A visual assessment of these mortars allowed the collection to be divided into three groups – grey, rose and white:

- Grey mortars: with significant content of charcoal, form the largest group. Most of the identified fragments are window tracery parts (Fig.1), and consoles; some pieces could have originally been the ceiling bosses.
- Rose-coloured: addition of crushed ceramic. The defined fragments from this group are probably parts of two gallery balustrades and of vault ribs (Fig.2).
- White mortars: with slight presence of ceramic or charcoal particles (non-intentional). It is difficult to recognise by visual asessment only – because weathering and dirt allows it to be mistaken for grey mortar. However, it can be observed among sculpted pieces of ceiling bosses (Fig.3). Such white fine mortar was probably intended for indoor details with refined sculptural forms.

The definition of function is according to inventory books and articles from the 1960's by Roman Domagała [2, 3]. It is not possible to identify the exact location of particular details as the castle was destroyed. So far, the research focused mostly on fragments with tracery decoration (that is, window tracery and balustrades) as the largest group of objects which are relatively easy to identify thanks to ornamental forms, and represent two significant types of mortars – grey- and rose-coloured [11]. The choice of samples for research by means of microscopy [12] was extended also to fragments of consoles and vault ribs, from these two mortar groups. The samples were taken from pieces 'typical' to both groups, and of those that differ in appearance. From fragments that consist of two layers of mortar, samples were taken to compare the composition of materials, to ascertain if it is a mark of medieval technique or rather modern reconstruction.

3 Condition Assessment

The façade elements were exposed to weathering processes for over a century. Demolition of the castle by the citizens of Toruń in 1454 was the actual cause of damage. Broken gypsum elements with crushed masonry were covered with earth for next 500 years until the archaeological excavations. Today, it is neither possible to unequivocally identify the exact original location of particular objects in the destroyed building, nor to reconstruct the destruction processes that took place into rubble. It can only be assumed how many different factors these architectonic details have been exposed to during their almost 700-year-history. Taking this context into consideration, along with the solubility of gypsum (over

2g/l) and weakening of gypsum mortars under the influence of moisture [13], one must admit that the relics of medieval decoration of the castle are surprisingly well preserved.

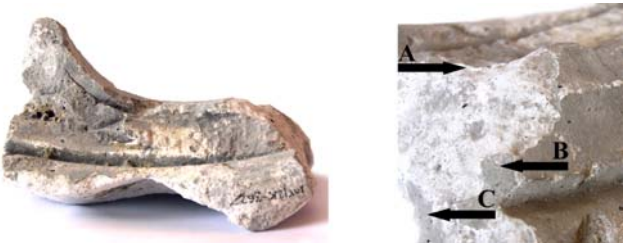

Fig. 4 Window tracery fragment MT/ZK-362. Left – principal view. Right – detail, weathered fracture surface: A – dense material layer of relief surface, B – dense material layer of old fracture surface, C – fresh fracture showing the actual colour of mortar

3.1 Condition of grey mortars – window tracery fragments

In most cases one profiled surface is preserved, while the other is strongly weathered. On some fragments the profiles are fully recognisable, while the opposite side (surface that was mounted into brickwork) shows deterioration. These changes could have been influenced by the original location of the tracery. Preserved relief and some fracture surfaces are coherent. On some fragments, a surface layer of approximately 1mm forms (Fig. 4-A), which itself is covered by dust and soil. The underlying material is slightly weakened, and is a probable cause of the partial loss of the original surface. Recrystallisation processes in these areas could cause this higher density of the surface. An assessment of fresher fractures shows that material in deeper parts is well preserved and hard (Fig. 4-c). Weathered areas are chalking, these are discolouring into white, and displaying loss of material (Fig. 4).

There are two examples from window tracery fragments that differ in appearance and condition. Piece numbered MT/ZK-359 is made of light grey mortar with a warm shade. The shape of relief is easily recognisable on one side, while on the other side it is washed out. However the mortar is hard and there is no evidence of chalking. The surface is rough, with remains of the original smooth surface observed in the cavities of the relief. This material is similar in appearance to five consoles from the collection. The other piece is made of mortar in a distinctly darker shade (MT/ZK-356). Some local sanding occurs, but the material is not strongly powdered as described above.

3.2 Condition of rose mortars

Tracery balustrades from the castle's ambulatory are mechanically damaged, but the material is in relatively good condition. Powdering of surfaces occurs, especially on apparently weathered parts (like hand-modelled side of MT/ZK-20, see Figs. 2 and 6). However, the surfaces of the fractures are homogenous – the phenomena of a dense surface covering loose material, which was observed in the case of grey group, is not noticeable. A few pieces identified as vault rib fragments (and some unidentified parts) appear to be made from softer mortar, and loss of material occured through powdering (MT/ZK-302).

4 Techniques of production of decorative details

4.1 Casting in moulds

Most of the elements were cast in gypsum mortar and their surface was, probably partially, sculpted (carved, smoothed) after setting. Pieces are monolithic, which indicates, that an exact amount of mortar was prepared for casting the elements. The consoles and bosses were cast as whole elements. Window tracery had to be made in pieces, to assure stability of large openwork and to allow mounting on site.

Traces of tools are recognizable on some elements. As the setting process allowed the removal of moulds and shuttering, the profiles were finished. Areas of further work were marked with lines, engraved by stylus (Fig. 5-A). To smooth surfaces or finish the edges, flat tools, such as knifes or spatulas were used (Fig. 5-D). Some profiles were worked with stonecutter's chisels (Fig. 5-B), which indicates that the material after drying had levels of hardness comparable to natural stone.

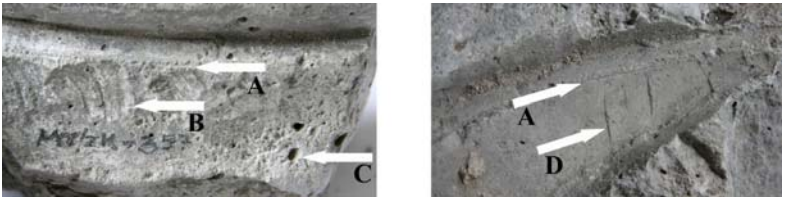

Fig. 5 Marks of technique of production of architectonic details: A – engraved line, B – chisel traces, C – air bubbles, D – traces of flat tool; window tracery fragments inv no. MT/ZK-357 (left) and MT/ZK-365 (right) [photo: J. Raczkowski and M.Jakubek]

4.2 Casting of elements combined with free-hand modelling

The fragments of rose-coloured pieces identified as fragments of balustrades were formed by a combination of techniques. First, the profiled pieces were cast. After setting, their reverse sides were worked out with a chisel, to obtain an adherent surface (Fig. 6-A). A layer of fresh mortar was then applied and modelled into shape to correspond with the cast profile (Fig. 6-B). This indicates that the mortar was capable of being used in free-hand modelling, at least in this application.

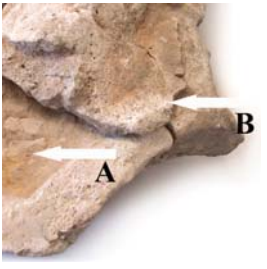

Fig. 6 Detail of balustrade fragment inv. No. MT/ZK-20, reverse side (see Fig.2); cast part worked out with chisel (A) and a layer of mortar applied with free-hand (B)

5 Chemical composition and structure

5.1 Thermal differential analysis

The samples were ground and dried at 60°C for 24 hours. Measurement conditions: oven temperatures 20 – 1000°C, sensitivity (TG) 200 mg, heating rate 10°C/min, atmosphere – air, ceramic crucible.

Table 1 Results of thermal differential analysis of grey-coloured mortars

object	description	$CaSO_4x2H_2O$	bound water	$CaCO_3$	residue
MT/ZK-355	appearance "typical" for grey group, as described in 3.1.	73.87	1.01	6.11	19.01
MT/ZK-357 (1)		61.28	0.67	8.44	29.61
MT/ZK-357 (2)		57.59	1.28	4.57	36.56
MT/ZK-362		70.46	1.12	6.09	22.33
MT/ZK-359	warmer colour, higher hardness	64.81	0.87	4.74	29.58
MT/ZK-351	darker colour, higher hardness	65.95	0.78	4.99	28.28
MT/ZK-356		66.29	0.59	6.04	27.08

Table 2 Results of thermal differential analysis of rose-coloured mortars

object	description	$CaSO_4x2H_2O$	bound water	$CaCO_3$	residue
MT/ZK-20 (1)	casted part	64.10	0.66	2.26	32.98
MT/ZK-20 (2)	casted part	64.39	0.43	1.96	33.22
MT/ZK-20 (3)	free-hand modelled	64.32	1.15	6.99	27.54
MT/ZK-342 (1)	casted part	72.12	0.75	2.74	24.39
MT/ZK-342 (2)	free-hand modelled part	71.23	0.73	3.72	24.32
MT/ZK-345	free-hand modelled part	67.09	0.43	3.38	29.10

All the analysed mortars are based on gypsum, and contain $CaCO_3$. In the grey group, the content of calcium carbonate differs from 4.57 to 8.44, but most often it is about 5-6%. In the rose-coloured group the content is 1.96 to 6.99, but the average rate is 3.5%.

Regarding the calcium carbonate content, two extreme results from the grey group are obtained from samples taken from two areas of the same window tracery (MT/ZK-357). Such inhomogenity could have originated during mixing or perhaps through weathering (dissolution and recrystallisation processes). The results should be considered as representative of two contrasting mortar groups.

5.2 Analysis of thin sections – in transmitted light and by SEM/EDX

To achieve information about the mortar's composition the microfabrics have been analysed in detail by means of microscopy.

The grey mortars (Figs. 7, 8-left, 9) contain charcoal and quartz particles ≤ 0.5mm (sometimes with rests of ceramic matrix, small additions of crushed brick are possible). This group shows evidence of high firing of gypsum, namely: I. Thermally originated $CaSO_4$ (so-called thermal anhydrite) in dihydrate matrix, characterized by holes in anhydrite grains (Fig.7); II. Lime fired together with gypsum. Marl impurities can occur as inclusions in grains of the gypsum firing product (Fig. 9). Some limestone fragments are present, grain size and crystal shape indicate their origin as naturally occurring lime within a gypsum deposit (Fig. 9-left), no calcium hydroxide was added. The microfabric is dense, corresponding to the well preserved state of these mortars.

Gypsum mortars from the rose coloured group (Fig. 8, right) contain crushed brick particles ≤ 0.7mm in size, and quartz particles that bear relicts of a ceramic matrix (Fig. 8-F). There was no addition of pure sand. There are single particles of limestone (from a gypsum rock) and charcoal present. No marl impurities, no intentional additions of lime and no primary anhydrite have been observed. Well preserved particles of limestone that occur in MT/ZK-20 (Fig. 8-G) indicate firing temperature below 800°C. In contrast, in sample MT/ZK-302 particles of the firing product contain anhydrite grains showing holes as described above that

indicate high firing. It can be recognized from the microfabrics that the weathering tendency of this object is not a result of binder dissolution, but that the higher porosity is rather an effect of the addition of more water during the production of mortar.

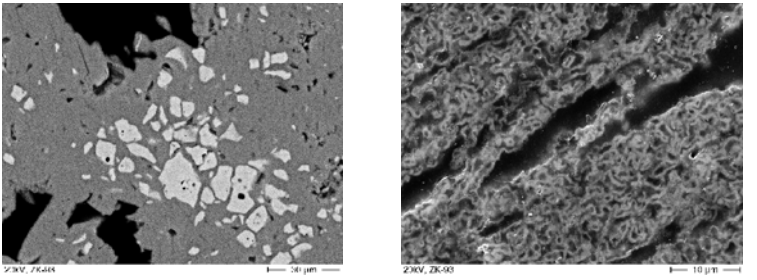

Fig. 7 BSE images of grey mortar sample (MT/ZK-93), marks of high firing. Left: anhydrite grains with holes (surrounded by dense dihydrate matrix). Right: lime structure originating from raw material

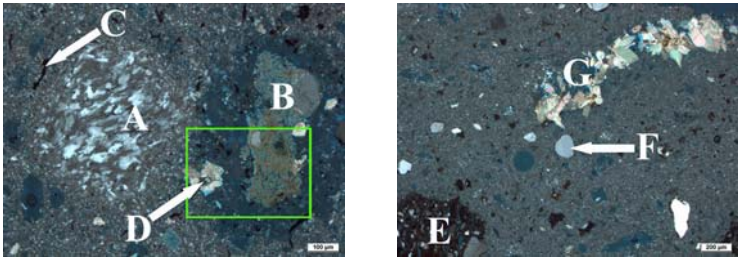

Fig. 8 Thin sections in transmitted light (+pol). Left – sample MT/ZK 353: A – preserved grain of firing product (dihydrate), B – calcareous marl, C – example of charcoal particle (the cause of grey colour), D – particle of limestone, green marking – the area of BSE-image, see Fig.9. Right – sample MT/ZK-20: E – large grain of crushed brick, smaller particles are spread in matrix (the cause of rose-colour), F – quartz grain with rests of ceramic matrix, G – limestone particles (no changes caused by firing)

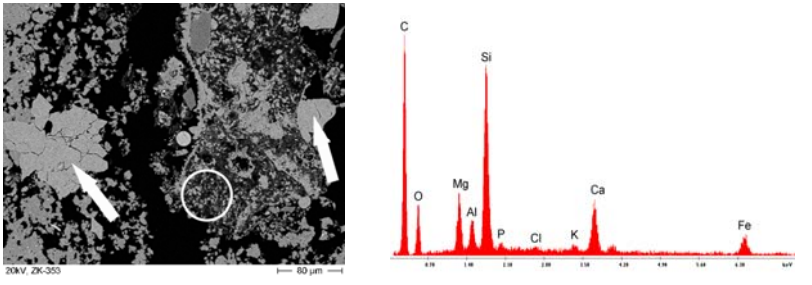

Fig. 9 Sample of grey mortar, MT/ZK-353, the green marked area from Fig.8. Left - BSE image, showing particles of limestone (arrows) and areas of calcareous marl (circle). Right - EDX spectrum of calcareous marl (area marked by circle in the left image)

6 Conclusions

Research into fragments of mortar from the Teutonic Order Caste in Toruń revealed the material characteristics of two kinds of medieval gypsum mortars, which were used for the production of architectonic decorative details.

It is evident that mortar groups differ not only in their main aggregate addition, which defines the colour (charcoal – grey, crushed brick – pink). There are differences in function (grey – mostly window tracery, rose – gallery ballustrades) and technique (hand-modelling on pieces from rose-coloured group). There are perceptible differences of character of both groups in their deterioration. However, it is very difficult to identify the destructive factors; this hinders the analysis of the relation between the composition and the durability of the mortars.

The research into the composition and structure showed that the grey group contains a larger amount of calcium carbonate, which originates from gypsum rock impurities. Also marl impurities are observed only in this group. These details suggest differences in raw materials, or in manufacturing processes of the binder. For further conclusions to be drawn, the research methods would need to be extended and material samples taken from other medieval objects as well as from gypsum deposits. To better understand the inhomogenities of the mortars, resulting from the production process and weathering would require more detailed analysis, with a sufficient number of samples to ensure a statistically significant sample to support general conclusions.

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I.24

Traditional Mortars with Burned Alum Shale as Artificial Pozzolan

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Abstract From the mid-18th century extensive research in Sweden and in present day Finland was focused on the development of mortars with hydraulic and pozzolanic properties. The results were mainly published by the Royal Swedish Academy of Science. The aim was to replace the imported Italian pozzolan and Dutch trass with a pozzolan produced in Sweden. Several products based on burned alum shale were developed. Cambrian alum shales with a high content of bitumen were fired without additional fuel in order to produce pozzolanic shale ash. The bituminous alum shale was used directly as fuel in the lime burning process from the late 18th century. The alum shale mortars have a red-brown colour due to the high content of iron oxides. The mortars are hard, strong and generally have good durability both as masonry mortars and renders. Microscopic analysis shows that often only a skeleton remains of the shale particles and that a large part of the particles has been consumed by the pozzolanic reaction. The field of application was initially mainly structures in contact with water, such as locks in canals and harbours, but building construction was also an early application.

1 Introduction

In the 17th century, waterside construction in Sweden was largely managed by Dutch engineers using Dutch techniques and pozzolanic trass mortars. One example is the city of Gothenburg, which was established on the marshy banks near the mouth of the Göta River in 1621. It was built by Dutch engineers using a Dutch city plan.

Later on during the 18th century mercantilist ideas grew stronger; these were accompanied by an increasing belief in the need to make knowledge and natural resources useful. According to this economic theory, the wealth of the nation was important. Wealth for the people was not considered a useful target; quite the

contrary, poverty for the common people was seen as a necessary motivation for people to work. This focus on the wealth of the nation rather than its population was reflected in many leading-edge building projects at the time in Sweden as well as in other parts of Europe. A number of demanding canal building projects were completed in Sweden during the 18th century and the first half of the 19th century. These required a suitable building material of which mortars that could harden under water were an important part. The political leadership in Sweden during the mid-18th century was much in favour of research. As a result of this a number of prominent researchers in the field of chemistry and mineralogy were engaged in the development of suitable mortars that could be based on Swedish materials [1-5]. The line that was most favoured was the use of synthetic pozzolans based on shale ash sourced from burned alum shale. As a result, Sweden concentrated on the development of mortars with these properties while other European countries were more focused on the development of hydraulic binders.

2 Limestone and Cambrian alum shales used for lime and pozzolan production in Sweden

The limestone used for lime production in Sweden is of two main types. One type is a sedimentary limestone from the counties of Skåne, Öland, Gotland Västergötland, Östergötland, Närke and Jämtland. Their chemical composition ranges from a pure limestone at a few sites to those with a high content of silica; the age of these limestones range from Tertiary to Cambrian. The other rock type used is a Pre-Cambrian metamorphic marble of a calcitic and dolomitic composition from southern central Sweden.

Alum shales of Cambrian age are widespread in Scandinavia and on the eastern side of the Baltic Sea. These are characterised by a high content of organic material, commonly about 10% and sometimes as high as 30%. They are also characterised by the high content of elements such as uranium, thorium, vanadium and molybdenum [6]. These shales occur in several areas in Sweden, but it is only the alum shales on the island of Öland and in the counties of Västergötland, Östergötland and Närke that have organic contents high enough for use as a fuel.

3 Development of mortars with artificial pozzolans

There are several early examples of mortars with burned alum shale. Early occurrences include 12th century lime paintings in Fornåsa [7] and medieval masonry churches in the county of Jämtland in northern central Sweden. In these cases the alum shale was probably burned with the limestone. Alum shale mortars were used in a few rare cases in the masonry of medieval castles in central

Sweden [8]. These examples may sometimes reflect local practices where alum shale mortars were intentionally used as early as the medieval period.

The following description of the early development of hydraulic and pozzolanic materials in Sweden is based mainly on Johansson [9] and to some extent Strömbäck [10].

A large part of the technology used for waterside construction in Sweden during the 17th and the first half of the 18th century was imported from the Netherlands where the techniques were partly developed during the expansion of Amsterdam in the early 17th century. This prompted Sven Rinman to make a visit to the Netherlands in 1746–47. He was later involved in research on the topic of shale ash production at Garphyttan in 1770–71. The purpose of this shale ash production plant was the development of a cement that could be used for waterside construction. Rinman studied 23 different mortar mixes based on burned alum shale, brick dust, slag and trass; he showed that the mortars based on hard burned, partly melted, alum shale and lime did harden in water and that these mortars had properties comparable to the trass mortars. The mortars produced had no added aggregate and therefore the burned alum shale served also as an aggregate in these mortars. Production of Garphytte Cement continued from 1779 to 1828 with an annual production of 50 tons. The cement was delivered to mines and used in the construction of locks, houses and bridges such as the Norrbro Bridge in Stockholm (1788).

Johan Ulfström was responsible for the repair of canal locks in the Hjälmare Canal in 1772. He developed a mortar called "Ulfström Cement" based on a burned alum shale or trass which was mixed to a stiff paste with hydraulic lime and water for two hours. The mortar had to be used within a few hours after mixing.

Another researcher, Bengt Qwist Andersson, was responsible for cement and clinker production at Brinkebergskulle from 1770. He performed tests on different imported natural pozzolans as well as burned alum shale. Assessment of the burned alum shale used here demonstrated that it had properties similar to volcanic pozzolans.

The alum shale mortars were further developed in connection with the building of several canals and locks in Sweden during the late 18th and early 19th centuries. There was at this time an active programme of research and development in this field. The most important work was probably conducted by Gustaf Erik Pasch, who in 1817 began researching mortars for the construction of the Göta Canal. In his research he investigated the importance of the burning temperature and particle size distribution in alum shale ash. The alum shales could be burned at low temperatures but the important factor was that the particles were finely milled. He also investigated the mix proportions of the mortars.

4 Production and utilisation

Alum shale lime mortar was called “cement”, while “Swedish Cement” was a name used by Sven Rinman. The manufacture of alum shale lime mortar required an industrial process that was initiated just after the first successful attempts at production had been completed. Manufacturing was concentrated at two major cement factories. One of them was at Garphyttan which was commissioned in 1771 as a direct result of Sven Rinman’s trials in 1770–71. Alum shale lime mortar was made here until about 1828, for use in hydraulic engineering projects etc, in Mälardalen and Stockholm, and possibly also for the 1800 Locks at Trollhättan. Another factory was established at Brinkebergskulle. Planning for a “cement and clinker works” was started as early as 1761, but the manufacture of clinker only began in 1770 and the manufacture of cement probably did not start until 1772 when the work on Gustaf’s Locks commenced (Fig. 1). Qwist Andersson was responsible for production in both cases.

The mortar was not solely used for infrastructure projects, although it is main application was initially the locks in the Hjälmare Canal and Brinkebergskulle (1772 and 1772–78 respectively), it was also used in housing projects. The Old Town Hall in Skövde (1775–76) is a very early example and is probably the first of its kind in Sweden.

Alum shale lime mortar from Brinkebergskulle was used for the locks in the Hjälmare Canal and Brinkebergskulle, and also as a cement mortar for joints in the construction of various buildings at the neighbouring Onsjö Manor (1774–93), as well as joints in the locks that were constructed in the Göta River at the end of the 1700s and possibly also in the 1800 Locks at Trollhättan. All these projects were in the west of Sweden.

Fig. 1 Gustaf´s Locks at Brinkebergskulle in the Göta river, constructed 1772-78 with an alum shale mortar from the cement factory at Brinkebergskulle. Photo: Sölve Johansson 1989.

Consequently, with the development of two alum shale lime factories, at Garphyttan and Brinkebergskulle, this type of mortar gained a strong position. The mortar was utilised in demanding construction and building projects during the 1800s until the introduction of Portland cement at the beginning of the 1860s, and above all from the start of the 1880s when domestic production of Portland cement was in force in Sweden.

Alum shale lime mortar was used extensively during the 1800s for projects such as the Göta Canal (1810–32) etc. This mortar was further developed by Gustaf Erik Pasch, who experimented with the choice of lime and mixing ratios. Natural hydraulic lime, both from orthoceratite limestone and strong bituminous antraconite, was preferred following comprehensive trials. Knowledge concerning production and utilisation of alum shale lime mortar was subsequently spread in Sweden through publication in the building handbooks of the 1800s and the early 1900s.

Alum shale lime mortar was also manufactured at Vargön under the name of "Vargö cement" during the period 1840–88, for projects such as the Locks in Trollhättan (1838–44), Stockholm Lock (1843–50), Saima Canal in Finland (1847–56) and the Dalsland Canal (1864–68). The initiative for this cement manufacture was taken by colonel engineer Nils Ericson.

In addition, local manufacturing of alum shale lime mortar probably occurred in Västergötland, where a very large number of buildings have been reported as using this type of mortar. This applies not only to the prominent buildings commissioned by the state, such as law courts and church buildings, but also to modest private buildings and housing.

Alum shale lime mortar was utilised above all for bricklaying and jointing, but it has also been used for rendering and broom finishing. The latter was used especially on exposed façades facing south and west. It was also utilised as a set mortar in the mounting of façade ornamentation, for example on Karlstad Town Hall. This type of façade ornamentation consisted of gypsum and natural cement.

Knowledge about the production and use of alum shale lime mortar obviously did not disappear with the rising popularity of Portland cement in construction and hydraulic engineering projects in the 1880s. Its use did however become limited. Alum shale lime mortar or rather alum shale lime cement mortar was used in the making of red Örebro render during the 1910s and 1920s. The burnt alum shale for this production was brought from Lanna and Latorp, from sites such as Garphyttan. This mortar is still produced as a restoration mortar for buildings originally built using the Örebro render.

The usage of alum shale mortar for house building increased during the 19th century. In the 1920s the process was adapted for the production of autoclave-aerated concrete. Production continued until the 1970s when it was abandoned due to the high radon emissions deriving from the uranium content in the shale ash present in these blocks.

5 Microstructural characteristics

5.1 Methods

The quantitative microscopic analysis was performed according to the methods described by Lindqvist & Sandström [11] and the COM-C1 method [12]. The chemical analysis of acid-soluble components was performed according to the methods described in Lindqvist et al [13].

5.2 Microstructural characteristics

The colour of the paste in the shale ash mortars is a relatively dark red which is mainly due to the presence of iron oxides and hydroxides from the burned shale. In several cases the paste is uncarbonated or not fully carbonated; an uncarbonated paste implies the presence of CSH gel. The cement index, assessed through analysis of acid-soluble components, gives a hydraulicity that ranges from that of a pure lime mortar to a strongly hydraulic mortar. There are small remnants of unhydrated cement clinker grains in some of the mortars which probably come from the burning of a lime shale mix both in the medieval mortars and in the 18th and 19th century mortars – a technique favoured by Sven Rinman in the 1770s. The main part of the CSH-gel is formed through a pozzolanic reaction which is probably based on the formation of reactive glass during the burning process.

The air content in the mortars shows a large variation. The shape of the air voids varies from irregular and elongated to well rounded. Fluorescent microscopy shows that there are generally very few cracks; these are mainly in the form of shrinkage cracks and cracks between different layers of renders, and occasionally as open cracks between the different layers in the same layer of render. In some cases the shrinkage cracks can occur around and within shale ash particles.

The aggregate is mostly fine grained with a maximum grain size of 2 mm or 4 mm with a well graded size distribution. Other properties, such as the shape of the aggregate, show no difference when compared to other mortar types from the same region and time.

Preserved shale particles, which are elongated often with an ellipsoid shape, display internal shrinkage cracks and adhesion cracks due to the shrinkage of the shale ash particles. The finer particles have largely reacted leaving just the larger shale ash particles which have to a large extent, also reacted to different degree. These range from intact or almost intact particles, to mainly fine-grained particles, where only a skeleton of the iron oxides and hydroxides remain (Fig. 2).

The mix proportions, based on point counting, vary from very binder-rich to those that compare with modern pozzolanic mortars.

Detailed analysis using electron microscopy demonstrates that shale ash particles that may seem inert at low magnification show a reaction at higher magnification. Shale ash particles may display sharp grain boundaries in the low magnification BSE images as well as in the chemical distribution. At higher magnification it can be seen that there is a zone of paste that is enriched in Si surrounding the shale ash particle.

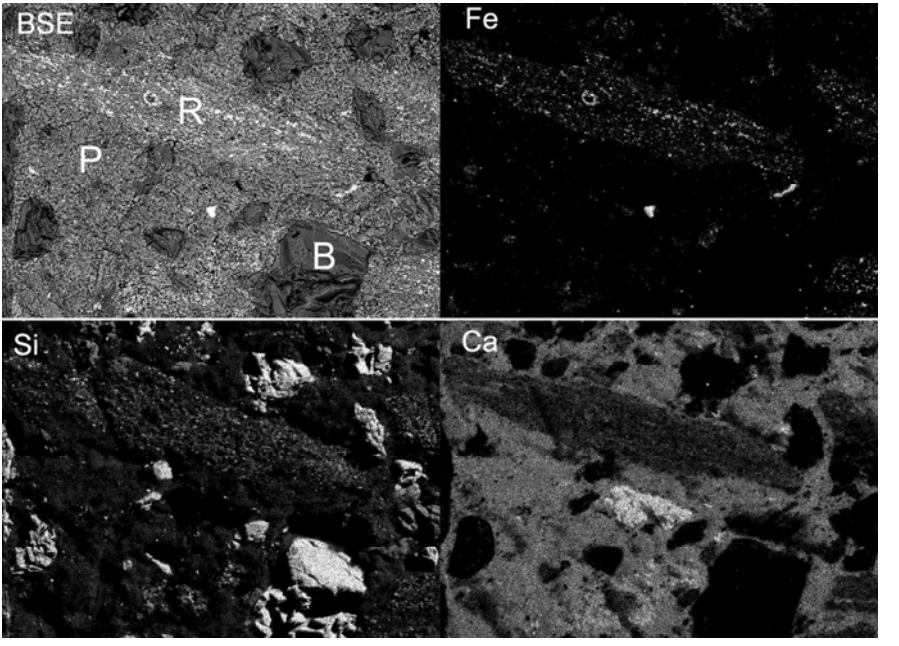

Fig. 2 Shows the back scatter electron image (BSE) combined with EDS maps of the distribution of iron (Fe), silica (Si) and calcium of an almost totally reacted shale ash particle. The instrumental magnification is 200X.

X-ray diffraction shows a broad hump in the range 10° to 20° 2θ and around 30° 2θ implying that the sample contains amorphous CSH gel. XRD analysis also shows the presence of the minerals calcite, hematite and the zeolite gismondite [9].

6 State of preservation

The old canals and locks that are mentioned in the text are protected as fixed ancient monuments in accordance with Swedish legislation concerning the preservation of historic monuments and the buildings that have been examined in most cases are architectural monuments. This signifies that these constructions and buildings are well protected. It is necessary however, in connection with

measures taken on these objects, to ensure that all forms of mortar are protected in practice, e.g. jointing mortar, grout and finishing mortar.

7 Acknowledgement

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I.25

Mineralogical and Microstructural Analysis of Mortars from Kushite Archaeological Sites

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Abstract This paper presents the XRD, XRF and porosimetry analyses and SEM-EDX observations of nine mortars: three Egyptian plasters (New Kingdom, 15th - 11th century BC) and six Meroitic mortars (1st century AD) collected on temples, palace and pyramids in archaeological sites located between the Third and Fourth Cataract. The two first Egyptian samples were mainly composed of gypsum plaster. The third one and a binding mortar collected on a Meroitic pyramid were composed of siliceous sand bound by about 30% kaolinite-rich clay. A coating mortar collected on another Meroitic pyramid, probably highly lixiviated, had a similar composition with only 11% clay. The other Meroitic samples appeared as conventional fully carbonated lime-sand mortars. The compositions of the decorative surface layers varied from clay to lime or lime-and-gypsum, in the form of painting or applied as fresco. This extreme diversity of compositions observed is particularly interesting from an archaeological point of view. The knowledge of the various techniques used enables us to have a better understanding of foreign influences on building workers in ancient North Sudan.

1 Introduction

Building materials often contain a lot of archaeological information and reveal the history of techniques. The use of mortars as a facing material is a major feature of Kushite architecture, and knowing the initial composition of these mortars is therefore a matter of importance both for archaeology and for the faithful restoration of the monuments concerned. However, until the year 2000, this issue only received very little attention [1, 2].

In a first study presented in HMC08 [3], the analysis of Meroitic mortars (two first centuries AD) coming from Kushite archaeological sites around the ancient

city of Merowe led us to propose the hypothesis that these mortars were originally lime-and-gypsum based. This study was recently completed by petrography [4]. Moreover, analyses of a gypsum-rich caliche from Omdurman (200 km upstream Merowe) and a Sudanese gypsum from the Red Sea, with respectively 0.18 and 0.94% SrO, are compatible with our hypothesis, mainly based on the strontium sulphate as a tracer of a previous presence of gypsum in our mortars.

Two other samples coming from Doukki Gel, located 500 km north from other sites, with a low SrO content, clearly did not belong to the same series. So it was particularly interesting to check if other mortars coming from sites near Doukki Gel had a composition similar to those already studied or were made using different techniques. Thus, this paper presents the chemical, mineralogical and microscopic analyses of these two Doukki Gel mortars, in comparison with seven new samples collected in archaeological sites located at or near Doukki Gel, between the Third and Fourth Cataract.

2 Origin of the samples

The series presented here is made up of four binding mortars used for sealing bricks and five coating mortars having a protective or decorative function (Fig.1).

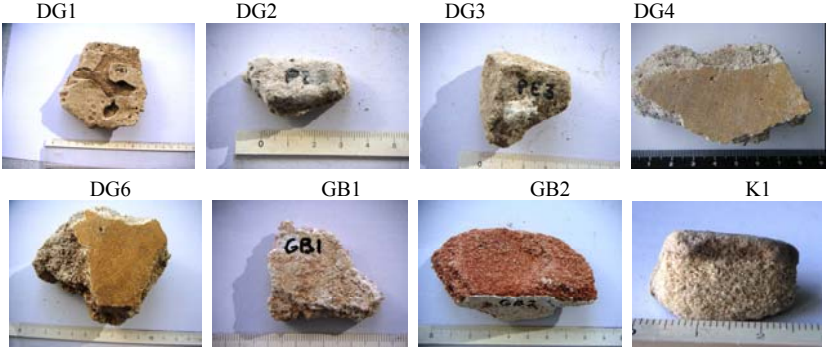

Fig. 1 Photos of 8 samples (DG5 similar to DG4)

Three Egyptian plasters or binding mortars were collected in Doukki Gel:

- DG1, from Hatshepsut's temple (15th century BC),
- DG2, Akhenaton's temple (14th century BC),
- DG3, Ramesside temple (13-11th century BC).

Three Meroitic facing mortars were also collected in Doukki Gel, in the Amun temple of Natakamani (1st century AD): DG4 and DG5 from the previous study and a new mortar DG6.

Two facing mortars came from Gebel Barkal:

- GB1, from the palace of Natakamani (1st century AD),
- GB2, collected on a Meroitic pyramid (1st -3rd century AD).

The ninth sample was a binding mortar K1 from a late Meroitic pyramid in Kawa (1st -3rd century AD).

3 Analytical techniques

It is necessary to use complementary analytical techniques for chemical, mineralogical and microstructural characterizations to obtain optimum understanding of these materials [5]. The mineralogical and chemical analyses were carried out on powdered samples, eventually after separation of the surface layer. X-Ray Diffraction (XRD) was used for identifying the nature of crystalline phases, such as binder components, sand or impurities. The elemental quantitative composition was determined by X-Ray Fluorescence (XRF) on calcined samples.

The porosity was measured by mercury intrusion porosimetry on small pieces of dried mortar. Microscopic observations were performed on polished sections by Scanning Electron Microscope (SEM), associated with EDX for identifying the chemical elements.

Finally, samples with clay binder were analyzed by ^{27}Al MAS-NMR in order to determine a possible evolution of aluminium coordination in the clay.

4 Results

The results of the main mineralogical, chemical and microstructural analyses will be described as follows.

4.1 Mineralogy

Table 1 gives the mineralogical composition of the core of each dried sample determined by X-ray diffraction. These results clearly show three families of mortars, based on gypsum, clay and lime or calcite binders.

The first two Egyptian mortars are based on calcium sulphate, in the form of gypsum for DG1 and gypsum, hemi-hydrate and anhydrite for DG2. Quartz (siliceous sand) is also present as a secondary or minor phase.

The third Egyptian mortar DG3 and the two Meroitic mortars GB2 and K1 appear composed of siliceous sand only bound by kaolinite, a clay mineral.

The other Meroitic facing mortars from Doukki Gel (DG4 to DG6) and Gebel Barkal GB1 have a similar composition corresponding to a lime-based mortar, with a high content of quartz and calcite. GB1 contains also calcium sulphate as minor phase.

Table 1 Mineralogical composition by XRD (+++ Major phase, ++Secondary phase, + Minor phase, (+) Traces)

	Gypsum		*Clay*			*Lime*			
	DG1	DG2	DG3	GB2	K1	DG4	DG5	DG6	GB1
Quartz	+	++	+++	+++	+++	+++	+++	+++	+++
Calcite	+	-	-	-	-	+++	+++	++	+++
Gypsum	+++	+++	-						(+)
H-hydrate		++	-						+
Anhydrite		+++	-						
Cordierite	+	-	-		(+)				
Feldspars		+	(+)		+	+	(+)	(+)	(+)
Kaolinite		+	+++	+	++	-	-	-	

4.2 Chemical composition

The results of X-ray fluorescence are reported in Table 2. Chemical elements are expressed in their oxide form. The loss on ignition (LOI) measured at 950°C gives a good estimation of carbonates content when present and helps to estimate the binder content.

Table 2 Chemical composition by XRF (expressed in %)

	Gypsum		*Clay*			*Lime*			
	DG1	DG2	DG3	GB2	K1	DG4	DG5	DG6	GB1
SiO_2	10.03	18.77	80.65	91.97	79.05	30.85	33.99	31.27	38.83
Al_2O_3	1.77	3.42	12.42	4.39	10.84	1.38	1.84	1.61	2.08
Fe_2O_3	0.84	1.84	1.28	1.05	2.34	0.92	1.07	1.01	1.21
CaO	29.67	27.63	0.16	0.08	0.73	23.75	24.13	30.03	26.48
MgO	0.59	0.65	0.12	0.06	0.45	9.92	9.07	5.27	1.11
K_2O	0.14	0.28	0.19	0.06	0.71	0.23	0.33	0.13	0.13
Na_2O	0.14	0.35	0.04	0.08	0.26	0.53	0.40	0.09	0.57
SO_3	36.02	36.66	<DL	<DL	<DL	0.33	0.40	0.26	3.61
SrO	0.05	0.04	<DL	<DL	<DL	0.02	0.03	0.04	0.11
LOI	20.45	10.05	5.20	2.01	4.58	32.13	28.29	29.07	25.49
TOTAL	99.87	100.14	100.51	99.91	99.93	100.42	100.09	99.18	99.97

The presence of calcium sulphate in the two first Egyptian mortars is confirmed by their large content of sulphur (SO_3) and calcium.

The clay mortars DG6, GB2 and K1 are characterized by a very high content of silica and a quasi-absence of calcium.

The other Meroitic mortars present a similar composition, with high calcium content and LOI, those from Doukki Gel having a higher proportion of magnesium. The presence of calcium sulphate in GB1 results in 3.6% SO_3 in the chemical composition.

4.3 Porosity

Table 3 gives the total porosity measured on five mortars. Porosities are quite variable, the extreme values being measured on the mortars from the Gebel Barkal pyramid (22%) and the Kawa pyramid (39%). The other facing mortars from Doukki Gel and Gebel Barkal have the same level of porosity, about 30%.

Table 3 Porosity of mortars

Samples	DG5	DG6	GB1	GB2	K1
Porosity (%)	32.8	30.2	27.1	21.9	38.7

4.4 SEM-EDX observations

Four samples representative of the different families were observed by SEM on polished sections in order to have a better understanding of their microstructure: the first Egyptian plaster, the new facing mortar from Doukki Gel and the two mortars from Gebel Barkal.

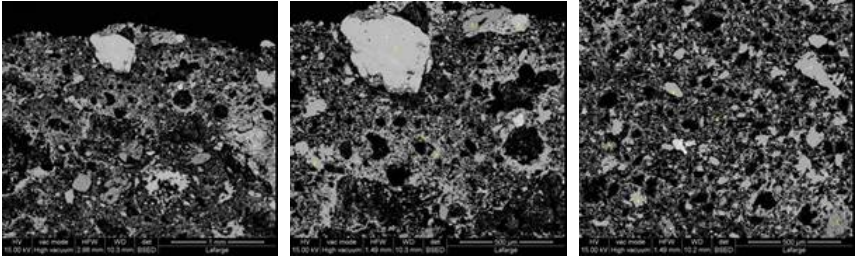

Fig. 2 SEM observation of DG1 (gypsum mortar)

The Egyptian plaster DG1 (Fig. 2) appears with a bi-layers structure. The observation of the core shows a fairly porous structure, with a combination of fine gypsum needles and large grains. Needles typically come from the hydration of hemi-hydrate, while the large grains may be residual gypsum from an incomplete burning. The upper layer (several mm thick), probably due to settling, has a more compact structure than the core and a higher proportion of large grains of gypsum.

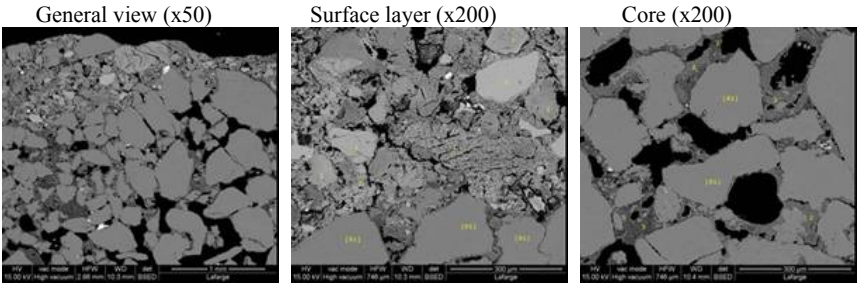

Fig. 3 SEM observation of GB2 (clay mortar)

The core of the clay mortar GB2 (Fig. 3) is composed of a quite porous and probably very permeable structure, with angular grains of quartz interconnected by a few points of adhesive clay. This mortar is covered by a very compact painting layer mainly consisting of calcium carbonate with traces of magnesium, without sand.

SEM observation of the core of the facing mortar DG6 (Fig. 4) shows siliceous sand in a calcium-rich binder. EDX analysis gives a widespread presence of Mg associated with Ca, indicating a magnesian calcite. The decorative surface layer consists of silicon, aluminium and iron, without calcium or magnesium, very probably clay minerals. Its interpenetration with the sub-layer suggests an application as a fresco.

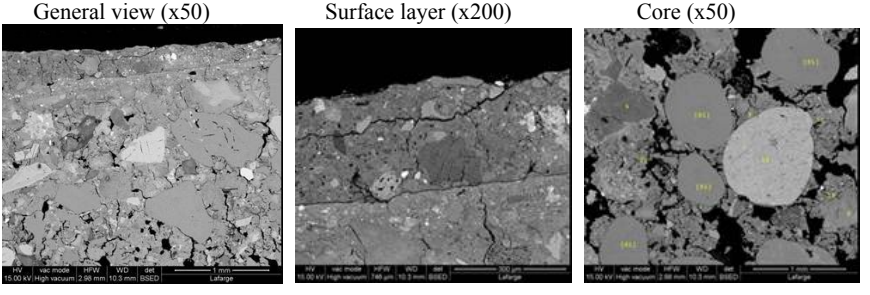

Fig. 4 SEM observation of DG6 (calcite mortar)

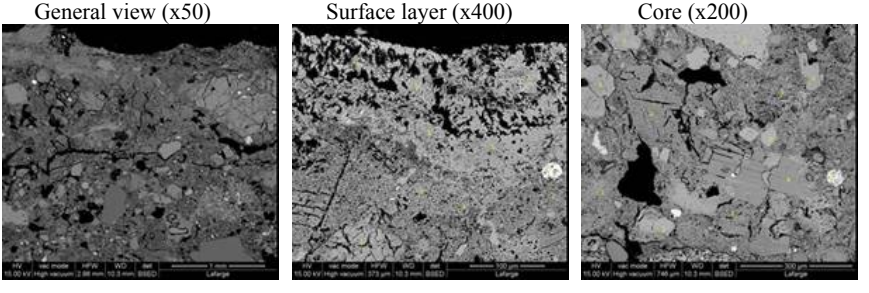

Fig. 5 SEM observation of GB1 (calcite mortar)

The sample GB1 (Fig. 5) also appears as a mortar of carbonated lime and silica sand. EDX confirms the presence of calcium sulphate. The lighter surface layer also contains calcite and calcium sulphate; its silica content, determined by XRF on a separate specimen, is only 3 times lower than the core.

4.5 ^{27}Al MAS-NMR analysis

Two clay mortars DG3 and GB2 were analysed by ^{27}Al MAS-NMR in order to measure the coordination state of Al atoms in the clay structure. For both samples, Al was almost totally in the form Al(VI), with a large peak at 3.4 ppm, showing that clay mineral was not modified by any reaction such as geopolymerisation [6]. Traces of Al(IV) were only identified by very small peaks around 70 ppm, with intensity slightly over the detection limit.

5 Interpretation

All results show that the studied mortars may be classified into three categories. An estimation of their quantitative composition, calculated from the chemical and mineralogical analyses, is reported in table 4. Calcium sulphate was calculated from SO_3, taking into account the possible formation of $SrSO_4$ from SrO. Magnesium and excess calcium not combined as sulphate were considered in the form of carbonates and expressed as "limestone". Kaolinite was calculated from Al content using the theoretical composition $Al_2Si_2O_5(OH)_4$ Finally, sand was considered as the residual part, corresponding to quartz and minor phases. A good accordance was checked between the theoretical LOI of calculated phases and the experimental values. For gypsum mortars, a possible distribution gypsum-anhydrite was calculated by estimating the water content from the LOI and the calculated content of limestone.

Table 4 Estimated present composition of mortars (mass %)

		Sand	Limestone	Gypsum	Kaolinite	Anhydrite
Gypsum mortars	DG1	13	9	77	-	0
	DG2	22	5	48	-	24
Clay mortars	DG3	69	-	-	31	-
	GB2	89	-	-	11	-
	K1	73	-	-	27	-
Lime mortars	DG4	37	63	1	-	-
	DG5	38	62	1	-	-
	DG6	35	64	1	-	-
	GB1	47	45	8	-	-

The two Egyptian gypsum mortars are similar and contain approximately 75% calcium sulphate, in the form of gypsum, hemi-hydrate and anhydrite (NB: calculations only based on gypsum and anhydrite).

The content of kaolinite in clay mortars varies from 11% to 31%. ^{27}Al NMR analysis of DG3 and GB2 shows that kaolinite structure has not been modified by reaction that could explain their durability such as geopolymerisation. This also indicates that clay was used in its raw state, without any burning process. The two binding mortars, positioned between bricks, were probably well protected from leaching, thus explaining their higher kaolinite content. The surface mortar GB2 has been probably more leached and has the lowest kaolinite content. The presence of a hard and compact painting of calcium carbonate has undoubtedly contributed greatly to its durability.

In the series of lime mortars, the three samples from Doukki Gel are very similar, with about 63% of carbonated lime in the form of magnesian calcite. SEM shows that DG6 is covered by a clay decorative layer applied as a fresco.

The mortar from Gebel Barkal GB1 is quite different, with lower content of calcite, and better calcium purity. The external layer is also based on calcite and silica. The low, but significant presence of gypsum (or hemi-hydrate) in this mortar cannot be considered only as an impurity and could correspond to the residual amount of a gypsum binder, associated with lime or crushed limestone, as supposed in our previous study [3].

6 Conclusions

The analyses carried out on this new series show three very different types of compositions, with gypsum plasters, clay-sand mortars and more conventional lime-sand mortars. The composition of the decorative surface layers varies from clay to lime or lime-and-gypsum, in the form of painting or applied as fresco.

This extreme diversity of compositions observed in these mortars and their decorative or protective layers is particularly interesting from an archaeological point of view. The knowledge of the various techniques used enables us to have a better understanding of foreign influences on building workers in ancient North Sudan [7].

It thus appears that gypsum mortars, based on techniques and raw materials coming from Egypt, were used only during the Egyptian colonization. Lime mortars were known and used at least since the 1st century AD. Finally, clay mortars were known as early as the Ramesside time, and were still in use in the 1st century AD and maybe later.

7 Acknowledgments

We want to thank very much all the colleagues that put the samples studied here at our disposal: the National Corporation for Antiquities and Museums, Vincent Rondot, Head of the French section, Charles Bonnet in Doukki Gel, Murtada Bushara Mohamed in Gebel Barkal and Derek Welsby in Kawa. We want also to thank Jean-Baptiste d'Espinose from ESPCI in Paris for the NMR analyses, the Lafarge Group for its financial and technical support, and particularly the Analysis Department and the Microstructure Group at the Lafarge Research Centre that carried out the analyses.

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I.26

Identification of Mortars in the Ottoman Era in Algeria through Historical Documentation and Laboratory Analyses

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Abstract In the Algerian traditional and historical architecture, there is a variety of mortars which were used as: jointing mortar and finishing mortar. We found out that they were different according to their regions and cities. Although Algeria conceals a very rich patrimonial park, our interest is mainly focused on the mortars used in the buildings in the Ottoman Era. Through a specific historical documentation of the Ottoman Empire, which is constituted by the registers of the property "*Habus*", we were able to identify all the used materials, the manufacturing of various mortars and especially their implementation. The archival information was compared to the analyses of mortar samples. Samples of mortars were collected and described in situ, and a number of laboratory tests were carried out to determine their physical characteristics, chemical and mineralogical compositions.

1 Introduction

The Ottoman Era in Algeria that extends from the 16th to 19th century was very rich in architectural constructions. Cities and particularly Algiers expanded significantly at that time and many buildings, nowadays regarded as our architectural heritage including palaces, mosques, military constructions and minor architecture (houses) within the central city and outside their walls were constructed.

This dynamism has also been reflected by the appearance of a building art, and know-how related to the construction techniques and preservation of buildings. These building techniques resulted in the use of different materials, particularly for the jointing of masonry and coating, i.e. mortars. The exploitation of the unique documents known as "*Habus"* allowed us to identify all the materials used

for preparing mortars and their different applications. The diversity of the Ottoman buildings varies according to their size and their geographic locations. In our study we had to limit our investigations to the most representative buildings in the city of Algiers. The following buildings were selected:

- Citadel of Algiers: the seat of Ottoman power, made up of various structures; the Palace and Mosque of the Dey, Bey Palace, Summer Pavilion, the Hammam of the Dey, District of Janissaries, Skifa casemates and powder magazine. The construction of this set was between the 16th and 17th centuries.

- Casbah of Algiers: The medina, which forms the city notable for its minor Ottoman architecture (the houses), all designed from the 16th to the 18th century.

-Djenane Mahieddine: A Fahs house (outside the medina and the ramparts), a villa mostly used in summer, built between the 16th and 17th centuries.

2 Historical approach

2.1 The Habus documents

This not-well known documentation was recently studied by S. Chergui [1]. On the eve of the French Occupation of Algeria, the urban properties of Algiers were divided among three main beneficiaries: Al-Baylik, Habus institutions and individual owners.

- The *baylik* properties are properties exclusively subject to the authority of the Dey or pashas, they are established by means of acquisition, inheritance, donation as well as forfeiture.
- *Habus* properties: These ones, known as *habus* possessions in the profit of religious institutions or public groups.
- Individual owners.

Through the use of the archival documents related to administrative and financial management of this *Habus* category "Real estate", we were able to understand the form of management, the operation and the mechanisms of construction and preservation of architectural heritage of properties based on the *habus* and therefore the identification of materials used in the Ottoman Era for making mortars.

2.2 Mortars of the Ottoman Era according to historical sources and Habus documents

Mortar, identified in the *Habus* documents by the generic term "Baghli" or "Khumra [2], is a lime-based binder. The qualities of the binder permitted different constructions of walls but also arches and domes. The mortar could have

multiple applications, e.g. jointing, grouting or filler but the basic components remained the same: sand and lime. To this mixing were added other components such as broken tiles or crushed bricks. According to [3], mortar was composed of red sand argillaceous of Pliocene formations, mixed with 'greasy' lime, while, Rozer [4] states that the mortar of the Ottoman Empire was composed of lime and red clay from diluvial ground.

The manufacturing of lime [5] took places in the areas close to the city. The quality of white limestone is pure and soft. The burned material (quicklime - Calcium oxide) was slaked by masons and transformed into lime at the construction site.

The bookkeeping records for the Habus mentions the use of two types of lime, the first called "Djir Ghabra" that means, the lime powder meaning the quicklime and the second "Djir Dhars", that means, the slaked lime [6]. In the books of Shawwal 1148 / 1735 to 1736, it is noted that DjirDhars is a result of slaking (tardjīh). The book of Rabi al-awal 1150/1737- 8 states that a quantity of quicklime (Djir Ghabra) was slaked directly on site. These two types of lime were used in various operations [7] such as: roughcasting (plaster) (talbīs) or restoration (Djir Ghabra li tarqī) or the painting (Djir dhara 'lil bayyād).

Mortar was made according to precise proportions (a portion of lime for two to three parts sand), the grain sizes largely depended on the use of mortar, i.e. Jointing or coating. During the rebuilding of Al-Sayyida Mosque [8], the use of one part of coarse sand (raml hasbā) for the mortar of fillings and the fine sand (raml daqīq) for roughcasting (lil-talbis) was mentioned in the records.

3 Description of samples

The mortar can have multiple uses such as jointing of masonry, finishing, coating and sealing for terrace. In this study we were interested in jointing and finishing mortar (plaster) used at the various sites previously mentioned.

These mortars present visual differences in their colours and textures, which led to the choice of nine samples: five samples of jointing mortar and four of finishing mortar.

3.1 Mortars of jointing

The Citadel of Algiers: three samples of jointing mortar were selected:

- The powder magazine (MJ1): It is a yellowish mortar containing large quantities of lime particles of more or less important dimensions. It also contains grains of broken gravel. It is a friable material (Fig. 1a).

- The Skifa (MJ2): it is a mortar of reddish to brownish colour containing the lime grains. This mortar is very friable and seems porous when judged by the naked eye (Fig. 1b)
- The mosque of Dey (MJ3): It is a pinkish colour mortar, containing lime grains (inclusions). This mortar is very friable and seems porous when observed by the naked eye. When crushed, it is composed of very fine lime and red sand particles (Fig. 1c).

The Casbah of Algiers (MJ4): It is a pinkish colour mortar, which seems very compact but friable when crushed in hands. It contains a certain number of pores (Fig. 1d).

Mahieddine Villa (MJ5): It is a pinkish colour mortar. It seems very compact but can be crushed by hand. It contains some brown spots (in much reduced quantity) and small grains of lime (Fig. 1e)

a) MJ1 b) MJ2 c) MJ3 d) MJ4 e) MJ5

Fig. 1 Photographs of different samples of jointing mortars

3.2 Mortars of coating

The Citadel of Algiers: two samples of coating mortar were selected:

- The powder magazine (MF1): mortar of very clear orange pink colour, including scattered brown spots and lime grains. It is a friable material when crushed by hand and a certain number of pores can be observed by the naked eye (Fig. 2a).
- The mosque of Dey (MF2): mortar of very clear pink colour which includes scattered brown spots and lime grains. It is compact (Fig. 2b).

The Casbah of Algiers: The mortar of coating (MF3) presents a very moderate colour which varies between the yellow, pink and white. This mortar includes brownish red spots and lime grains. It is friable when crushed by hand (Fig. 2c).

The Mahieddine villa: Mortar of coating (MF4): It is composed of two parts: The first part of a thickness of up to 2 to 2.5 cm of pink colour. It is a reddish colour and includes brown spots of various dimensions. It is very friable when crushed by hand and presents certain number of pores visible by the naked eye.

The second part is thin (0.5 cm). Its colour is whitish and includes black spots which are particles of gravel (broken stones) and spots brown clay or red sand particles (Fig. 2d).

a) MF1 b) MF2 c) MF3 d) MF4

Fig. 2 Photographs of different samples of coating mortar

4 The experimental part

Several laboratory tests have been carried out in order to determine the physical characteristics of the collected samples and their mineralogical and chemical compositions.

4.1 Physical characteristics

The following characteristics were considered; bulk density; specific density; the concentration of free lime CaO (based on the solubility of calcium oxide and hydroxide in a sucrose solution, the volume of hydrochloric acid required for neutralization of the alkaline solution of calcium saccharate, determines the content of free lime); pH; moisture content; rate of organic mass Cmoc (using the French standard XP P 94-047: this test can determine the mass loss of a previously dried sample in an oven at a temperature of 450°C).

4.1.1 Bulk density, Specific density; Concentration of lime free (CaO) and pH

The results are presented in Tables 1 and 2**.**

Table 1 The jointing mortars

Samples	bulk density g/cm3	specific density g/cm3	CaO% (wt,-)	pH
MJ1 (The powder magazine)	1.78	2.52	0.21	9.42
MJ2 (The Skifa)	2.81	3.30	0.17	9.39
MJ3 (The mosque of Dey)	1.78	2.27	0.24	9.96
MJ4 (The Casbah of Algiers)	2.01	2.18	0.33	9.85
MJ5 (Mahieddine Villa)	1.67	2.13	0.22	10.58

Table 2 The coating mortars

Samples	bulk density g/cm3	specific density g/cm3	CaO% (wt.-)	pH
MF1 (The powder magazine)	1.67	2.04	0.44	9.92
MF2 (The mosque of Dey)	2.02	2.31	0.56	9.20
MF3 (The Casbah of Algiers)	1.47	1.98	0.28	9.32
MF4 (Mahieddine Villa)	1.80	2.48	0.32	9.72

4.1.2 Moisture content and organic mass

The results are presented in Tables 3 and 4**.**

Table 3 The jointing mortars

Samples	H% (wt.-)	Cmoc% (wt.-)
MJ1 (The powder magazine)	1.37	0.07
MJ2 (The Skifa)	12.27	0.13
MJ3 (The mosque of Dey)	2.38	0.02
MJ4 (The Casbah of Algiers)	7.42	0.03
MJ5 (Mahieddine Villa)	3.42	0.03

Table 4 The coating mortars

Samples	H% (wt.-)	Cmoc% (wt.-)
MF1 (The powder magazine)	1.99	0.03
MF2 (The mosque of Dey)	2.01	0.02
MF3 (The Casbah of Algiers)	6.21	0.03
MF4 (Mahieddine Villa)	3.46	0.00

The various tests carried out, enabled us to determine certain physical characteristics of the analyzed mortar samples:

- The mortar samples studied are very friable and soluble in water so do not allow trials to determine the absorption rate and porosity. The Comparison between bulk and specific densities of each sample shows that the specific density is significantly greater than the bulk density in an order ranging from 1.08 to 1.44 confirming that all samples studied are very porous mortar.
- The moisture content varies between samples and it is strongly related to the environment and also confirms the porosity of the mortars studied, which weakens them and increases their vulnerability.
- There is a presence of free lime CaO (not bound) but at reduced rates and therefore does not increase the vulnerability of the material.
- The pH of all the samples varies from 9.20 to 10.6, therefore these mortars are basic, and also composed of alkaline oxide “clayey alkaline”

- The presence of an organic matter in all the samples was determined except in the mortar of finishing of the Mahieddine Villa. The organic matter rate in all the samples is quite reduced and variable from 0.02% to 0.13%.

4.1.3 Chemical analysis

Elementary chemical analyses were carried out by X-Ray Fluorescence (XRF) of various components and their proportions expressed as a percentage.

Table 5 The jointing and coating mortars

N°	Samples	Loss to ignition %	Total %	SiO2 Si2 %	Al2O3 Al2 %	Fe2O3 Fe2 %	CaO Ca %
01	MJ1	19.5	100.0	49.64	6.63	2.86	16.59
02	MF1	13.5	100.0	62.12	4.89	1.76	15.29
03	MJ3	28.9	100.0	22.84	6.05	4.92	13.60
04	MJ5	15.3	100.0	52.98	9.99	3.27	13.25
05	MF3	10.3	100.0	51.71	10.54	4.11	18.47

Table 6 The jointing and coating mortars

N°	Samples	MgO Mg %	SO3 S2 %	K2O K2 %	Na2O Na2 %	P2O5 P2 %	TiO2 Ti2 %
01	MJ1	0.90	0.28	1.63	1.60	0.08	0.32
02	MF1	0.35	0.08	0.96	0.84	0.06	0.17
03	MJ3	0.72	0.17	1.73	0.68	0.05	0.41
04	MJ5	0.61	0.13	2.76	1.24	0.05	0.41
05	MF3	1.37	0.15	1.81	0.90	0.12	0.49

4.1.4 Mineralogical analysis (XRD)

This analysis was carried out through X-Ray diffraction (XRD). Mineralogical analyses were performed on five mortar samples: powder magazine (MJ1and MF1), mosque of Dey (MJ3), Mahieddine Villa (MJ5), Casbah of Algiers(MF3).

The various tests carried out, enabled us to identify the chemical and mineralogical components of the analyzed mortars:

- The chemical analysis revealed the composition of different samples of mortars, the same chemical components and in similar proportions. A great proportion of silica is in hydrated form SiO_2 whose origin can be quartz or clay; there is also a great proportion of CaO and Al2O3. One finds in smaller quantities the other components like iron oxide, sulphur trioxide, potassium, oxide of sodium, titanium dioxide and magnesium oxide. These are minerals that are found in the basic composition of clay.

- Chemical analysis has also highlighted the presence of a component of phosphorus pentoxide P205 which could be organic
- The mineralogical analysis confirms the results of the chemical analysis; indeed, this reveals that the essential components of the analyzed mortars are quartz in free form and the white feldspar which (albite) is a group of the silicates which may have feldspathic and micaceous sand origins. In addition there is the presence of calcite whose origin could be lime. The other components include muscovite which can have as similar origin in feldspars or clay (earth or plundered bricks) and the potassium which can be associated with other minerals but which can also have as its origin an organic component because it can be found in the ash or in the composition of bone.
- The colour of the mortar is according to the rate of iron oxide; indeed it is the iron oxide which gives this pink to red colour. In case its rate is low in the mortar, this last has a very clear colour as the sample MF1 whose rate is of 1.76%, which corresponds to its aspect with the naked eye, a very clear orange pink colour.

5 Conclusion

Through the various analyses, we were able to check and to confirm essential facts regarding the jointing and coating mortars used in the Ottoman period in the city of Algiers:

- The similarity between the various samples despite the diversity of the sites and the buildings, leads us to say that there was a common knowledge in the city of Algiers about how to prepare a good quality mortar, which lasted several centuries, from the 16th to the 18th century. These similarities are about the manufacture of mortars, their components and their respective proportions within the composition of the mortar.
- These mortars are based on lime and clay as it was mentioned in historical documents and archives. The composition of these mortars is quite precise in the proportions of the components: the most important components in terms of quantity are quartz and the feldspars which one can find in the siliceous sand or the clay which are used like grease-removers, then the quicklime, used as a binder, in a ratio of 1/3 to 1/4 compared to the first component. These are the same proportions which were mentioned in the historical documents and archives of the Ottoman Era.
- The analysed mortars contained organic components, probably bones or ashes.
- Plundered brick which is a clayey element was found and identified.

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I.27

Historic Documents in Understanding and Evaluation of Historic Lime Mortars

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Abstract Sophisticated analysing proceedings have been used in the past to assess the composition of hardened mortars. Chemical and mechanical tests combined with microscopic investigations seem to provide all the information required for the design of repair mortars which physically and visually are appropriate for restoration purposes. Lime putty and hydrated lime of varying quality meanwhile are currently available. Nevertheless the results are not always convincing. The limit of the analysing techniques has become evident in conservation practise. Knowledge of how mortars have been fabricated, mixed, stored and applied is as important as the chemical composition. The authors have therefore collected information on the fabrication, compositions and use of mortars revealed by an examination of written historic sources.

1 Introduction

Laboratory tests on new mortars for restoration or repair having the same composition as a historic prototype rarely show neither the same aspect nor the same mechanical behaviour. One reason is a lack of knowledge of the ancient techniques of lime burning, slaking and tooling. Studying the historic documents therefore is not only relevant for historical research but is also of technical interest. Mortar production in pre-industrial time depended on the specific geological situation. Lime for the construction of the town hall of Bremen, for example, was obtained by burning shells due to a lack of limestone in northern Germany. The focus of this paper is on documents from the late middle ages from Southern Germany and Zurich where limestone was available.

2 Historic sources

2.1 Original mortar samples - limits of technical analysis

The most important source for historic mortar technology is the monument itself. Laboratory investigations on historic mortar samples provide information on the type of binder and aggregates and the binder aggregate ratio. In some cases the lime slaking process can be determined. More difficult is the identification of the origin of the ingredients. Sometimes hydraulic material is found close to pure lime mortar in the same part of an old building. This may occur when lime of different provenance has been used or when a pozzolanic component has been added. Information on the origin of the limestone would help to interpret the chemical analysis in such a case.

Particle size of the original binder and original water content (water-binder-ratio) of the fresh mortar can not be determined. The various methods of slaking, mixing, tooling the same ingredients produce mortars with different characteristics like bulk density and texture. In conservation practise frequently the question arises which slaking method should be adopted for a repair mortar to match with the original mortar. Burnt lime could have been slaked with a surplus of water and matured for days, months or years. In other cases it was dry slaked under a layer of sand. A third method consisted in grinding burnt limestone and using it unslaked to prepare the so called *hot mortar.* The applied methods can not always be concluded from laboratory analysis (Figs. 1 and 2).

Fig. 1 Presumably dry slaked medieval mortar with fine cracks in lime lump

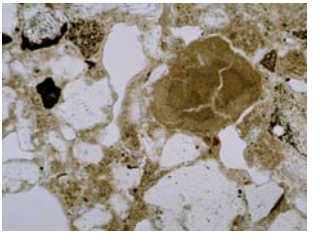

Fig. 2 Thin section of laboratory hot mortar (Foto: K. Kraus, IfS)

2.2 Written documents

Eckert evaluated a multitude of historic texts related to the fabrication and use of lime mortar and traced developments in mortar technology from roman antiquity to modern times [8]. In Italy a detailed collection of mortar recipes was published by *Archolao* [1]. Mostly these recipes came from theoretical treatises of architecture from the 15th to the 19th century. In early middle ages contemporary

descriptions of mortar fabrication are rare. The few known texts reveal the symbolic meaning of every human action in that time. The documents are more religious contemplation than technical account. More reliable documents are preserved from the late middle ages. A very precious source is the *Baumeisterbuch* of *Endres Tucher* [5]. *Tucher* was the public master builder of Nuremberg from 1464 to 75. The detailed description of his professional duties gives a very close view on organisation, construction and municipal life in the 15th century.

A document of similar importance is the *Zuricher Baumeisterbuch* from 1573 [6]. Both towns, Nuremberg and Zurich had a high building activity at that time. The availability of building material especially of limestone was similar. Thus it could be expected that fabrication and employ of lime mortar was similar as well.

In this paper both books are studied together with about 30 unpublished documents, mostly building accounts from Zurich, in order to get an insight into the local conditions of mortar fabrication at that time [9].

2.3 Depictive representations

Though they are widely published, representations of building sites and of craftsmen still offer details on the fabrication of mortar which scarcely have been discussed until now.

Eckert investigated the medieval representations on mortar fabrication collected and published by *Binding* [8, 2, 3]. More than 100 pictures from 11th to 15th century are preserved. The largest number of illustrations date from the 15th century (79 documents). Most of them show mortar as a pile of material, presumably sand and quicklime which is chopped or turned with a hoe.

Fig. 3 Mortar prepared in an open hut

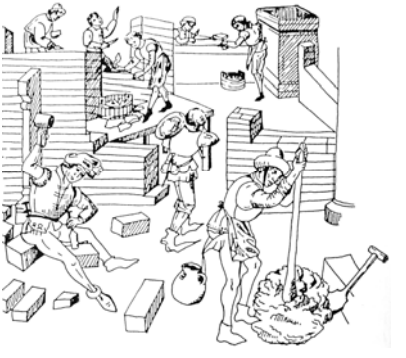

Fig. 4 Ramming mortar with rounded stake

Frequently a water bin is shown close to the pile. Sometimes the pile is protected by a roof (Fig. 3). In 17 pictures mortar is prepared in a case or frame of

timber which could indicate the preparation and maturing of lime putty. The only picture showing a kiln on the construction site is an early mosaic from Palermo (12th century). Lime here is slaked in a closed case and seems rather liquid. An example for ramming an almost dry mixture is seen in Fig. 4. The procedure of ramming or beating can help to crush pieces of unslaked quicklime and to homogenise the lime-sand-mix. Ramming also consolidates the sand and lime putty by extruding surplus of water and air. The binder-sand contact is improved and workability increases compared to mixing by chopping and turning over.

3 Mortar fabrication in Nuremberg and Zurich around 1500

3.1 Provenance of limestone

Both towns, Nuremberg and Zurich profited from limestone deposits. *Tucher* enumerates four quarries around Nuremberg which were about 20 km distant. This distance corresponded to one day of travelling. A fifth quarry was explored some 40 kilometres away at Deinschwang. Lime from Deinschwang was of better quality according to the master builder and therefore was worth the higher costs and efforts of transportation. *Tucher* commends the good yield and workability of this lime which was equally suitable for masonry mortar, rendering and limewash.

In Zurich the supply of lime was worse. The reason for this was not a lack of natural deposits but neglect by the building master. Quarries around Zurich were situated in distances between 0.8 and 24 kilometres. Additionally the quarries around *Rüti* (43 km distance) could easily be assessed using the lake as way of transportation. The limestone in this case was burnt at or close to the quarry and the burnt material (quicklime) was packed and transported in *Röhrli*, special sealed barrels which protected the hazardous material from air and water. Another source of limestone was the river Sihl. Here pebbles could be collected and burned during the winter, when the quarries were inaccessible.

Rights of ways could have presented another impediment to procure limestone. Litigations of this type are documented for both towns.

3.2 Sand

Sand usually is the most important component by volume in mortar. Nevertheless *Tucher* does not mention sand at all. In Zurich every citizen had to procure the sand he needed individually. In spite of that rule, one resolution concerning sand is documented charging the master builder with the provisioning of enough sand in the municipal lime hut to accommodate the demand. In 30 accounts of building materials from the years 1531 to 1752 the purchase of sand

occurs only once. This means that suitable sand must have been easily available and presumably free of costs in both cities.

3.3 Fabrication and storage

3.3.1 Nuremberg

None of the documents referred to in this study treats the process of lime burning itself but it is mentioned where the kilns were situated and how the production was planned in advance.

Two kilns were situated on the territory of Nuremberg. The public master builder was responsible for the provisioning of the town with building material. *Tucher* knew the exact quantities of limestone and the amount of wood one filling of a kiln would need. Providing enough firewood often represented a major problem. The surroundings of Nuremberg had been stubbed out due to the large demand for timber and fuel. Wood had to be ordered long time in advance. As *Tucher* complains the firewood sometimes had been stolen. Thus the heat obtained in the kiln was insufficient for lime burning. This could endanger a whole building project.

Lime also was burnt by peasants in the vicinity. This gave them a little secondary income. When needed *Tucher* had one or two supplementary kilns erected directly on the market place. This was necessary when the price for lime increased due to price-fixing agreements of the peasants or in cases of increasing demand.

The burnt lime was stored dry in special huts. No indication of pits for slaking can be found in the *Baumeisterbuch*. The product was sold as quicklime, but the order is reported that a building master must have the lime slaked before handing it out. The product then is sold *'melbsweis'*. This unusual German term signifies 'like flour' which would indicate that the pieces of quicklime had been reduced to powder in the slaking process. In fact quicklime breaks into pieces when the amount of water added is less or just exactly sufficient to turn all the oxide of Calcium into hydroxide. Only with excess of water it becomes a paste or liquid lime putty. Thus in Nuremberg in the end of the 15th century probably lime was pre-slaked and transported in a wet state to the building site, where it was mixed with sand and water.

3.3.2 Zurich

Most limekilns in Zurich belonged to the brickyards but the municipality of Zurich also maintained one kiln [6]. In 1540 lime here was stored in special barrels mainly as quicklime for use in masonry mortar and some as lime putty for limewash. This changed in the following years. Preserved inventories of the lime huts indicate that from 1600 to 1612 lime mainly was stored as lime putty and

between 1620 and 1670 the whole municipal stock was lime putty. The reason for this change is not yet understood. Around 1600 there was an increasing demand for stucco on interior walls. This might explain the large storage of lime putty. Before, masonry mortar and plaster had been produced with the same type of binder but using different sands. Stucco needed a fine graded, homogeneous binder. The total absence of quicklime in the stock is nevertheless striking and it would be of interest to investigate whether lime putty has been used for setting mortar at that time. It was not before 1670 that quicklime reappeared in the inventories.

3.4 Mortar fabrication

Numerous German terms like *mortarruhrer* (mortar stirrer) *mortarkocher* (mortar cooker) or the latin *caementarius* describe the profession of a mortar maker. Representations of craftsmen from the 15th century in Nuremberg show the mortar maker in an almost stereotype manner (Fig. 5). Only one folio represents a closed mortar case with a pile of sand or dry slaked lime (a sand-lime-paste or powder) and two water bins close beside (Fig. 6). The timber case here is divided into two sections, both filled with mortar. The horizontal surface indicates a rather liquid consistency. This could show the process of slaking burnt lime and maturing lime putty but the absence of pieces of burnt limestone in the otherwise detailed representation makes it more liable that a pre-slaked mixture is diluted for a limewash or rendering mortar. The mortar maker was responsible for the fabrication of mortar for the stonemasons, plasterers and the roofers.

Fig. 5 Mortar maker in Nuremberg in 1425

Fig. 6 Preparation of lime mortar in 1522

Even though his wage was inferior to a mason's he was not an untrained worker or helper. However reliable craftsmen were rare in medieval towns and good mortar was not always guaranteed.

Tucher complains about unskilled workers unable to produce reasonable mortar for the roofer and therewith endangering the building project. And in Zurich it was reported that in 1541 the mortar sold of the municipal building yard repeatedly was not properly slaked but *burnt*.

In summer 1541 the lime hut in Zurich was reorganized. The building yard with the lime hut was situated outside the town. Here mortar was prepared and stored together with the municipal provision of tiles. Regularly the sale of tiles and *mortar* (not *lime* as usually was sold in other towns) was recorded. According to *Guex* mortar was prepared at the lime hut by dry slaking with water and sand [6]. The accounts also refer to the delivered quantities of lime and sand. The given quantities allow a rough estimation of the most common binder aggregate ratio. A ratio of 1:3 is assessed which seems reasonable and typical for masonry mortar in regions with limestone deposits and normal graded sand.

4 Conclusions

Whether better lime was obtained by slaking and maturing or by dry slaking depended on the features of the available limestone variety. In pre-industrial times the possibilities of mortar fabrication were determined by the specific local conditions. The practise of burning lime pebbles reported in Zurich could explain larger scatterings in the chemical composition of the binding matrix observed in some analysis, because material transported by the river was more heterogeneous then quarry material. Even today the qualities of burnt limestone are difficult to predict. Recent analytical research in Germany to establish a prediction model revealed the complexity of this issue [10].

Apart from local geological conditions, infrastructure, economic situation and changes in the architectural treatment of surfaces sometimes political realities had an influence on mortar fabrication. Lime burning and slaking was organized by the civil administration. In the 15th century mainly dry slaked lime or lime paste were applied. Lime putty apparently became widespread in Zurich in the 17th century. No indication for grinding burnt lime could be found for preparation of hot mortar. Which technology exactly has been applied for different purposes is not yet fully understood. Current analytical research focuses on detecting the characteristics of hot lime, dry slaked or matured putty binders.

Comparing the documents related to mortar fabrication in the late middle ages of Zurich and Nuremberg, this paper shows that mortar composition is too complex to be summarized in a couple of generalised formulas. Collecting and evaluating historic documents can provide a better understanding of regional phenomena. Together with specific analytical investigation of historic specimens

as well as on restoration mortars it should become possible to distinguish local findings and avoid inaccurate generalisations.

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6 Photographic credits

Fig. 1: Photography: Neuwald-Burg 2008
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Fig. 3: Binding (2001) p.30, Abb. 67 (Berlin, Staatliche Museen zu Berlin, Kupferstichkabinett, MS 78 E1, fol 11, Rudolf von Ems Weltchronik (Toggenburg Bibel) Illumination
Fig. 4: Binding (2001) p. 170, fig. 534a. (Strasbourg, Bibl. Nationale et Universitaire, Ms. 532, fol. 3, Augustinus, Cité de Dieu, Illumination, Netherlands)
Fig. 5: Hausbuch der Zwölfbrüderstiftungen, Amb. 317.2° Folio 36 recto (Mendel I), Staatsbibliothek Nürnberg
Fig. 6: Hausbuch der Zwölfbrüderstiftungen, Amb. 279.2° Folio 13 verso (Landauer I), Staatsbibliothek Nürnberg

I.28

Mortars and Plasters under the Mosaics and the Wall Paintings of the Roman Villa at Piazza Armerina, Sicily

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Abstract The Roman Villa at Piazza Armerina in Sicily, built in many successive steps over the 2nd and 3rd centuries A.D., is renowned all over the world for both the wealth and the refinement of its mosaic floors. In February 2007 the Regional Government of Sicily started a restoration project of the whole archaeological site. The systematic survey and study of all decorative elements highlighted the value of wall paintings, which until then were almost unknown except for casual approaches to specific problems of conservation, carried on without any relation to the far and away famous mosaics. This paper shows the results of a physical chemical investigation of the mortars used for both floors and walls, which were extensively sampled both indoor and outdoor, including the crushed brick mortars of the basins at the monumental front entrance of the Villa. The mineralogical petrographic study of mortars and plasters was performed by XR diffractometry and by optical microscopy using polarized light through thin sections. Pigments were analyzed by micro-Raman spectroscopy, simultaneous thermal analysis was also performed in a few cases, in order to further investigate the recipe of the mixture.The results describe the composition of mortar under the mosaics and afford an unpublished view of both materials and techniques used in the wall paintings of the Villa at Piazza Armerina, giving the opportunity for interesting comparison with others archaeological sites under study.

1 Introduction

The Villa Romana del Casale in the neighbourhood of Piazza Armerina, Sicily, was built in many successive steps over the 2nd and 3rd centuries AD, and it is one of the most luxurious of the Roman Empire especially noteworthy for the finest mosaics which decorate almost every room [1]. When the villa was discovered during the ‘50s, minor importance was given to the traces of colours on the walls

hidden by a thick and strong layer of sinter due to alluvial debris. The restoration project of the whole archaeological site that started in 2007 highlighted the value of wall paintings, which until then were almost unknown [2]. In fact, every wall, both indoor and outdoor is decorated with subjects related to the use of the rooms: the paintings on most of the external surfaces look like the coloured marbles of the opus sectile in the Basilica, in the rooms floored with figurative mosaics the wall paintings are figurative as well, harmonized as for both the colours and the subjects.

The painting layer is often severely decayed by different phenomena mainly crystallization of soluble salts, i.e. efflorescences, that induced decoesion of the surface layers of plasters, including the painted film; moreover mostly walls are covered by a thick sinter. Therefore, the knowledge of composition and texture of the layers of mortar and plaster became a key step in order to achieve proper restoration intervention [3].

2 Materials and methods

The mortars and the plaster were extensively sampled both indoor and outdoor, including the crushed brick mortars of the basins at the monumental front entrance of the Villa, (Table 1).

The mineralogical-petrographic and the physical chemical investigations of mortars and plasters were performed by XR diffractometry and by optical microscopy using polarized light through thin sections. Micro-Raman spectroscopy was employed for the detection of some specific areas of thin sections where some recrystallization processes are visible.

Optical microscopy, both in reflected and in transmitted light on thin-sections, to analyze composition and texture; the thin sections were observed by means of an Olympus petrographic microscope equipped with a digital camera and Image Pro Plus software.

X ray diffraction was performed to identify the crystalline phases, by CuKα radiation on powdered samples in the 2θ range from 4 to 60 degrees, after separation of the layers of mortar.

MicroRaman spectroscopy was perfomed by means of a Renishaw Invia Raman Spectrometer, using two different excitation wavelength, 633nm and 532 nm. Spectra were collected by means of a CCD sensor air cooled by Peltier effect, in a raman shift range from 200 to 3000 cm^{-1}.

Table 1 Characteristics of collected samples

Sample	Material	Location	Note
09PA 04	Painted plaster	Room of “Dominus”	
09PA11	Painted plaster	Monumental door,	Painted band in the bedrock. A

		external, left	fragment already detached with a strong biological deterioration, it contains pointing, finish, paint and deposit layers.
09PA 12	Painted plaster	Monumental door, external, right	The residual band in the bedrock is very broken up. The fragment seems to contain just one layer of paint.
09PA 13	Crushed brick mortar	External basin, left external lining	
09PA 14	Crushed brick mortar	Musive internal basin, right internal lining	Thick layer of mortar beneath.
09PA 15	Painted plaster	External wall, right	
09PA 20	Painted plaster	External wall, right	
09PA 21	Plaster	Parete esterna frigidarium	Painted plaster covered with scale/crosta
09PA 22	Sinter on painted plaster	palestra	powder
09PA 23	Painted plaster	Four-sided portico wall	Triple layer of plaster, the sample concerns the second layer (the most ancient painting)
09PA 24	Fragments of painted mortar	Four-sided portico wall	Triple layer of plaster, the sample concerns the third layer (the most recent painting)
30PA 01	Mortar fragments	External wall of the octagonal hall	

3 Results and discussion

The observation of the thin sections allowed to give the description of characteristics of the composition and the texture of the mortars. Their mineralogical composition has been verified by XRD (results are in table 2).

The joint mortars of the internal mosaic lining of the tanks, see figure 1, are crushed brick mortars, they also contain granules of vitrophires, quartz grains (600-1500 micron) and more rarely carbonate ones, even of bioclastic origin and sporadic feldspar ones. The inert ones have very variable dimensions, from some mm to the dimension of a silt. The ratio Inert/Binder (I/B) varies between 0.4 and 0.7. Macroporosity is less than 5%. In the binder around the inert one there are thick spherulitic concretion (100 micron) and fringes of radiate calcite. In these concretions, the analysis by means of Microraman spectroscopy has revealed the presence of strontianite. The setting of this mortar has been realized in various levels.

Table 2 Results of XRD analysis of the samples

Sample	Calcite	Magnesite	Quartz	Feldspar	Kieserite
09PA11	++++		+++	+++	
09PA 12	+++++		+++	traces	
09PA 13A	++++		++	traces	+
09PA 13B	++++		+	traces	+
09PA 14	+++	+	+	traces	
09PA 15A	++++		++++	traces	+
09PA 21	+++++		++	+	+
09PA 23	++++		++++	+	
09PA 24	++++		++++	traces	

Key: the number of + indicates the relative abundances of crystalline phases within the sample.

The results of X ray diffractometry indicate that the most present mineralogical phases are calcite and quartz, often associated with feldspar. The presence of Kieserite, a magnesium sulphate $MgSO_4.H_2O$, is related to the presence of sulphatic water in the environment of the villa that caused severe problems both to mosaics and wall paintings, mostly due to formation of efflorescences.

Fig. 1 joint mortar of the internal mosaic lining of the tank at the monumental door

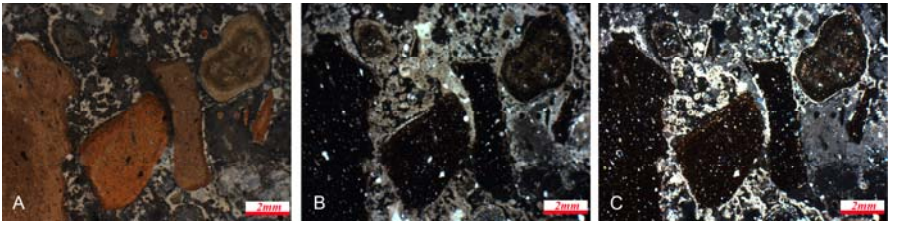

Fig. 2 micrographs of the thin section of the sample 09PA14: A reflected light, B ppl (plane polarized light) and C xpl (cross polarized light)

The mortars of the external lining of the tanks are crushed brick mortars as well, and they do not differ from the ones of the internal lining either for the inert/binder ratio (I/B 0.4-0.7), or for the composition or the granulometry of the inert ones. Only the porosity is a little larger 5%-10%. The superficial layer differs; it is not covered by tesserae, but it is covered by a layer of lime with a I/B ratio 1.5, in this are present inerts which composition reflect the one of the local rocks, consisting of quartz and carbonates, also bioclastic ones, and rare granules of feldspar and muscovite, and some fragments of vitrophires and igneous rocks. The lesser attention of the setting of this mortar that did not have a waterproof function is highlighted by the presence of not dissolved, cracked and inert lacking lumps of binder.

The mortars from the zone of the thermal baths belong to two typologies: the external wall of the frigidarium, sample 09PA21, is lined by a lime with a I/B ratio of about 0,6 and aggregate made by granules of broken up local rock (quartz, rare feldspars, carbonates and bioclastes), and, unlike the others, it is characterized by the presence of a thick rating of withdrawal fractures; on the contrary a remarkable cohesion characterizes the sample of external wall of the octagonal hall, sample 30PA01, that is the entrance environment to the thermal complex, where the humidity rate in the air is always really high, the figures are painted on a single layer of crushed brick mortar, which was very well smoothed on the surface.

Fig. 3 Polished cross section in reflect light of the crushed brick mortar with a red painted layer coming from the external wall of the octagonal hall

The paintings on the surfaces of the Villa perimetric wall and on the individual included buildings were realized on two overlapping mortar layer linings, the external one, which has a variable thickness from 1500 to 600 micron, is formed just by binder, appearing collophorm, with rare presence of some granule of inert of dimension between 400 and 15 micron, consisting of carbonatic rocks and quartz. Porosity is at maximum 5%.

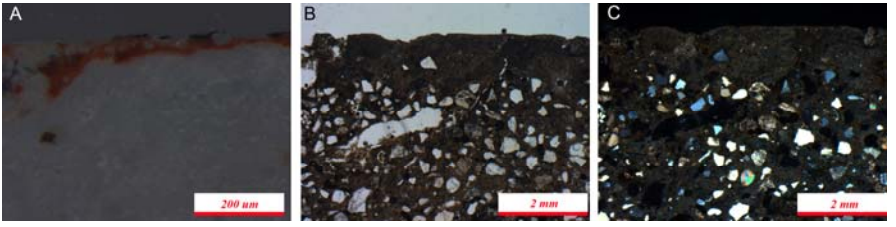

Fig. 4 micrographs of the thin section of sample 09PA12: A reflected light, B ppl and C xpl

The adhesion to brickwork layer contains as aggregate quartz grains that are fairly assorted concerning the granulometry, the dimension are variable between 400 and 30 micron, with a mode that varies from 150 micron in same sample to about 30 in others, e.g. 09 PA11. The binder shows collophorm texture. The ratio inert/binder varies from 0.80, sample 09PA12, to 0.30, with a majority of values around 0.5. Porosity is quite variable from 5% to 30%, in the most of the cases is 10% and it spreads in macropores, of about 400-200 micron in diameter with irregular shapes, and in mostly spherical bubbles of small dimension, ranging from 50 to 150 micron.

The covered household room mortars, sample 09PA04, do not essentially differ from the ones on the open air masonry lining; microscopic analysis of thin section of sample 09PA04 shows that the painting is approximately 25 micron thin and it is applied on a layer of almost inert free carbonatic binder, with rare quartz aggregates. There are some macropores shaped as fenestae and some micropores irregularly shaped. The inner layer, in contact with the masonry, is a mortar with quartz aggregates that are well selected as for particle size, bimodal distribution, 125 and 25 micron respectively, spherical pores with variable diameter are present.

The in situ observations on the frescos of the four-sided portico have revealed the overlapping of two pictorial series, as shown in figure 5, applied on substrate mortars, whose characteristics do not essentially differ from the ones already described.

Fig. 5 the two pictorial layers on the four-sided portico wall

The thickness of the pictorial film goes from 100, sample 09PA24, to 20 micron, sample 09PA23, each pictorial film is applied on a layer of plaster that is almost completely composed by binder superposed on the reinforcing mortar. Yet, it is evident that the reinforcing mortar of the most recent pictorial series is a lot richer in binder, i.e. I/B=0,2, than other samples. Also in this case the aggregates are mostly composed by quartz grains and less by carbonate rocks, sparitic and microsparitic, by rare feldspars, even rarer muscovite lamellae and casual bioclasts, this highlights that the material comes from local arenaceous outcrop. The binder has a collophorm texture also in this case.

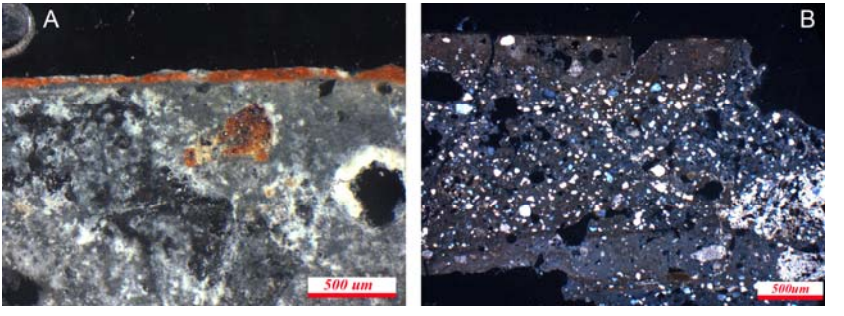

Fig. 6 Micrographs of the sample 09PA23 taken from the oldest pictorial layer. A reflected light and B xpl.

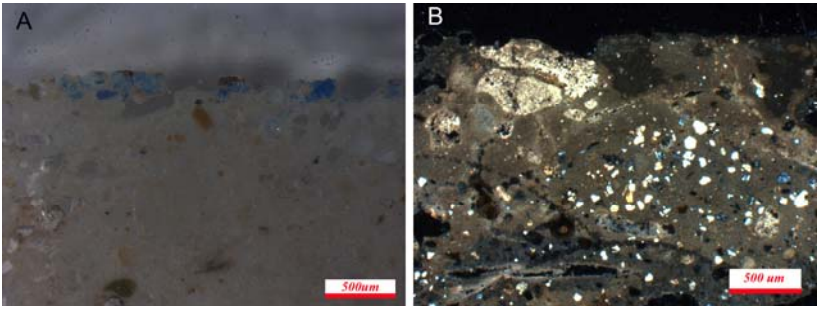

Fig. 7 Micrographs of the sample 09PA24 taken from the most recent pictorial layer, A reflected light and B ppl

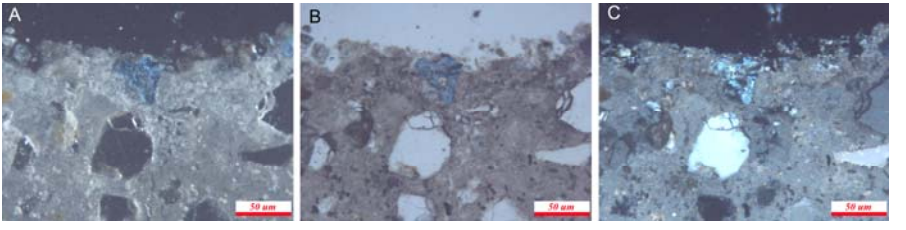

Fig. 8 Sample 09PA24 micrographs of the grains of the Egyptian blue: A in reflected light, B ppl and C xpl. In the latter it is evident the birefractivity of the crystals.

4 Concluding remarks

The composition and the stratigraphy of the wall mortars varies all over the site according the real use of the Villa rooms.

The substratum of wall painting of internal and external walls consists of two levels: external level is perhaps a pure binder, the inner one is a mortar rich in quartz aggregates

The painted layer, brown in colour as observed on thin section in ppl, is 100 to 20 micron thick and has generally a colloidal texture, excluding Egyptian blue that is birefractive in xpl. Except for some fortuitous cases, in presence of microfracture of the layer of "pure binder", is not observed any diffusion of the pigments towards the inner layers, in fact there is, in general, a marked line of boundary. Two overlapped layers of paintings separated by a thin veil of lime were found in the peristyle and in the external wall of the Villa, which testify repainting of the wall.

The sample of external wall painting of the complex of thermae presents a crushed bricks mortar, this latter is also the substratum of mosaic internal covering and painted external surfaces of basins located on open air near the monumental gate of the villa. The contemporary presence of the mortar aggregates, used for the

water contact, the cocciopesto and the vitrophires is quite spread in Roman age mortars, as a matter of fact it had been already well-grounded in Thermae waterworks [4] to guarantee an hydraulic effect such has been verified in historic mortars from completely different sites [5, 6].

For the correct formulation of the restoration protocol [7, 8] both of the mosaics and the wall pantings was truly important the diagnostic phase of the materials with which the Villa was built, of the techniques used by the ancient workers, and in particular of the study of the composition, the texture and the condition of the mosaic allurement mortars, of the wall finishing and pictorial supporting surfaces of the frescos mortars.

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I.29

How Did Expertise in Maritime Hydraulic Concrete Spread through the Roman Empire?

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Abstract The long passage in Vitruvius' *De architectura* concerning the methods and materials for building concrete harbour structures in the sea (5.12.2-5) is unique in ancient literature and consequently frequently cited by modern scholars. Less well known are passages elsewhere in Vitruvius that deal with hydraulic concrete in marine structures, and similar comments in the works of Strabo, Pliny the Elder, Seneca, Suetonius, and Dio Cassius. These authors all comment on the need for a crucial ingredient, *pulvis puteolanus* volcanic ash from the region around ancient Puteoli on the Bay of Naples. None of these passages, however, concern engineering works outside central Italy, although the ROMACONS Project has documented the use of *pulvis puteolanus* (now popularly called *pozzolana*) in Roman harbour structures throughout the Mediterranean. It seems likely that information concerning the ideal materials for placing hydraulic concrete, and their ratios, was spread not only by the movement of central Italian engineers around the Mediterranean but also by the circulation of sub-literary engineering manuals.

1 Introduction: Roman Maritime Concrete

Since 2001 Oleson, in collaboration with Christopher Brandon and Robert Hohlfelder, has co-directed the Roman Maritime Concrete Study (ROMACONS), collecting 36 large diameter cores from numerous maritime structures at 10 Roman harbour sites in Italy, Israel, Egypt, Greece, and Turkey [4, 8, 12, 18, 19, 20, 21]. We also replicated an 8 cubic metre block in the sea with concrete prepared according to Vitruvius' specifications [18]. The concrete in the cores from the Roman harbours we sampled varies to some extent both in the composition of the mortar and the type of aggregate, but every structure tested made use of *pulvis Puteolanus*, now popularly called *pozzolana*, a type of

powdery, pumiceous, incoherent volcanic ash erupted from Campi Flegrei volcanoes around the Gulf of Pozzuoli at the northwest sector of the Bay of Naples [1, 12, 13, 14, 15]. The term "*pozzolana*" can be confusing, but it long ago became embedded in the archaeological literature; here it refers only to the volcanic ash from the Campi Flegrei. We have also found that this material was used in the mortar of a marine fish-tank on the coast of Portugal, outside the Straits of Gibraltar. The benefit of hydraulic pozzolanic mortar is that it can set and cure in the water, out of contact with atmospheric CO_2, allowing concrete for harbour structures to be placed in inundated, or even completely submerged, forms. The pozzolana also enhances the long-term durability of the concrete [15].

This more than Mediterranean-wide trade in a bulk building material is not mentioned in surviving ancient literary or inscriptional sources, but clearly it was important to Roman harbour engineers for nearly 300 years. Harbours, of course, were the most important element in the physical infrastructure that made the Roman imperial economy, and thus the Roman imperial socio-political system, possible.

Various questions must be posed about the origins and spread of the technology for using hydraulic concrete made of hydrated lime and *pozzolana*, particularly in immense marine structures built far from Central Italy [21]. When was the formula discovered, and to what degree did engineers understand the mechanism of its function, and the capabilities of the material? How was the mortar prepared and mixed, and how was the concrete placed in the sea? Did Roman engineers make use of any other volcanic additives to contribute to the hydraulic qualities of their mortars, particularly around the city of Rome? How did the knowledge of the properties of *pozzolana* travel to large and small marine construction sites outside of Italy: through the movement of engineers, or by means of technical handbooks on harbour engineering? A careful consideration of the ancient Roman literary and inscriptional sources concerned with maritime concrete construction can help resolve some of these questions. Important Latin and Greek terms are provided within these translations in parentheses, and sections of the original Latin text follow the translation of particularly important or ambiguous phrases or passages.

2 The Testimony of Ancient Authors for Roman Maritime Concrete

We are fortunate that the handbook *On Architecture* (*De architectura*) by Vitruvius, completed around 20 BC, contains several explicit passages on *pozzolana* and its use in marine concrete, including discussion of the method of placement in formwork. Vitruvius is insistent that the *pozzolana* (*pulvis*, lit. "powdery earth") intended for mortar used in submarine construction should be sourced from the Bay of Naples (*De arch.* 5.12.2), or—more specifically—the area around Baiae. "There is a kind of powdery earth (*pulvis*) that by its nature

produces wonderful results. It originates (*nascitur*) in the neighbourhood of Baiae and the territory of the municipalities around Mount Vesuvius. This material, when mixed with lime (*calx*) and rubble (*caementum*), not only furnishes strength to other buildings, but also, when piers (*moles*) are built in the sea, they set under water." (*De arch.* 2.6.1)

Vitruvius goes on to speculate that the natural subterranean heat of this region is the cause of this useful capacity for setting underwater and the tuff (*tofus*) that occurs there, rising up from beneath the earth, is without natural moisture. "Therefore when three substances [lime, tuff, and *pozzolana*?] formed in a similar manner by the violence of fire, come into one mixture and take on the moisture all at once, they cohere. Hardened by the liquid they quickly form a solid mass, and neither waves nor the effect of water can dissolve them. It seems certain that the natural moisture (*liquor*) has been snatched from the tuff and *pozzolana* (? *ex tofo terraque*) in the same manner as it is from limestone in lime-kilns (*quemadmodum in fornacibus et a calce*). Therefore, when unlike and unequal substances have been separated then united again into one substance, the hot thirst for moisture, suddenly quenched with water, boils with the heat hidden in the conjoined forms and causes them to unite furiously and quickly to take on the unified strength of a solid." (*De arch.* 2.6.1-4).

Although the meaning is not entirely clear, Vitruvius seems to suggest that all three elements lack the liquid element (*liquor*) but have a latent heat (cf. *De arch*. 2.5.2-3). This heat is released by contact with water in an exothermic reaction [10]. There are echoes of this explanation in a passage of Dio Cassius' *History* in which he describes the properties of the *pozzolana* used in the harbour Agrippa built in 37 BC near Baiae, a seaside resort renowned for its thermal waters.

"Now besides these products, the hill behind Baiae furnishes an earth (*gē*), the special nature of which I will describe. The subterranean heat cannot burn anything because its scorching properties are quenched by the admixture of ground water, but it can still separate and melt the substances with which it comes into contact. In consequence, the soft part of the earth is melted out by the heat, while the hard and as it were bony part is left behind. Hence the masses of earth necessarily become porous and when exposed to the dry air crumble into dust (*kónis*). When this dust is mixed with water and lime (*konía*) they become a compact mass, and as long as they remain in the water they continue to set and harden. The reason for this is that the brittle element in them is disintegrated and broken up by the fire, which possesses the same nature, but by the admixture of moisture it is chilled, and so once again becomes completely dense and indissoluble." (48.51.3-4)

In his *Questions about Nature* (*Quaestiones Naturales*), the first-century philosopher Seneca mentions *pozzolana* in the context of water that leaves a calcium carbonate deposit. "The water [of the Hebrus River] is adulterated and throws a sediment (*limus*) of such a nature that it cements and hardens objects. In just the same manner that the powdery earth of Puteoli (*Puteolanus pulvis*)

becomes rock if it touches water, so by contrast, if this water touches something solid it clings to it and forms concretions." (*QN* 3.20.3)

There is a similar comment in Pliny's *Natural History*: "But other creations belong to the Earth itself. For who could marvel enough that on the hills of Puteoli there exists a dust (*pulvis*)—so named because it is the most insignificant part of the Earth—that, as soon as it comes into contact with the waves of the sea and is submerged, becomes a single stone mass, impregnable to the waves and every day stronger, especially if mixed with stones quarried at Cumae." (*HN* 35.166)

Seneca and Pliny both undoubtedly knew that *pozzolana* had to be mixed with lime to make a proper mortar, so they may just be glossing over the full formula to make a rhetorical point. On the other hand, these observant natural scientists may simply be referring to natural concretes or volcanic tuffs that form through lithification of volcanic ash during alteration by ground and surface waters, or even to the secondary mineral cements formed by the alteration of coastal deposits of volcanic ash in seawater [12]. It is possible that builders or engineers in the late third century BC noticed this phenomenon and experimented with the substitution of *pozzolana* for beach or river sands in their mortars.

Early experimentation with pozzolanic mortar for maritime construction probably took place at Puteoli, which in the third and second centuries BC was the only important port in the vicinity of the *pozzolana* deposits of the Campi Flegrei volcano. Until completion of the Claudian and Trajanic harbours at Portus, Puteoli served as the major harbour for the city of Rome, 200 km away, particularly for grain imports [16]. At some point early in the second century BC, a long breakwater composed of large, closely spaced concrete piers (*pilae*) connected by low concrete vaults was constructed to accommodate the growing sea trade serving Rome. In the early first century AD Strabo praises the natural suitability of the local "sand-ash" at Puteoli for the construction of concrete breakwaters. "Puteoli has become a very great emporium, since it has an artificially constructed harbour, something made possible by the natural qualities of the local sand (*ámmos*), which is well suited to the lime and takes a firm set and solidity. Therefore, by mixing the sand-ash (*ammokonía,*i.e. *pozzolana*) with the lime, they can run moles out into the sea and in this way make the exposed shore into a protected bay, so that the biggest cargo ships can anchor there safely." (*Geography* 5.4.6)

Although there are ancient and modern representations of the harbour works at Puteoli, the ancient remains unfortunately now are inaccessible beneath a modern breakwater.

There are numerous concrete harbour installations around the northern shores of the Bay of Naples, many of them associated with the massive installations of the Praetorian Fleet at Misenum. A tomb monument found in the region was dedicated to a Lucius Iulius Valens who was a *caementarius* ("worker in concrete") with the *Classis Praetoria Misensium* (*CIL* 10.1.3414). Since he was a *dupliciarius*, a soldier receiving double salary because of a special skill, Lucius might have been some sort of engineer of maritime concrete construction.

Pliny mentions the importation of *Puteolanus pulvis* to Portus to make concrete for one of the breakwaters of the emperor Claudius' new harbour basin. He describes a gigantic ship built for the emperor Caligula to carry an Egyptian obelisk to Rome that was sunk on site and used as a kind of caisson. "It is certain that nothing more amazing than this ship has ever been seen on the sea… Its length took up a large part of the left side of the port facilities of Ostia, for under the emperor Claudius it was sunk there. Three great masses as high as towers were built on it for this purpose with the dusty earth of Puteoli (*Puteolano pulvere*), and brought here." (*Nat.* 16.202)

The impossible suggestion that the concrete towers were built on the ship before it arrived at Portus may result from textual corruption, or from confusion with the procedures involved in using a floating ship as a caisson. Suetonius, in his *Life of Claudius* (20.3), states that the ship was scuttled, and then piers were built on top.

Vitruvius provides us with our only detailed description of how Roman builders constructed concrete structures in the sea with pozzolanic mortar [2, 3, 14, 18, 19]. "If, however, we have no natural harbour situation suitable for protecting ships from storms, we must proceed as follows. If there is an anchorage on one side and no river mouth interferes, then a mole composed of concrete structures (*structurae*) or rubble mounds (*aggeres*) is to be built on the other side and the harbour enclosure constructed in this manner. Those concrete structures that are to be in the water must be made in the following fashion. Volcanic ash (*pulvis*) is to be brought from that region which runs from Cumae to the promontory of Minerva (the Bay of Naples), and this is to be mixed so that in the trough the proportions are two parts ash to one of lime. Next, in the designated spot, formwork (*arcae*) enclosed by stout posts and tie beams (*stipitibus robusteis et catenis inclusae*) must be let down into the water and fixed firmly in position. Then the area within it at the bottom, below the water, must be levelled and cleared out, (working) from a platform of small crossbeams (*ex transtris*?). There, the aggregate, and the mortar from the trough mixed as described above, must be heaped up (*caementis ex mortario materia mixta…ibi congerendum*), until the space left for the concrete within the form has been filled…" (*De arch.* 5.12)

In addition to *pozzolana* from Puteoli, there are volcanic sand deposits in the region of Rome that are effective pozzolanic mortar aggregates. The Romans made good use of them for terrestrial structures [1, 9, 10, 11, 12]. Vitruvius, however, is careful to distinguish the origin and character of these red, black, and light grey sands, which he called *harenae fossiciae* ("quarry sands") from the fine-grained grey *pulvis* that came from Puteoli (*De arch.* 2.4, 2.6.4-6). He recommends the *harenae fossiciae* for structures on land: "When the lime (*calx*) has been slaked, then the mortar is to be mixed in such a manner that—if pit sand (*harena fossicia*) is used—three parts sand and one part lime are poured in." (*De arch.* 2.5.1) For marine structures, the Vitruvian ratio was two measures of *pulvis Puteolanus* to one of lime (*De arch.* 5.12.2). For structures on land, Pliny (*HN* 36.175) specifies a pozzolanic mortar with a ratio of four measures of *harena*

fossicia to one of lime. Vitruvius is careful to note that, while there are quarries for *harena fossicia* in the volcanic landscape of Etruria, north of Rome, deposits of *pulvis* do not occur there. "Since there are also numerous hot springs in Etruria, the question remains why one does not find there also the volcanic powder (*pulvis*) through which in the same manner concrete sets underwater (*sub aqua structura*)." (*De arch*. 2.6.4-5)

Vitruvius sums up his discussion of *harenae fossiciae* and *pulvis Puteolanus* with the comment that "Some materials have advantages for structures on land (*terrenis aedificiis*), others for moles built in the sea (*maritimis molibus*)." (*De arch.* 2.6.6) The distinctive application of the two volcanic products is reflected in the cores taken by the ROMACONS project, even at sites such as Portus, where imported *pozzolana* was used for the structures below water and local *harena fossicia* for structures above.

The importance of lime in ancient concrete work cannot be underestimated. The lime paste, however, drives the chemical reaction that produces the hydraulic properties in the mortar [12], and the Romans recognized an array of limes with varying properties. Lime paste, in fact, was and remains the most expensive ingredient in a concrete mix [5, 13], and Pliny (*HN* 36.176) states that skimping on lime in a mortar mix was the main reason for the collapse of buildings in Rome. This type of fraud remains a serious problem in developing countries. Vitruvius emphasizes the need for selectivity (*De arch.* 2.5.1; cf. Pliny *HN* 36.174): "…one must be careful that, in regard to lime (*calx*), it is burned from white rock, whether (hard) stone or (softer) *silex*. The lime from close-grained, harder stone will be the most useful in structural forms, while that made from porous stone will be best in plaster." Vitruvius explicitly states that the lime should be slaked before it is added to the mortar mix (*De arch.* 2.5.1). Pliny (*HN* 36.176) refers to "old building laws" requiring the ageing of *intrita*—which in the context should be slaked lime putty—for three years prior to use.

3 How did expertise with this technology spread?

Clearly, Roman engineers had a very nuanced understanding and strong opinions based on empirical experience regarding the geologic materials that went into both terrestrial and submarine mortars. The ROMACONS Project has revealed that the practice of obtaining *pulvis Puteolanus* from the Campi Flegrei area was applied throughout the Mediterranean, despite the presence of suitable pozzolans outside Italy, at Santorini or Melos, for example. Indeed, French engineers used "Santorini earth" for marine structures associated with the Corinth and Suez canals [6]. Roman engineers also had a sophisticated knowledge of both stationary and floating forms for placing pozzolanic concrete in the marine environment, and of stationary cofferdams that could be pumped dry to allow the placement of non-hydraulic concretes below water level [2, 3, 19].

How did this information about the proper materials and techniques for marine construction travel around the entire Mediterranean world, from Alexandria and Caesarea Maritima on the east to Portugal on the west? For example, the core of the two enormous breakwaters sheltering the outer basin at Caesarea was composed of approximately 35,000 cubic metres of hydraulic concrete. The mortar was made with *pulvis Puteolanus* shipped 2,000 km from the Puteoli region, approximately 24,000 cubic metres weighing 52,000 tons [8]. It seems likely that Herod requested technical assistance from Rome for his enormous project, probably from his friend Agrippa, who had built the harbour of Portus Iulius near Puteoli. Agrippa would have sent harbour engineers out from Italy, military engineers, like the *caementarius* Valens mentioned above who was stationed with the fleet at Misenum. These engineers, reflecting the same practical expertise as their contemporary Vitruvius — himself a retired military engineer — evidently recommended the use of *pulvis Puteolanus*, augmented with local sand, coarse aggregate, and lime [20]. Elaborate single-use barge forms identical to those documented at Caesarea were used in the construction of concrete structures in the harbour of Alexandria in the first century AD [2, 3, 7]. While the movement of military engineers around the Mediterranean is the most likely explanation for the spread of this type of harbour construction technology, it is also possible that sub-literary technical manuals incorporating the technical information in written and graphic form moved with these engineers, or even independently. The traces of manuals of this type (*commentarii*) have been discerned in the archaeological evidence for military and agricultural equipment, and wooden pumps, and there is no reason they could not have existed for the elements of concrete construction in the sea as well [17]. The existence of such manuals would help explain the use of *pulvis Puteolanus* in the maritime concrete of small, out of the way Roman harbours such as that at Chersonisos on Crete, where imperial involvement is unlikely [4, 21].

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I.30

Thermal Activation of Kaolinite Used as Hydraulic Additive of Old Lime Mixtures: a Literature Study

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Abstract This paper reports the results obtained in the study of thermal activation of kaolinite used as a hydraulic agent in old aerial lime mixtures. This study has been carried out in order to obtain a better knowledge of the old lime mixtures containing kaolinite and to set up a 'modern' hydraulic additive with improved qualities. In particular, this paper deals with changes that could have happened in the kaolinite structure when this mineral was burnt inside the old lime furnaces. With this aim in mind, a large number of bibliographic references have been studied. Results obtained show that the kaolin could have burnt in the same furnaces used for the lime production but that these two materials may have burnt separately and probably at different temperatures.

1 Introduction

The use of burnt kaolin as a hydraulic additive in aerial lime mixtures has been described in a previous paper presented at the first "Historic Mortar Conference" [1] in which a large number of X-ray Diffraction (XRD) analyses had been considered to underline the use of these mixtures in Medieval and Modern constructions in the Liguria region (northern Italy, Mediterranean area).

To fully understand the physical and chemical characteristics of these mixtures and the reasons for their high resistance to mechanical, biological and chemical stresses [1], a study on the thermal activation of kaolinite has been initiated at the University of Genoa's Laboratory of Materials Engineering [2].

The aim of this research was the comprehension of the modality of use of this particular mineral in the above mentioned mixtures. In order to reach this aim, the changes to the structure of kaolinite when it is burnt under the same conditions that must have taken placed inside the old lime furnaces, was studied.

Part of this research has been based on the study of a large number of bibliographic references which have proved useful in understanding the changes that occur in the structure of kaolinite when it is subjected to increased temperatures. A further study has focused on a number of experiments that were carried out to determine the optimal partial pressure of water that must be created inside the furnaces to obtain a highly reactive material. One of the main reactions that occur inside the furnaces where the kaolin is fired, is a dehydroxylation process; this therefore means that the partial pressure of water in the atmosphere of the furnaces can affect this reaction.

A fellow research group from the University of Genoa [3] has demonstrated the influence of the partial pressure of water on the production of quicklime and that past lime producers did indeed have knowledge of this effect. Through the study of past documents it has been revealed that during the firing, basins of water were placed outside the main door of furnaces, presumably to increase the inner partial pressure of water.

This paper deals with the results of the first part of the research which aims to highlight characteristics of the old productive process of kaolin that was used in lime mixtures.

2 Kaolinite and metakaolinite reactivity

As it is well known, kaolinite is a silicate mineral structurally belonging to the phyllosilicates group [4]. Its' formula can be written as: $Al_2Si_2O_5(OH)_4$ and in this way it is easy to see that the *Si* - *Al* ratio is 1:1.

Even from a structural point of view, kaolinite is made up of an aluminium hydroxide layer (abbreviated as: "O") where the aluminium has an octahedral coordination with the groups O^- and OH^-, and by a silicon dioxide layer (abbreviated as: "T") where the silicon has a tetrahedral coordination with the O^- groups. These two layers are linked by the O^- groups in the upper vertex of the silica tetrahedrons, which are under the aluminium layer. Over and under this structure, made up of two layers, there are empty spaces and new double structures of T-O which are repeated.

In a hypothetical perfect crystal, this configuration is electronically neutral but with some overcharges due to the polarisation of the ionic bonds of the aluminium and silicon in the upper face of the octahedral layer, the lower face of the tetrahedral layer and along the borders of the sheets.

The presence of defects such as deficiencies in the lattice due to the absence of anionic groups or ionic substitutions in the octahedral and tetrahedral layers etc (sometimes magnesium and iron ions, amongst others, can replace the aluminium and silicon) can increase the reactivity of the crystal. In fact, each of the above mentioned defects can be recognised as an 'active site' useful in creating new

bonds and, consequently, it becomes clear that an increase in the number of active sites results in an increase in the crystal's reactivity.

Thus, the firing of kaolinite (which leads to the production of so called 'meta-kaolinite') increases the reactivity of the mineral, because it increases the number of defects, in particular, the number of ionic groups with an excess charge [5]; it is for this reason this treatment is also called 'activation'.

3 Effects of thermal treatment on the kaolinite structure

Considering the temperature range 373 K to 1223 K (because it is difficult to assume that the average temperature inside an old furnace could have been above 1223 K [3]) and summarising the knowledge reported in scientific literature, it is possible to state that the main structural changes involved in the firing of kaolinite are as follows:

- between 273 K and 673 K the so called 'pre-dehydroxylation' process takes place which, at most, involves the loss of only one hydroxyl anion for each base module of the crystal structure. It is very simple to check this weight loss when the thermal treatment takes place under vacuum, but when the activation process takes place under atmospheric pressure, this change is almost absent [6, 7].
- Between 673 and 923 K the 'true' dehydroxylation process, which involves some of the main changes of the entire thermal treatment, takes place. If this change is studied using Differential Thermal Analysis, it is possible to verify that the maximum peak of the reaction is at about 823 K. This means that at this temperature the maximum removal of hydroxyl groups linked to the aluminium layer takes place. Thus, the aluminium ions change their configuration, keeping bonded only some hydroxyl groups of the mineral structure (including the innermost hydroxyl groups). At the same time a chipping process of the silica layer takes place, which involves a long range order destruction of the kaolinite structure (for this reason, kaolinite becomes amorphous to the XRD analysis). According to Massiot and his research group [8], under controlled conditions the dehydroxylation process appears as a reaction placed between a pure diffusive mechanism and a boundary-controlled reaction. The flexure point found in the sigmoid curve of dehydroxylation (proportionally low: α = 0.2) and the results of XRD analysis of the same samples, suggest that the long range order destruction of the structure along the z axis is quicker than the chipping of the sheets. Still according to Massiot, between 723 K and 1213 K the silica layer becomes amorphous with a short range order, but at the same time it creates new bonds to form a silicon network with three-dimensional characteristics (abbreviated as: Q_4 [5, 8]).

- Diffractometric analysis carried out by a few authors in the temperature range of 923 K to 1123 K, has underlined some new arrangements in the amorphous structure of meta-kaolinite. At higher temperatures these new arrangements become the new crystalline phases: mullite and cristobalite [6].
- At the same time, through the use of NMR analysis carried out on ^{27}Al, it is possible to notice that between 823 K and 1173 K the aluminium acquires a new configuration with different coordination values [8, 9]. In fact, this change seems to conduce the aluminium to acquire – at the same time - the coordination numbers IV, V and VI with the surrounding anion groups (those which still remain) with each of these forms appearing with different percentages. Massiot estimated these percentages as: 60% of Al_{IV}, 30% of Al_V and 10% of Al_{VI} [8]. Lambert [10] suggested a relation of 30-50-10 and Rocha [11] a relation of 40-40-20 (these differences can be due to the different experimental conditions).
- In the FTIR analysis carried out on samples treated between 1123 K and 1223 K the Al-OH bonds disappear [6]; this can be a confirmation of the above mentioned reorganisation of the aluminium ions. At 1193 K the formation process of a spinel-like new phase begins, made of SiO_2 and $\gamma - Al_2O_3$ compounds, which is the precursor of the above mentioned crystalline phases; for some authors, the first nucleation centres of this phase appear at about 1123 K [9]. In fact, between 1123 and 1473 K the spinel-like phase remains until its final disappearance [4, 9]. At the same time, at about 1253 K and 1473 K respectively, the mullite phase and the cristobalite phase start to take shape, marking the complete segregation of silicon from aluminium. This segregation starts in earnest at 1213 K [9] but it is clear that the first segregation step occurs from about 723 K when the first three-dimensional bonds of silicon are formed.

Fig. 1 shows that after this treatment the metakaolinite structure is still phyllosilicate-like but the sheets display a small extension and many gaps that are reminiscent of the original structure [12]. In the upper layer of aluminium there are only a few hydroxyl groups (which should be comparable to 10% of the original anionic groups) as suggested by other research groups whose descriptions can be variable The sheet pictured by Traorè (Fig.1) is not altered by the state of tension that derives from the changes in the aluminium layer (which is still linked to the silicon layer beneath). According to the suggestions of some authors who assert that the reactivity of meta-kaolinite depends on the ‘active sites’ represented by ionic groups with overcharge [5, 6], it is possible to see that in this picture the upper layer of aluminium is characterised by a surplus of positive charges and the lower layer of silicon by a surplus of negative charges due to the several free corners of silica tetrahedrons.

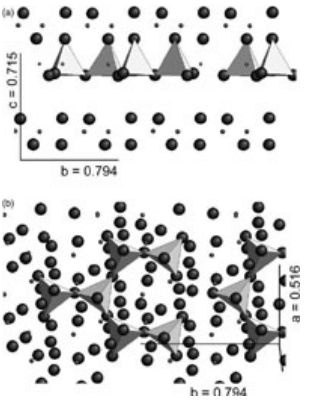

Fig. 1 Schematic representation of metakaolinite as proposed by Traoré [12].

Thus, in respect to the original structure of kaolinite, it is clear that the number of sites where new chemical bonds can be formed (e.g. between silica and calcium ions; Fig. 2) are increased which in turn results in an increase in reactivity.

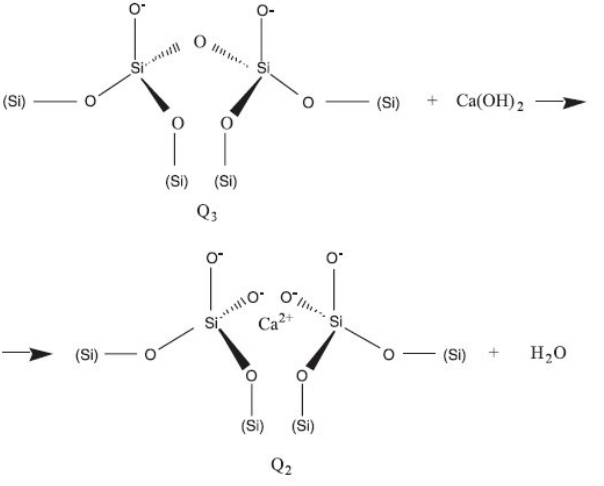

Fig. 2 Schematic representation of the interaction between silica and calcium hydroxide in aqueous solution as proposed by Zendri [5].

4 Observation of the structural change of kaolinite and on the reactivity of the burnt material

In summarising the above mentioned observations, it is possible to highlight that in the long disruption process of the kaolinite structure, the best temperature

range for which it is possible to obtain a highly reactive material is between 773 K and 1193 K and that, within this range the dominant changes occur at about 823 K. At this temperature the majority of transformations involving the aluminium layer take place, including the loss of the main part of the hydroxyl groups and the breaking apart of the silica layer. The temperature of 823 K is not a fixed point because there can be some little shifts due, for example, to the imperfections in the crystal lattice, to the impurities of the raw mineral or to the fineness of the kaolinite particles [6].

Formation of the three dimensional bond of silicon, which can reduce meta-kaolinite reactivity, starts at 773 K when the long range order destruction of the mineral begins.

At around 900 K, the meta-kaolinite sheets are shattered and altered by the state of tension that derives from the changes that take place in the aluminium layer which is still linked to the silica layer; this type of structure must therefore have a large number of active sites. The nucleation process of these crystalline phases begins at 923 K, however they only become clearly visible at higher temperatures which can result in a decrease in the disordered state. At 903 K the anionic groups bonded to the aluminium appear to have left their sites with the rest of the anionic groups - the inner groups - disappearing at about 1173 K.

On the whole, it is clear that the number of hydroxyl groups which leave the kaolin structure during thermal treatment can't be considered to be individual representatives of the amorphous grade of the material (and, consequently its reactivity), because in the same temperature range other changes occur which can reduce the reactivity. It is also clear that the most reactive product can be obtained in the above mentioned temperature range of 773 K and 1193 K, probably nearer to the upper limit. In fact, some authors found the maximum disorder of the meta-kaolinite structure to occur between the 973 K and the 993 K range; such a narrow temperature range can be due to the characteristics of the raw mineral, or to the experimental conditions, but it is stressed within the literature, that between 923 and 1123 K it is still possible to obtain a product with a good reactivity.

5 Conclusions

If we compare the above mentioned temperature range with the temperatures that could have been reached inside the old lime furnaces (probably below 1173 K [3]) and with the temperature necessary to burn limestone, it is possible to understand that the thermal activation of kaolin could be carried out inside these furnaces.

If this hypothesis is correct it is important to consider the problem of firing and in particular if these two materials, limestone and kaolin, could be fired together. XRD analysis of old mortars and plasters containing kaolin show weak traces of unfired kaolinite [1], indicating that not all the hydraulic additive used in those

mixtures had reached the above mentioned temperatures and, in particular, that some parts of that mineral did not reach 673 K (the lower limit of the temperature range necessary to start the dehydroxylation process). This could have happened for many reasons for example: because blocks of kaolin were away from the fire (may be the limestone, which needs a higher temperature, was closer to the fire than the kaolin) or because blocks of kaolin could have been fired at different times and at a temperature lower than that of the limestone. On the other hand, it is also possible that blocks of kaolin could have been fired in different furnaces, but at present there is no evidence to support this hypothesis.

It is unlikely that the limestone and kaolin were not mixed together during the firing process because the temperatures reached in the furnaces, testified by the uncooked kaolin, were too low to obtain a good quicklime. Furthermore, firing mixtures of calcium carbonate and kaolinite lead to the formation of gehlenite [12, 13], through a direct reaction between metakaolinite and calcium oxide and consequently, a complete absence of this stable compound in all the XRD analysis carried out on the samples gathered in Liguria, seems to confirm a separate thermal treatment of limestone and kaolin. This also seems to be confirmed by the absence of references to kaolin supplies in past documents which refer to the production and supply of quicklime in the vicinity of Genoa; this lack of information will be discussed in depth in a future paper.

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I.31

Radiocarbon Dating of Lumps of not Completely Mixed Lime Contained in Old Constructions: the Sampling Problem

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Abstract This paper deals with the technical and methodological sampling problems of lumps of not completely mixed lime putty in mixtures, in order to obtain a suitable material for the radiocarbon dating of mortars and plasters. Sampling of this type of lumps, in fact, allows us to be able to use a suitable material for the radiocarbon dating of lime mixtures (e.g. mortars, plasters, lime bed of mosaics, frescos paintings, etc.) because in this way it is possible to avoid the contamination problems deriving from sources of carbon such as the "^{14}C-dead" of limestone sand or of not completely burned limestone. From an archaeological point of view, this sampling procedure gives the possibility to obtain an accurate radiocarbon dating for each piece of masonry considered without any considerable damage.

1 Introduction

Mortars have been exploited as material for radiocarbon dating for a long time [1-7]. The basic principle of the method is quite simple: lime is produced from limestone (essentially $CaCO_3$, calcium carbonate) of geological origin ("dead" in terms of radiocarbon concentration) which, in the past, was burnt at about 1173 K to produce CaO (quicklime). Lime was used, for example, for mortars and render, by slaking quicklime with water and mixing this slaked lime with sand (aggregates). When in place, these mixtures (essentially formed by $Ca(OH)_2$ + aggregates) harden by absorbing CO_2 from the atmosphere and becoming again calcium carbonate ($Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$). As a result of this process, the calcium carbonate contained in the mortar reflects the atmospheric ^{14}C concentration at the time of hardening and thus, this material can be used for radiocarbon dating.

Despite the fact that this method may be very simple in its principles, several studies have shown its drawbacks and limitations [8] which are mainly due to the contamination of the samples from carbonaceous substances such as pieces of incompletely burnt limestone containing "^{14}C-dead" and aggregates of fossil origin (e.g. limestone sand).

Furthermore, although more recent studies have shown that accurate sample processing treatments allow the significant reduction of these error sources [6], a new, different sampling procedure based on the selection of lumps of incompletely mixed lime, often visible in the mixtures, is a very interesting alternative for the absolute dating of lime that does not deal with the problems of contamination. This method was demonstrated by the author in a paper published in the *Radiocarbon* journal [9]. The correct selection of lime lumps carried out with the aid of an optical stereo microscope, allows pure lime samples reflecting the atmospheric ^{14}C concentration of the time of the mixture hardening to be obtained, without doubts of contamination problems deriving from any sources of old ^{14}C".

2 The case history and the main characteristics of the lime lump sampling and dating method

Since 2007 we have applied this sampling and dating method to 11 samples of lime lumps coming from four different buildings: the Medieval church of S. Nicolò of Capodimonte (Camogli, Genoa – Italy; [9]); the Medieval Crypt of the Reggio Emilia Cathedral (Reggio Emilia - Italy); the Medieval Castle of Zuccarello (Zuccarello, Savona - Italy) and the Medieval Castle of Donnetta (Torriglia, Genoa - Italy). The above mentioned samples were the only samples picked up in these buildings and for each sample we obtained results that perfectly met the dating obtained by other archaeological methods.

In the same manner some years ago other researchers carried out radiocarbon dating of lime lumps on the alto-Medieval castle of Aghinolfi (Massa Carrara – Italy; [10]) and on the basilica of S. Lorenzo Maggiore in Milan (Milan – Italy; [11]) which have had a very important role in the comprehension of the history of these two buildings.

This case history provides evidence of the importance of this sampling and dating method in the field of archaeology. In fact, this method has some very suitable characteristics for the majority of archaeological research carried on in both the field of excavations and in the field of building archaeology. Radiocarbon dating can be done with a very small quantity of lime (20 milligrams) if Accelerator Mass Spectrometry is used: this quantity is perfectly comparable with the dimensions of a single lime lump obtainable from the majority of aerial lime mixtures we have studied. This means that each time the work necessary to obtain a suitable sample of lime for a radiocarbon dating involves the destruction of a

very small part of the object (this does not always happen with other dating methods).

Besides, the cost of a single dating is not so expensive as the other dating methods (e.g. thermoluminescence), and these items are more and more important if we compare this cost with the typical budget of archaeological research.

Furthermore, thanks to the fact that reused pieces of masonry containing mortars or plasters can be easily recognised, it is possible to avoid the problem of the dating of reused materials as, instead, happens with some other materials like brick, when the thermoluminescence method is applied to some samples of reused material.

However, not all the characteristics of this sampling and dating method match all the needs of archaeologists and, as happens with other dating methods, this method has some application problems. In fact, some issues are still to be addressed such as the quite large calendar time ranges resulting from the calibration of the conventional radiocarbon ages, that often make the results not so useful to resolve archaeological problems. This problem is strictly related to the shape of the calibration curve in the studied temporal range which is not discussed here. Nevertheless, in this circumstance we can underline that the application of advanced statistical tools, such as Bayesian based methods, to constraint radiocarbon determination with stratigraphic or historical information can be expected to be a fundamental help to reduce the calendar time ranges [9]. The main objective of this paper is to underline the problems connected to the sampling method of the lime lumps for the radiocarbon dating.

3 The sampling method of lumps of lime putty for radiocarbon dating

The above mentioned dating, developed in recent years by different research groups, shows that the dating of lumps of incompletely mixed lime is a very promising method to obtain absolute and direct dating mortars, plasters, renders, mosaic substrate, frescos paintings, etc.

However, at the same time, these cases show that the method relies on the correct sampling of lime lumps (it is for this reason, that in the previous paragraphs this method has been called: “sampling and dating method”). Thus, in order to clarify, as best as possible, the work necessary to achieve the correct results, it is necessary to concentrate our attention to the sampling method and in doing this, it is necessary to consider the problems in two sectors: the problems related to the on site sampling and the problems related to the identification of lumps of pure lime which are not mixed.

3.1 Problems related to the on site sampling of lime lumps

The first thing to consider is the condition of the structure (building out of the ground, underground walls, frescos layers, mosaic substrate, etc.).

If we work in the field of building archaeology, in which we can't often reach the inner part of the walls but only their surfaces, the thickness of mortar joints must be large enough to allow the selection of suitable samples. Basically, this problem depends on the characteristics of masonry that sometimes does not allow a correct lump sampling (this is the case of most parts of the Roman and Medieval constructions made with squared off blocks, laid upon very thin mortar joints).

This problem is less relevant when a wall section is accessible and this happens very often in the archaeological excavations where it is common to find underground masonry.

But if we can reach the inner part of the masonry, another two problems must be considered: the problem of the possible dissolution and re-carbonation cycle of calcium carbonate of lumps due to the water circulation of soil and the problem of the depth of sampling into the wall.

For the first problem, it is necessary to underline that, at present, we have not yet met cases of dating alteration due to this cycle but, sometimes we gave up the sampling work because we had the suspicion that samples could have been affected. This is the case of some Roman mosaics found during the excavation of the crypt of the Reggio Emilia cathedral, where we gave up the radiocarbon dating of lime lumps because we suspected that the increase and decrease of the ground water, that surely involved those mosaics, could affect the results of our samples.

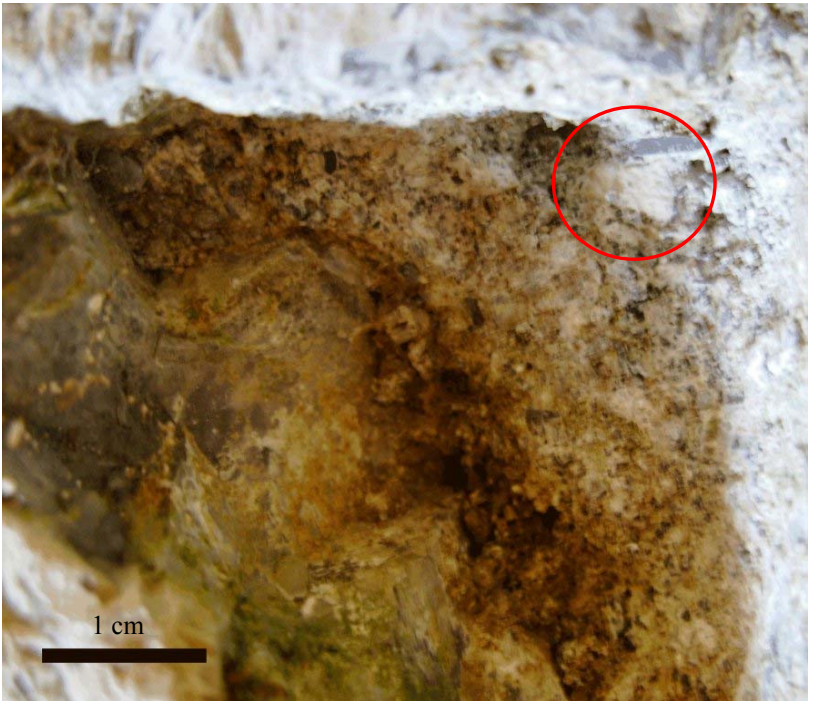

Fig. 1 Mortar joint with lump of lime (upper right corner, inside the red circle)

For the second problem (the depth of sampling into the wall) we must consider that the depth must be sufficient to avoid sampling of mixtures not belonging to the original construction (for example, some plasters applied on the wall after its construction). Furthermore, it must not be too deep to avoid the problem of incompletely carbonated lime lumps or the problem of a delayed carbonation process (with respect to the construction time of the wall). In fact, in some cases, non-carbonated or partially carbonated samples have been found inside the walls.

The carbonation process begins from the external surfaces of the walls and carries on towards the inner parts at a more and more reduced speed. As a consequence of this mechanism, there is the possibility to have samples subjected to a "delayed" carbonation, if we gather samples in the most inner parts of the masonry and this problem should be taken into great consideration during the sampling work.

The mass of a single lump (that must be at least 20 milligrams), has to be evaluated directly *in situ* in order to have enough material for the radiocarbon dating. If a single lump is not considered to be large enough, it is possible to collect more than one lump. We only need to be very careful in collecting samples from the same part of the masonry that in archaeological terms means from the same stratigraphic unit.

3.2 Problems related to the identification of pure lime lumps

After the on-site sampling and before the radiocarbon dating treatment, it is necessary to check the samples picked up on-site under a stereo optical microscope. This work is necessary in order to verify if the sample is really a pure carbonated slaked lime lump and in order to remove mechanically all the pieces of limestone aggregate pieces that can be attached on the surface of lump.

In order to verify if the sample is a lump really suitable for the radiocarbon dating and not an incompletely ^{14}C-dead burnt lime (that is a piece of unburned stone, unsuitable for the radiocarbon dating) it is possible to proceed in two ways: by an observation of the lump surface with a magnifying glass and by a very simple test of its hardness.

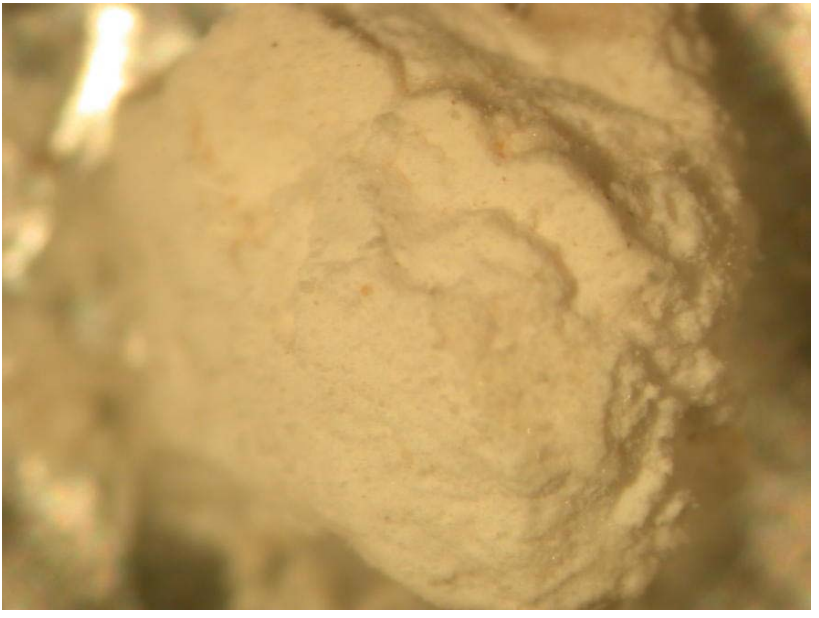

Fig. 2 Image of a lump lime taken at the optical microscope

In fact, often during the on-site work it is possible to find lumps of incompletely ^{14}C-dead burned lime (pieces of unburned stone) that look like small white and rounded lumps, similar to the lime lump of carbonated slaked lime. But under a magnifying glass, like the glasses of a stereo microscope, even at low magnification (e.g. 10x) it is possible to verify that the surface of lumps of carbonated slaked lime look floury (Fig. 2), instead the surface of uncooked lumps appear to be thick in the manner of a stone.

Besides, if we try to scratch an unburned piece of stone with, for example, a needle point, it is simple to recognize the typical hardness of stones. Instead, if we

try to scratch a lump of carbonated slaked lime, it is possible to observe a softness that sometimes can make it very hard to treat the samples.

Pieces of limestone sand can be removed from the lump surface by using tools, for example, a scalpel. In order to remove as many pieces of sand as possible, this work must be carried out by the use of the above mentioned microscope and must be carried out with great care because it is very easy to damage or destroy the sample because, as we have already said, it is very delicate.

Samples obtained in this way are perfectly suitable for a radiocarbon dating.

4 Conclusion

From the case history we faced it is possible to assert that the radiocarbon dating of lime lumps of carbonated slaked lime is one of the most interesting dating methods for constructions available at present.

In this method the sampling work is one of the most important parts of all the processes that involve archaeological knowledge, chemical and physical knowledge and the knowledge of building materials. In fact, in order to avoid the most elementary dating problems like the dating of hidden repairs, it is necessary to begin the sampling work with a very careful stratigraphic analysis of the object that must be dated (this point is essential to obtain archaeologically correct results) and, after this work, it is necessary to work carefully on the lime lumps both, on site and in the laboratory.

However, the results obtained in recent years are still not enough to allow us to understand completely the potentialities of this method. In fact, some things are still unknown. For example, we must underline that up until now, we have performed dating of lime lumps on samples coming from mixtures containing aerial lime or, at least, feeble hydraulic lime. We have come to know these binders thanks to the theoretical and practical studies that have been performed recently in many parts of the world. But we don't know exactly what happens in mixtures made with moderately or highly natural hydraulic limes; a type of binder often used in the past. We know, for example, that in mixtures with this type of binder there is always a surplus of calcium hydroxide so that the carbonation reaction is still important, but we don't know what happens to the lumps. For instance, we don't know if it is possible to find as many lumps in mixtures made with natural hydraulic limes as in the mixtures with aerial limes and if the presence of silicon dioxide and aluminium oxide in the lime oblige us to discover bigger lumps than the 20 milligram lumps that we sample in the aerial lime mixtures. Or again, if the presence of silicon dioxide and aluminium oxide in the lime can effect the radiocarbon dating.

Thus, in the next few years we must improve our knowledge about these types of binders and, above all, our knowledge regarding their lumps. In doing this, we must consider that, at present, there are only a few articles in the scientific

literature that deal with problems of lime lumps and that these papers do not deal with the problem of their formation processes [12]. Thus, one of the first things that we must understand is exactly what the lime lumps are and how they take form inside the mixtures. Otherwise, we will run the risk of making serious archaeological errors.

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I.32

The Earliest Use of Lime and Gypsum Mortars in Cyprus

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Abstract In Cyprus, lime and gypsum mortars have been used in architecture since the prehistoric period. Although the production of lime and gypsum seems to have been known since the Neolithic period, coinciding with the first permanent habitation on the island, it was widely disseminated in later periods. This paper is based on the first all-encompassing research derived from microscopic and laboratory analyses (chemical, mineral) of more than 100 samples collected from various pre-historic sites, followed by observations on their microstructure with the help of a scanning electron microscope (SEM). Through this research the chronological development and successive use of ancient mortars on the island was identified. The position of Cyprus with respect to the rest of the ancient world in terms of the technology of construction materials was investigated, and matters were examined with regard to the origin, manufacture and selective use of these materials.

1 Introduction

Lime and gypsum mortars were used extensively in various structures in Cyprus, employed mainly as plaster coatings. The results of an all-encompassing research aiming to investigate the chronological evolution of the two main types of mortars during the earliest periods of antiquity are presented in this paper. This research aims to investigate the different methods of their preparation and to identify the pyrotechnology known during the earliest periods of antiquity. The absence until today of a comprehensive study on the old mortars of the island adds to the value of this research. It is anticipated that the results of this research will constitute the first database for mortar investigation throughout the different periods of antiquity of the island and will form the basis for the development of compatible mortars for conservation purposes. It is worth mentioning that lime and gypsum have been in use without any significant changes in the vernacular architecture of the last century on the island before the introduction of cement.

Lime and gypsum, which have been the two main mortar binders since antiquity, are derived from the burning of limestone and gypsum rocks. The discovery of lime and gypsum plasters [1] introduced a revolutionary pyrochemical industry, in which the natural rocks underwent a chemical change when heated and when crushed to powder and mixed with water, created a paste that could be easily worked. The physical properties and chemical composition of lime and gypsum mortars are identical to those of the corresponding natural rocks, although their microstructure is different. The technology in the production of pozzolanic or crushed brick-lime mortars is more complex. These can be manufactured by mixing lime with pulverized clay materials called pozzolanes (natural or artificial). When split into thin parts, the pozzolanes react with lime at normal temperatures in the presence of water or moisture to form stable calcium silicate/aluminate hydrates. The hydraulic character of mortars is due to the reactions between the pozzolanic material and the matrix.

It is noteworthy that during prehistoric periods, in most areas, either gypsum or lime was preferred. In the Levant (Syro-Palestine coast), Anatolia and Greece [2, 3], lime plaster was almost exclusively the material of choice. In these areas [4] the use of gypsum plasters in the earliest periods of antiquity is rather limited. However, gypsum is the material of choice in the area of the Tigris and Euphrates and further to the east [1, 5]. Recent studies have shown that in ancient Egypt, lime was also used: a fact that contradicts the previous information for the exclusive use of gypsum in this region [6]. Geographically, Cyprus constitutes an interesting case, as it is located in the lime region between the Levant, Anatolia and Greece [1], but it has very notable deposits of gypsum.

2 Experimental

This research was based on *in situ* observation of 120 samples of lime and gypsum mortars collected from various archaeological sites from prehistoric Cyprus, followed by laboratory analyses. The number of layers was counted and the thickness of each was measured, and the bond at each interface was investigated in detail. Special attention was given to the presence of admixtures and additives and their distribution throughout the mortars. Some of them were rather porous crushable materials, but most were dense and coherent. The samples also differed in terms of grain size, colour, texture and surface roughness.

2.1 Methodology

All of the samples selected were thoroughly observed in the laboratory under the stereoscope, followed by the preparation of thin sections of each specimen. These were examined under a petrographic microscope for the identification of the binder and the aggregates. These preliminary microscope observations led to a

selection of samples (70) for further scientific analysis: chemical and mineral analyses using X-Ray Diffraction (XRD). From the results of these analyses, the 20 most characteristic and representative examples were subjected to a more detailed investigation. Differential thermal analysis (DTA) and thermogravimetry (TG) were employed to determine the nature of the mortar constituents and to investigate the degree of their hydraulicity. For detailed observation and examination of the microstructure of the samples in the micron particle size, a SEM equipped with a microanalyser (EDS) was employed to determine the exact composition of mortars in different parts of the sample and to detect the binders, aggregates, and reaction products.

2.2 Experimental data and results

2.2.1 In situ observations

The coating plaster of the walls very often was set in thin, successive layers in order to avoid collapsing under their own weight. The placement of successive layers to produce a thicker coating was also observed in the wider area of the Near East [7]. The final thin coating of lime, often applied above a base mud layer, contributed to better adhesion of the coating to the structure of the wall. In the lower part of the vertical wall where it meets the horizontal floor, a series of small rounded stones was sometimes laid to ease the curvature of the wall coating [8], which continued as a floor coating. The floor plaster often constituted two or three successive layers. A fine-grained coating was often laid on one or two coarser substrates and sometimes placed on a base layer of flat stones [8]. This technique also has been widely observed in the Middle East since the Neolithic period [9]. These successive layers of different floors during the earliest periods were associated not only with construction technology but also with the duration of the structures. The thickness of the floors also was affected by social factors and particularly by the neolithic custom of burial beneath the plaster floors - a practice that resulted in extensive use of plaster. This custom was widespread not only in Cyprus [8] but also in the Near East [7].

2.2.2 Laboratory data and results

The investigation showed that during the Neolithic period lime and gypsum, either separately or in combination, were used as plaster coatings for walls and floors. The samples selected were derived from the two most important settlements of this period: Kalavasos-Tenta and Khirokitia. Floors and walls were usually coated with a thin, whitish plaster layer laid on a base of friable mud plaster. Samples were selected from the hardest and most dense final plaster layers. The plaster samples taken from Kalavasos-Tenta can be divided into separate categories according to their mineral and chemical composition [8]:

gypsum plasters, lime plasters, and gypsum-lime or lime-gypsum plasters. Samples having both calcite and gypsum as their main components belong to the last two categories. The samples having a high percentage (more than 10% and less than 40%) of sulphur trioxide (SO_3) are considered gypsum-lime, whereas the samples with lower percentage of SO_3 (less than 10%) are considered lime-gypsum. On the other hand, the samples from Khirokitia are mainly lime plasters.

The examination with a petrographic microscope and SEM revealed that gypsum is the binding material in the gypsum and gypsum-lime mortars. The structure of these neolithic plasters is very different from the irregular microcrystalline morphology of the natural gypsum rock but also differs from the needle-like structure of the contemporary gypsum plasters, probably due to the non-controlled heating procedure and the age of the samples. In the gypsum-lime mortars, gypsum crystals often surround the grains of calcite, giving the impression that the calcite is acting as an aggregate (Fig. 1a).

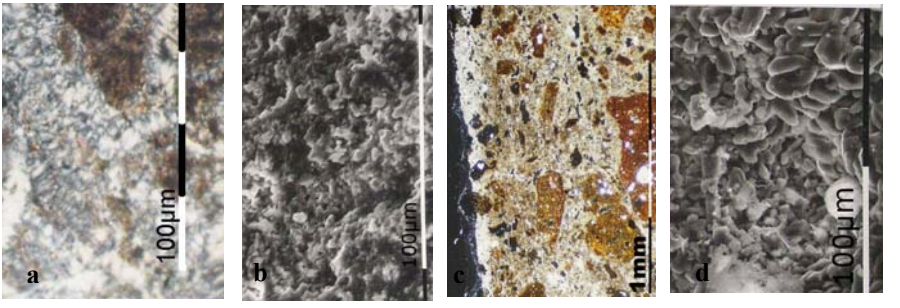

Fig. 1 Thin sections and SEM photos showing the structure of a gypsum-lime mortar (a-thin section), a lime mortar (b-SEM photo), a brick-lime mortar (c-thin section) and a gypsum mortar (d-SEM photo)

The observation of the samples of Kalavasos-Tenta and Khirokitia, which are mainly of a calcitic composition, revealed that in these cases, lime constitutes the binder. The observation of thin sections of the lime mortars confirmed the existence of siliceous aggregates. There were often pieces of igneous rocks (diabase) and a few silicates (quartz, pyroxenes and feldspars). The calcination of lime was mainly confirmed by the small size of the grains (less than 1 micron), their geometry, and their uniformity, all of which were distinguished in the SEM (Fig. 1b). The crystalline form of the lime is different from the crystalline structure of the raw material used for its manufacture, as the large volume change during the calcination process creates large strains in the surface layer of the reaction product, causing it to crack into small (less than 1 micron) particles. Thus, fine grained calcium carbonate is produced with particles less than 1 micron in size [1, 4]. During hydration, the lime forms a colloidal hydroxide and an extremely fine-grained calcium carbonate on recarbonation [4].

This very early use of lime mortars in Cyprus is not surprising since the invention of lime in the Near East can be dated back to the earliest periods of

antiquity. According to J.D. Frierman [10], the production of lime originated in Anatolia and then spread to the Levant. More recent studies [1, 11] have shown that the invention of lime in the Near East can be dated back to the Epi-Paleolithic period (12000 B.C.) while the earliest use of lime in architecture took place in the Early Natufian period (10300 B.C.). This plaster production expanded in the Aceramic Neolithic period and particularly in the 7th and 6th millennium when thick plaster floors were widely adopted [1].

The fossils, observed mainly in thin sections of lime and lime-gypsum mortars, suggest the presence of aggregates of calcitic composition. According to Leslie and Hughes [12], small lime lumps of under-burnt or over-burnt quicklime often can be recognized in the historic lime mortars, showing that the calcination process was not complete. The presence of lime lumps is sometimes interpreted as having been caused by a practice where damp aggregate is deliberately mixed with roughly crushed quicklime [12]. This was a typical ancient and traditional technique [4]. The use of lime and gypsum plasters appears to be connected to the emergence of permanent architecture during the Neolithic period of the island, accompanied by the need for building materials resistant to environmental conditions. This theory is also supported by Kingery [1], who reported that "the appearance of permanent architecture brought with it the desirability of building materials resistant to environmental weathering." It is noteworthy that in Cyprus during the Neolithic period, the knowledge of the technology for plaster production, in relation to the rest of the civilization, either suggests a sophisticated culture that was introduced to the island from abroad or constitutes an evolution of an earlier local civilization.

Chalcolithic mortars were mainly collected from Kissonerga-Mosphilia, one of the most important sites of this period. Their detailed investigation showed that the lime heating process was widespread on the island during this period, as several plaster floors of considerable thickness were found, all consisting of one or two dense layers of lime, 5-10 cm thick. These thick lime floors were quite different from the neolithic thin final layers of lime. The study of the thin sections showed that the binder is microcrystalline-calcite. The examination of the microstructure of the plasters using the SEM revealed a uniform fine-grained material (calcite grains 1-3 micra). The physical (hardness and thickness) and chemical characteristics, as well as the microstructure of the chalcolithic floors, suggest that the combustion process of limestone was widespread during this period. It is noteworthy that lime plaster floors have existed since the Neolithic period, but in most cases they just constituted one or two very thin upper layers. Thus, the process of heating limestone, although known during the Neolithic period, was widely disseminated during the Chalcolithic period.

The results for the Bronze Age lime plasters were based on analyses of samples selected from five very significant sites of the Late Bronze Age (Kalavasos-Ayios Dhimitrios, Maroni-Vournes, Hala Sultan Tekke, Maa-Palaiokastro and Alassa-Palaiotaverna). In the primary rooms of important public buildings, the coatings of the flooring were thick and consisted of hard calcitic material [8] that was

recognised as lime under the SEM. The discovery and use of crushed brick-lime mortars for the first time in the Late Bronze Age constitutes the most important evolution in the manufacture of lime mortars during this period. Their main use was in floors, where the capillary rise of water was expected (bath rooms and laboratory areas) and in various water-related structures (water channels). Small reddish particles were observed in all samples during examination under an optical microscope. These particles were recognized as ceramic fragments in thin sections. The high quantities of aluminum, iron, and silicon oxides are directly related to the addition of clay ceramic material during the preparation of the mortars. The identification by XRD of ghelenite, a mineral that is seldom found in nature but is characteristic of the use of ceramics heated to 800-1060^{o}C or natural hydraulic lime, is worth noting. The presence of anorthite in some samples also confirms the use of ceramics [14].

The observations under the SEM showed that crushed brick-lime mortars have a compact microstructure of the type formed in hydraulic mortars. The ceramic fragments in the thin sections appeared as reddish clay inclusions (Fig. 1c). The ceramic is extremely fine and uniformly distributed, with grains smaller than one millimetre. The small size of the ceramic grains considerably increases the interaction surface area of the ceramic with the calcium. During the consolidation phase, the grains of the ceramic, particularly their periphery, seem to react with calcium hydroxide to create calcium silicate and aluminate hydrates, which results in the hydraulicity of the mortars. The pozzolanicity of these mortars is attributed to the adhesion reactions occurring at the ceramic matrix interface. It is known that brick powder has a high pozzolanicity when it is heated to low temperatures. Ancient ceramics were often heated to relatively low temperatures, and so they were suitable as pozzolanic additives. The thermal curves confirmed that the examined crushed brick-lime mortars were hydraulic. Weight loss between 200 and 600^{o}C is attributed to the loss of structurally bound (hydraulic) water, i.e. due to the decomposition of calcium silicate and calcium aluminate hydrates. The Late Bronze Age crushed brick-lime mortars consist of 5-8% structurally bound water, so they present a moderate hydraulic character.

The appearance of the crushed brick-lime plasters in Cyprus during this period can be associated with the overall prosperity of the era and particularly with the emergence of urban centres. The appearance of crushed brick-lime mortars seems to occur simultaneously in the Mycenaean world. Recent studies have shown the use of natural pozzolanic additives in the later Minoan periods in Crete [15]. On the other hand, in the Levant, the earliest use of lime plasters with hydraulic properties is dated to the Early Bronze Age, and thus appears to precede the use of the similar mortars in Cyprus [8].

With the exception of the widespread use of gypsum plasters in the settlement of Kalavasos-Tenta, gypsum plasters are to be found mainly during the Late Bronze Age for special applications (i.e. as a material for the fastening of wooden elements). The limited use of gypsum is surprising, since the island has very notable deposits of gypsum rocks. Observations by SEM on the Late Bronze Age

gypsum plasters revealed the existence of various well-shaped elongated or rather rounded crystals (Fig. 1d). The microstructure of these samples is very similar to the structure of other historic gypsum mortars, but differs from contemporary ones [16, 1, 4]. According to Middendorf [16], a long-term weathered historic mortar is made up of large rounded crystals due to accumulated crystallization process induced by wet and dry cycles during weathering processes, and thus differs from contemporary gypsum mortars. The procedure described by Strahan [17] was followed for further verification of the manufacturing method of gypsum mortars. According to this theory, the final gypsum product of calcination can be distinguished from the natural rock by the diagram of XRD when samples are mixed with acetone. By using acetone slurry on a quartz plate, the preferred orientation of the crystals is duplicated. The relationship between the three major gypsum XRD peaks was investigated (7.56, 4.28, 3.06 angstroms) and the intensity of the peak of 7.56 angstrom (first peak) was compared to the other two. According to Strahan, the peak of 7.56 angstroms is consistently lower than the other two in the plasters. The prehistoric plasters examined showed the first peak to be lower than the others, confirming this assumption.

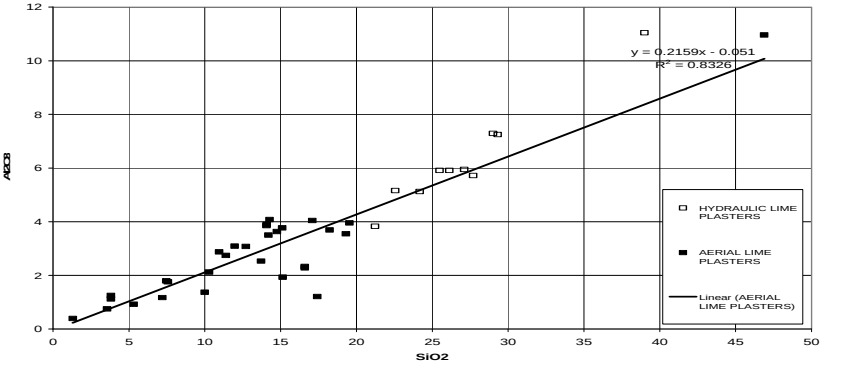

Fig. 2 Relationship between SiO_2 and Al_2O_3

3 Discussion and Conclusions

The analyses under an SEM indicated that most of the samples have a compact microstructure typical of old historic mortars, with aggregates well-embedded in the matrices [1, 4]. The relationship between silicon and aluminum oxides, and also between aluminum and ferric oxides, is linear in most of the aerial lime and crushed brick-lime plasters (Fig. 2). This leads to the conclusion that these oxides are related to the existence of clay minerals in aerial lime mortars and ceramic additives in crushed brick-lime mortars. The relationship between silicon and calcium oxides appears to be of an inverse nature in all lime mortars. Gypsum

mortars constitute a different case with a limited content of aggregates. The diagrams and the analyses showed that the gypsum mortars of all periods were prepared by the calcination of pure gypsum rocks, whereas lime mortars always had other additives, either due to the composition of the raw material or to the addition of aggregates during the manufacturing process.

This research demonstrated the need for the use of a combination of different characterization techniques for the detailed study of ancient mortars [18]. It is obvious that the investigation of the various types of plasters gives information about the knowledge level of technology, the economy and organization of the production of a region, and the distribution of raw materials and finished products.

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I.33

Characterization of Roman Mortars and Plasters in Tarsus (Cilicia-Turkey)

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Abstract Tarsus, located in southern Anatolia (Asia Minor), was one of the important urban-centres of the Roman Province Cilicia. This paper aims to provide an extensive characterization of the mortar and plaster samples from several Roman structures in Tarsus. To determine the properties of the samples, a set of chemical, physical, and mechanical tests were carried out and the results were evaluated. The presence of calcareous aggregates required the use of quantitative microscopic methods to determine the mix proportions. The results showed that all samples are lime mortars with limestone and river sand aggregates. It is also evident that gypsum is a constituent of the binder in most of the samples.

1 Introduction

Tarsus, with its long history reaching to Neolithic period, had become an important settlement for Romans from the 1st century B.C. and held its position for centuries [1]. Excavations and surveys have been carried out on the sites enclosing Roman remains since the 1980s, yet there are no extensive studies regarding the characterization of historic mortars and plasters that were used in these constructions. Samples taken from four Roman sites in the city has been the subject of this paper: The Temple (Donuktaş), Roman Road, Roman Bath, and Cleopatra Gate. Studies on the characterization of historic building materials would obviously support and enrich the scientific research conducted on these sites. Furthermore, such studies would lead to a better understanding of the local construction techniques and allow comparisons to similar sites in Anatolia and the Middle East.

2 Materials and methods

Thirteen mortar and plaster samples were studied from the four historical sites mentioned above. The Temple (known as Donuktaş) is an extensive structure and one of the most important monuments of the Roman era in the city. It has a rectangular plan with dimensions approximately 103 m x 43 m [2]. DT1 and DT2 are the samples taken from the thick (6.50 m) outer walls of the Temple. RY1 and RY3 were collected from the remains surrounding the Roman Road, which was discovered during the excavations in 1993. Samples RH1, RH2, RH3, RH4, RH5, RH6, RH7 were taken from different levels and parts of the Roman Bath, which is also an outstanding structure of large size and noted for its partly standing dome. KLK1 and KLK2 are samples from the Gate, also known as "Cleopatra Gate," which had been part of the city walls. The locations and general observations of the samples are shown in Table 1. The samples, weighing approximately 60-80 g, were carefully removed with a chisel from the sound parts of the masonry, labelled, and transferred to the laboratory safely in plastic bags. [3]

Table 1 Descriptions of the samples (DT1,DT2 are taken from The Roman Temple, RY1,RY3 are taken from Roman Road, RH1,RH2,RH3,RH4,RH5,RH6,RH7 are taken from Roman Bath, KLK1,KLK2 are taken from Cleopatra Gate)

Sample No	Function/ Location	Construction type	Description
DT1	Masonry mortar / Wall	Rubble stone +mortar	High strength mortar with white coloured binder and sand aggregate under 2 mm
DT2	Masonry mortar / Wall	Rubble stone +mortar	High strength mortar with white coloured binder and sand aggregate under 2 mm
RY1	Masonry mortar / Pavement	Rubble stone +mortar	High strength mortar with yellow-white coloured binder and sand aggregate under 5 mm
RY3	Joint mortar/ Wall	Brick +mortar	Joint mortar with yellow-white coloured binder and fine sand aggregate and organic additives
RH1	Masonry mortar / Wall	Rubble stone +mortar	High strength mortar with yellow-white coloured binder and sand aggregate under 5 mm
RH2	Joint mortar/ Wall	Brick +mortar	Joint mortar with yellow-white coloured binder and sand aggregate under 2 mm
RH3	Plaster/ Wall	Render over brick +mortar wall	Render with white coloured binder and sand aggregates under 2 mm and lime lumps

RH4	Plaster /Pool wall	Render over brick +mortar wall	Render with yellow-white coloured binder and sand aggregates under 4 mm
RH5	Joint mortar / Arch	Brick +mortar	Joint mortar with yellow-white coloured binder and sand aggregate under 3 mm
RH6	Masonry mortar / Wall	Rubble stone +mortar	Mortar with yellow-white coloured binder and sand aggregate under 3 mm
RH7	Masonry mortar /Dome	Rubble stone +mortar	Mortar with yellow-white coloured binder and sand aggregate under 5 mm
KLK1	Masonry mortar / Wall	Rubble stone +mortar	High strength mortar with yellow-white coloured binder and sand aggregate under 2 mm
KLK2	Masonry mortar / Wall	Ashlar stone +mortar	High strength mortar with yellow-white coloured binder and sand aggregate under 5 mm

This project followed methods and standards proposed in former related studies for the characterization of historic mortars and plasters to analyze and evaluate the samples. Chemical analyses, such as acid loss and ignition loss tests, were carried out in order to understand the properties of binder and aggregates and binder/aggregate ratios [4, 5]. The grading curves of the aggregates were determined by means of sieve analysis, and graded aggregates then were observed under stereo-microscope [4, 5]. The mineralogy of the binder and aggregates was carefully determined through polarized-light microscopy after thin section preparations of the samples and X-Ray diffraction (XRD) analyses [6]. Physical tests were conducted to identify the bulk density and porosity of the samples [7, 8]. In order to understand the mechanical properties, mechanical tests were conducted on irregular lumps by using point-load tester [9].

3 Results and discussion

3.1 Physico-mechanical characteristics

The physical and mechanical properties of the samples are presented in Table 2. The density values ranging between 1.15 and 2.21 g/cm^3 are typical for historic mortars and plasters [10]. Porosities are rather variable. This variability is mainly related to binder composition as well as different binder/aggregate ratios. [11]

Compressive strength values have been calculated using the equations in the ASTM standard [9]. The only conflict was the strength conversion index values

used in the calculation of the uniaxial compressive strength (MPa), which were designed for rocks. A suitable index for the mortar samples was calculated by using the correlation between uniaxial compressive strength values and point-load strength values. Cube specimens of adequate size (4x4x4 cm) were cut out of mortar lumps from the samples and subjected to the uniaxial compressive strength test. The irregular lumps of the same samples were tested using point-load tester. The ratios of the two values were calculated, and the median was accepted as the strength conversion index.

The visual analyses are compatible with the compressive strength values. The samples evaluated visually as high-strength mortars with less friability have higher values (3.16 MPa- 4.93 MPa), whereas samples indicated as low-strength mortars show lower values (0.55 MPa -1.84 MPa).

Table 2 Results of the analyses and evaluation

Sample No	Acid loss B+CA content (%)	PBW (%)	SBW (%)	$CaCO_3$ (%)	CA (%)	B:A Ratio	B	A	D (g/cm^3)	P (%)	CS (MPa)
DT1	70.9	2.41	7.39	53.3	20	1:3	Ct,G	Q,C,V	1.71	32.69	3.16
DT2	66.7	4.05	20.77	30.2	35	1:3	Ct,G	Q,C,V	2.21	8.30	3.50
RY1	70.4	1.62	7.04	60.2	35	1:3	Ct	Q,C,V,S	2.19	15.35	3.73
RY3	80.9	1.47	4.74	74.2	40	1:2	Ct	Q,C,V	1.15	52.08	1.84
RH1	75.2	1.05	3.15	68.3	35	1:2	Ct	Q,C,F,V	1.99	19.56	3.23
RH2	65.5	0.62	2.49	82.6	15	1:1	Ct	Q,C,F,V	1.49	36.03	3.18
RH3	45.6	6.53	1.40	65.5	-	1:1	Ct,G	Q,F,V	1.38	26.93	4.87
RH4	71.5	2.05	5.25	61.6	20	2:3	Ct,G	Q,F,C	1.30	46.21	0.99
RH5	68.2	8.34	18.14	36.6	10	1:3	Ct	Q,C,F,V,B	1.86	15.66	0.86
RH6	64.6	5.29	14.18	42.2	17	1:3	Ct,G	Q,C,F,V	1.78	23.52	2.49
RH7	58.0	0.68	5.11	70.0	33	1:3	Ct	Q,C,F,V,B	1.57	35.22	0.55
KLK1	18.5* +72.3**	16.73	3.84	17.9	-	1:1	Ct,G	V, Cc	1.54	14.49	4.93
KLK2	33.0* +64.3**	15.89	5.91	18.0	15	2:3	Ct,G	V, Cc	1.80	6.02	4.04

B:Binder , A:Aggregate, CA: Calcareous aggregate, PBW: Physically bound water, SBW: Structurally bound water, D:Bulk density, P:Total porosity, CS: Compressive strength

*: lime, **:gypsum

Ct: Calcite, G:Gypsum, Q:Quartz,V:Volcanic, C:Carbonates/Limestone, S: Shells, F:Feldspars, B: Brick particles and dust, Cc:Charcoal

3.2 Binder identification and characterization

The XRD results indicate that calcite is the main component of the binder of the samples; however, the presence of gypsum, ranging from traces to very strong peaks, is remarkable in most of the samples (Fig. 1). Quartz is present as a result of the fine aggregate grains passed through a 63 μm sieve.

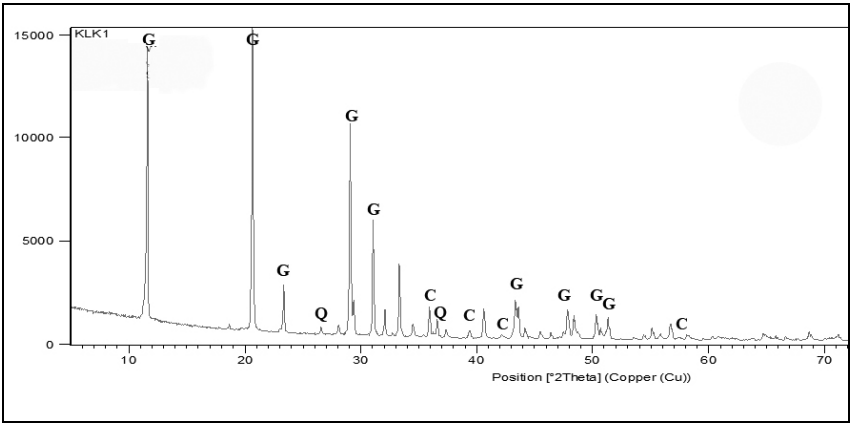

Fig. 1 XRD pattern of sample KLK1 (G: Gypsum-($Ca(SO_4)(H_2O)_2$, C:Calcite-$Ca(CO_3)$, Q:Quartz –(SiO_2)

Dissolving samples in HCl acid to determine binder/aggregate ratios of the mortars is a simple and generally used method [12, 13, 14]. On the other hand, the method is not suitable for mortars with calcareous aggregate, since the aggregates also would dissolve in the solution [15]. The investigation of the thin sections under polarized-light microscope indicates the presence of calcareous aggregates in most of the samples. Hence, quantitative microscopic methods were used to determine the mix proportions [16]. The percentages of calcareous aggregates in the mixtures were also defined by comparative evaluation of the results of acid loss and ignition loss tests. The binder/aggregate ratios are variant, including ratios such as 1:1, 2:3, 1:2, and 1:3. The proportions of calcareous aggregates are shown in Table 2.

KLK1 and KLK2 are two samples containing high amounts of gypsum that did not react and dissolve in HCl (10%) acid. These samples were treated by the chemical method stated by Middendorf and Knöfel [17], and gypsum and lime contents of the binder are given separately in Table 2.

3.3 Aggregate identification and characterization

The mineralogical analysis shows that the aggregates are composed of mainly quartz, limestone, feldspar, and volcanic rocks (Fig. 2). Traces of shells and

charcoal are present in several samples. It is apparent that the aggregates are river sand, and they can be classified by colour into two groups: dark-coloured river sand and light-coloured river sand.

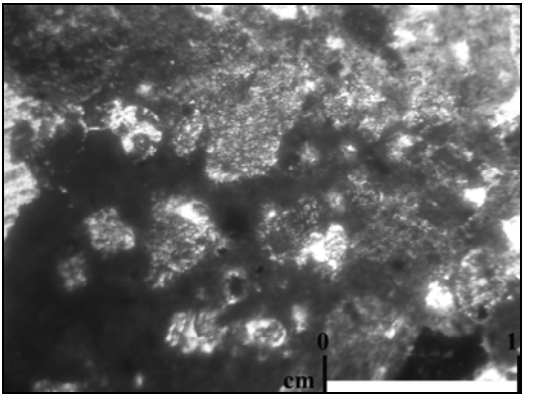

Fig. 2 Thin section image under polarized-light microscope of sample RH6 showing mainly limestone and quartz

The grain size distributions of most of the samples are within ideal ranges when compared to the Fuller curve (Figs. 3, 4, 5). The maximum grain size for these samples is 4 mm. The three samples with coarse aggregates (>8 mm) have been taken either from the core of the walls (DT2-DT3) or the sub-level of the pavement (RY1). The plasters and joint mortars contain finer aggregates despite the presence of coarse grains in samples taken from rubble stone masonry.

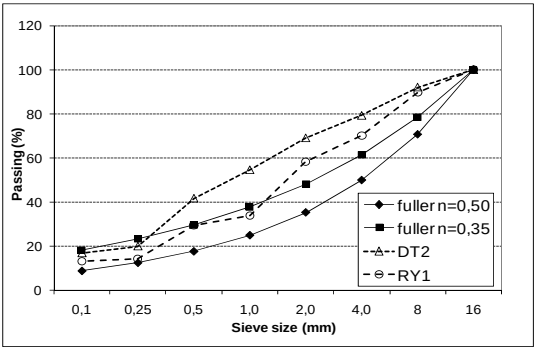

Fig. 3 Particle size distribution of the aggregates having the maximum size of 16 mm.

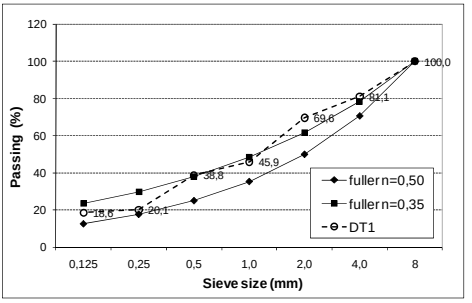

Fig. 4 Particle size distribution of the aggregates having the maximum size of 8 mm.

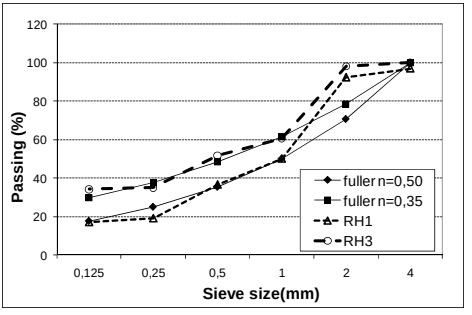

Fig. 5 Particle size distribution of the aggregates having the maximum size of 4 mm.

4 Conclusions

The aim of this study was to identify and characterize the binders and aggregates of mortars used in four different Roman sites in order to understand the construction techniques in Plain Cilicia.

The results indicate that all samples are lime mortars with limestone and river sand aggregates. The XRD results indicate that the samples with different porosity than that of typical lime mortars contain gypsum as a constituent of the binder. Gypsum content ranges from trace amounts to a high quantity. Samples KLK1 and KLK2 contain much higher amounts of gypsum than the others. After a comprehensive research on the historical background of the site and further studies on the other related monuments of the era in the region, it would be appropriate to identify the mortar containing both lime and a high gypsum content either as a mortar type used in the Roman period or to indicate some medieval repairs.

The aggregates are river sands definitely taken from the several rivers of the region.

The presence of calcareous aggregates complicates the evaluation of binder/aggregate proportions and the predictions of binder hydraulicity according

to CO_2/H_2O ratios. Advanced instrumental analysis, such as SEM-EDS analysis, becomes fundamental for samples with calcareous aggregates in order to understand hydraulic additives. Quantitative microscopic analysis is a convenient method to determine mixing ratios in such cases.

It can be stated that aggregate gradation curves of the samples with higher mechanical properties comply with the Fuller curve.

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I.34

Development of an Analytical Protocol for Characterisation of Historical Mortars

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Abstract The definition of the composition, the technological process and, last but not least, the provenance of the raw materials of historical mortars is still difficult and unsatisfactory, notwithstanding a number of guide-lines proposed in the last years. Problems are usually associated with the composite nature of materials. On the contrary, in case of archaeological building investigations conservation scientists call for a valid and reliable analytical tool to classify mortars by the compositional and morphological points of view and to enlighten the conservation history and the sequence of the building interventions. The paper describes the development of an integrated protocol of chemical, mineralogical and microscopic analyses for the characterisation of mortars. The key idea was to set up and standardize an analytical methodology whose basic objective is the identification of major and minor constituent materials and binder/ aggregate ratio. The protocol defined and optimised every step of the techniques usually carried out for the analysis of historical mortars, i.e. sampling, sample preparation, assessment of reproducibility and sensitivity of measurements and data treatment. Specimens of mortars were prepared with a calcitic binder, carbonated and analysed by Optical and Electronic Microscopy, Infrared and Atomic Spectroscopy, Thermogravimetry and X Ray Diffraction. The paper presents the preliminary results.

I.35

Mapping of Mortars and Ashlars in Watchtowers of Reconquest Ages in Cuenca District, Spain

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Abstract In the inner tablelands of Spain, in Cuenca district, at only 150kms south east from Madrid we can discover a dense net of watchtowers, dated on the last years of the 12th century, scattered all over the territory. These enigmatic constructions, following the results of the presented, research have a Muslim origin and a Christian maintenance, due to their control of the territory and bonded with the regulation of the displacements of livestock during the seasons. Have they a military or a civil function? Both of the possibilities are documented…at the same time, a part from a morphological and typological developed study, the research has opened an interesting study about the features of the mortar and the ashlars used in the district during the Reconquest Ages. The direct analysis shows the use of specific masonries, both for religious, and for civil constructions, made by manageable ashlars, set in regular rows, with a deep filling of lime mortars. These mortars, rich in lime, as the chemical analysis show could guarantee the good performances of the walls during the ages, in spite of the use of sedimentary and low quality limestone ashlars. The result of the research is a useful "pattern book" of the masonries of the watchtowers and Reconquest buildings in the district, throughout the centuries and during their reparations.

1 The context and the object of the study

The study spreads out a wide area of the *Cuenca* Province territory, in an inner district of the interior flatland of Spain, close to a river district (called *Jucar* and *Cabriel* river basins). A series of towers appears throughout this extended hill-waved landscape: *Piqueras, Barchín, Olmeda, Chumillas, Honrubia, Gascas, Buenache, Solera Valhermoso* villages give evidence of the presence of well conserved or ruined free standing towers. The surface, that the study includes, is an area of approximately 50.000 hectares. For this reason, due to the huge

extension of the analysed territory, some planned and scheduled stages of study were recommended. Definitively this research is opened to different disciplines that allow to go deeply into the origin and role played by these towers along the Ages.

The study begins with the comprehension of the area where the towers are built with reference to physical, climatical ecological and geological aspects.

After this regional vision, the work tries to focus on historical *data* and sources, to establish the construction age of the towers, their features and their relation with other detached buildings of the area (like churches, for examples).

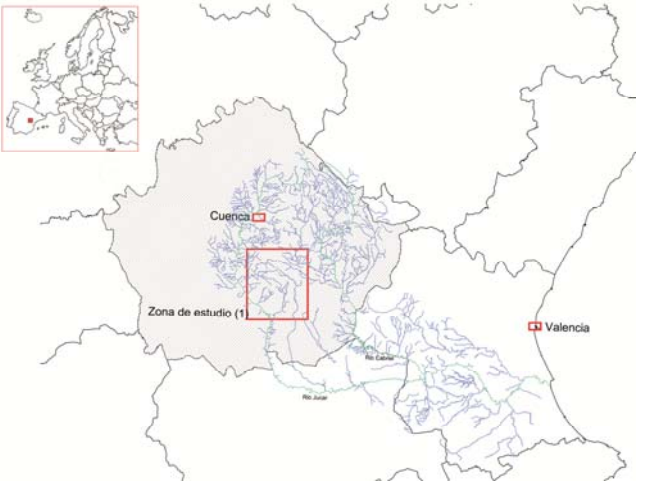

Fig. 1 the context and localization of the towers (in the red square)

The road links are important elements to consider in the anthropological study of the area, because these connections completely cross Cuenca's Province throughout the centuries. The historical paths, bonded with the local cattle raising economy, are fundamental for the complete comprehension of the evolution of the landscape and for the understanding of the presence of the towers. From the first Iberian villages to the ancient Roman's routes net, from Visigothic legacy to Muslim/Christian employment. Always, throughout History, the trades and the woollen activities feed the maintenance of the territory and its roads links.

Therefore the towers would be connected with these cattle historical routes, above all from the Recoquest Ages. This term refers to the eight centuries during which the Christian kings of the Spanish kingdoms gradually reclaimed their country from the Moors, who had invaded the Iberian Peninsula. Nevertheless King *Alfonso VIII*, considered this area, in his advance towards on the South, as a strategic location. The monarch comes up to the Province, with the support of the Military Order of *Santiago*, in the year 1177, being especially interested in the management of the tolls of routes and passes.

Fig. 2 A tower example: the case of study of *Valhermoso*

The territory where the towers are located has been so little altered by such external agents like, infrastructures or human changes through the ages. For this reason the group of towers is an untouched and great example of defensive typology in the Region. They are still identical watchtowers along the topography of the county. The analysis has shown that the towers present some repeated features, visible in all the cases of study. For example the location of the watchtowers is always on top of reduced rocky platform, their situation is constantly in a narrow valley close to a creek or river. In each case of study the towers are flanked, by routes, ways or paths which are tracing in general with a specific orientation.

As a matter of fact, the position of the buildings is always related to the cattle raising roads, usually crossing the Peninsula from North to South.

All of them attend to a typology of free standing tower with a regular rectangular layout, with small imbalances due to irrelevant adjustments to the topography. Their height changes according to their state of conservation. It's quite frequent to recognize a main access, around 5 m of height, with an arch shaped by rough stones.

It's quite difficult to recognize a tower in an absolutely well conserved state; anyway, with the studying of some examples, like *Cervera* o *Piqueras* [13] towers, it is possible to recognize the battlements, their maintenance and their evolution.

The study of modulation and proportion of these buildings is also quite interesting. We have witness of the employment of a module, of 47 cm. This module would fit with the measure of the "cubit" of Castille, called *codo*. (In

reference to the human dimension that measure from the elbow to the top of the finger).

2 Historical notes

So when can we go back into the centuries to discover the beginning of the construction of these buildings? In the early stage of expansion of the Christian kingdoms, at the end of the XII C., the area was exploited with clearly commercial lenses. Furthermore the Military Order of *Santiago*, as an estate to the service of the kingdom, starts the maintenance of the previous Muslim emplacements [2, 4].

The towers would play the rule of "body of vigilance" of the great extension of territory towards the South of the Peninsula. At the same time their function was to guarantee and control the correct development of pastures, the forest management, and the control of the passes [10].

On the other hand, the reference of historic documents would testify as the towers (so as to detail the *Valhermoso* one) are maintained and repaired with the arrival, in the Region, of the military order of *Santiago* (1234).

The function of these Towers, therefore, is deeply related to the control of the routes and passes more than that with an exclusive warlike function.

In the analysis of possible visual relations among these buildings, it is verified that the watchtowers are not connected to one another.

Visual basins are generated from each tower, thanks to the management of the cartographic information (going on from a two-dimensional vision to a three-dimensional one) Two hypotheses appear from each type of building visibility: diurnal, within a distance of 15 km, and night visibility, within a distance of 30 km.

The overlapping of these visual basins on the 3D model, confirms that the towers are not visually connected.

Rather on the contrary, the visual basins are complementary, covering the surface of every municipal area [2, 3]. This might confirm the watch role of the buildings in the control of the territory, based on visual complementation and complete managing of lands.

3 Constructive features and details

The study tries to focus on the masonries of the towers so as to date he buildings through disciplines like constructive analysis, stratigraphy and petrography.

The walls are perfectly built with horizontal rows by ashlars, proceeding from quarries near to the emplacement. We can recognize different raw materials, depending on the local availability, sandstones, limestones; conglomerates are

used with no distinction in the masonries. The walls are received with lime mortar and arid of variable granulometry; in occasions ashes are used to improve the hydration.

Fig. 3 Masonries study: exterior disposition of ashlars and interior filling technique

The walls are formed of two external faces formed with rows, of 25 cm of height, as previously indicated. Among them there's a huge filling formed of pieces of minor granulometry, wastes of stones and pebbles. In some points it is also possible to estimate that the filling is formed of regular layers of approximately 10 cm of thickness.

The process of study started with the comparison of the towers, not well dated, with some buildings, with a precise dating. In the area, churches and military constructions were used as references of masonry constructions and finishing.

The towers always present a regular disposition of ashlars, of 25x20x20 cm, well shaped especially in the corners. It is not so common that in this area of study, you should see such well ordered and set masonries [6, 8]. We can see that Muslim buildings (IX-X C.) are used to be built with a filling core [1], but with bigger rough stones, of 50x25x30cm, disposed in variable vertical/horizontal corners are progressively well shaped (XIV-XV C.) with carved ashlars and keystones of the arches.

The final contribution to the demonstration of the homogeneous nature of this set of medieval towers is provided by the petrographic analysis of the mortars.

Fig. 4 Masonries study: classification of pathologies (structures and surfaces)

4 Lime mortars: results and discussion

The analysis results from the 14 samples, selected from the 7 towers analysed, are quite uniform and homogeneous.

The *de visu* macroscopic analysis of the mortars (14 samples) shows homogeneous and porous matrixes. The tonality is the characteristic of major differentiation of the samples, variable between the range of pink and brownish colours [14].

There are also visible some ceramic fragments and impurities, carbonate crusts not well grounded, with an average size of 1.2mm. For this reason the mortars are not so smooth and with a grain texture. The analysis done on the samples are the following ones:

MO (Optical microscopy)

Optical microscopic methods are commonly applied using a polarising petrographic miscroscope to study thin section material. In this case, although the binder diffraction is mostly very good identification of the type of binder (gypsum, lime or gypsum and lime) is mostly possible.

SEM (scanning electron microscopy)

Using SEM, the structure of the tower mortars can be analysed at high magnifications and three dimensions on rough, broken surfaces to directly visualize the components of the mortar. SEM analysis is important, in this way, for the characterization of very fine-grained lime mortars, and the higher magnifications allow the recognition of the micro-structure of hydrated hydraulic phases.

FTIR (Infra-Red spectroscopy)

By using Infra-Red spectroscopy, especially Fourier Transform Infra Red spectroscopy, in addition to the identification of the main mineral phases in a binder, small quantities of admixtures and additives can be identified. In general this method relies on the interaction between applied infra-red radiation and the molecules in compounds.

Thanks to the results of the study, we have witnessed that the mortars are mainly composed of a microcrystalline binder of calcium carbonate $CaCO_3$(without traces of $CaSO_4 \cdot 2H_2O$.) and the aggregates are constituted by quartz matrix and a low proportion of clays. This latter one is in charge of the tonality of the mortars (depending on the content of Fe3+ the mortars can turn into a brownish/pink colour). All the samples contain, in a different percentage, nitrate-bearing grounds that were identified so much in the sample to hand, as with the FTIR.

In general the granulometry (reduced, with approximate values) suggests a very similar proportion of dry: binder around 9:1. So, finally we can describe the samples as mortars with binding material and finely crystallized calcite, well carbonated. Otherwise the aggregates are mainly calcite consisting of coarse clastic quartz grains [16].

5 Conclusion

Generally, the constructive system of the towers, the way of their implantation in the landscape, their dating, their relation with road links are fundamental keys for their study.

At the same time the uniform and “standardized” mortars used in the walls, the ashlars, their dimensions, modules and features... are other basic elements of comparison and study.

The research tries to focus on these buildings not as isolated elements, but as a group of monuments, deeply related and rooted to the landscape and the territory.

This might relate to the proper system of land organization of the Santiago Military Order. At the same time this perfectly articulated system gives solution to the problem of the management of big territorial extensions, where the density of population was especially low.

Another important documentary evidence to confirm the unit of this set of towers is based on several constructive features, visible in the buildings.

The towers answer to a constructive basic system, which is closer to the beginning of a Romanesque architecture of repopulation, than to constructive Gothic systems, as it was claimed at some point.

The new settlers of the *Reconquest,* devoted themselves to execute their works with great solidity but without great technical complexity [3, 15]. To this one,

another reference might be added: the clear influence of Roman and Muslim legacies that should have influenced the new settlers at the end of the XII C.

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I.36

Stone-Imitating Plasters in the Renaissance Ducal Palace in Mantua (Italy): Characteristics and Decay with Relation to Microstructure

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Abstract The plasters of the 16th century *Cavallerizza* Courtyard in the Ducal Palace in Mantua (Italy) were designed to imitate natural stones (rustication work, carved marble, etc.). They were produced for both aesthetic and manufacturing purposes with highly variable formulations, resulting in highly variable microstructures of the final elements. Because the plasters have been exposed to high concentrations of atmospheric pollutants in the last decades, they currently exhibit severe decay, differing on the basis of microstructural characteristics. The aim of this paper is to analyze the complex interaction between environmental aggressiveness, plaster microstructure, and degradation phenomena in view of their restoration. Plaster samples were collected from the Loggia side of the courtyard at short distance from one another, so that exposure conditions could be considered constant. The samples were characterized in terms of mineralogical composition, overall open porosity, and pore size distribution; and the degree of the chemical attack for each sample was assessed by comparing the salt contents of the inner and external layers. In light of microstructure characterization and chemical attack evaluation, guidelines for restoration of the plasters were proposed.

1 Introduction

Stone-imitating plasters were widely used in historical architecture in place of natural stones for covering surfaces and creating carved elements, especially when economic constraints and/or scarce local availability made the use of natural stones impossible. Hence, as stone-imitating plasters primarily contribute to the image of historical architecture (exactly like natural stones), their conservation and restoration are fundamental for the preservation of a building's cultural value.

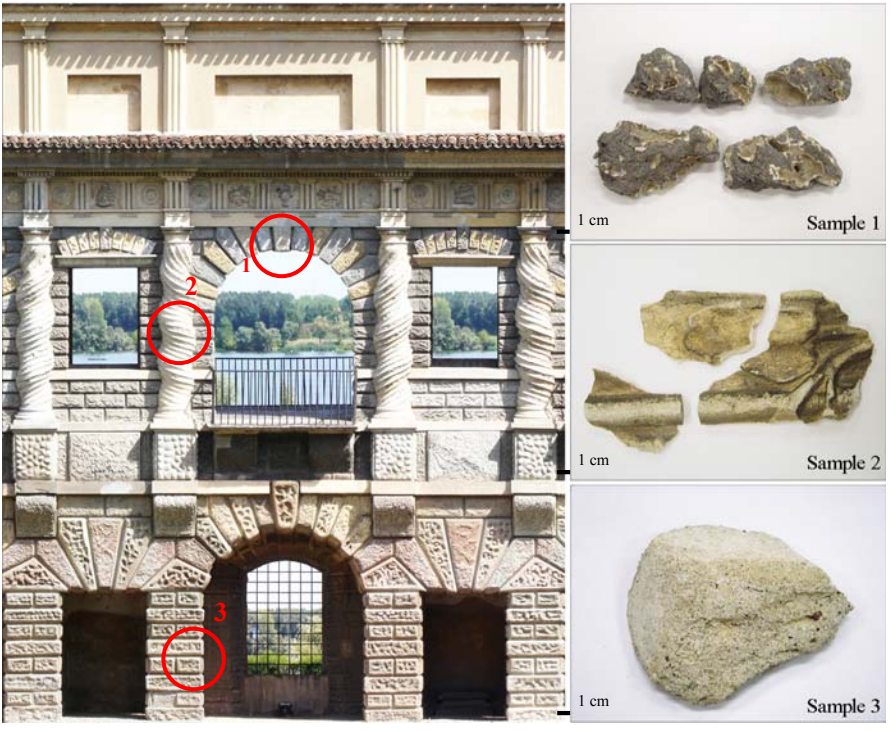

Fig. 1 View of the Loggia side of the courtyard (left) and details of the samples (right)

However, the nature and microstructural characteristics of such plasters are variable in relation to the richness of their final stone-imitating effects, and their decay might differ greatly, even among plasters exposed to the same environmental conditions. Therefore, accurate microstructural diagnostic investigations are necessary in order to outline effective and compatible restoration procedures (re-adhesion, consolidation, substitution, etc.) [1].

In this paper, the complex interaction between environmental aggressiveness, microstructural characteristics, and degradation phenomena is analyzed for the plasters of the *Cavallerizza* courtyard in the Ducal Palace in Mantua (XVI century, Italy), and restoration guidelines are proposed. The evaluation of environmental aggressiveness was performed according to previously proposed methodologies [2-3].

2 Materials and Methods

2.1 Samples

The four sides of the *Cavallerizza* courtyard (*Loggia dei Marmi* [Marble Loggia], *Rustica* [Rustic], *Galleria dei Marmi* [Marble Gallery], and *Loggiato* [Loggia]) were built in different phases from 1536-1604 [4-6], the first two sides by Giulio Romano and the other two by Giovanbattista Bertani. The Loggia side directly overlooks the *Lago Inferiore* [Inferior Lake] (Fig. 1, left).

Three samples of decayed plasters were collected from the *Loggiato* side of the courtyard at a close distance from one another, so that exposure conditions could be considered constant (Fig. 1, right). The sampling points and descriptions of the samples are reported in Table 1.

Table 1 Identification and description of the plaster samples

No.	Sampling point (Fig. 1)	Description of the layers (from the external surface)
1	Ornamentation of an arch (first floor)	Paint layer (<1 mm), with wide gaps; dark grey inner mortar (4-5 cm), crumbly and prone to pulverization
2	Flower-style decoration from a tortile column (first floor)	Hard and resistant paste (0.5-1 cm), with some dark deposits; underlying "adhesive" paste layer (≈1 mm), where detachment from the column occurred
3	Rustication plaster from a pillar (ground floor)	Slight pale-yellow paint; inner mortar (2-3 cm), quite compact

2.2 Samples characterization

The different layers of the samples (Table 1) were investigated separately. Open porosity, mean pore radius, and pore size distribution were determined by mercury intrusion porosimetry (MIP, Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba) for the inner part of samples 1-3 and for the "adhesive" layer in sample 2, while the surface paint in sample 1 was too inclined to pulverization to be analyzed by MIP.

The mineralogical composition of samples 1-3, the "adhesive" layer in sample 2, and the surface paint layer in sample 1 were assessed with powder X-ray diffraction (XRD, Philips Diffractometer PW 1840, 40 kV/20 mA, Cu Kα anode). XRD analysis was also performed on surface samples (≈3 mm) of each plaster to determine if decay by-products, such as gypsum, are present due to environmental attack.

Finally, a quantitative evaluation of chemical attack (mainly sulphation) of the samples was carried out by comparing the content of soluble salts in the most external layer (≈3 mm) and in the inner part (depth 1-2 cm). The salt content was determined by sample grinding, salt extraction with distilled boiling water, filtration, and ion chromatography (IC, Dionex ICS 1000).

3 Results and discussion

Environmental aggressiveness evaluation revealed the courtyard plasters have been exposed to extremely severe conditions in the last decades. In fact, presumably due to the proximity of a thermo-electric power station (only a few kilometres away), the atmospheric pollutants in the surroundings of the Palace reached very high concentration levels in the past. In particular, annual average concentration of SO_2 (currently amounting to ≈5 μg/m^3) used to be about five times higher in the '90s and even ten times higher in the '80s [7]. Similarly, NO_2 annual average concentration (currently amounting to ≈30 μg/m^3) used to be about three times higher in the '80s [7].

The investigated plasters exhibited quite different microstructural features, which have resulted in different degradation states. Microstructure variability can be explained considering both the complex articulation of the courtyard's construction phases – covering a 66-year period under the direction of different architects – and the different manufacturing technologies required to shape such rich manneristic decorations and to imitate various kinds of stone. Sample 1, having a very high open porosity and a large amount of "macro-pores", i.e. with radius >1 μm (Fig. 2 and Table 2), is a roughly compacted plaster used to imitate a bush-hammered stone ashlar. The mortar seems to have been made of lime binder and sand composed mainly of quartz, feldspar, and traces of dolomite (Table 3). Likely because of the raw finishing of the plaster, a lime paint with protective and decorative functions was added; this paint, now completely carbonated, also contains 4.4 wt% gypsum (calculated on the basis of the $SO_4^=$ content detected by IC, Tables 3 and 4).

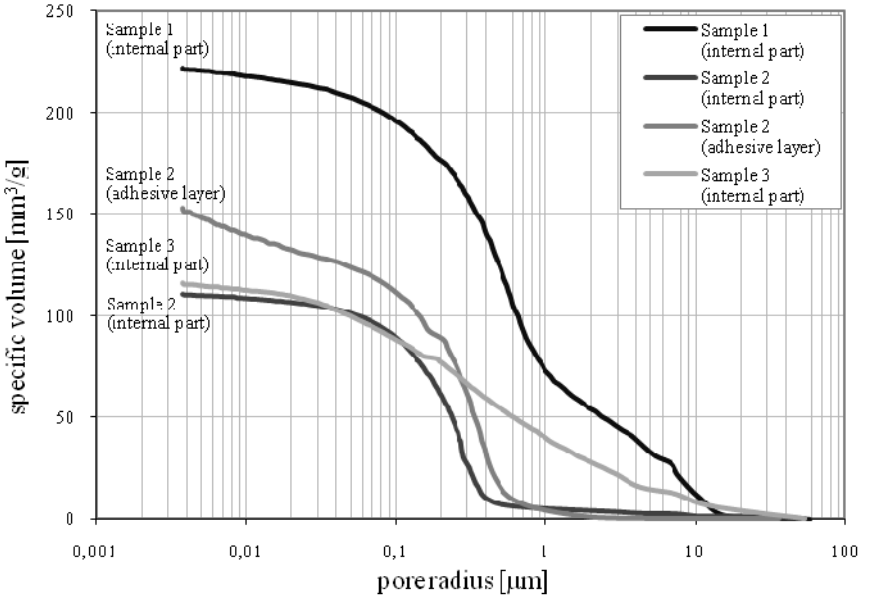

Fig. 2 Pore size distribution of the samples

The presence of gypsum in the surface paint could be due either to the addition of gypsum to the binder fraction in order to reduce the plaster's hardening time, or to the transformation of calcite into gypsum via environmental chemical attack (rising dampness is excluded due to the first floor location of the sample). Considering that sulphates were found in the external part of the underlying mortar ($SO_4^=$ =0.68 wt%, Table 4), which had been exposed to environmental attack after the detachment of the overlying paint, as well as in the more internal part of the mortar ($SO_4^=$ =0.42 wt%), the ascription of gypsum to calcite sulphation due to atmospheric pollutants seems reasonable, as gypsum content gradually decreases with depth. Similarly, the high amount of nitrates and chlorides detected in the surface paint layer (0.48 wt% and 0.17 wt% respectively, Table 4) seems to be a consequence of environmental attack as well. The chemical attack to the lime surface paint led to its detachment from the substrate, enhancing the sulphation of the underlying parts.

Sample 2, having a relatively low open porosity, a very fine mean pore radius, and a low percentage of macro-pores (Table 2 and Fig. 2), is a paste intended to imitate carved marble. The omission of aggregates and a careful manufacturing process were necessary to mould the fine flower-style decorations on the tortile columns and resulted in a reduction of the size and number of the pores. The sample consisted of only calcite and dolomite produced by the binder carbonation (Table 3), and it was very hard. The high content of dolomite resulting from

binder hardening can be explained considering that magnesium-rich limes were often used for moulded plasters and pastes to increase plasticity and adherence to substrates [8-9]. The "adhesive" layer between the moulded part and the column proved to be a paste made of calcite and dolomite as well (Table 3), with a porosity similar to the overlying moulded part and a slightly larger average pore radius (0.36 μm, Table 2), which implies careful manufacturing for this support layer as well.

With regard to the conservation state of sample 2, the XRD performed on the external part of the sample (≈3 mm) identified the presence of gypsum, which was not detected in the underlying internal part (Table 3). The IC analysis confirmed the sulphate content in the external part is almost double that in the internal part (2.01 wt% and 1.23 wt% respectively, Table 4). This result suggests that an intense sulphation action must have occurred in the past, when atmospheric SO_2 concentrations were ≈50 μg/m^3. However, the surface of the sample seems unaffected by huge material loss (thanks to the compact microstructure of the plaster), and the flower-style decoration is still visible and recognizable. On the other hand, the detachment of the sample occurred along the "adhesive" layer, suggesting that, despite the use of magnesium-rich lime, the paste adherence failed.

Table 2 Results of MIP analysis (OP = open porosity; pores r>1 μm = pores with radius >1 μm ; pores r>0.1 μm = pores with radius >0.1 μm; r_m = mean pore radius)

Sample	Part	OP [%]	pores r>1 μm [%]	pores r>0.1 μm [%]	r_m [μm]
1	Internal	36.1	32.7	88.2	0.48
2	Internal	22.7	4.7	80.6	0.27
	Adhesive	19.3	2.8	72.8	0.36
3	Internal	24.2	34.3	75.7	0.26

Table 3 Results of XRD analysis (C = calcite; D = dolomite; Q = quartz; F = feldspar (albite); G = gypsum; +++ = dominantly present; ++ = present; + = traces; - = not present)

Sample	Part	C	D	Q	F	G
1	Surface paint	++	-	+	-	+
	External	++	+	+++	++	-
	Internal	++	+	+++	++	-
2	External	+++	+++	-	-	+
	Internal	+++	+++	-	-	-
	Adhesive	+++	+++	-	-	-
3	External	++	+	+++	++	-
	Internal	++	+	+++	+	-

Table 4 Results of IC analysis (wt%)

Sample	Part	$SO_4^=$	NO_3^-	Cl^-
1	Surface paint	3.10	0.48	0.17
	External	0.68	0.27	0.10
	Internal	0.42	0.25	0.11
2	External	2.01	0.05	0.02
	Internal	1.23	0.05	0.01
3	External	1.40	0.58	0.03
	Internal	0.68	0.44	0.05

Sample 3, although having relatively low porosity, has the highest percentage of coarse pores among the examined samples (34.3% of pores with r>1 μm, Table 2). The rough compaction of the plaster was necessary to achieve the rustication appearance and is responsible for the high number of macropores. The thickness and coarse placing of such plaster was made possible by the insertion of brick fragments as a reinforcement for supporting the fresh plaster (Fig. 3).

Fig. 3 Brick fragments insertion in the rustication plaster.

XRD analysis was performed on the whole sample (calcite, dolomite, quartz and feldspar were detected, as noted in Table 3) and separately on the binder and aggregate fractions, according to the methodology in [10]. Calcite is ascribable to the binder, and dolomite is contained in the aggregate alongside quartz and feldspar. Hence, the sand presumably came from the Mincio river, which originates in the Dolomites and forms the Lago Inferiore near the courtyard.

The external part of the sample (≈3 mm) showed a sulphate content double that of the internal part (1.4 wt% and 0.68 wt% respectively, Tab. 3), suggesting that intense sulphation occurred in this sample as well.

4 Conclusions

In light of the microstructural characterization results and the assessment of decay causes, and considering that the environmental aggression seems to have significantly decreased after the reconversion of the nearby power-station, some guidelines for restoration can be proposed. In sample 1, the paint detachment due to sulphation exposed the underlying parts (likely designed to be protected by the surface paint) to environmental attack, leading to prevalent material pulverization and loss. For the missing areas, replacement with a compatible plaster – in terms of formulation, grain size distribution, texture, physical-mechanical properties, etc. [9] – should be considered, while consolidation seems suitable for the parts still present. The application of a new final paint layer of the same kind and colour of the existing one seems the most compatible protection solution. In sample 2, the detachment from the tortile column occurred alongside the "adhesive" layer and, in spite of the intense sulphation, the moulded surface is still well-conserved and unaffected by significant material loss. Therefore, re-adhesion of the detached parts, e.g. by means of lime mortar added with epoxy resin, the moulding should be cleaned and a final protection treatment applied. Finally, in the case of sample 3, which appears to be compact and not affected by pulverization despite the sulphation of the most external layer, the re-adhesion of the detached parts and the filling of the lacking parts with a compatible restoration plaster should be considered.

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Physico-Chemical Characterization of the Plasters from the Church of *Santissimo Sacramento* in Alcântara, Lisbon

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Abstract The Santissimo Sacramento Convent, in Alcântara quarter in Lisbon, was an innovative architectural project in the 17th century and one of the most important ecclesiastic structures at that period in Lisbon. An intervention aiming at the restoration of the monument's interior plasters was planned in 2009 and is currently being carried out. In this article, the main results obtained in the physico-chemical characterization of the internal plasters from Santissimo Sacramento church, including mortars, stuccos, and pigments, are presented; the diagnosis methodology was applied for both the evaluation of the state of conservation of the renders and the recommendations made for the repair mortars. The results obtained indicate that the mortars are in very good condition, being composed of aerial calcitic lime with siliceous and basaltic aggregates; the stuccos are composed of gypsum and aerial calcitic lime, and the decorative layers are of lime with some precious pigments, such as ultramarine (lapis lazuli) and gildings.

1 Introduction

The *Santissimo Sacramento* Church of Lisbon (Fig. 1), located in the ancient convent of the same name, is an excellent example of the architectural richness of Lisbon in the XV century and one of the most important constructions built during the Spanish dynasty (1580-1640). The convent was established in 1605 and the construction works ended in 1620, but the Church was rebuilt in 1635 due to its lack of light and also reduced internal spaces. It survived the earthquake of Lisbon in 1755, however it became poorer and its decline started in 1834 with the suppression of the religious orders in Portugal. At the beginning of the XX century

the convent passed under the control of the Army and suffered several alterations. Finally, at the end of the '90s, the convent was acquired by the Foreign Affairs Office, which decided to refurbish the entire complex.

The Church presents a Greek cross plan with a dome widely decorated with plasters and mural paintings of great quality. The mortars are well-preserved and present interesting mural paintings simulating rose marble.

This paper presents the results obtained in the characterization of the internal renders (mortars, stuccos, and mural paintings) of the *Santíssimo Sacramento* Church in Lisbon. This characterization was carried out as the first step to define the conservation strategy.

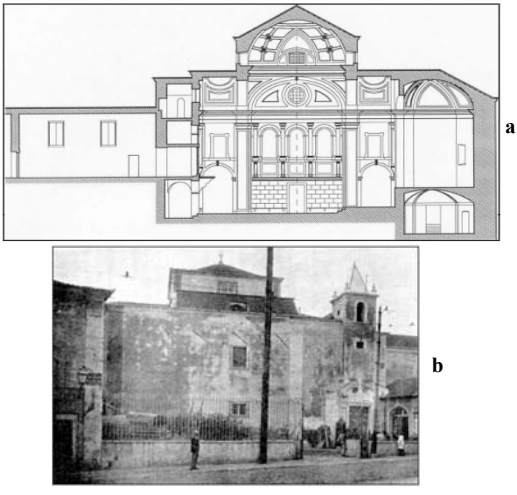

Fig. 1 a) Section of the *Santíssimo Sacramento* Church; b) Picture of the Church, 1929 [1].

2 Samples and methodology

2.1 Samples

The selection of the sampling sites was carried out according the LNEC's methodology for the characterization of renders in ancient buildings [2, 3] following two archaeological and historical studies of the Sacramento complex [4, 5]. The aim was to identify the different plastering materials, to study their compositions, and determine their state of conservation. Thirteen samples of mortars, plasters, and mural paintings were collected from different zones, as shown in Fig. 2 and described in Tables 1 and 2.

Table 1 Identification of the samples, type and their localization.

Samples Identification	Layers Identification	Constitution	Localization
1	S1	Mortar	West wall , South part
	SP8	Mural Painting	
	SB5	Stucco	
1 A	SP7	Mural Painting	West wall , South part
	S1A	Mortar	
2	S2	Mortar	Dome vault
	SB6	Stucco	
	SP11	Mural Painting	

Table 2 Identification of the samples, type and their localization (cont.)

Samples Identification	Layers Identification	Constitution	Localization
3	S3	Mortar	North wall , West part
	SB7	Stucco	
	SP9	Mural Painting	
4	S4	Mortar	Dome's moulding
	SB8 -1st Layer	Stucco	
	SB8 -2nd Layer	Plaster	
	SP10	Mural Painting	
5	S5	Mortar	South wall , East part
6	SB9	Stucco	Dome – South vault, East part
7	SB10	Stucco	Dome – South vault, West part
8	SP1	Mural Painting	Dome – red painting, marble imitation
9	SP2	Mural Painting	Dome – blue painting
10	SP3	Mural Painting	Dome vault – grapes
11	SP4	Mural Painting	Dome vault – leaf
12	SP5	Mural Painting	Dome vault – grapevine leaf
13	SP6	Mural Painting	Dome vault – golden sunbeam

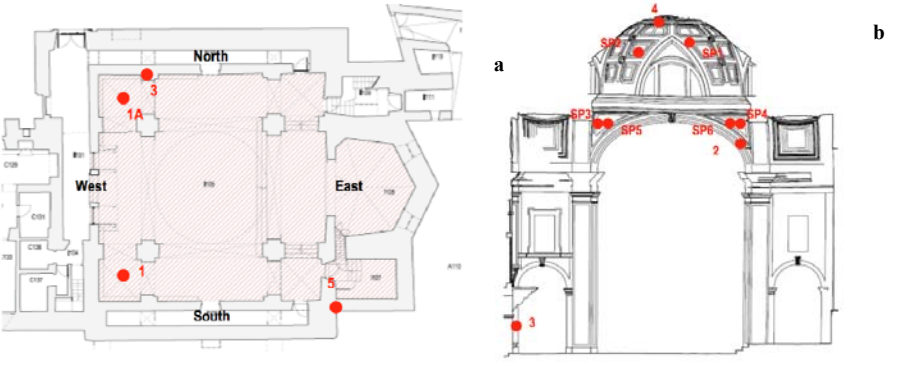

Fig. 2 a, b) Plan and section of *Santíssimo Sacramento* Church showing the sample sites selected [4].

2.2 Characterization methodology

A great number of physical and chemical techniques can be applied in the characterization of old mortars and plasters. The physico-chemical characterization methodology developed by the authors [2, 3] comprises a wide range of techniques that complement each other, including XRD, TGA-DTA, optical microscopy and petrography, SEM-EDS, micro-FTIR, grain size analysis, chemical analysis, capillarity coefficient, and compression strength. The characterization concentrates on the renders from the walls, the roof, and the dome, and it includes mortars, stuccos, and mural paintings. The main objectives of the characterization of these materials were the determination of their stratigraphy, composition, and conservation/degradation state of the renders.

3 Results and discussion

3.1 XRD Analysis

Tables 3 and 4 present the mineralogical composition of the mortars and stuccos, respectively, obtained by XRD analysis. The results show that the mortars of *Santissimo Sacramento's* Church are essentially of two types. The first group (S1, S1A, S3, S5) is composed of calcitic lime binder with siliceous and basaltic aggregates. This group is contaminated with chlorides, which seem to come from the marine aerosol and/or by the use of unwashed sea sand. The second group of mortars (S2, S4) contain a lower quantity of calcitic lime binder, a remarkable

quantity of gypsum, and silicious aggregates only; they are more contaminated with chlorides than the mortars in the first group.

Table 3 Mineralogical composition of the mortars assessed by XRD.

Crystalline phases	S1				S1A	S2		S3	S4	S5
	1st L	2nd L		3rd L	G	G	F	G	G	G
	G	G	F	G						
Quartz	+++	+++	T/+	+++	+++	++/+++	+/++	+++	+++	+++/++++
Feldspars	+/++	+/++	T	++	+/++	++	T/+	++	+/++	++
Mica	?	?	-	?	-	-	-	-	-	-
Pyroxene	T	T	-	T	T/+	-	-	T	-	T
Calcite	+++	+++	+++/++++	+++	+++	++	+++	+++	++/+++	++/+++
Gypsum	-	-	-	-	-	+	++	-	+/++	-
Halite	T	T/+	T/+	T	T	T/+	+	T	T	T
Hematite	T	T	T	T	T	-	-	T	-	T

+++ abundant, ++ present, + small amount, T traces, ? doubts in presence, - undetected
L – Layer ; G – Overall fraction ; F – Binder rich fraction

Table 4 Mineralogical composition of the stuccos assessed by XRD.

Crystalline phases	SB5	SB6	SB7	SB8		SB9	SB10
				1st L	2nd L		
Quartz	-	+	-	-	-	+	+
Feldspars	T	+	?/T	-	-	-	-
Calcite	+++	+++/+++	+++	+++	+++	+++	+++
Gypsum	+++	++	+++	+++	+++	-	-
Anhydrite	T	-	?	T	T	-	-
Halite	-	-	-	-	-	T	T

The stuccos, with exception of samples SB9 and SB10, are essentially made of mixes of calcite with gypsum; samples SB5, SB6 and SB8 present a calcite:gypsum ratio of aproximately 1:1.

3.2 Thermal Analysis

The TG-DTA analysis confirmed the XRD results, presenting for the lime mortar samples (Fig. 3a) an important weight loss in the range between 550 and 900 ºC, corresponding to the decarbonation of calcium carbonate. The gypsum-rich stucco samples (Fig. 3b) presented a typical weight loss between 25 and 200ºC, corresponding to the decomposition of gypsum.

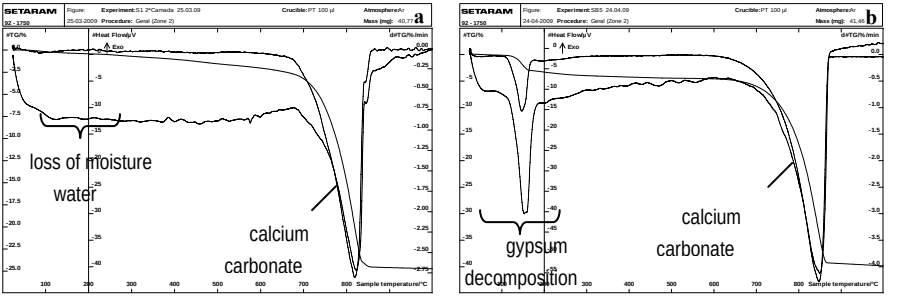

Fig. 3 TGA/DTA curves of: a) Mortar S1- 2nd Layer; b) stucco SB5.

3.3 Chemical and Grain Size Analysis

Mortar samples S1 and S2 were selected for chemical analysis because they represent the two groups of mortars in analysis. The chemical data (Table 5) confirm the XRD and TGA/DTA results and highlight the fact that sample S1 has a higher quantity of binder than S2. Additionally, mortar S2 is much richer in soluble salts, specifically chlorides and sulphates (gypsum as binder according to XRD).

Table 5 Chemical data (wt %) of the soluble fraction of mortars S1 and S2.

Sample identification	Insoluble Residue	Sodium (Na^+)	Potassium (K^+)	Sulphate (SO_3)	Chloride (Cl^-)	Soluble silica
S1	43.75	0.38	0.09	0.05	1.73	0.21
S2	58.48	0.57	0.14	2.67	2.99	0.17

The grain size distribution of the insoluble residues (siliceous sand), presented in Fig. 4, is very important for the production of compatible mortars for restoration works. These results revealed that the mortar S2 is mainly composed of aggregates with diameters between 0.315 and 1.25 mm, while sample S1 shows a more homogeneous grain-size distribution, which is related to its different composition and functionality.

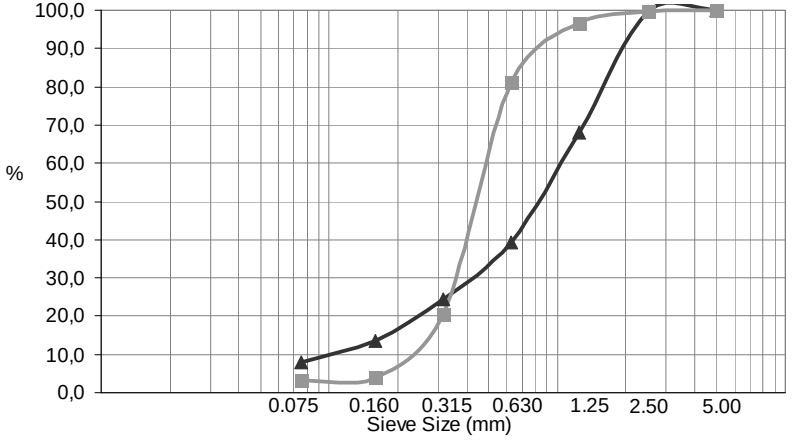

Fig. 4 Grain-size distribution of the sand of the mortars (a) S1 (▲) and (b) S2 (■).

3.4 Optical Microscopy Analysis

3.4.1 Stereo zoom observation

Impregnated polished sections were observed under a stereomicroscope. Observation shows that all mortars contain rounded lime lumps (Fig. 5), which could indicate that the lime was slaked with a minimum amount of water to convert CaO into $Ca(OH)_2$ [6, 7]. Both basaltic and siliceous aggregates are visible in mortar S1, while S2 presents only siliceous aggregates. All samples contain shell fragments, suggesting the marine origin of the aggregates.

All of the renders are covered by white stucco and decorated with a painting layer or with a *fresco* mural painting. The observation of render S1 shows the existence of an older painting layer (SP8), which was covered by the white stucco and a new painting layer. This layer structure seems to be an indication of an earlier intervention on the render, probably in the 19th century, since some artificial pigments, identified in the dome and applied in the same period, were synthesized only after the beginning of that century.

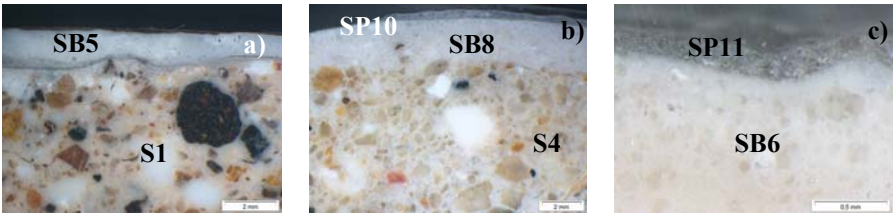

Fig. 5 Renders, polished cross sections, observation at stereo zoom microscope: a) S1 mortar and its stucco SB5; b) S4 mortar, with its stucco SB8 and the greyish painting layer SP10; c) Detail of the painting layer (SP11) and stucco SB6.

The microscopic analyses of the mural paintings samples reveal the use of a great number of inorganic pigments (ultramarine; azurite; iron ochres, red and green earths; gold leaf) as can be seen in Fig. 6. Clearly, the paintings originally consisted of a blue layer of natural ultramarine (*lapis lazuli*) [8], which was replaced more recently by other aesthetic solutions, probably because of its degradation phenomena.

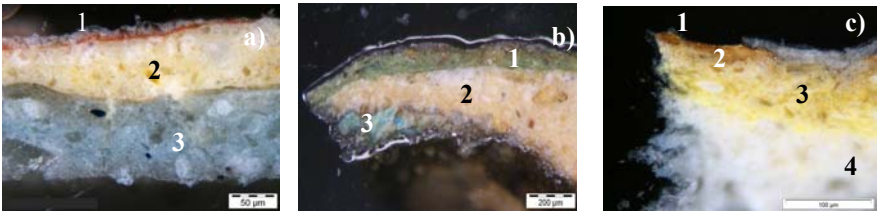

Fig. 6 Observation of polished sections of the mural paintings with stereo zoom microscope: a) SP1 with the superficial red earth layer (1), its preparation (2) and the oldest layer (3) which presents particles of natural ultramarine (*lapis lazuli*); b) SP5 with the superficial layer (1) of green earth pigment, its yellowish preparation (2) and the oldest layer of azurite (3); c) SP6 with the superficial thin gold foil (1), its adhesive (2), the yellow preparation (*bolos*) and the white preparation coating (4, usually made of gypsum) for the gilding.

3.4.2 Petrographic observation

The observation with petrographic microscope underlines that the siliceous and basaltic grains present a sub-rolled morphology, suggesting an alluvial origin of the aggregates. Moreover, reaction rims are evident around the basaltic aggregates (Fig. 7b), suggesting the occurrence of pozzolanic reactions between these aggregates and the calcitic lime. Such reactions create neoformation products, such as calcium-silico-aluminates, normally responsible for the improved mechanical resistance of these old mortars.

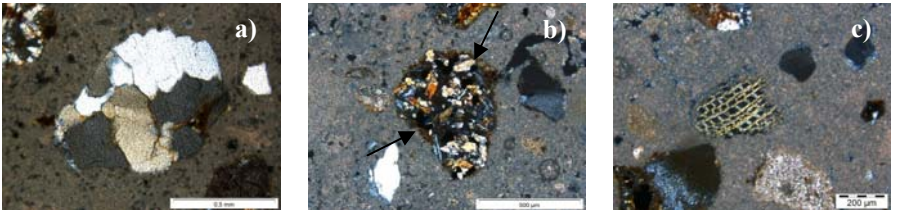

Fig. 7 Thin-section S1 mortar observation: a) Grain of quartzitic sand; b) Basaltic sand grain with reaction rim (interface aggregate/paste); c) Wood particle.

3.5 Scanning Electron Microscopy Analysis (SEM/EDS)

Mortars analysis with SEM/EDS showed that all mortars have a compact matrix, typical of old lime mortars, with aggregates well incorporated into the calcitic binder (Fig. 8b). In addition to the confirmation of the nature of the aggregates (Fig. 8b) and halite (Fig. 8a), it was possible to determine the presence of biological colonization [9]. The SEM analysis determined that the stuccos are composed of gypsum and calcite and identified the painting layer SP7 of mortar S1 as a lime-based painting with a red earth pigment.

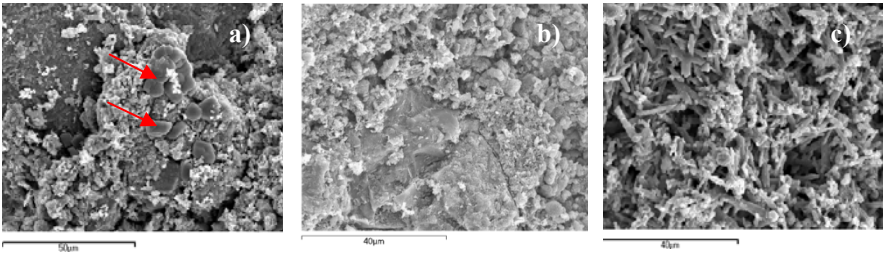

Fig. 8 SEM micrographs observed in the S1 render; a) halite crystals in the mortar; b) basaltic grain with neoformation products; c) detail of the stucco SB5 presenting a gypsum and calcitic binder nature.

3.6 Micro-FTIR

In order to identify the possible presence of organic compounds, namely natural additives or recent restoration products, micro-FTIR analyses were performed in mortars S1 and S4, which presented the highest weight losses by TG-DTA, in the range of 220 to 400º C. The results obtained (Figs. 9, 10) from the residue of the samples after extraction in ether indicate the presence, in remarkable quantity, of Paraloid B-72, an acrylic resin commonly used as consolidant and protective since the ’60s.

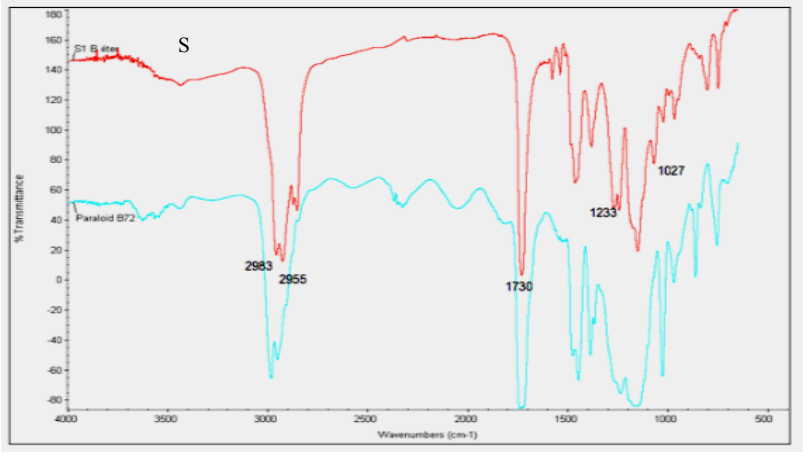

Fig. 9 Micro-FT-IR spectrums of the mortars S1.

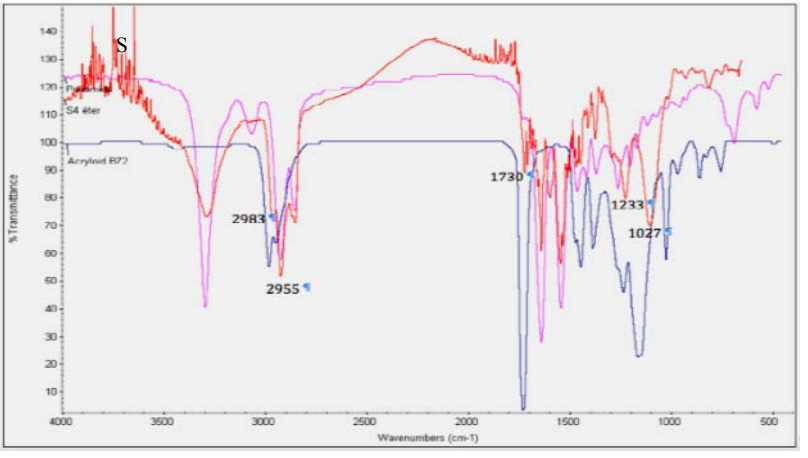

Fig. 10 Micro-FT-IR spectrums of the mortars S4.

Besides the Polaroid B-72, mortar S4 also contains a small quantity of a polyamide, not well identified. These results show that there was a restoration intervention in the internal renders of the church, which was probably executed during the last occupation of the convent (second half of the 20th century).

3.7 Physical analysis

After some preliminary *in-situ* analysis, additional physical and mechanical tests were performed in the most representative mortar samples. Table 6 reports the absorption capillarity coefficient and compressive strength of the mortars S1

and S2, including the assessment of the influence of the stucco (SB5) on the mortars S1's performance.

Table 6 Physical-mechanical results of analysed samples.

Samples	Capillarity Coefficient by Contact at 5 min (Ccc5) ($kg/m^2.min^{1/2}$)	Maximum absorption value (kg/m^2) (saturation time)	Compression Strength (N/mm^2)
S1+SP7+SB5	0.11	2.2 (>24h)	2.40
S1	0.89	0.3 (24h)	2.45
S2	1,54	0.3 (30min)	3.20
Reference mortar*	1.1-1.6	0.3 (>24h)	0.6-1.6

*Calcitic mortar prepared in laboratory (90 days)

As seen in Table 6, the lime-gypsum mortar S2 has the highest absorption capillarity coefficient, and the lime mortar with a stucco layer, sample S1, has a lower value. However, the compressive strength of mortar S2 is higher than that of mortar S1, and the presence of the stucco did not induce a variation in the mechanical resistance of plaster S1. These mortars do have good mechanical resistance, confirming the need to preserve and restore the existing plasters.

4 Conclusions

The results showed that the plasters are composed of several layers of a calcitic lime-based mortar, a stucco, and a lime-based mural painting. The mortars vary somewhat in composition: a first group (mortars S1, S3, S5) has a calcitic lime binder, with aggregates composed of siliceous and basaltic grains; a second group (mortars S2 and S4) has a binder composed of calcitic lime and gypsum and contains only siliceous sand. Moreover, the physical analyses emphasize that the first group of samples has a lower mechanical resistance and a lower absorption capillary coefficient compared with the second.

The presence of basaltic aggregates in the first group has facilitated pozzolanic reactions, improving the mechanical strength of these mortars. The lime-gypsum mortars of the second group are consistent with the spread of gypsum plasters for interior decoration during the Baroque and Neoclassic periods in Portugal [10]. All mortars present fragments of shell, which, given the sub-rolled morphology of the sand grains, are indicative of a marine origin of the aggregates. This feature can also explain the contamination by chlorides, probably due to the use of unwashed marine aggregates.

The stuccos are composed by gypsum and/or calcitic lime. The presence of anhydrite also was detected in stuccos SB5 and SB8, probably introduced to increase their mechanical resistance and workability.

The mural paintings are composed of many different pigments, such as ultramarine blue (both natural and artificial), yellow, red, and green earths, azurite and gold leaf, and prepared with various materials, including barite, lead white, gypsum, and calcite as binder media. Moreover, two different painting phases were identified: the first with more precious pigments (including the natural blue ultramarine – *lapis lazuli*), datable from the construction of the complex (17th century), and the second one with the strongest colours but the poorest materials (ex. natural earths), probably dating back to the 19th century.

The results obtained indicate that the mortars are in very good condition, with only superficial degradation. Notably, even gypsum-based plasters are in rather good condition despite water leakage through the church's roof during a period before the beginning of the present intervention. Hence, considering both the historic and artistic value of the building, the existing plasters were conserved and restored using materials with the same compositional and aesthetic characteristics.

5 Acknowledgements

The authors acknowledge the support of the National Laboratory of Civil Engineering (LNEC), where the experimental work presented here was carried out. They also wish to thank the technical support of Prof. José Mirão from the University of Evora in the petrographical analysis, Dr. Isabel Ribeiro and Dr. Sara Valadas from *Instituto dos Museus e da Conservação* (IMC) in the micro-FTIR analysis, and Dr. Dora Soares from LNEC in the chemical analysis.

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I.38

Air Lime Mortars with Vegetable Fat Addition: Characteristics and Research Needs

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Abstract Although history reveals that air lime mortars with added vegetable fat (ALVF) were used very often in the past, little knowledge about them survives to modern times. Little is known about the influence of fat addition on the mortars' durability, and some details about their manufacture and application are completely unknown. Even less is understood about the mechanisms that explain the behavior of ALVF-based mortars that also contain pozzolans. This paper reviews current knowledge about the characteristics of ALVF-based mortars in order to highlight questions that must be addressed in future research.

1 Introduction

The use of ALVF-based mortars dates back to the Roman Empire, as noted by Vitruvius [1, 2]. Portuguese architect Quirino da Fonseca published a book in the early 1990s, in which he mentioned the addition of small amounts of vegetable oil during the lime slaking process [3, 4]. He also mentioned that these materials were used by historic Portuguese masons to build fortresses, including Nossa Senhora da Conceição on Gerum island, Ormuz, in the Persian Gulf (Iran). The construction of that fortress took place in 1507 and comprised eight outer towers surrounding a central one.

In 1873, more than three hundred years after the construction of Nossa Senhora da Conceição, A.W. Stiffe, a lieutenant of the British navy, visited the interior of the fortress (Fig. 1) and described its conservation status for the Geographical Magazine. He stated that "*The mortar used was excellent, and much more durable than the stones* " [5]. This account provides a good impression of the durability of those mortars, primarily because they were placed in harsh conditions near the sea.

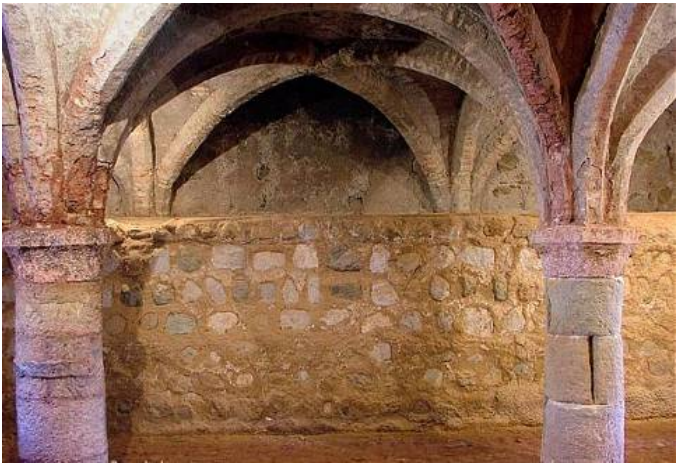

Fig. 1 Portuguese fortress of "Nossa Senhora da Conceição" (Persian Gulf, Iran)

In 1570, the Venetian architect Palladio, mentioned the use of linseed and nut oils to obtain waterproof lime-pozzolan mortars [6]. Manuel Azevedo Fortes, in his book "The Portuguese Engineer" published in 1729, mentioned the use of olive oil in the air lime slaking process, recommending that the olive oil should be added to lime while it is in a boiling state [4].

2 The Present

Since the middle of the 1990s a Portuguese manufacturer has sold an air lime called "D. Fradique" that is produced with the addition of olive oil waste. The production of this air lime started after the Portuguese architect Quirino da Fonseca was chosen to be in charge of the conservation works of the walls of the Castle S.Jorge in Lisbon. He then tried to reproduce the characteristics of ancient ALVF-based mortars. The firm responsible for the production of air lime uses a quasi-industrial process. After the calcination of limestone rocks they are ground in a jaw mill. The air lime is slaked by hand and the olive oil wastes are added at this time. Quirino da Fonseca recommends the following proportions to the manufacture of this air lime: 25kg of lime; 1.5kg of olive oil wastes; 10l of water. Of course the manufacturer uses other proportions that are under commercial secrecy [4]. The hardening of this air lime occurs by a carbonation mechanism, as with other air limes.

Table 1 Comparison between "D.Fradique" air lime mortars versus current air lime mortars [3]

Tests						Commercial air lime based mortars slaked with olive oil waste	Current air lime mortars
Mortar paste	Density (Kg/m^3)					1745	1999
	Workability (flow table %)					81	77
Hardened mortar	Apparent density (Kg/m^3)					1614	1783
	Watertight capacity	Vapor permeability	Vapor permeability coefficient (ng/m.s.Pa)			29.1	26.46
			Difussion layer thickness equivalent to a 1cm render			0.12	0.14
		Cappillarity coefficient (Kg/m^2.h^{0,5})				0.13	10.2
		a) Moistute test	1cm-1/2h	b) Wetting delay (h)		0	271.6
				d) Wetting intensity (mV.hx10^3)		0	60.21
			5cm-28h	Wetting delay (h)		38.69	146.02
				Wetting intensity (mV.hx10^3)		0.97	38.31
	Fungal development resistance					Medium	High

a) Moisture test: Measurement of electric current inside mortar layers. Mortar specimens possess 1.5cm thickness and are applied over a fiber-cement sheet. Then mortar specimens are submitted to a water film.

b) Wetting delay: Time between the moment that mortar specimens contact the water film and the beginning of water detection by moisture apparatus, which happens when electric current decreases to 95%.

c) Test time: Time between electric current decrease due to specimen wetting and the moment that electric current reaches 95% again.

d) Wetting intensity. Area below the curve of electric current, mV, with time.

According to some authors [4] the mortars made with commercial air lime slaked with olive oil wastes have several advantages over current air lime-based mortars (Table 1):

- Higher workability;
- Higher water vapor permeability
- Lower water absorption by capillarity
- Higher waterproofing behavior
- Higher resistance to fungal development

In a study of the behavior of several mortars used as renders for rock masonry, Sá [4] found that although mortars based on commercial air lime slaked with olive oil wastes are more waterproof than other mortars, they also have low impact resistance and low adhesion resistance (Table 2).

Table 2 Comparison of mortars properties [4]

Test	Mortars according to the binder used			
	Commercial air lime slaked with olive oil wastes (1:3)	Air lime	Hydraulic lime (1:3)	Air lime and cement (0.5:0.5:3)
Flexural resistance-Rt (MPa)	0.22	0.21	0.20	0.47
Compression resistance-Rc (MPa)	0.65	0.44	1.56	2.67
Rt/Rc	0.34	0.48	0.13	0.17
Impact resistance with a sphere Ø impact (mm)	18.6	20.7	12.6	11.8
Adhesion resistance (MPa)	0.048	0.056	0.057	0.129
Water absorption by Carsten tubes-10 min (cm^3)	0.1	36.1	2.1	3.1
Water absorption by capillarity (water mass after 5min - g)	2.22	23.92	9.66	8.57

The presence of the vegetable oil creates a less porous structure, which delays the carbonation process while also delaying the resistance development. Veiga [7] mentioned that the use of renders based on this particular type of lime may lead to some failures that can be explained by the carbonation delaying effect mentioned above.

Vegetable oils are composed of glycerides (esters of glycerol and fatty acids), which are not chemically stable in highly alkaline environments like cement

mortar. The carboxyl group of the fatty acid anion will coordinate strongly with calcium oxide in such environments [8].

Other authors [9] study the water-resistance of hydraulic binders mixed with vegetable oil fat. These authors mention that using just 0.5% vegetable oil by cement weight allows good mortar performance and that rapeseed oil is one of the cheapest and most effective oils, more so even than olive oil.

The majority of additives used to enhance waterproofing of concrete and mortars (resins and polymers) come from the oil industry [10]. Therefore, sustainable development requires that new environmental friendly additives must be investigated. It is not without irony that the past can teach us something in this area.

Holz [11] mentioned that one of the disadvantages of the use of mortar renders based on vegetable oils is that UV lights can oxidize the fatty acids, reducing the waterproofing ability near the surface. Cechova et al. [12] study mortars with 1% of linseed oil addition. These authors state that oil addition increases both flexural and compressive strength of hydraulic mortars, but for air lime mortars an inverse behavior was observed. Both mortars demonstrate a decrease in water absorption, but this effect is more profound for air lime mortars, for which water absorption is ten times lower.

More recent investigations [13] confirm that oil addition delays setting time because it slows down the penetration of water molecules to the grains of binder. Further, mortar performance is dependent on the quantity of oil used. The use of 1% linseed oil improves mortar strength, but when 3% is used air lime mortars exhibit a strength reduction. Results also show that oil addition improves resistance to salt and freeze-thaw cycles for both percentages [13].

3 Research Needs

Current knowledge about air lime mortars containing vegetable fat is an area with many gaps to be filled. It is important to know how the slaking process influences the properties and the durability of mortars. Although oil addition increases the mortar's resistance to water, that must be controlled in order to avoid water vapour reduction. The mechanisms for lime-pozzolan mortars with vegetable oil also deserve research efforts. It is important to determine whether the addition of oil during lime production oil influences the carbonation process, the pozzolanic reaction, or the formation of hydraulic phases. Different vegetable oils must be studied, in particular rapeseed soil, because it is a low cost additive in Portugal.

4 Conclusions

Air lime mortars with vegetable fat addition have been used since ancient times, apparently with very good results. The interest in these mortars has been revived for historic reasons but also for purposes of sustainability. The use of air lime mortars with vegetable fat addition still requires further investigation.

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I.39

Characterisation of Dolomitic Lime Mortars from the Benedictine Monastery in Riesa, Saxony (Germany)

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Abstract The binders of joint mortars and plasters used during several construction phases in the history of the Benedictine monastery in Riesa have been identified as dolomitic lime. Magnesite and/or hydromagnesite could be determined as the magnesium bearing carbonate phases beside calcite in the binder. Most of the mortars contain carbonate lumps, partially with altered silicate mineral inclusions, that represent remnants of the original structure of the late Palaeozoic dolomitic limestones which were used as the local raw material for lime production over the centuries. Low contents of aluminous silicates in the limestone might have contributed to the formation of hydraulic components and hydrotalcite, which has been determined by XRD in some of the samples investigated.

1 Introduction

The Benedictine monastery in Riesa, a city situated about 40 km north-west of Dresden at the river Elbe, was founded in the year 1119 and is one of the oldest buildings of its kind in Saxony. Several times in history it was destroyed and reconstructed. Most of the buildings were converted after secularization in the 16th century. The last restoration intervention dated from 1909. Large parts of the façade were in bad condition after another 80 years of exposure. The eastern wing, the dormitory of the former monastery complex, was thoroughly restored from the late 1990s onward. In the framework of restoration measures, investigations into the building's history made evident several construction periods from the Romanesque (13th century) until the early 20th century.

Mortar samples from historical plasters and joint mortars, assigned to different construction periods by the restorer, were taken at the eastern façade for

mineralogical characterisation (Table 1). The aim of this study was to derive information about the types of mortar used in different construction periods.

Table 1 Samples from the east façade of the eastern wing of the Benedictine monastery in Riesa (E - from the exterior, I - from the interior)

Sample number	Position	Construction period	Peculiarities
RIE-FM 1 (E)	Joint mortar from deep inside the base (gap in the stonework)	Early Gothic	Brownish mortar, no lumps visible in the binder.
RIE-FM 2 (E)	Joint mortar from the window jamb of the third window right of the main entrance, top floor	Romanesque	Light mortar, rich in binder; no lumps visible in the binder; crushed ceramics in the aggregate.
RIE-FM 3 (E)	Joint mortar, above first window to the north, top floor	Romanesque	Reddish mortar, rich in binder; occasionally white lumps.
RIE-PU 1 (E)	Plaster from the northern part, between first floor and top floor	Romanesque	Beige mortar, rich in binder; no lumps visible in the binder.
RIE-PU 2 (E)	Plaster from the northern part, between first floor and top floor	Romanesque	Light pink mortar, rich in binder; occasionally white lumps.
RIE-PU 3 (E)	Plaster from the first floor, northern part	Early Gothic	Beige mortar, rich in binder, no lumps visible in the binder.
RIE-PU 4 (E)	Plaster from the first floor, right of the main entrance	Renaissance / Baroque (?)	Beige mortar with quartz aggregate up to 5 mm, occasionally white lumps in the binder.
RIE-PU 5 (E)	Plaster from the first floor, right of the main entrance	Late 19th century	Beige-grey mortar with quartz aggregate up to 5 mm; occasionally light beige lumps in the binder.
RIE-PU 6 (E)	Plaster on bricked up Romanesque portal	1909	Light mortar, no lumps visible in the binder.
RIE-PU 7 (E)	Plaster from the top floor, right of the sixth window from north	Gothic	Light brownish mortar, rich in binder, without visible lumps.
RIE-PU 8 (I)	Plaster on window jamb, top floor, third window from south	Romanesque	Light mortar, rich in binder; occasionally white lumps.
RIE-PU 9 (I)	Plaster on window jamb, top floor, second window from south	Romanesque	Light beige mortar, rich in binder; no lumps visible in the binder.
RIE-PU 10 (I)	Plaster layer right below RIE-PU 9	Romanesque	Brownish mortar, rich in binder; occasionally lumps in the binder.
RIE-PU 11 (I)	Transition layer between joint mortar and plaster, right below RIE-PU 10	Romanesque	Light mortar, rich in binder, with quartz and rock aggregate up to 10 mm; occasionally lumps.
RIE-PU 12 (I)	Plaster from the top floor, left of the fourth window from north	Renaissance / Baroque (?)	Light mortar, rich in binder; no lumps visible in the binder.

2 Analytical methods

All samples were first examined under the stereo microscope. Part of every sample was used for polished thin sections, another for phase analysis of the binder using X-ray diffraction (XRD) and thermal analysis with combined Differential Thermal Analysis (DTA) and Thermogravimetry (TG). The pieces used for XRD and DTA/TG were carefully ground in an agate mortar; coarse aggregate grains were separated by sieving to get a concentrate enriched in binder. The binder concentrate was ground < 63µm for XRD and thermal analysis. XRD was performed with Siemens D5000 equipment ($Co_{K\alpha}$, 40 kV, 30 mA, 5-80°, step 0.02°, step time 2s), DTA/TG was performed with a Netzsch STA 409 PG (in static air, temperature range 25-1000°C, heating rate 10 K/min). Some of the thin sections were coated with carbon and additionally investigated under a Zeiss EVO 50 scanning electron microscope (SEM) coupled with a ROENTEC detector XFlash 3001 for elemental analysis by energy-dispersive spectroscopy (EDS). Results of chemical analyses were calculated as oxides. Due to artificial side effects resulting from the coating and impregnation of materials with organic resin during preparation, CO_2 contents were not determined. The presence of carbonate, however, is indicated by an excess of oxygen in the analyses concerned.

3 Results

3.1 Aggregate

Analysis of aggregates under the petrographic microscope allowed a survey of the aggregate used within the mortars during various construction periods. Grains with diameters below 2 mm (95-99%) dominate the aggregate of nearly all mortar samples investigated. Remarkable amounts of bigger grains (up to 10%) were only found in samples RIE-FM 3, RIE-PU 10, and RIE-PU 11. Most of the grains are sub-rounded to well-rounded, indicating an origin from natural sands. Quartz and fragments of polycrystalline quartz, porphyry, and occasionally volcanic tuff are dominant. Samples RIE-FM 2 and RIE-PU 8 additionally contain crushed ceramics. Slag particles were found in samples RIE-PU 5 and RIE-PU 6. The pink and reddish colours of some mortars are a result of the high amounts of red quartz in the aggregate (RIE-FM 3, RIE-PU 2).

3.2 Binder

Binders of the mortars were characterised by combined XRD and DTA/TG analysis (Table 2). XRD can identify crystalline phases but not amorphous

compounds; randomly ordered phases with low crystallinity and/or very small crystalline particles (< 0.1 μm) cannot be detected well, especially when their content in the sample is small [1]; as a result some phases could be found by DTA, but not by XRD analysis.

As can be seen from Table 2, all mortars contain both calcium carbonate phases and magnesium carbonate phases. Differentiation between the hydrous magnesium carbonates nesquehonite (N) and hydromagnesite (HM) can be problematic in thermal analysis, especially in the presence of gypsum [1]. Therefore, thermal effects between 200 and 550°C were generally assigned to "hydrous magnesium carbonate". Traces of crystalline HM were detected in two samples by XRD (RIE-PU 7 and 12), but no N was found. Hydrotalcite (HT) could be clearly detected in the XRD diagrams of some of the samples. Thermal effects of HT are superimposed by those of other compounds.

Table 2 Phases in the binder enriched fraction of mortars from the east façade of the eastern wing of the Benedictine monastery in Riesa (E - from the exterior, I - from the interior). ++ = dominantly present, + = present, (+) = possibly present, - = not detected. Components from aggregate (quartz, feldspar, mica) are neglected.

Sample number	Calcite		Aragonite		Magnesite		Hydrous Magnesium Carbonate		Hydrotalcite		Gypsum	
	XRD	DTA	XRD	DTA	XRD	DTA	XRD	DTA	XRD	DTA	XRD	DTA
RIE-FM 1 (E)	++	++	+	(+)*	-	-	-	++	+	(+)*	-	-
RIE-FM 2 (E)	++	++	+	(+)*	++	++	-	+	(+)	(+)*	-	-
RIE-FM 3 (E)	++	++	-	-	(+)	++	-	-	-	-	++	++
RIE-PU 1 (E)	++	++	-	-	-	(+)	-	+	-	-	++	++
RIE-PU 2 (E)	++	++	-	-	+	++	-	-	-	-	++	++
RIE-PU 3 (E)	++	++	-	-	-	+	-	-	-	-	++	++
RIE-PU 4 (E)	++	++	-	-	-	+	-	-	-	-	++	++
RIE-PU 5 (E)	++	++	+	(+)*	-	++	-	-	-	-	++	++
RIE-PU 6 (E)	++	++	-	-	-	++	-	-	-	-	++	++
RIE-PU 7 (E)	++	++	++	(+)*	-	++	(+)**	++	-	-	+	+
RIE-PU 8 (I)	++	++	-	-	++	++	-	-	-	-	-	-
RIE-PU 9 (I)	++	++	-	-	++	++	-	-	-	-	++	++
RIE-PU 10 (I)	++	++	-	-	-	(+)	-	++	-	-	(+)	(+)
RIE-PU 11 (I)	++	++	-	-	-	(+)	-	++	+	(+)*	-	-
RIE-PU 12(E)	++	++	-	-	++	++	(+)**	++	-	-	-	-

* Thermal effects superimposed by those of other more dominant phases ** hydromagnesite

Microscopic identification of single phases within the binder is impossible due to the very fine grain size. In most of the samples, however, the binder matrix contains carbonate lumps in the dimension of some 100 μm to some mm which appear darker and denser than the matrix with a fine-grained structure. Sometimes

they show internal structures with darker patches or small inclusions. Aggregate is not present within these lumps. Some of the lumps are criss-crossed by cracks which do not continue in the matrix. A typical example is shown in the photomicrographs in Fig. 1. As can be seen from the element mapping images and from point analyses with EDS, the lumps contain calcium and magnesium carbonates and very small inclusions (< 100 µm) rich in silicon and aluminium. Figs. 1d and 1f clearly demonstrate the spatial distribution of separate magnesium and calcium carbonate phases in the lumps as well as in the binder matrix. Some of the inclusions were investigated in more detail by SEM/EDS analyses. Examples are given in Fig. 2. Inclusions show a core with high silicon and/or aluminium contents, respectively.

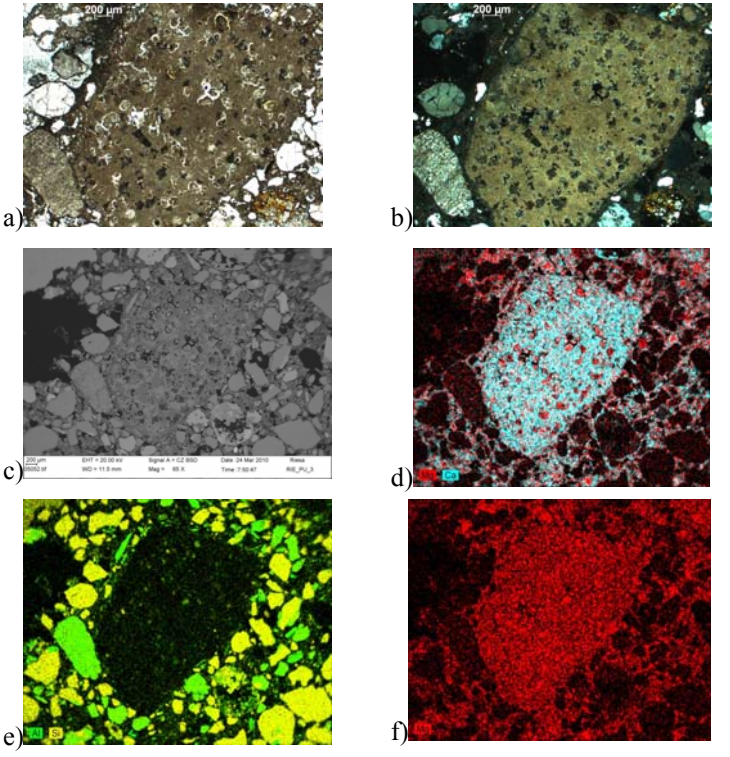

Fig. 1 Lump in the binder matrix of sample RIE-PU 3 (diameter > 3 mm) in photomicrographs from petrographic microscope (a - Nicols parallel, b - Nicols crossed) and SEM (c - back scattered electron (BSE) image, d-f - mapping of element distribution by EDS: d) Mg, Ca; e) Si, Al; f) Mg).

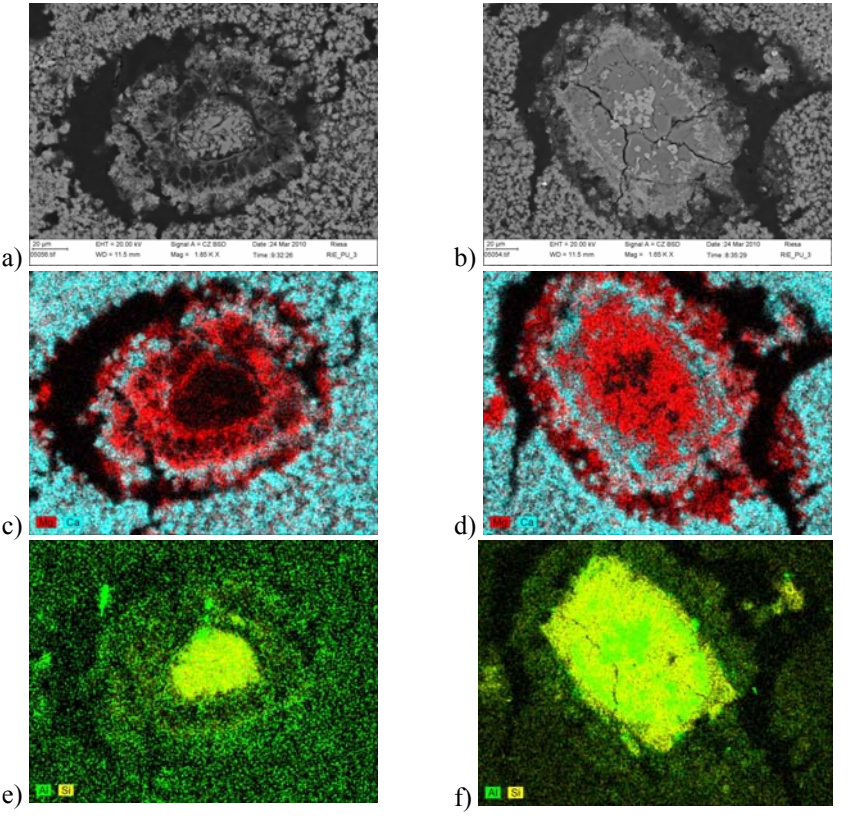

Fig. 2 Inclusions in the lump displayed in Fig. 1 (RIE-PU 3) at higher magnitude in SEM (a, b - back scattered electron (BSE) image, c-f - mapping of element distribution by EDS).

According to EDS analysis, the inclusion in Fig. 2a consists of 97 wt% SiO_2 in the core and 28 wt% MgO and 58 wt% SiO_2 within the inner rim. The inclusion in Fig. 2b contains SiO_2 (41 wt%), Al_2O_3 (28 wt%) and K_2O (27 wt%) within the core and high contents of MgO (40 wt%) and SiO_2 (51 wt%) and additionally Al_2O_3 (7 wt%) within the inner rim. The amount of CaO is low (< 1.7 wt%) in both the core and the inner rims. The adjoining outer rims show an alternating dominance of Ca and Mg phases, converting from silicates/alumino-silicates near the core to carbonates in the outer zones. The inclusions could be interpreted as silicate minerals (such as K-feldspar) from the raw limestone that have been affected by the burning process. The lumps may therefore be remnants of small dolomite pieces which, although calcined and slaked, i.e. chemically altered, still show patterns of the original petrographic structure of the raw material (fine-grained, with silicate inclusions).

4 Discussion and conclusions

Investigations into the binders of the 13th - early 20th century joint mortars and plasters from the eastern wing of the Riesa monastery have demonstrated the permanent use of dolomite or dolostone in local lime production over the centuries. It is thought that the dolomite was sourced from deposits of late Palaeozoic origin (Zechstein) located about 15 km south-west of Riesa.

The occurrence of magnesite (M) and /or hydromagnesite (HM) phases beside calcite (CC) in the binder are in good accordance with the results obtained from historical dolomitic lime mortars studied by other authors [2-5]. Brucite was not detected in Riesa although it is also known to be present in historical binders [4, 5].

The samples investigated in this study can be divided into three groups according to the type of magnesium phases in the binder:

1) Samples with only HM beside CC (FM 1) or very small contents of M (questionable) beside CC and HM (PU 10, PU 11). They come from the interior wall (PU 10, PU 11) or from inside the wall (FM 1).
2) Samples with both M and HM beside CC (FM 2, PU 1, PU 7, PU 12). These mortars come from the exterior; some of them contain gypsum.
3) Samples with M as the only magnesium phase beside CC (FM 3, PU 2 - PU 6, PU 8, PU 9). Most of these samples come from the exterior of the building. Samples PU 8 and PU 9 from the interior were taken from the window jamb that has been affected by external influences like rain. 7 of these 8 samples additionally contain gypsum as an indicator of chemical weathering due to environmental influences.

There is no relation between construction age of the mortars and the phase content of their binders.

As known from other investigations [6], behaviour of the magnesium phases during burning, slaking and setting of the lime is somewhat different from that of the calcium phases. After the de-carbonation of dolomite during burning, Ca and Mg form new spatially separate phases, i.e. hydroxides from slaking and carbonates from setting. Size and spatial distribution of the coexisting calcium and magnesium carbonates in the binder and in enclosed lumps are displayed in Fig. 1. Although the thermodynamically stable magnesium carbonate phase is magnesite [7], the occurrence of hydrous magnesium carbonates (HM, N) has often been reported from field studies as well as from laboratory investigations of dolomitic binders [2-6]. Samples in this study with only HM (group 1) come from sheltered positions and might represent the first stage of carbonation of the magnesium phase by the formation of amorphous, hydrous magnesium carbonate (brucite is absent). Samples from the exterior, which are exposed to long-term, intensive contact with the air and rain water, frequently contain only M beside CC.

Gypsum, formed through the chemical weathering (due to air pollution) of the plasters, is present within the majority of samples from the exterior and is also

evident as salt efflorescence together with magnesium sulphate on the building's surface.

The occurrence of M might indicate a "mature" stage of the development of the magnesium carbonate phase towards the stable state. This is in good accordance with the investigations of micro-scale profiles on Baroque dolomitic lime plasters at a façade in Altenburg (Germany) by Zier and Seifert [8]. These authors found differences in the phase content of the surface layer of the plaster (0-1 mm depth, with CC, very small amounts of M, and gypsum) and the adjacent deeper layers (2-5 mm depth: CC and M; 5-10 mm depth: CC and HM / M; > 10 mm depth: CC and HM). Further investigations are needed to elucidate possible interactions of magnesium carbonate and sulphate formation in polluted environments. Hydrotalcite, which was determined in three of the samples, might have formed through the reaction of magnesium with aluminous silicate compounds from the raw dolomite (Fig. 2) or from the aggregate.

5 Acknowledgements

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Characterisation of Ancient Gypsum Mortars from the Archaeological Site of Amathus, Cyprus

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Abstract The purpose of the present research work was the mineralogical, mechanical and microstructure characterization of the gypsum mortars sampled from the internal parts of the crepis (foundation) of the Aphrodite temple and the walls of the early Christian basilica from the archaeological site of Amathus, Cyprus. The project is part of the studies carried out by the French Archaeological School of Athens in view of a possible anastylosis of the temple. The tests included (a) wet chemical analysis for the oxide determination, (b) XRD analysis, with nickel-filtered CuKα radiation, (c) TG/DTA analysis in the range of 25-1000°C, (d) scanning electron microscopy coupled with microanalysis, (e) optical microscopy performed in thin sections in transmitted light and (f) mechanical tests for the determination of the tensile strength. The examined binders were composed by hydrous calcium sulphate ($CaSO_4 \cdot 2H_2O$) and small proportion of $CaCO_3$ and SiO_2, whose detection was attributed to their presence in the initial mineral gypsum.

1 Introduction

Amathus was one of the most ancient royal cities of Cyprus, on the southern coast, about 24 miles west of Larnaca and 6 miles east of Limassol. The ancient city of Amathus was inhabited since the 11th century B.C. and destined to become one of the leading states of the Cypriot Iron Age, no less powerful and prosperous than the Greek city kingdoms. It was a rich and densely populated kingdom with a flourishing agriculture, and it was important because of its port, from where it exported copper and timber. In the Roman era it became the capital of one of the four administrative regions of Cyprus. The dominant feature at Amathus is its acropolis, the upper city. The easily fortified hill was undoubtedly the site of the

original settlement and the home to the great goddess who protected it. Her original name is unknown, but by Classical times she was firmly identified with Aphrodite. In Late Antiquity (3rd-7th centuries AD), the temple was replaced by an early Christian basilica, but little remains apart from the foundations. Excavations in the area began in 1980 and continue by teams of Cypriot and French archaeologists, bringing to light the Acropolis, the temple of Aphrodite, the Market, the city's Walls, the Basilica, and the Port.

The study of ancient mortars is of great importance from an archaeological and technological point of view. Ancient mortars are an important source of information, and their analysis may give an indication of the composition of mortar mixtures used during the different periods, as well as their state of preservation. Mud, gypsum, and lime had traditionally been the three most common binder types during the construction history of mankind [1]. The binder glues aggregates and other particles together and provides adhesion to the substrate. Due to their physical or chemical reaction, binders play the major role in the final strength of the mortar.

Gypsum is a relatively easily mined rock, chemically known as hydrous calcium sulphate. When heated to approximately 130°C, part of the water is driven off according to the reaction

$$2CaSO_4 .2H_2O \rightarrow (CaSO_4). ½ H2O + 1.5H_2O. \quad (1)$$

When recombined with water, an interlocking crystalline structure of hydrous calcium sulphate ($2CaSO_4.2H_2O$) is re-established. The structure is made up of sheets of Ca^{2+} and SO_4^{2-} ions held together by hydrogen bonds in the water molecules.

The oldest use of burnt gypsum occurred in dynastic Egypt from 5000 to 3400 B.C. It was used along with Nile mud as mortar during building and as plaster of walls and floors in tombs [2]. About 2000 BC, the ancient Minoans built a sandstone-paved road extending from the southern to the northern coast of the island of Crete. The mortar used to affix the sandstone pavement was a clay/gypsum mixture [3]. It also was used in other countries in the Middle East and in medieval times for masonry mortars in the region around Lübeck in Northern Germany [4] and in the Paris region. In many cases, gypsum mortars placed between the carefully squared stone blocks were not actually used as joints, but mainly as filling material in order to accurately arrange stone blocks on the structure.

The use of gypsum in construction was known in Cyprus since Prehistory. Abundant reserves of this mineral are found in Cyprus and are nowadays an important product for export. Gypsum belongs to the geological formation of Kalavasos. In Cyprus, gypsum appears as laminated, i.e. in thin alternating layers, as laminated with concretions, and as selenite with twin crystals. [5].

Chemical examination of ancient gypsum mortars by Lucas [6] has shown that the ancient Egyptians never used lime until the Roman Period. Lucas explained

that gypsum was preferred over lime because of the scarcity of fuel. Gypsum was generally quarried in a very impure state and usually contained calcium carbonate. He also stated that the gypsum used was often impure and contained natural admixtures of calcium carbonate and quartz sand. Ghorab et al [7] analysed, by XRD, samples from the Gizeh Pyramids and from the Sphinx. The minerals identified were gypsum, anhydrite, calcite, and silica. Gypsum was predominant in the Sphinx. According to Regourd [8], the Cheops and Unas pyramids were built in 2500 and 2250 BC with mortar in which gypsum microcrystals occur as the product of the anhydrite transformation. Sabnis and White [9] found that the ultimate strength of gypsum mortar is based largely on the water-to-gypsum ratio and on the aggregate-to-gypsum ratio. They report that increasing the aggregate ratio from zero to 1.2 reduced compression strength by up to 50%. An increase in water ratio from 0.3 to 0.4 also reduced compressive strength by 27-34%.

2 Experimental

In order to obtain information about the Amathus mortars' composition, mortar samples were smoothly separated and sieved through ISO 565 series of sieves. This enabled estimation of the proportions of binder/aggregate within the mortar. The most significant fraction of the grain-size distribution, for the aim of this research, is that of <63 μm consisting mostly of the binder.

Chemical analysis of the principal components was carried out by attack with a sodium carbonate-borax alkaline flux and the subsequent analysis of the elements by traditional chemical methods.

The mortars' binders were characterized by a Nicolet 560 IR Magna Fourier transform spectrophotometer, in the range of 4000- 400 cm^{-1} with 200 successive scans. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector and with an attenuated total reflectance (ATR) unit. The spectra rationed against a potassium bromide (KBr) background. The ATR sampling compartment is a ZnSe crystal (refractive index 2.4) with an angle of incidence of 45° oriented horizontally. The size of the rectangular surface area of the ATR crystal is 60 mm × 10 mm.

Mineralogical analysis was carried out by X-ray diffraction (XRD), using a Bruker D8-Focus diffractometer with nickel-filtered CuKα1 radiation (=1.5405 Å), 40 kV and 40 mA.

TG/DTA analysis was conducted with a Setaram-Labsys thermal analyzer. Type S-thermocouple is used for temperature measurements in this instrument. The sample was placed in a ceramic crucible and heated from room temperature to 1200°C at a heating rate of 5°C/min using air as a medium under static condition. TG/DTA were done simultaneously.

The fragments-test method was used to estimate the tensile strength of the ancient mortar [10]. For that purpose, the installation of the Laboratory of

Reinforced Concrete at the NTUA was used. A small specimen of 40 mm x 20 mm x 28 mm was cut from the original piece, glued in a special mould using a strong epoxy resin, and subjected to direct tension.

Optical microscopy was performed on thin and polished sections. Thin sections were produced by vacuum impregnation of the selected sample with epoxy resin, followed by cutting, grinding, and polishing, until a final thickness of 20 μm was reached.

The microstructure of the mortar samples was evaluated by scanning electron microscopy (SEM) using a Jeol 6380 LV SEM. Experimental conditions involved 20 kV accelerating voltage using a backscattered electron detector. SEM was performed in polished sections. Microanalysis was performed by an Oxford INCA Energy Dispersive Spectrometer (EDS) connected to the SEM.

3 Results and Discussions

All the examined mortars presented a very dense structure, making the crushing process very hard. The direct tension test revealed a quite high value of tensile strength f_{tu}= 1.93 MPa. The mortars' apparent porosity was found equal to 25.3%.

The detected aggregates were very fine and they did not present well-defined edges. The chemical analysis of a typical mortar binder is given in Table 1.

Table 1 Chemical Analysis of a typical mortar's binder

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI_{1000}
Weight (%)	1.07	0.14	0.10	37.40	0.48	0.34	0.68	31.88	11.21

The examined mortars' binders are mainly composed of up to 38% of CaO and up to 32% of SO_3, whereas loss of ignition at 1000^{o}C is in the range of 11%-12%. The measurements also showed that silica and aluminium/iron oxide are found in very small proportion, rather as impurities and not as part of the binder. As a result, it is a gypsum mortar, which contains about 68.5% of $CaSO_4$ .2H2O.

The results of chemical analysis were confirmed by the mineralogical analysis. The X-ray diffraction pattern of a typical mortar binder is presented in Fig. 1. The presence of principal reflections at the d-spacings 7.5900, 4.27885, 3.0613, 2.8754, and 2.6830 Å and their intensity confirmed that the major phase of the sample is gypsum. The additional weak reflection occurring at the d-spacing 3.0289 Å also indicated the presence of a small amount of calcium carbonate. No detectable amounts of bassanite or anhydrite were present.

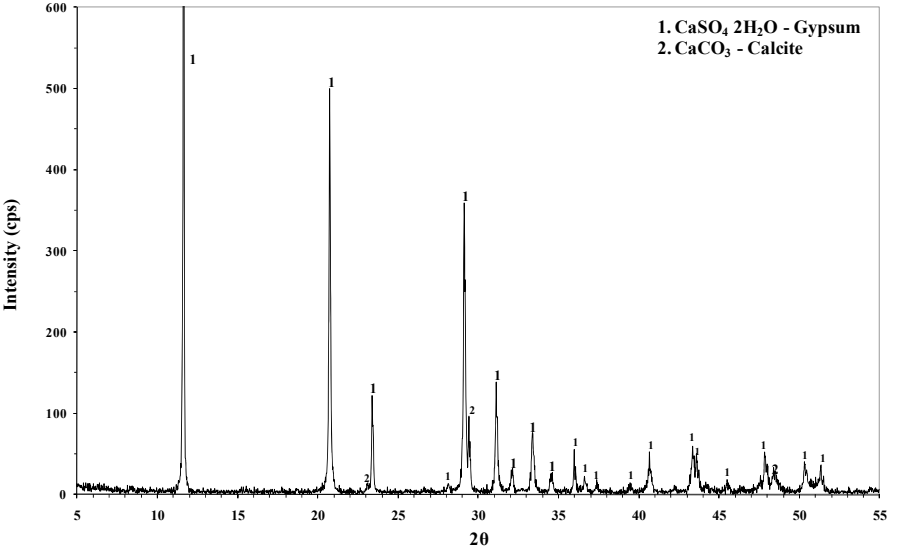

Fig. 1 X-ray diffraction pattern of a typical mortar binder

As mentioned above, the binder was produced after a thermal treatment (130-170°C) of mineral gypsum, which is dehydrated partially in order to produce hemi-hydrate. During hydration, hydrous calcium sulphate ($CaSO_4.2H_2O$) is re-established. The detection of $CaCO_3$ (10%) should be attributed either to the remains of the fine calcareous aggregates in the binder or to the presence of calcite as an impurity in the initial mineral gypsum.

TG-DTA analysis results are in agreement with XRD data. Fig. 2 illustrates removal of hygroscopic water at 100°C, followed by the water of crystallization during the transition to the hemihydrate form. The endothermic peak at 165°C, relates to the loss of 1.5 molecules of water from $CaSO_4.2H_2O$. The second endothermic peak at 190°C represents the loss of the remaining $1/2H_2O$ during the formation of $CaSO_4$. The exothermic peak at 380°C corresponds to the phase transformation from soluble to insoluble anhydrite. A small endothermic peak was also detected at 800°C, which was attributed to the presence of calcite (previously observed by XRD). Carbonates show distinctive endothermic peaks, whose position may vary depending on grain size, atmosphere, and other concomitant factors. They are due to the escape of CO_2 during the breakdown of their structure. Continued heating above 1100°C reduces the insoluble anhydrite to CaO and sulphur trioxide gas (SO_3).

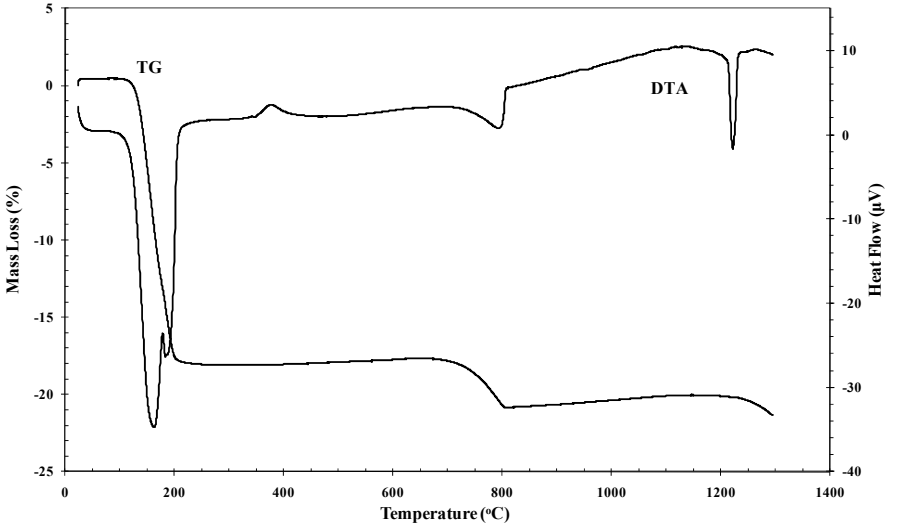

Fig. 2 T.G. and D.T.A. analysis of a typical mortar binder

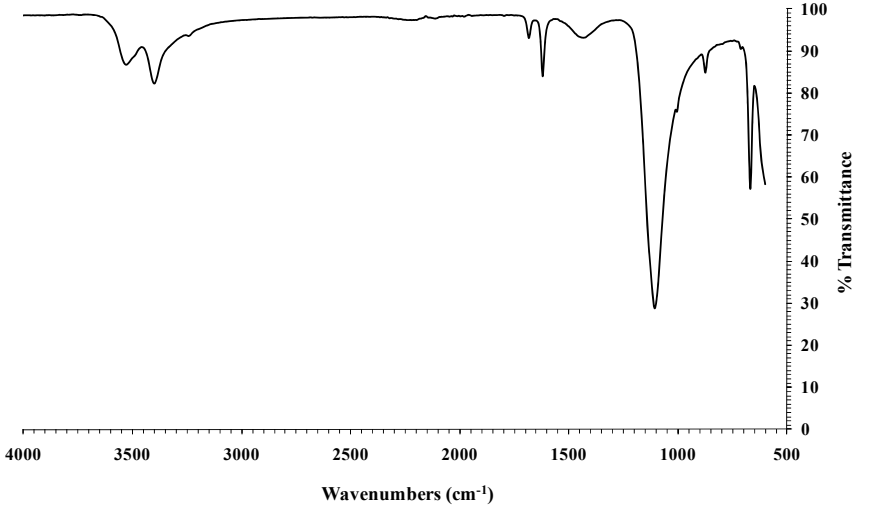

Fig. 3 FT-IR spectra of the examined mortar binder

Fig. 3 presents the FT-IR spectra of a typical mortar binder. The observed bands in the area of 3500 cm^{-1} attest the presence of water of crystallization. The ν3 and ν1 H_2O vibrations are detected near 3620 and 3400 cm^{-1}, but sometimes depend on the degree of hydrogen bonding in the mineral lattice. The two water-bending vibrations are observed at 1620 and 1682 cm^{-1}. The absorption taken

from the area of 1100-900 cm^{-1} corresponds to vibration of valence O-S. Fundamental sulphate vibrations occur for the sulphate ion due to symmetric (ν1, 981 cm^{-1}) and asymmetric (ν3, 1104 cm^{-1}) stretching. A strong doublet is observed near 600 and 670 cm^{-1} due to the ν4 $(SO_4)^{2-}$ bending vibrations. The weak band at 1460 cm^{-1} indicates the presence of carbonate species in the sample.

The morphology of the examined gypsum mortars and their association with calcite and quartz sand was observed under OM and SEM (Figs. 4, 5).

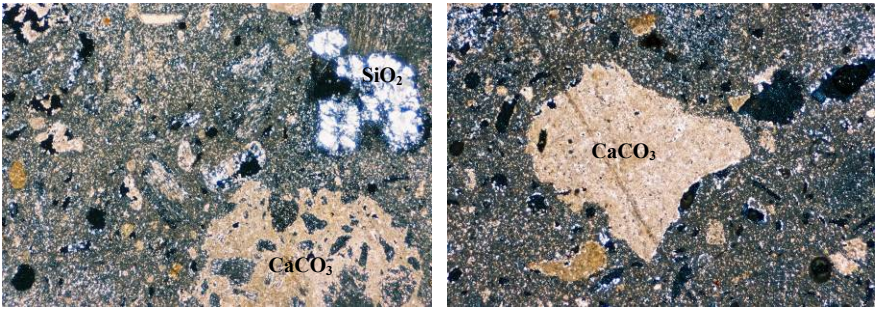

Fig. 4 Thin-section observation of the mortars. Gypsum matrix with calcite-quartz inclusions

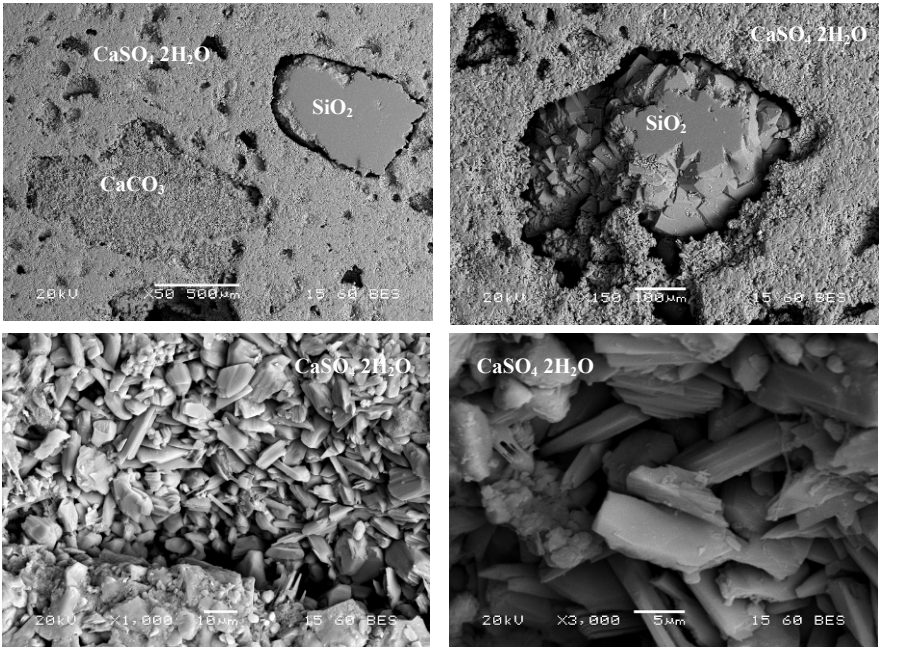

Fig. 5 SEM micrographs. Matrix of gypsum idiomorphic crystals with calcite-quartz inclusions

The white micritic calcite inclusions, as well as those of quartz, were easily distinguished in optical microscopic analyses. Analysis of the mortars by SEM/EDS showed that all mortars have a compact microstructure. Gypsum is the

most abundant phase. A tightly intertwined network of well-formed idiomorphic crystals and flaky particles made up of small crystals (10-20 μm) is observed. Nevertheless, the presence of microscopic cracks was noticed. These cracks were attributed to the initial shrinkage of the mortar. The porosity consists of small, interconnected pores with approximately 1 μm size and large spherical pores (>50 μm) formed by trapped air in the initial raw material powder. Calcite and quartz were observed in low proportion as inclusions inside the gypsum of matrix. Both inclusions did not present well-defined edges, a fact that confirmed the absence of crushed aggregates added in the initial mortar.

4 Conclusions

The mineralogical, mechanical, and microstructural characterization of the gypsum mortars sampled from the internal parts of the crepis (foundation) of the Aphrodite temple and the walls of the early Christian basilica from the archaeological site of Anathus, Cyprus, reveals that they are made of gypsum, which contains natural admixtures of calcite and quartz. Gypsum forms a tightly intertwined network of well-formed idiomorphic crystals and flaky particles made up of small crystals and shows a quite high tensile strength. Calcite and quartz were observed as inclusions, with not well-defined edges inside the gypsum matrix.

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Mineralogical and Petrographic Characterization of Ancient Roman Maritime Concretes from Mediterranean Harbours

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Abstract Eleven hydraulic concretes from ancient Roman harbours around the Mediterranean seacoast were drilled by the Romacons team in 2002–2009. In 2008–2009 the same team extracted three new cores from a reproduction of a Vitruvian concrete *pila*, cast in seawater at Brindisi harbour in 2004, and previously cored at 6, 12 and 24 months curing. New geochemical and mineralogical analyses of representative ancient mortars, and the concrete reproduction in Brindisi, are summarized here. In addition, the progress of the pozzolanic reaction in the various hydraulic concretes is evaluated, through compositional and microstructural examinations.

1 Drill cores from ancient Roman harbour concretes

Hydraulic, pozzolanic concretes, first developed by the Romans in the 2nd century BCE, were widely used in important harbour constructions along the Mediterranean seacoast. The excellent durability of these structures has allowed them to persist, intact, in seawater for 2000 years. The purpose of this paper is to summarize chemical, mineralogical and petrographic data for cores of Roman marine structures drilled by the ROMACONS group between 2002-2009 in eleven different harbours, and a historically accurate experimental *pila* cast under sea water in 2004 in the modern harbour of Brindisi [1, 2, 3]. The first group was drilled in 2001-2008 from harbours along the Italian peninsula, from the ports of

Claudius (POR.2002) and Trajan (PTR.2002) in Ostia Antica, Nero at Anzio (ANZ.2002), Cosa (PCO.2003) and Santa Liberata breakwaters (SLI.2003; SLI.2004) on the Tuscany coast, Baia (BAI.2006) in the Gulf of Naples, and Egnazia (EGN.2008) on the Adriatic coast close to Brindisi. The second group, drilled from 2005-2009, comes from more distant harbours, such as Caesarea Palestinae (CAE.2005) in Israel, Chersonisos (CHR.2007) in Crete, Alexandria (ALE.2007) in Egypt and, finally, Pompeiopolis (POM.2009), near Mersin, in Turkey. The microstructures and compositions of the ancient mortars and their aggregates were investigated with petrographic studies of 5x7cm "panoramic" thin sections, X-ray diffraction (XRD), and major element chemical analyses (Tables 1–4). The characteristics of the ancient concretes are compared with the Brindisi reproduction drilled at 6 (BRI.2005.01), 12 (BRI.2005.02), 24 (BRI.2006), 42 (BRI.2008), 60 months (BRI.2009) curing; new results from the 2008-2009 cores describe recent changes during the last two years of curing. These data begin to clarify the provenance of raw materials and the diverse concrete mix designs of the various harbours, which always include coarse tuff aggregate (*caementa*), lime hydrated in seawater, and vitric, pozzolanic volcanic ash, the *pulvis Puteolanus* of Vitruvius [4, 5]. Ongoing analyses are currently building on these initial results.

2 Concrete cores from Baia, Egnazia and Brindisi (2006-2008)

In 2006 ROMACONS extracted five cores from the sunken remains of harbour moles at **Baia** (BAI.2006.01), two *pilae* at Secca Fumosa (BAI.2006.03), and the submerged remains of Portus Iulius (BAI.2006.02, 04, 05) mainly from the first century BC [1, 6]. The coarse aggregate is mainly 10 to 15 cm-sized vitric-tuff, from local Phlegrean Fields deposits. The volcanic aggregate has sanidine and analcime, clay mineral as illite, zeolites (phillipsite and chabazite) and hydrotalcite. Mortars generally have dark vitric ash-tuff and pumiceous scoria, and phenocrysts (sanidine and augite). The cementitious binding matrix is mainly microcrystalline sparry calcite plus a very small amount of amorphous gel-like C-S-H. There are centimeter-sized dull white clasts, which are apparently lime that reacted to form tobermorite [7, 8], plus a little calcite, brucite and vaterite (tables 1, 2). These textures attest to different stages of lime dissolution. Porosity is lower than the other mortars, and the hydraulic index (defined as H.I. = (SiO_2 wt. % + Al_2O_3 wt. % + Fe_2O_3 wt. %) / (CaO wt. %.+ MgO wt. %)), is very high.

In 2008, ROMACONS drilled the large, tall pila near the north side of the ancient **Egnazia** harbour, on the Adriatic coast, near Brindisi, which is probably early Imperial in age, first century BC. The coarse aggregate is porous, fossiliferous grainstone, from the local 'Tufi delle Murge' Pleistocene calcarenite [9]. The mortar is granular, somewhat porous, and strongly enriched in pozzolanic materials. The tuff-aggregate consists of volcanic rock fragments, ash with subordinated pumiceous scorias filled by zeolites, sanidine and augite

phenocrysts, and local carbonate rock fragments. The cementitious matrix is composed mainly of amorphous gel-like C-S-H, with subordinate microcrystalline sparry calcite, and rare dull grains of reacted lime. In addition, XRD shows calcite, ettringite and tobermorite (Tables 1, 2). Porosity is very high as is the hydraulic index.

Table 1 Representative geochemical analyses of seawater ancient mortars, from Baia (Naples), Alexandria (Egypt), Chersonisos (Crete), Egnazia (Brindisi), and Pompeiopolis (Turkey), extracted by the ROMACONS group between 2006-2009. Symbols legend: S.S.: soluble silica; I.R.: insoluble residue; H.I.: hydraulic index.

Mortars	**Baia**		**Alexandria**		**Chersonisos**		**Egnazia**		**Pomp.**
Core:	Bai.06.1	Bai.06.2	Ale.07.3	Ale.07.2	Chr.07.1	Chr.07.2	Egn.08.1	Egn.08.2	Pom.09.2
Wt.%	-	-	3/1	-	Medium	Medium	Medium	Medium	-
L.o.i.	13.4	9.0	25.6	21.4	36.4	19.5	20.4	19.0	15.0
SiO_2	43.3	52.8	29.0	36.3	15.3	39.1	43.2	44.1	42.9
Al_2O_3	12.9	15.7	8.8	10.4	4.5	11.4	11.7	12.8	12.4
Fe_2O_3	2.3	3.0	1.6	2.2	1.2	2.3	2.3	2.2	2.7
CaO	17.7	2.1	26.9	18.6	24.8	9.6	7.7	10.4	17.9
MgO	1.8	6.0	0.8	2.4	14.5	9.6	4.0	0.7	1.1
SO_3	0.2	0.2	1.3	1.1	0.5	0.4	0.5	0.4	0.1
Na_2O	3.1	4.3	2.3	3.4	1.4	3.9	4.3	4.2	2.8
K_2O	4.8	6.2	2.5	3.1	1.1	3.4	3.7	4.1	4.4
SrO	< 0.03	0.1	0.7	0.4	0.0	0.0	0.0	0.0	0.0
Mn_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
P_2O_5	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
TiO_2	0.3	0.3	0.2	0.3	0.1	0.4	0.3	0.3	0.3
Cl-	1.5	1.1	n.d.	n.d.	n.d.	n.d.	1.4	1.4	0.4
$CaCO_3$	6.8	4.5	29.5	22.8	65.5	17.0	11.5	9	8.8
S.S.	15.7	0.8	14.1	9.7	0.8	2.5	2.1	7.3	17.3
I.R.	34.8	71.5	19.9	34.9	20.1	48.2	33.6	38.4	23.2
S.S./I.R.	0.5	0.0	0.7	0.3	0.0	0.1	0.1	0.2	0.7
H.I.	3.0	8.8	1.4	2.3	0.5	2.8	4.9	5.3	3.0

In May 2008 a fourth **Brindisi** core (BRI.2008.01) was drilled from the *pila* reproduction [3, 10], and a fifth core was drilled in November 2009 (BRI.2009) (Tables 3, 4). The cementitious matrix of the 2009 mortar shows very low birefringence, and an amorphous gel-like C-S-H apparently predominates. Paradoxically, the 2008 mortar shows a stronger evolution of cement textures, with two distinctive constituents: a densely opaque brownish matrix in plane polarized light (PPL), luminescent in natural light, probably composed of altered fine vitric ash-tuff, and a fine grained, 1st order birefringent microcrystalline cementitious phase. The mortar aggregate has numerous, still glassy, pumiceous

fragments of the Bacoli tuff, sanidine and augite. Traces of ash dissolution are widespread, sometimes associated with precipitation of birefringent cements. Mechanical compression tests on 2008 and 2009 cores give heterogeneous results, although there is a low increase in averaged strengths compared with 2006 [2, 3].

Table 2 X-ray diffraction of components of ancient mortars. Seawater cement phases include: Arg: Aragonite; Brc: Brucite; Bsn: Bassanite; Cal: Calcite; Clc: Clinochlore; Cbz: Chabazite; Etr: Ettringite; Fl: Fluorite; Gp: Gypsum; Hl: Halite; Hyc: Hydrocalumite; Hyt: Hydrotalcite; Phi: Phillipsite; Nordstrandite; Str: Strätlingite; Tbm: Tobermorite; Vat: Vaterite. Volcanic pozzolan (tuff pumice and lava fragments) includes crystal fragments and phenocrysts: An: Anorthite; Anl: analcime; Bio: Biotite; Di: Diopside; Hem: Hematite; Sa: Sanidine; and authigenic alteration components: Alb: Albite; Cal: Calcite; Cbz: Chabazite; Hal: Halloysite; Ill: Illite; Kao: Kaolinite; Phi: Phillipsite. Sedimentary sands and coarse aggregates include: Cal: Calcite; Qtz: Quartz; Mic: Microcline; Prg:.. Potassic-pargasite; Sa: Sanidine.

Specimen	Predominant Seawater Cements	Subordinate Seawater Cements	Pozzolanic Aggregate	Other Primary Aggregates	Notes
Bai.06.1-3	Cal, Tbm	Phi,Cbz, Hyt	Sa. Anl. Ill	–	Mortar composition
Bai.06.2-4	Cal	Phi, Cbz ± Hyt	Sa. Anl ± Ill	–	
Bai.06.1	Tbm, Cal, Vat ± Brc	–	–	–	Dull grains
Bai.05.1	–	Phi, Cbz	Sa. Anl. Ill	–	Tuff *caementa*
Ale.07.3/1-2	Cal, Tbm ± Etr	Phi	Sa	Cal	Mortar composition
Ale.07.2	Cal, Tbm ± Etr	Phi	Sa	Cal	
Ale.07.1	Cal, Tbm, Etr	Phi	Sa	Cal	
Ale.07.2-3	–	Hl	–	Cal, Arg	Gravel-sized aggregate
Ale.07.1	–	Hl, Brc	–	Cal, Arg	
Chr.07.1	Cal, Tbm	Phi	Sa	Cal, Dol	Mortar composition
Chr.07.2	Cal	Phi	Sa	Cal, Dol	
Chr.07.1	–	Hl	± Ms, Chl	Cal, Dol ± Qtz	Gravel-sized aggregate
Chr.07.2	–	Hl ± Brc	–	Dol. Cal	
Egn.08.1	Cal ± Etr	Phi, Cbz, Gp ± Hl	Sa. Anl. Ill	Cal	Mortar composition
Egn.08.2	Cal, Etr ±Tbm	Phi, Cbz, Gp ± Bsn	Sa. Anl. Ill	Cal ± Qtz	
Egn.08.1-2	–	Etr ± Hl	± Ill	Cal ± Arg	Gravel-sized aggregate
Pom.09.2 Top	Cal, Tbm	Phi, Cbz	Sa, Anl	–	Mortar
Pom.09.2 Bottom	–	–	–	Sa, Prg	Cobble aggregate
Pom.09.2 Bottom	–	–	–	Cal (stony coral)	Cobble aggregate

3 Concrete cores from more distant harbours (2005-2009)

New analyses regarding the concretes of the Caesarea Palestinae harbour [11, 12], the Chersonisos harbour in Crete [13], and a mineralogic-petrographic characterization of the Caesarea Palestinae concretes as compared with those of Santa Liberata [7] provide a foundation for evaluating the compositions of concretes and technical expertise of concrete engineers far from Rome [4].

In 2007, ROMACONS extracted four cores from submerged first century BC structures in the eastern harbour basin at **Alexandria**. Two cores (ALE.2007.01 and 02) were recovered from a thin bed of concrete within a single-use barge form at the base of Antirhodos Island [11]. A third core (ALE.2007.03) was taken from the largest of several large *pilae* extending south from the modern western breakwater. These concretes closely resemble those of Caesarea [12]. The coarse-size aggregate is composed of a bioclastic grainstone (Cal + Arg), probably the local eolianite limestone, while the fine-aggregate in the mortar is composed of fine vitric ash-tuffs, pumiceous scorias filled by zeolites, phenocrysts (sanidine and augite), and local carbonate rock fragments.

Table 3 Representative geochemical analyses of seawater reproducing Vitruvian mortar of Brindisi, cored by the ROMACONS team between 2008-2009. Symbols legend: S.S.: soluble silica; I.R.: insoluble residue; H.I.: hydraulic index.

Mortars	**Brindisi 2008: 42 months**					**Brindisi 2009: 60 months**			
Core:	Bri.08.1	Bri.08.1	Bri.08.1	Bri.08.2	Bri.08.2	Bri.09.1	Bri.09.1	Bri.09.1	Bri.09.1
Wt.%	Top.1	Top.2	Med.	Top	Bottom	Top	Med.1	Med.2	Bottom
L.o.i.	17.7	12.8	15.4	15.1	16.6	28.0	26.8	15.0	22.2
SiO_2	43.9	51.3	45.3	47.8	45.1	35.4	34.1	45.1	39.4
Al_2O_3	12.2	14.4	12.6	13.3	12.5	10.5	10.2	13.4	11.7
Fe_2O_3	2.9	3.4	2.9	3.1	2.8	2.1	2.1	2.8	2.4
CaO	12.2	4.8	13.0	8.7	12.0	14.4	17.3	12.2	14.0
MgO	1.2	1.2	1.2	1.0	0.9	0.7	0.8	0.9	0.9
SO_3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Na_2O	2.3	3.3	2.5	2.7	2.5	2.8	2.9	3.3	2.9
K_2O	6.4	7.7	6.1	7.1	6.4	4.6	4.5	5.9	5.0
SrO	0.0	0.0	<0.03	0.0	0.0	0.0	0.0	0.0	0.0
Mn_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
P_2O_5	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
TiO_2	0.4	0.4	0.3	0.4	0.4	0.3	0.3	0.3	0.3
$CaCO_3$	n.d.	n.d.	n.d.	n.d.	n.d.	3.5	6.3	5.0	7.0
S.S.	n.d.	n.d.	n.d.	n.d.	n.d.	9.9	11.7	9.0	9.2
I.R.	n.d.	n.d.	n.d.	n.d.	n.d.	35.1	30.5	49.4	42.1
H.I.	4.4	11.5	4.3	6.6	4.7	3.2	2.6	4.7	3.6

Table 4 X-ray Diffraction analyses of Brindisi mortar reproductions. See Table 2 for mineral abbreviations.

Specimen	Predominant Seawater Cement Phases	Subordinate Seawater Cement Phases	Pozzolanic Aggregate	Notes
Bacoli Tuff	Phi-K, Cbz-Ca natural rock cements	–	Anl, Sa	Pumiceous lithified tuff Phlegrean Fields
Bri.05.1 top	Cal, Vat	Hyc, Chm	Anl, Sa	Mortar composition
Bri.05.1 bottom	Cal, Vat	Hyc, Chm, Por	Anl, Sa	
Bri.05.1	Cal, Vat	Hyc	Anl, Sa	Binding matrix
Bri.05.1	Cal, Vat	Hyc	Anl, Di	Tuff pozzolan (pumice)
Bri.05.2	Cal, Vat	Chz-Ca, Phi-Na	Anl, Sa	Binding matrix
Bri.06.3	Cal, Vat	Phi-Na	Anl, Sa	Binding matrix
Bri.08	Cal, Phi-K	Cbz-Ca, Hyc, ± Hl	Sa, Anl, Ill	Mortar composition (six samples average)
Bri.08.1 top	Cal, Vat, Hyc	Cbz-Ca, Phi-Na	Sa, Anl, Ill	Binding matrix
Bri.08.2 bottom	Cal, Vat, Hyc	Phi-Na	Anl, Sa, Ill	Binding matrix
Bri.08.w1	Cal, Por	Vat, Hyc, Sjg	Cal, Por	White inclusion
Bri.08.w2	Cal, Vat	Hyc, Sjg	Cal, Vat	White inclusion
Bri.08	Phi-K, Cbz-Ca	Cal	Anl, Ill, Sa	Tuff *caementa*
Bri.09.C2	Cal, Vat	Hyc	Anl, Di	Binding matrix
Bri.09.C2	Cal, Por	Ett, Hyc	-	White inclusion

The cementitious binding matrix has a pervasive sub-millimetric sparry calcite, plus microcrystalline ettringite, and amorphous gel-like C-S-H. Furthermore, XRD shows pervasive tobermorite cement, as well as dull white, microcrystalline inclusions, with tobermorite assemblages. Round pores in the mortar are filled by zeolites with a "rosette-like" morphology. Porosity is generally high, while the hydraulic index is very low (Table 1). The tuff has sanidine, augite, and authigenic phillipsite, apparently compatible with Phlegrean pyroclastic deposits.

Two cores were recovered from the first century BC/AD breakwater at **Chersonisos** harbour, also in 2007. The mortar of core CHR.07.01, from a submerged *pila*, is very crumbly, and poor cohesion caused much of the core to grind away. The porous mortar, appears to be low in lime (Table 1), either because of an originally lime-poor mix, or because leaching, increasing porosity, and erosion hastened its decay. The mortar fabric appears poorly sorted and mixed, and includes fairly large chunks of tuff up to 2.8 cm, large voids where a crumbly black material has fallen out, and clusters of dull white nodules, apparently hydrated lime clasts, ranging from 2–4 cm. Core two (CHR.07.02) comes from a quay wall, exposed above the waterline. It has a very porous, poorly compacted,

and incoherent granular mortar, also perhaps poor in lime. Dull white nodules, 4–25 cm are widespread. Petrographic examinations show that the amount of the tuff-aggregate in the mortar is very low, and is partially replaced by red-bricks of *cocciopesto*; in addition the general appearance suggests a lower level of pozzolanic reaction than in the other mortars (Tables 1, 2). Overall, pumiceous scorias, sanidine phenocrysts, ash-tuff with zeolite fillings, and carbonate rock fragments form the fine aggregate. The cementitious binding matrix is essentially amorphous gel-like C-S-H, with subordinated sparry calcite, ettringite, and rare white dull grains of tobermorite, apparently derived from hydrated lime. The volcanic aggregates show sanidine plus phillipsite, which are compatible with the Phlegrean vitric tuff deposits. Total porosity is the highest, and the hydraulic index is one of the lowest.

In 2009 ROMACONS extracted two cores from the west breakwater of **Pompeiopolis** harbour, whose age is not well known. The top surface of the mole is currently above sea level, so it was possible to drill the complete height of the structure. Core POM.2009.01 has friable mortar and hard, closely packed, riverbed cobbles and pebbles, ~5–20 cm in diameter. The poorly compacted mortar presents many voids and large dull white nodules, along with pumice clasts and green sand. In contrast, the POM.2009.02 core has a very hard, well mixed, hydraulic mortar, containing vitric fine tuff-aggregate with fragments of pumiceous scorias filled by zeolites, volcanoclasts, shards, sanidine, analcime and augite phenocrysts, similar to Phlegrean Fields vitric tuff. Petrographic examinations of coarse aggregate show the presence of amphibolite metamorphic rocks (Sa + Prg), stony corals, and travertine. The cementitious binding matrix is commonly birefringent and has microcrystalline sparry calcite, plus subordinated amorphous gel-like C-S-H, and frequently dull clasts of reacted lime. XRD analyses on dull grains indicate the presence of calcite and tobermorite. Both Pompeiopolis cores have a large proportion of coarse aggregate relative to mortar, ~64–54%, while this proportion ranges ~40%–60% mortar in the concrete sampled at sites along the Italian coast, and Alexandria and Caesarea.

4 Conclusions

Introductory chemical, mineralogical, and petrographic analyses of the hydraulic mortars of maritime structures from numerous ancient Roman harbours indicate that all contain distinctive pumiceous vitric tuff pozzolan with sanidine, apparently from Phlegrean Fields pyroclastic deposits, the *pulvis Puteolanus* of Vitruvius [1, 4]. However, the proportions of the vitric tuff used as mortar pozzolan vary. This is the predominant pozzolan at harbours of the Italian peninsula near Naples, such as Baia, Anzio, as well as Ostia [8]. However, the tuff forms a smaller fraction of the total mortar aggregate in other harbours, as at Alexandria, Caesarea, and Chersonisos. Here, the mortar contains limestone

aggregate, and at Egnazia, limestone, with occasional ceramics, as well. These compositions suggest that the Roman concrete engineers strove to include some measure of the tuff in the mortar and concrete formulations. The coarse aggregate varies as well, from Phlegrean tuff at Baia, for example, to predominantly limestone at Alexandria and Caesarea, dolomitic limestone at Chersonisos, and to river cobbles of diverse petrographic composition at Pompeiopolis. The microcrystalline cementitious matrix is often associated with gel-like C-S-H, and white dull residual grains of hydrated lime show progressive stages of dissolution.

Further analytical work will clarify the diverse aggregate compositions and their influence of pozzolanic cement development and durability.

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Gravel Lime? Research into Danube Gravel as the Main Ingredient of the Historic Mortars at Castle Prandegg in Upper Austria

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Abstract Lime was, aside from clay, the main historic mortar material for castles in the northern part of Upper Austria. As there are no geological sources of limestone in the region, the question posed was - how were the necessary amounts of quicklime produced and transported? The assumption that the source of the historic quicklime could be burned Danube pebbles arose as results of analyses on the historic mortar samples from the castle ruin of Prandegg showed constant slight impurities of magnesia/silica and non-burnable pebbles with glass-like surfaces in the cores of the ruin walls. The hydraulic properties of the mortars could be traced to the mixture of limestone and quartz pebbles common in Danube gravel. A complete reconstruction of the historic mortar of Prandegg was performed by burning Danube river gravel as part of an archaeological experiment. During the slaking all burned limestone pebbles completely turned into a homogeneous lime putty. The reconstructed "Danube gravel" lime mortar was then confirmed as the historical source as it showed, aside from the magnesia and silica phases, a general similarity to the historic mortar in its chemical and physical structure.

1 The thesis of "Danube gravel lime" in Prandegg

1.1 Historic mortar and geological sources of limestone

Lime is the most common binder for the construction of historic stone walls of the castles in the region of "Mühlviertel" (which is the northern part of Upper-Austria) and was (aside from clay) the only material from which a stable mortar and plaster could be formed.

The problem raised by the use of lime is that there are no bedrock sources of limestone in the region at all. The geology of the area consists of granite, sand and clay. Deposits of limestone are found about 50 km south of the river Danube in the regions near Molln and Reichraming at the so called "Reichraminger Back-mountains", where limestone is still mined today (for example: the Röfix Company in Molln). This posed the question - how could such a large amount of quicklime be transported over such a distance (about 80 km) to Prandegg?

Some evidence about the origin of lime in the Mühlviertel-region was found by Götting and Grüll in their book [1] about the castles of Upper Austria, published in 1956. Here in just a few sentences the search of limestone-chips on the gravel-banks of the river Danube is described, where the tributaries Salzach, Traun and Enns, which originate in the limestone-mountains near Molln, carry limestone-gravel to their estuaries. There is a record from 1650 that for the building of the castle Windhaag near Perg, Danube quicklime was burned in the small village of Au at the Danube. This village is less than 30 km away from Prandegg, so it seemed likely that for the castles of the nearby Mühlviertel-region, Danube gravel was calcined there. Some of the lime-kilns burning the Danube gravel remained active until WW2. One, at Pulgarn at the Danube, was in use until the construction of a dam which flooded the area in 1945.

Danube gravel generally contains a lot of different limestones; the tributaries with limestone carrying sediment bed-loads in particular display a large amount of limestone variation. In the case of the historic lime-kiln of Au at the Danube, the limestone would be sourced from the rivers Enns and Traun and their headwaters, the Steyr, the Laussa-stream, the Krems-stream, the Reichraming and the Krumme Steyerling, which all carry limestone-gravel from their origins in the Limestone Alps of the Reichraminger Back-Mountains, the Ennstal-Alps, the Sengsen-Mountains or the north side of the Dead-Mountains (fig.1). This, combined with the fact that the percentage of burnable material carried by the rivers is remarkably high, was most likely why a lime factory was situated there. Today this site is the location of the Brandner gravel processing plant. The manager Josef Schwarz, recalled stories from his predecessor who told him about the gravel burning traditions of his childhood. He also gave a lot of information about the consistence of the pebbles in the Enns estuary, and doubted the possibility that unsorted gravel from other Danube regions could be suitably burnt due to their high amount of quartz stone. He said, that during the spring-floods in the Enns-estuary the so called "Alte Haufen", ("old huddles") were washed into the Danube every year and were said to consist almost completely of different limestones; which therefore meant that they could be used without sorting.

Taken samples and the comparison of gravel from the headwater of the Reichraming and the Danube-estuary at the gravel plant Brandner showed an astounding similarity in their geological structure.

Fig. 1 Location map of the geological limestone sources and rivers in Upper Austria

Fig. 2 Different limestone rubble samples from Upper Austria
Below-the pebbles of the gravel plant Brandner at the Danube, *above left*-gravel from the Enns river in the mountains near Großraming, *above middle*-rubble from the Reichraming stream at its estuary in the Enns and *above right*-the material from a headwater of the Steyr near Schmidleithen near Obergrünburg.

A picture of the different rubble samples is provided in Figure 2. Results show that nearly all the material consists of different variations of limestone and marble, namely Wetterstein limestone, shallow water limestone, dolomite, coral rag, marbles, flysch limestone, gravel limestone and shelly limestone.

The headwaters, which transport the limestones from the cliffs of the Limestone-Mountains to the Enns, show nearly no crystalline stones. In the Danube gravel, aside from the clearly recognizable material of the Enns itself, some non-lime-based stones such as white quartzite can be found. These pebbles consist mainly of quartz and look similar to white limestone chips when they are dry. The Danube gravel here shows a mixture of the transported limestones of the Enns and the quartz and granite chips from the upstream regions of the Danube. This may be the reason for the diverse composition and physical characteristics of the historic mortar in Prandegg when compared to modern pure lime putty. Because of the different stones and lime variations in the burning material, it seems possible that this could cause additional hydraulic qualities in the mortar when hardening.

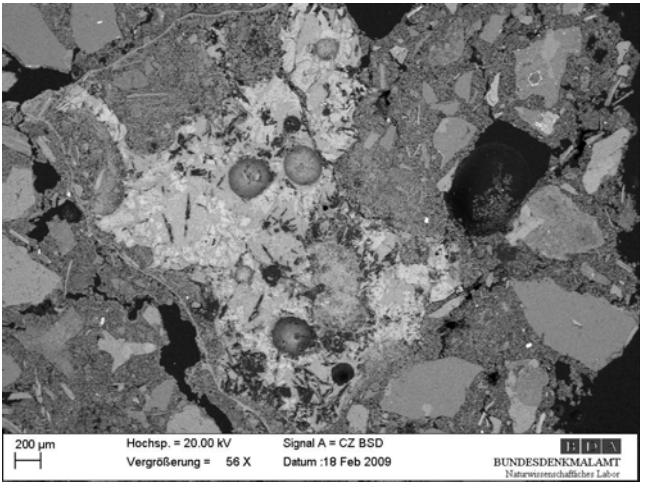

Fig. 3 Thin section of Prandegg mortar at field 1[2]

A laboratory analysis of the historic mortar samples from Prandegg showed constant slight impurities of magnesia and silica in the pure calcium carbonate "*Kalkputz mit geringem, natürlichem Anteil von Si und Mg*", which, according to Dr. Pintèr, a chemist from the BDA laboratory [2], could be caused by the calcification of the different gravel materials. Nearly every mortar sample from Prandegg shows a certain amount of magnesia and silica in its chemical composition.

Because of the very specific characteristics of this material, it cannot be compared with the modern hydraulic lime mortars, trass, natural hydraulic lime (NHL) or even hydraulic lime (HL), which lead to a much harder and denser

mortar structure; instead it has to be considered as an independent variation of historic lime mortar, the so called "gravel lime" mortar. A comparison to the modern lime putty used in 2005 at Prandegg showed exactly this lack of magnesia and silica, which could be an answer to the durability problems of modern lime mortars when used for the repair of layers in historic buildings.

Fig. 4 Partly calcined gravel chip in the core mortar of the tower at Prandegg

Further evidence for the theory of Danube gravel as the source of quicklime showed up recently during various inspections at the ruin itself. Burned Danube pebbles were found directly in the core of the historic walls (fig.4). These pebbles are mostly silica stones which show a glass-like layer on their surface. This was likely caused by the heat of kiln as the silica pebbles were not removed prior to burning and so were burned and slaked with the limestone. Another pebble, found in the mortar of the watchtower, was clearly identifiable as a partly burned limestone river pebble with a rough burned outer shell. As a result all gravel that is seen in the mortar during restoration works or inspections is being kept and documented.

1.2 The reconstruction of the Danube Gravel lime

Immediately after the first evidence of gravel as the original source for the mortars of Prandegg became apparent, an idea was proposed to burn Danube rubble as an archaeological experiment to directly confirm this theory. In the beginning there were doubts as to whether it would be possible to get the right gravel material, because the sediment banks of the "Alte Haufen" ("old huddles") in the Danube no longer exist after the introduction of river regulations and the building of dams; however the gravel plant Brandner offered gravel dug directly

out of the riverbed at the estuary; this gravel is removed from the riverbed to deepen it for shipping purposes and provided the correct material for the experiment.

Fig. 5 Burning Danube gravel in 2009 with Dr. Karl Stingl and Mr. Vösenhuber

A total amount of one cubic meter of Danube gravel was taken to Mauerbach, where the Bundesdenkmalamt (office for the preservation of monuments) built a historic field kiln to burn a certain amount of limestone every year (fig.5). This oven was constructed according to historical archetypes and was fired constantly for three days with wood as a sole fuel source to allow the burning temperature and procedure to be as similar to that of the medieval times. Before filling the oven, all the gravel chips were sorted, documented and if possible determined and named by the geologist Karl Stingl from the University of Graz. Here a variety of different burnable limestones, such as Wetterstein lime, black lime, red lime, shallow water lime, grenoide, jura lime and dolomite, along with a few non burnable quartz-pebbles, were identified. The possibility existed for the quartz to cause a hydraulic effect (2CaO.SiO2) similar to the silica processes of modern NHL (3CaO.SiO2).

Once sorted about 0.3 m³ of gravel chips were placed in the oven. Restorer and lime burner Hannes Weissenbach doubted the success of the experiment as he thought the burning process would be too short to completely burn the more dense pebbles and that the amount of non-burnable “deaf” stones would be over 60%. For this reason the examination of the quicklime after the cooling of the kiln was even more exciting, although the much lesser weight of the quicklime-gravel was already very promising. Once cooled, the first slaking of a typical lime pebble was immediately conducted; results showed an instant vigorous exothermic reaction and the transformation of the gravel pebble into very homogeneous lime putty after only a few minutes (fig.6). It must be said, that the slaking reaction differs

clearly from that of normal modern quicklime, as the reaction changes between phases of high and low activity and the heating of the putty is lower, barely reaching boiling point.

Fig. 6 Three burned Danube pebbles starting their slaking reaction. The pebble on the left is a silica quartz and shows a glass-like surface like the one found in the core of the walls. Like the brown silica based sandstone below it will not slake and remain as "deaf" stone in the mortar.

This lime putty was immediately tested as a slurry in a test field at Prandegg and as a series of test-cube moulds. Here the gravel-lime showed a very soft and light consistence that was very easy and comfortable to work with. The first significant amount of gravel quicklime (about 10 kgs) was slaked this year at the ruins of Prandegg during the annual restoration works. There the different pebbles were slaked first individually and then together. Interestingly, all the quicklime pebbles slaked completely although each had a very distinct reaction. Even the Wetterstein limestones, which were classified as non-burnable by many experts, showed an intense reaction and were completely transformed into a lime putty. The significant percentage of silica sand in the limestones simply became part of the mixture; only the pure silica stones didn't change and remained as they were. They showed the typical glass like surface, which was also found on the pebbles in the historic mortars of the 15th century; providing further evidence for the gravel lime theory.

2 Conclusion

The mixture of the different quicklime pebbles turned into a very specific lime putty, which has in spite of its percentage of sand from the Wetterstein lime, a very smooth and soft consistency. The colour ranges from a yellow to a slightly red grey and differs clearly from the bright white of modern lime putties. When kept in an air proof bucket, the first hint of hydraulic hardening through reactions between the quartzite, dolomitic magnesia and silica, became evident as a jelly like mass on the floor of the bucket which gradually hardened and may continue to do so, without any contact with air or carbon dioxide.

The "Danube gravel lime" was confirmed through laboratory analysis as the source of the Prandegg mortars as it showed in the microscopic examination, aside from the magnesia and silica phases, a "*general similarity to the historic mortar in its chemical and physical structure*"[3]. The newly made mortar was used as a repair mortar in Prandegg for filling the washed out wall layers in a test field, which will, together with the test cubes, show how durable and weatherproof the mortar will be under field conditions.

The next step of the research will be to burn the pebbles again at the laboratory, where a reconstruction of the calcification process under laboratory conditions should show the exact chemical and physical reactions of the different limestone pebbles. The history of gravel-lime burning in Upper Austria will also be the topic of future papers and research.

3 Acknowledgements

This article is based on the paper "Dreckiger Kalk" (Dirty Lime) which can be downloaded from the author's homepage:
http://www.wacha.info/wacha_robert_transdata_1.html

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13. „*Zusammenfassend kann festgestellt werden, dass beide Proben sowohl morphologisch als auch in chemischer Zusammensetzung einander ähnlich sind* „ Pinter F (2010) Untersuchungsbericht Nr. 35/10 ‚Burgruine Prandegg, Abt. Konservierung und Restaurierung Bau- und Kunstdenkmalpflege- Naturwissenschaftliches Labor des Bundesdenkmalamtes, Arsenal, Vienna

I.43

19th Century "Novel" Building Materials: Examples of Various Historic Mortars under the Microscope

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Abstract Starting in the late 18th century, the age of industrialisation brought about a huge number of new technologies, amongst which novel binder systems of hydraulic nature were meant to answer the demand for improved mortar strength even at moist conditions. Such mortars form an important part of our today's architectural heritage and are therefore frequently encountered either as primary materials or as historic restoration mortars, when historic objects are studied in the course of restoration. Their proper identification, a prerequisite for any sound diagnosis and therapy, may be complicated by the fact that those building materials later on either ran out of use, or developed into more modern systems. The paper deals with the basic features of a choice of those cementing materials which were "novel" at their time: Sorel cements, iron hammer scale mortars, and natural Roman as well as early Portland cements. The analytical approach followed is based on light and scanning electron microscopy, believed to provide primary tools to identify the mortars and to understand some of their key properties.

1 Methods

Samples were studied on thin sections and polished sections by means of polarising microscopy (PM) at transmitted and incident light. The same sections were eventually observed by scanning electron microscopy (SEM), using back-scattered electron (BSE) facilities. Several instruments were employed both at high and at low vacuum, thus no apparatus specifications are given. In all cases was energy-dispersive X-ray systems (EDX) used for chemical analyses.

Microstructures of the matrix of a sample were studied preferentially on fresh fracture faces, using both secondary electron (SE) and BSE detectors.

2 Sorel cement mortars

Magnesia cement, also called Sorel cement after its inventor Stanislas Sorel, is in fact no cement according to today's terminology, since it is not resistant to water. The binder was first produced in 1867. In the late 19th century and probably until after World War I, Sorel cement was used for a wide range of applications, such as e.g. artificial stones, floorings, grindstones, repair mortars and even glues for broken stone parts. Today's use is mostly in the field of floor screeds for industrial purposes. More data related to this application are given e.g. in [1].

Sorel cement belongs to the class known as acid-base binders, with caustic magnesia, MgO, produced from calcining magnesite, $MgCO_3$, to which magnesium chloride, $MgCl_2$, is added either as solution or in the solid state [1]. The resulting salt is reported to be a magnesium oxychloride hydrate of the formula $3MgO{\cdot}MgCl_2{\cdot}11H_2O$ [2], probably in intimate mixture with magnesium hydroxide, $Mg(OH)_2$, precipitated in a colloidal form [3]. The binder starts to set after approx. 40 min and should be hard after 9 hrs at relatively low shrinkage. The final strength of a floor screed is impressing, with tensile strengths from 5 to 20 MPa and compressive strengths from 20 to 100 MPa. The low resistance to the action of moisture has however limited the application of Sorel cements.

Mortars and grouts from Sorel cement may contain considerable amounts of almost any kind of filler, and the use of wooden fibres in that context, increasing the thermal insulation capacity of a floor, has led to the name of *xylolith*.

Sorel cement mortars have been identified by the authors in a number of cases ranging from repair mortars and stuccoes for marble sculptures, glues for archaeological stone objects, inlays for structured façade renders, and floors. Some of those findings were related to outdoor applications where the material was strongly weathered but still in place.

Thin-sections under the polarising microscope show a brownish matrix which cannot be identified further, apart from several characteristic phases of residual or secondary nature. These comprise residual carbonates, brucite, $Mg(OH)_2$, in aggregates of tiny crystals, and hydromagnesite, $Mg_5[(OH)_2/(CO_3)_4]{\cdot}4H_2O$, as spherical grains of radial-fibrous appearance.

The mortar structure is largely dependant on type and amount of filler adjusted to the mode of application. Fig. 1 shows a *xylolith*-type flooring mortar with high internal porosity due to the abundant wood fibres and frequent air voids caused by the liquid consistency. Fig. 2 illustrates a 19th century stone repair mortar applied to a marble sculpture outdoors. Its abundant filler consists of limestone fragments; the lower water:cement ratio is reflected by residual periclase, MgO, and the air voids are filled with secondary hydromagnesite.

The microstructure of the Sorel cement matrix provides additional information to understand the high mechanical strength attributed to these mortars. The crystals of magnesium oxychloride appear in prismatic shapes from tiny acicular to coarser pillared, sometimes intergrown with platy crystals. The porosity within the matrix varies from fairly high, with pore sizes in the range of <5µm (Fig. 3), to relatively low, with just a few air voids in an otherwise compact structure (Fig. 4).

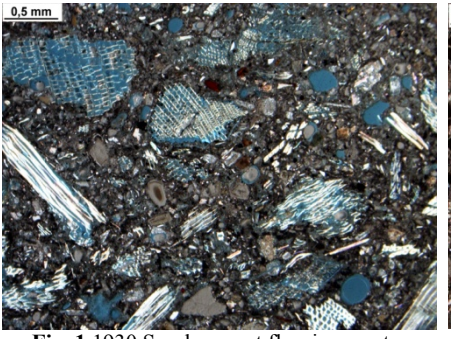

Fig. 1 1930 Sorel cement flooring mortar, filled with wood fibres; abundant air voids; blue resin, parallel Nicols

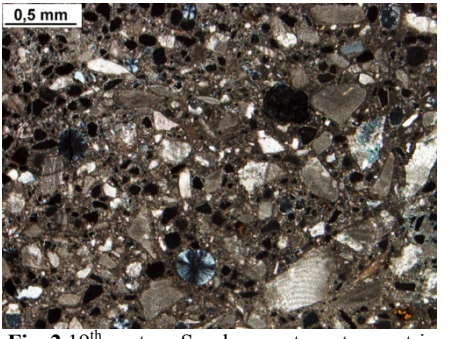

Fig. 2 19th century Sorel cement mortar; matrix with isotropic periclase, air voids filled with hydromagnesite; crossed Nicols.

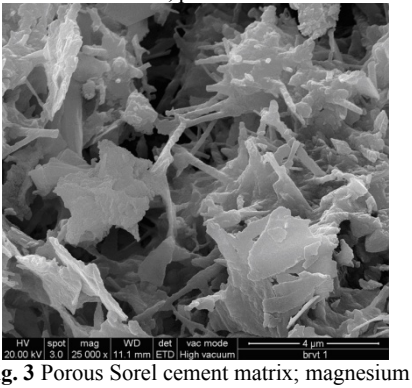

Fig. 3 Porous Sorel cement matrix; magnesium oxychloride hydrate crystals; SEM-SE

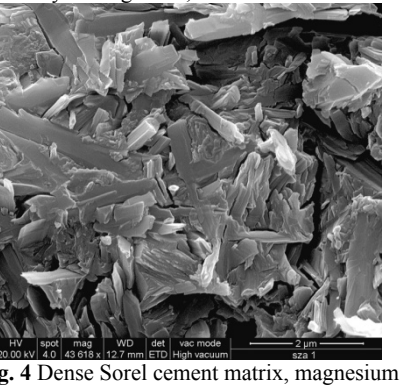

Fig. 4 Dense Sorel cement matrix, magnesium oxychloride hydrate crystals ; SEM-SE

3 Iron hammer scale mortars

High strength lime mortars of reddish to dark red colour can be found as 19th century materials for stone and masonry repair as well as for rejointing e.g. brick walls. The presence of iron in metallic form or as oxides can be suspected by visual inspection or sometimes even by the magnetic properties. Even if in the restoration community they are well known as hammer scale mortars, not much knowledge seems to exist about their properties and the mechanisms leading to the

strength they develop. Only few historic sources mention these mortars [4] which should not be confused with other types of putty prepared from iron cuttings.

Hammer scale is a waste product from iron smithing which consists mainly of tiny flakes of iron converted to iron oxides such as magnetite, Fe_3O_4, or haematite, Fe_2O_3. According to [4], the scale was ground and admixed to lime to prepare a mortar which was reported to harden considerably, particularly in moist places. The same article in [4] offers an explanation for the hardening of hammer scale mortars by addressing the well-known fact of rust subjected to volume expansion when forming from iron through the action of moisture and atmospheric acid.

The analysis of hammer scale mortars by means of microscopy and SEM supports the above hypothesis. Fig. 5 from a 19th century pointing mortar shows flakes of a dark grey iron phase, either haematite or magnetite. Both oxides have formed at high temperatures. Occasionally, metallic iron is still preserved in the core of such fragments (Fig. 6). Inert fillers such as e.g. quartz are also present.

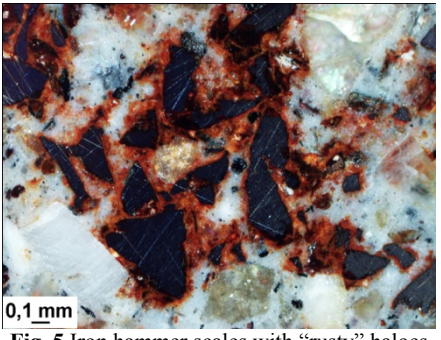

Fig. 5 Iron hammer scales with "rusty" haloes in a 19th cent. pointing mortar; incident light

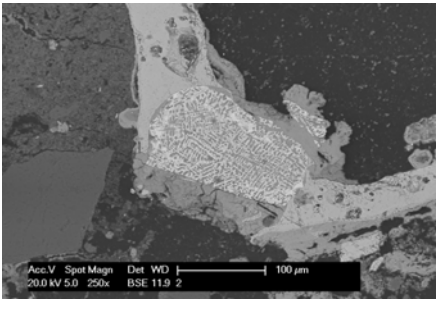

Fig. 6 Iron hammer scale with metal surrounded by iron oxide; SEM-BSE

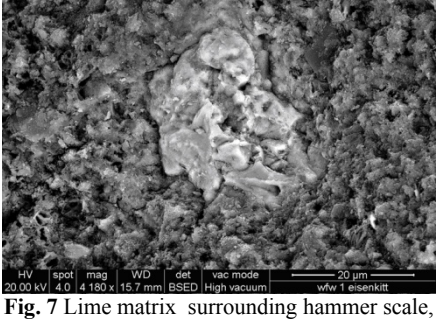

Fig. 7 Lime matrix surrounding hammer scale, densified by iron compounds; SEM-BSE

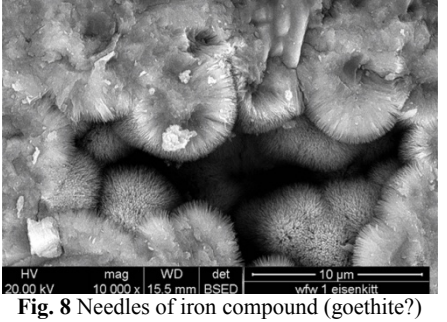

Fig. 8 Needles of iron compound (goethite?) around a binder pore; SEM-BSE

Most of the iron oxide scales are surrounded by irregular areas of red colour, where iron hydroxides and hydrated oxides have caused densification of the calcite matrix (Fig. 7). No evidence for the formation of a calcium ferritic phase could be found, and small needle-shaped crystals growing within the matrix (Fig. 8) contain just iron and no calcium and are hence likely to represent a

mineral of the goethite type, $FeO(OH)\cdot H_2O$. Even if an exact mineralogical identification of the phases involved has not been performed in the present study, the principles of reaction are clear: the oxidation – rusting – of the scales is accompanied by the migration of colloidal iron hydroxides into the lime matrix where they precipitate and crystallise in the binder pores, causing significant compaction. Similar effects by an analogous process had been described for crystalline marble whose cracks were "healed" by iron hydroxides having migrated from rusting iron rebars [5].

4 Roman cements

Several papers, e.g. [6, 7, 8, 9, 10, 11, 12, 13], have recently dealt with Roman cements (RC) - natural cements produced at temperatures well below sintering, i.e. in the range of about 800 to 900°C. These hydraulic binders played an important role in building construction and façade decoration especially in Western and Central Europe.

When analysing historic RC- mortars it should be kept in mind that they differ from Portland cement or NHL-mortars not so much in their chemical composition as in respect to mineral content and appearance of the residual clinker, along with the microstructure of the hydrated cement matrix. The nature of the raw feed, typically argillaceous limestone, and the low temperatures of calcination lead to the formation of characteristic cement compounds and binder microstructures. Their identification must be primarily based on microscopy and SEM. Weber and Gadermayr in [11] have presented the range of residual phases typically present in RCD-mortars, as well as their visual appearance under the polarising microscope and SEM. Fig. 9 shows a 19th century RC-mortar at low magnification, where the brownish colour and the abundant binder nodules form the primary features of distinction. The nodules mark areas of incomplete or non-ideal hydration due to non-reactive phases formed by either sub- or super-optimal calcination, both conditions being inherent to the process of production. The sub-optimal nodules are characterised by incomplete decomposition of carbonate and/or insufficient reactions with the silicates, while the super-optimal grains typically contain coarse belite, C_2S of the β-form, gehlenite, C_2A_2S, and sometimes even products of local melting (Fig. 10). Both nodule types seem to play an essential role as inert fillers.

The reactive portion of a RC "clinker" is known to consist of an amorphous phase and highly reactive α'-belite mixed with less reactive β-belite [7, 8].

Historic Roman cement mortars combine high strength with high porosity in the capillary range. This specific feature is even more pronounced for mortars with very low amounts of aggregate. SEM-studies of the matrix help understand the mentioned properties. As already stated e.g. in [8] and [11], the calcium silicate hydrates formed in a Roman cement paste is of an unusual coarse nature

with card house-like intergrowth (Fig. 11). Abundant calcite crystals formed in most of the historic mortars upon carbonation yield additional strength.

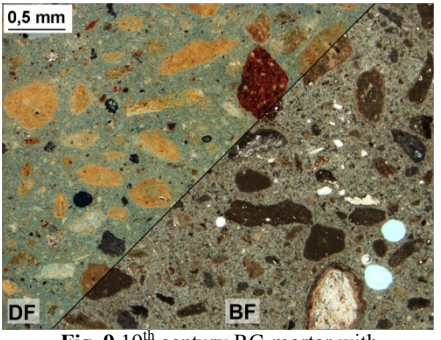

Fig. 9 19th century RC-mortar with characteristic binder nodules; the red grain is a brick fragment; transmitted light in bright field (BF) and dark field (DF)

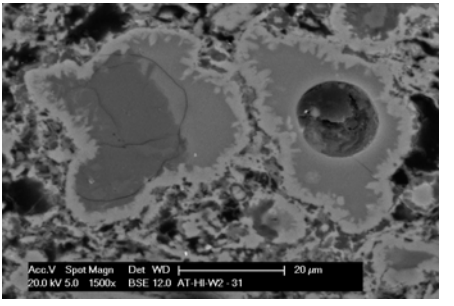

Fig. 10 RC binder residues with silica grains to which diffusion of Ca and alkalis has caused zoning with even local melting (right). Matrix with partially hydrated belites, C_2S; SEM-BSE

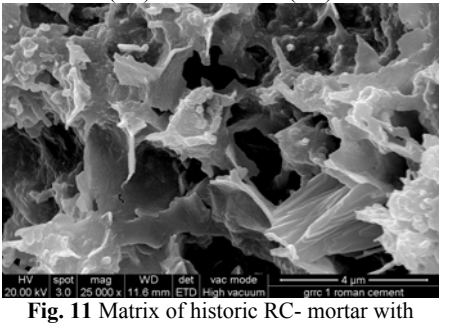

Fig. 11 Matrix of historic RC- mortar with coarse calcim silicate hydrate, C-S-H; SEM-SE

5 Early Portland cements

When dealing with early Portland cement (PC) mortars, it should be kept in mind that their binders differ from today's OPC. Analyses of early PC raise the suspicion that, for a period of probably about hundred years, the usual peak kiln temperatures were rather in the range of about 1200°C – the temperature of sintering for most raw feeds – than 1450°C as for OPC. The main clinker phase of modern PC (see e.g. [14]), i.e. alite, C_3S, is thus unlikely to occur in early cements, while the other phases of significance, such as belite, C_2S, aluminate, C_3A, and ferrite, C_4AF, would form before or as soon as the above point of sintering is reached.

Most early Portland cements lack therefore C_3S in favour of C_2S. It would be misleading, however, to consider them as binders similar to Roman cements, and

in fact all historic handbooks make a clear distinction between both cements, pointing to the slower set, more rapid strength gain, and higher final strength of PC (e.g. [15]). From the point of view of the clinker composition, the difference between early PC and RC can be explained by several factors: first, belite present in an early PC was most probably of the β-type in contrary to the α'-polymorph typical for RC; second, not the amorphous phase present in RC, but rather C_3A was the phase responsible for the onset of stiffening and early strength in PC pastes; finally, the higher temperatures of PC calcination would have caused higher rates of reaction within the raw feed, leading to coarser crystals, less solid solutions, and thus less binder residues in the final product as compared to RC.

A distinctive feature in sections of early PC-mortars viewed under the microscope is therefore the low amount or even lack of brownish binder nodules. As soon as, with temperatures of calcination exceeding about 1.100 °C, iron starts to be incorporated in the ferrite phase, the colour of the cement turns from yellowish-reddish to greenish-greyish. Fig. 12 and Fig. 13 show examples.

From modern PC mortars the early ones can be distinguished by their much coarser clinker residues – in the range of 200 µm or more as compared to 20 µm - and by the lack of C_3S in them.

Viewed by SEM on fractures, the microstructure of the hydrated matrix of historic Portland cement can be described as more compact than in Roman cements (Fig. 14), with C-S-H forming a dense framework even if some areas remain more open-porous. The hydrates are, however, much coarser than in modern cements (Fig. 15); when growing inside larger voids, they tend to develop acicular shapes. Rhombohedral crystals of calcite can be found quite frequently, since all of the samples investigated revealed full carbonation.

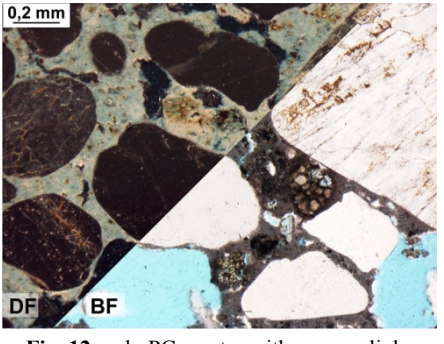

Fig. 12 early PC-mortar with coarse clinker residues with interstitial ferrite; transmitted light in bright field (BF) and dark field (DF)

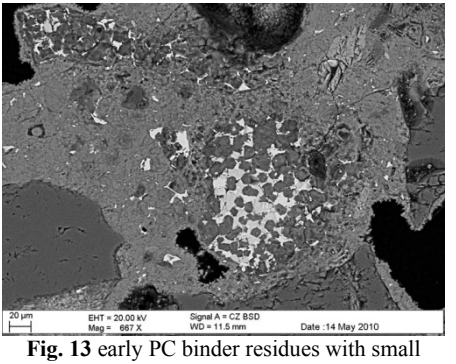

Fig. 13 early PC binder residues with small silica (dark grey), belite and ferrite, surrounded by a dense matrix of hydrates; SEM-BSE

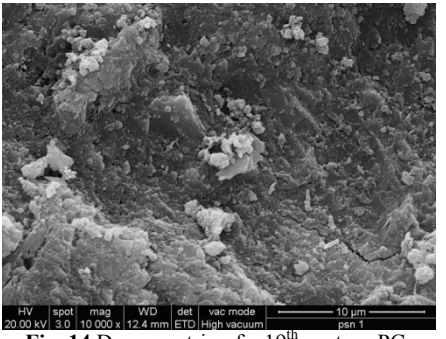

Fig. 14 Dense matrix of a 19th century PC-mortar; SEM-SE

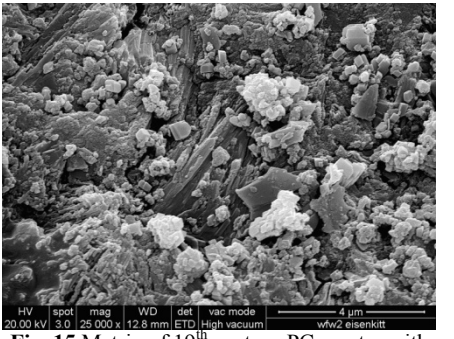

Fig. 15 Matrix of 19th century PC-mortar with coarse C-S-H and calcite; SEM-SE

6 Acknowledgements

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I.44

Characterization of Mortars in Historical Modern Monuments: a Realistic and an Analytical Approach

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Abstract Structures embedding historical, artistic and scientific values and built after 1830 (the date of the establishment of the Modern Greek state) are defined as modern monuments according to Greek legislation. Although the period of documentation is restricted to the last 180 years, extended field survey and visual examination, traced a wide range of structural mortar mixtures in support of typical bearing masonries. The continuous and successful use of wet slaked lime putties has been documented through historical, socioeconomic and technological analysis of local construction practice combined with applied research (in situ, in the lab, and through market study). The obtained integrated background knowledge, the regular long-term monitoring of the old and repair mortars in a real site environment and the attained overall experience support ongoing conservation projects. Since the analytical chemical approach is too sophisticated and expensive for ordinary conservation work, the least amount of key laboratory tests -adequate to characterize a mortar and to control the available market materials- is crucial to enhance interventions' quality and minimize the cost.

1 Introduction

Structures embedding historical, artistic and scientific values and built after 1830 (the date of the establishment of the Modern Greek state) are defined as modern monuments according to Greek legislation (law No 3028/2002, commonly called "archaeological law"). Considering that the majority of modern monuments are private, Greek Ephorates of Modern Monuments mainly supervise conservation projects financed by the private sector or by individual owners. A limited number of conservation projects of public modern monuments are undertaken by the Greek Ministry of Culture and/or co-financed by the European Community Support Frameworks.

In most private interventions, lack of money - or time or simply unwillingness to carry out any materials' research – merely leads to general recommendations to owners and/or contractors. As a result, the Ephorates' capability in controlling the quality of each conservation project is constrained. However, this approach is definitely inadequate for large scale, or international projects, as for example are the requirements of the National Strategic Reference Framework (NSRF) 2007-13. In this frame of responsibilities, the background knowledge on mortars technology [1-7] aspires to support ongoing conservation projects, private and public.

Indicatively, the present paper focuses on the pragmatic and/or analytical characterisation of masonry mortars -and specifically of the binders- with the aim to contribute scientifically and cost-effectively to their appropriate conservation.

2 Case studies

Typical bearing masonries of the - as previously defined - modern monuments consist of the building units and the bedding mortars. Knowledge on local traditional construction systems and materials are preserved in Greece, and will continue to live on, as long as old masons are still alive. Also, local sources of raw materials can still be identified (e.g. resources for stones extraction to be used as bearing elements or for lime production, earth quarries, wood forests etc). Today, conventional know-how in building construction usually contradicts to current European codes and standards [3] and to common economic immigrant masons' expertise. Since we are standing at a crucial crossroad, we are urged to seek out combined conservation strategies in terms of interdisciplinary perspective and international cooperation network [4].

Regarding structural mortars, three general types can be categorized according to their binder type: a) earthen or weak lime earthen mortars of C19, b) pure lime mortars rarely combined with local pozzolan of C19/C20 and c) lime cement synthesis of C20. At any case, the continuous use of wet slaked lime putties has been documented through historical, socioeconomic and technological analysis of the last two centuries in local construction [2] combined with applied research (in situ [5] , in the lab [6, 7], and through market study [3]).

2.1 Earthen or weak lime earthen mortars of C19

Naoussa, Prefecture of Hmathia • Listed unit of Mathieu's 'House-Mill'

Fig. 1 The storehouse before collapsing

Fig. 2 The storehouse under restoration

Table 1 The key role of local raw materials and know-how in authenticity preservation [3]

Date of construction	late C19
Original use and ownership	Storehouse of the main building unit of Mathieu's 'House-Mill'
Current use and ownership	Redundant, under expropriation by the Greek Ministry of Culture; intended use 'Museum of Tradition, of Historic Archives and Wine Museum of Naoussa town' (Fig. 1, Fig. 2)
Bearing structure	Stone masonries with wooden chainage (ground floor and all north walls) and timber framed (2 upper floors); wooden floors & roof
Study 2002-03 (emergency)	The study was carried out by E. Mavroudi and G. Zacharopoulou
Project 2002-03 (salvage)	Local knowledge was alive; no materials' research was carried out; local masons were aware of the traditional construction system and materials; they gathered earth (called 'pourohoma') from the old quarry and meticulously filled the masonry gaps and also reinforced the wooden structure under Ephorate's supervision & funding

2.2 Pure lime mortars combined with pozzolan of C19/C20

Municipality of Michaniona, Prefecture of Thessaloniki • The fort of Megalo Emvolo (Great Karabournou)

Stone: compressive strength fc=68.59 MPa (A.S.T.M. D 2938-71a), bulk density 2.74gr/cm^3, absorption 0.40%

Brick: BxLxH: (10.5-11.8)x(23-25) x(5.3-6.2), compressive strength fc=5.16 MPa, absorption 19.02%

Fig. 1 Sampling of (bedding) mortars and natural (stone) and artificial (brick) masonry units

Table 2 The need for better documentation of the local materials before restoration

Date of construction	1883-85 by German military engineers and early C20 additions
Original use and ownership	defensive Naval Fort of the Greek Army
Current use and ownership	redundant, Navy of the Greek Army
Bearing structure	brick vaulted, stone masonries with brick layers
Study	2008-09 in the frame of the 3rd Community Support Framework, ENM KM, O. Deligianni, G. Zacharopoulou et al.
Project	intended for the National Strategic Reference Framework (NSRF) 2007-13; the large scale of the monument and the demands of NSRF for using standardized materials requires better documentation of the authentic and new local materials available in the market; standardized materials vs. local materials (usually not standardized)

To identify the texture of the mineral aggregates the shape of the lime grains and their chemistry, Scanning Electron Microcopy (S.E.M) analytical techniques were applied on mortar fragments using the GSM 840A instrument (SEM laboratory of AUTh), after sampling of mortars and building units (Fig. 3). Good cohesion bonds were observed both at the matrix (Fig. 4) and at the binder/aggregate interface (Fig. 5) comparable to those obtain in lab research with lime putty samples [2, p. 200]. Besides, mechanical and physical characteristics were obtained in cooperation with the Laboratory of Public Works of Central Macedonia. Indicatively, the mortar's information is integrated as following:

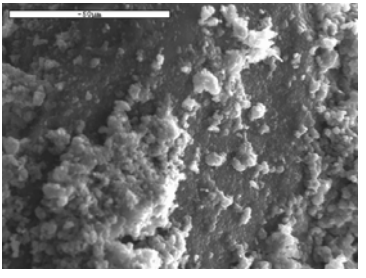

Fig. 2 Cohesiveness of the lime matrix

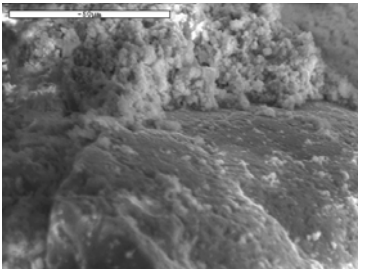

Fig. 3 Binder/aggregate interface

Table 3 Further investigation and interpretation towards authentic mortar's characterization

Sample code & location	**ΚΔ.π – masonry mortar**
Colour	10YR 8/1 white (according to Munsell soil color chart)
Binder	49-61% $Ca(OH)_2$ (or 68-85%, CaO), lime grains dm ~1μm÷5μm; homogeneous without grain aggregations (porous <10μm)
Aggregate	
-characterisation	river sand, siliceous origin, with little amount of added ceramic fragments >3mm from low fired crushed bricks (on going research)
-sieving curve (according to E105-86, tests 6 & 7)	even, 0-4.75mm (63.6% between No 200/7.5μm - No 10/2mm); 6% of grain size >4.75mm with equal amount of crushed bricks and sand
Absorption	19-21% (comparable to the hand-made bricks)
Compressive strength	compressive strength fc<2.5 MPa
B/Ag	binder/ aggregate ~1/2.5 (point counting)
w/b	use of matured lime putty; min. w/b to achieve lime's consistency

2.3 Lime (pozzolan) cement synthesis of early C20

Thessaloniki, Prefecture of Thessaloniki • The 'Casa Bianca'

Fig. 4 The 'Casa Bianca', 1994

Fig. 5 Internal bearing structure, 1994

Table 4 Description of the modern monument 'Casa Bianca'

Date of construction	1911-12 (transitional period in the use of binders)
Original use and ownership	lodge of Blanche and Fernandez Diaz (architect P. Arigoni)
Current use and ownership	since 1997, Cultural Centre of the Municipality of Thessaloniki
Bearing structure	stone masonries with brick layers (ground floor) & brick masonries (upper floors) both reinforced with metallic components (beams and anchors); internal wooden floors with the exception of the 'wet' rooms (kitchen and baths) where metallic beams bridged with special large bricks were used; external terrace constructed with a transitional type of 'early concrete – brick' Zöllner slab
Study	1993; research group of the Polytechnic School of AUTh; responsible of the static restoration, Prof. G. Penelis, civil engineer
Project	1994-1997, financed in the frame of 'Thessaloniki, Cultural Capital of Europe 1997'. Consultant engineer (on site), G. Zacharopoulou

Table 5 The supportive role of key laboratory tests in mortars characterization

Sample code & location	structural mortar of masonries (4 samples)
Colour	white-grey
Binder	$Ca(OH)_2$ ~40%, CaO: 28-34%, SiO_2: 29-30%, Al_2O_3: 5-7% (~15-18% soluble in 0.1N HCl); lime/pozzolan ~2/1.
Aggregate	
-characterisation	river sand, siliceous origin (with added local pozzolan or cement)
-sieving curve	0-5mm (50% passing 0,5μm) rich in fine particles;
Absorption	~14%
Compressive strength	compressive strength fc<2.0 MPa

After series of relevant research samples, hydrated lime (in dry form), cement and sand were proposed for the repair mortars; Lime/Cement/Aggregate /Water=1/1/6/2.4 per volume, compressive strength fc=3.25MPa, flexural strength f_f=1.05MPa, dynamic modulus of elasticity Ed=8041MPa.

According to current global knowledge and also to the local integrated background research [2-7] some kind of (local) pozzolan should have been added. Furthermore, lime is preferable in the form of matured wet slaked putty [1].

2.4 High calcium lime wet slaking at the worksite

Fig. 6 Asvestochori lime production area

Fig. 7 Wet slaking at the worksite, 2001

In 2001, the 10th Ephorate of Byzantine Antiquities (responsible for the Prefecture of Halkidiki and Mount Athos) was commissioned to restore the 'Russian Metohi' at Flogita area and to adapt it to the 'Christian Culture Center of Halkidiki' under the name 'Justinian Center'. Acknowledging the importance of using wet slaked matured lime putty, 10 tones of high calcium quicklime were bought from the Asvestochori lime production area (Fig. 8) and wet slaked at the worksite (Fig. 9) producing about 27 tn of putty.

The water added during slaking has been chosen correctly, as the settled water (w_s) after 24h was ≤40ml, according to EN 459-2:2001 [8], 5.9.2; it was measured w_s=13.5cm^3 (96% of the 30th day). Yield was also acceptable as being ≥26dm/10kg, according to EN 459-1, 4.5.2, Table 4: Physical requirements of quicklime. Also, available lime Ka=74.40% (limits only for dry forms in EN 459) and free water w_F=59%, according to EN 459-2, 5.11, (EN 459-1, Table 5; gives limits 45%≤ w_F ≤70%). Finally, bulk density=1.262gr/ml, acceptable as according to BS 890 ≤1.45g/ml (there are no limits about putties in EN 459).

Since then, lime putty has been successfully matured and used for all restoration works in the area for which the Ephorate is responsible.

3 Discussion and Conclusions

Although the period of documentation is restricted to the last 180 years extended field survey and observation in the Ephorate's area (Macedonia and Thrace) traced a wide range of structural mortar mixtures of typical bearing masonries. Those historical masonries are frequently and successfully used in mixed structures e.g. timber (Table 1), metal or concrete framed. These are

structural components consisting of natural or artificial masonry units, which are commonly laid with mortar (Tables 2, 4). As masonries are usually used for components subjected to compressive loading, they either have to withstand weights in vertical direction (walls, columns) or span across spaces and rooms (arches, vaults (Table 2), domes). They have also a limited capacity to support horizontal loads (earthquake, wind action) and bending moments.

During last decades, though, the efficiency of current masonry systems has been considerably improved in terms of higher allowable stresses and/or refined possibilities of design. This involves a more precise analysis, more demanding constructions, and more standardized materials' production. The key role of local raw materials and know-how both in mortars characterization and in monuments' authenticity preservation is usually undermined by the requirements for using standardized materials in interventions. Since local materials are usually not standardized, a further documentation of the authentic - and also new available materials - is needed, where the lab techniques are very supportive (Tables 3, 5). The comparative evaluation of the real structural behavior of modern masonry structures with stiff and brittle mortars and of the traditional masonry systems with soft lime based mortars, in terms of tensile strength, fracture energy and ductility, will help to reduce interventions and preserve authenticity in monuments [1].

Towards this aim, the authentic materials of a monument (binders, aggregates, masonry units etc) should be compared to the local available resources and construction know-how. Local integrated background research - incorporated historical, socioeconomic and technological analysis of local construction practice combined with applied research (in situ, in the lab, and through market study) - of the authentic and available today traditional and conventional raw and building materials should be extremely supportive in questioning and interpreting the documentation data of each monument.

Regarding mortars characterization [9, 10] only the absolutely necessary materials' research is then carried out, based on a step by step cost effective plan of research priorities in search of: a) the hydraulicity (or not) of the binder and its form (dry or putty), b) the (inert or active) aggregate nature (origin) and grading (sieving curve) and c) the mixture proportions i.e. the binder/aggregate ratio (B/Ag) and the water/binder ratio (w/b) [1, 9, 10]. Bearing in mind that there is a general consensus on the positive influence of key technological parameters, such as the proper aggregates selection, their even gradation, mortar's high degree of compaction and its low water/binder ratio (differentiating in lime putties [1]), it is derived that the binder form and type is crucial for the mortar's performance [1].

Integrating this approach in binders research, the bedding mortars of modern monuments of central Macedonia are characterized as: a) earthen or weak lime earthen mortars of C19 (Table 1), b) pure lime mortars rarely combined with (natural or artificial) active aggregates (pozzolan) of C19/C20 (Table 3) and c) lime (pozzolan) cement synthesis of C20 (Table 5). The strong and still alive tradition in the production and use of consistent wet slaked lime putties in Greece has been investigated and interpreted as owing to the plentiful, hard and high

calcium limestone deposits together with the efficient, empirically developed, know-how on production processes [2-7]. The laboratory research on lime putty product demonstrated the positive effect of the key missing link of maturation process on the service life of lime mortars [1]. It has been highlighted both scientifically [1-7] and pragmatically that the proper use of homogeneously matured lime putties with high water retentiveness capacity may control competently mortars' porosity, strength development rate and durability [1]. Furthermore, the market research revealed that although Greek SME's have developed a significant local know-how, they are hardly compensate the standardisation push that gradually tends to reduce heterogeneity of limes, in the move from (small scale) local towards (large scale) global markets [3, 4]. Considering that the know-how of the dry high calcium lime production was imported at early 70s, the production of natural (or artificial) hydraulic binders in dry form is never documented in Greece and also that the first cement factory constructed close to Athens in 1902 [2-3], as historical market research suggests, it is derived that most modern standardized dry binders – harmonized to European standards [1, 8] and gradually imported in Greece - are not necessarily the best or the unique answer for our interventions. However, the extent of the imported building materials, since 1830, should be further investigated and evaluated.

4 Acknowledgments

I wish to thank Ass. Prof. E. Pavlidou, physist and lect. L. Papadopoulou, geologist of the Aristotle University of Thessaloniki (AUTh) for supporting the ongoing SEM characterisation of mortars. Thanks are also due to Mr. I. Tragopoulos, civil engineer of the Laboratory of Public Works of Central Macedonia for contributing to the physical and mechanical characterisation of mortars.

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Theme II

Assessment of mortars and masonry

diagnostics and testing methods, complex evaluation of masonry and mortars, structural issues, damage and deterioration

II.01

Testing the Freeze/Thaw Cycles in Lime Mortar

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Abstract The purpose of this study is to evaluate the behaviour of lime mortars in cold climates, namely by the effect of freeze/thaw cycles. Twelve compositions of mortars were prepared varying the type of binder (air lime, hydraulic lime and air lime + cement), the grain size distribution of the sand and the use of an air entraining agent. Tests including the open porosity, mechanical strength and resistance to freeze/thaw cycles were conducted in order to evaluate the performance of lime mortars in cold climates. The analysis of results allowed to assess some relevant conclusions about the influence of the grain size of aggregate, the use of an air entraining agent and the behaviour of mortars with different types of binder. The open porosity depends mainly on the granulometry of sands while the mechanical strength is correlated with the binder type. These two characteristics have a great influence on the strength of mortar to freeze/thaw cycles and consequently on their performance in cold climates.

1 Introduction

Lime based mortars have been used in building construction for centuries, even millennia. Air lime was the most utilized binder and the final characteristics of historic mortars were strongly dependent on the civilizations that used them. As a consequence today a wide variety of mortars are found in historical buildings.

The appearance of cement as a binder in mortars led to its widespread and excessive use in most parts of a building, including in the conservation and rehabilitation of architectonic heritage. Their fast hardening and the fact that they confer a high mechanical strength were the determining factors for this overuse.

Since the appearance of cement, lime-based mortars fell into gradual disuse and the knowledge of craftsmen almost disappeared. Some decades ago, it was noted that the replacement of lime mortars by cement mortars in the conservation and

rehabilitation of old buildings was a serious error. Cement mortars are chemically and mechanically incompatible with old building materials, they are very strong, rapidly reaching maximum strength, have a hardening process that results in the release of soluble salts and still have a shorter life when compared to lime mortars. From this realization a new phase in the use of lime and a new search to optimize the behaviour of lime mortars, began.

Although the compatibility with old materials and elements and their protection are fundamental to mortars applied to architectonic heritage, the durability of such mortars is also important. A mortar has greater durability if it resists the action of degradation agents that act upon it. Such agents vary depending on the particular environment (region, climate) where the building is localized. In cold climates it is the effect of freeze/thaw cycles that is most important [1].

The presence of water, one of the main aggressors for building materials and for mortars in particular, increases the effect of freeze/thaw cycles in cold climates. Freeze/thaw is a cyclic process during which a change in volume occurs as water crystallizes within the mortar during freezing prior to its liquefaction during melting.

The durability of hardened mortars to freeze/thaw cycles is dependent on their ability to:

- resist water penetration;
- lose water quickly to prevent it freezing inside the mortar;
- present a porous structure that stands the strain caused by the increased volume of water as it passes between the solid and liquid state in successive cycles [2].

Based on previous assumptions, a research study was developed in order to assess the behaviour of mortars under the action of freeze/thaw cycles by varying the type of binder, the grain size distribution of the aggregate and the use of an air entraining agent. The assumptions associated with this objective were: (i) the variation of the type of binder generates mechanical resistance of different orders of magnitude and conditions to freeze/thaw cycles; (ii) the variation in particle size distribution of the aggregate and the use of an air entraining agent modify the microstructure of the hardened material generating different reactions to the freeze/thaw cycles.

2 Development and experimental characterization of mortars

The experimental methodologies were based on normative documents, when available and considered adequate. Mortar test normative documents are almost always specific to cement based mortars and are sometimes not adequate for the assessment of lime-based mortars. When needed, mortar test specifications

developed by the research team at the School of Science and Technology of Nova University of Lisbon (UNL), were used [3].

2.1 Mortar materials

The materials used in the experimental work were: a commercial washed river sand and two grain size controlled sands (AGS1 / 2 - coarse and FPS120 – fine sands), a commercial hydrated air lime (CL90 from Lusical), a commercial hydrated hydraulic lime (NHL5 from Secil), Portland cement (CEM I / BL 32.5 N from Secil), an air entraining agent (AER5 from SIKA) and public drinking water. The air entraining agent was applied following the commercial recommendations and the same quantity was always added. Fig. 1 represents the grain size distribution of used sands.

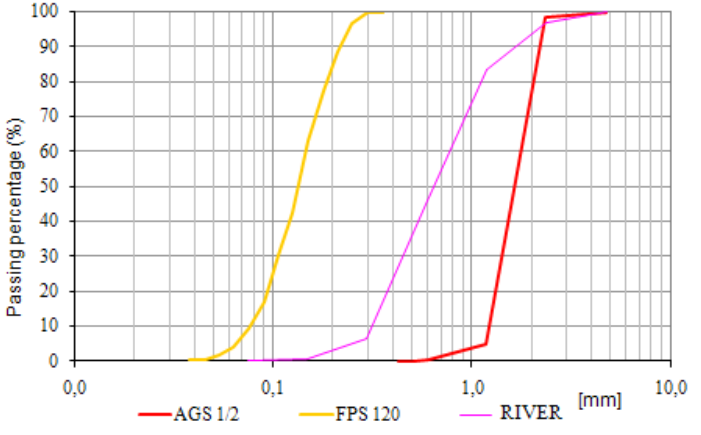

Fig. 1 Granulometric curve of used sands

2.2 Mortar preparation and test program

Twelve mortars were prepared with the materials and volumetric proportions described in Table 1. The general procedure used in the execution of the mortars was based on the European Standard EN 1015-2:1998 [4] with indications from the test card Fe 19 (UNL) [3]. The mortars were mechanically mixed in a laboratory mixer using a standard sequence of operations. The mortar was mechanically compacted in the moulds with twenty falls for each one of the two layers which complete the moulds. Impermeable metallic moulds, 4cm x 4cm x 16cm, were used with a minimum of grease to assure removal. Once moulded the samples were kept in controlled conditions at 20±2ºC and 65±5% relative

humidity. The curing time of the air lime mortar without an air entraining agent was 91 days, while the remaining mortars had a curing time of 61 days.

The test program consisted of determining the consistency of fresh mortars, their mechanical properties (flexural and compressive strength), open porosity and the resistance to freeze/thaw cycles of hardened mortar samples.

2.3 Fresh mortar characterization

Tests of flow table consistency were performed based on EN 1015-3:1999 [5]. The mortar displacement after 15 shots of the flow table in 15 seconds was registered. The values of flow for mortars without an air entraining agent had a benchmark at 175mm while in the mortars with an agent the same amount of water was used without a benchmark flow.

2.4 Hardened mortar characterization

The open porosity of the mortars was determined following test specification Fe 02 [3], based on the method of hydrostatic weighing after vacuum.

The mechanical strength was evaluated by three points of tensile strength and compressive strength. Tests were performed using a universal tensile machine according to Standard EN 1015-11:1999 [6].

Tests to assess the resistance to freeze/thaw cycles in lime mortars are not addressed in any current normative document. The existing standards relating to test methods for the determination of resistance to freeze/thaw cycles are specific to concrete and for natural stone. These procedures were considered too aggressive for lime mortars, mainly due to the fact that each cycle imposed the immersion of the samples. A different and original (based on the method described by Konow [7]) testing method was adopted with the objective of measuring the mass loss of the specimens to make a qualitative assessment of the damage over time.

The mortar samples were immersed in water until their weight was constant (less than 1% weight variation in 24h); they were then placed inside sealed airtight bags to retain their moisture conditions; the bags with the samples were conditioned inside an environmental chamber programmed to simulate freeze/thaw cycles. The environmental chamber was scheduled to carry out two cycles per day with a maximum temperature of 10ºC and a minimum temperature of -10ºC, stagnation in each defined an exposure time at extreme temperatures of 2 hours. The samples were weighed every 24 hours after two hours of rising temperature. The test was concluded when a substantial disintegration of the sample occurred (percentage of weight loss greater than 30% of the original mass of the sample), with a limit of 40 cycles. Three comparative indices corresponding to the percentage of mass lost at 10 (i10), 20 (i20) and 40 cycles (i40) were established (Table 1).

3 Results and discussion

This chapter presents the results of each test developed for each mortar and a relational analysis seeking to identify the characteristics of a mortar that produce the most promising test results of resistance to freeze/thaw cycles. Table 1 presents the constituents of each mortar, the volumetric ratio of binder: aggregate and the results of tests including the percentage of weight lost after 10, 20 and 40 freeze/thaw cycles. Some mortars disintegrated between the 20th and the 40th cycle.

Table 1 Table of test results

Material			binder: aggregate ratio (vol.)	Por.	F.S.	C.S.	Freeze-thaw [%]		
Binder	Sand	A.I.		[%]	[MPa]	[MPa]	i10	i20	i40
A	AGS1/2	-	1:2	31	0.17	0.46	1.1	19.3	-
	River	-	1:2	34	0.30	1.01	0.6	2.4	7.5
	FPS120	-	1:2	38	0.58	2.23	2.3	5.9	-
H	AGS1/2	-	1:3	29	0.11	0.53	0.4	1.9	4.6
	River	-	1:3	32	0.13	0.43	0.2	3.4	6.4
	FPS120	-	1:3	39	0.34	0.79	5.0	6.0	9.5
A+C	AGS1/2	-	1:1:6	30	0.76	3.95	0.7	2.6	28.9
	River	-	1:1:6	30	1.05	4.89	0.8	1.8	4.4
	FPS120	-	1:1:6	37	1.35	5.00	0.9	2.1	3.2
A	River	√	1:2	35	0.26	1.04	0.6	2.4	10.5
H		√	1:3	34	0.11	0.52	0.8	4.3	6.5
A+C		√	1:1:6	32	0.93	5.13	0.7	1.8	29.3

Type of binder: A-air lime, H-hydraulic lime, A+C-air lime + cement
Type of sand: AGS1/2-river, FPS120-with or without air entraining agent AI
Tests: Por-open porosity, FS-flexural strength, CS-compressive strength

3.1 Individual results

The lime+cement mortars are the ones with lower values of open porosity. Compared with air lime mortars, the introduction of cement (in lime+cement mortars) reduces its porosity. Hydraulic lime mortars show an intermediate behaviour. The porosity increases with the decreasing particle size of sand due to the higher specific surface of the smaller sand particles. As expected, the air entraining agent increases the porosity of the mortars.

The bastard air lime+cement mortars are the ones with the highest values of flexural strength, confirming that the incorporation of cement does indeed increase

the strength of the mortars. The hydraulic lime mortars present values of flexural strength even lower than those of air lime mortars, although these values may be partially justified by the different volumetric ratio of binder: aggregate used (the air lime mortar with a 1:2 ratio and the hydraulic lime mortar with a 1:3 ratio).

As before, the bastard mortars present higher values of compressive strength and the hydraulic lime mortars register the smaller values. The results of the mortars with an air entrainer were strange. According to the assessment, values of compressive strength increase with the use of air an entraining agent. The results obtained contradict the general opinion that the use of an air entraining agent increases the porosity of a mortar which therefore reduces its mechanical strength. This may be due to the fact that the increase in open porosity was not very high. Nevertheless test results of flexural and compressive strength should follow the same trend, which was not verified.

Air lime mortars presented different behaviour under freeze/thaw cycles depending on their components. The air lime mortars with river sand produced the best behaviour. Other sands resulted in mortars with a similar behaviour among themselves, with a poorer resistance to freeze/thaw than those with the river sand; often with these mortars the test ended before the completion of the 40 cycles.

Hydraulic lime mortars are the ones whose behaviour is more homogeneous with all hydraulic mortars experiencing a weight loss between 5% and 10% after 40 cycles. There is a general trend of inferior behaviour with the decreasing particle size of the aggregate.

Mortars with lime+cement and sand AGS1/2 are those that lost larger amounts of material after 40 cycles, despite a good performance after 20 cycles. The lime+cement mortars and sand FPS 120 are the ones with a better resistance to freeze/thaw cycles.

Fig. 2 shows a graphical representation of freeze/thaw cycle results excluding the mortars containing an air entraining agent. When comparing mortars with and without an air entraining agent, the difference in weight loss is minimal after 10 cycles. The results after 20 cycles do not follow the expected trend [8]. In fact, at this point of the test, mortars with an air entraining agent show a higher weight loss than those where the agent was not used. This trend is confirmed after 40 cycles using aerial lime and lime+cement mortars.

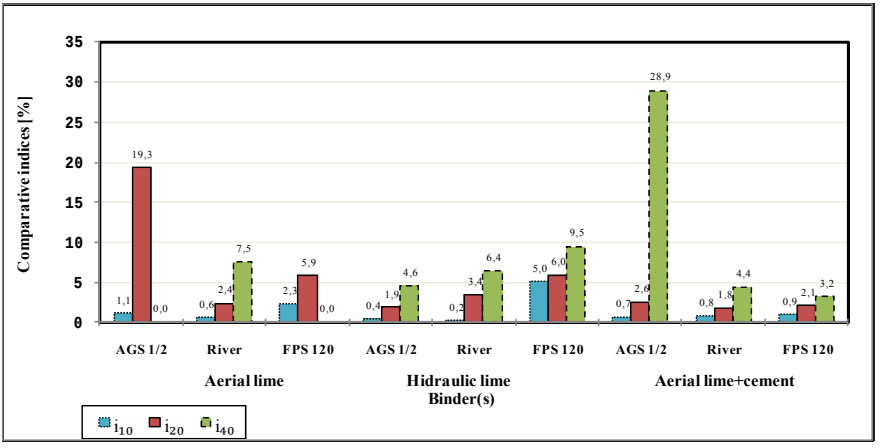

Fig. 2 Freeze/thaw cycles results of mortars without air entraining agent

3.2 Relational analysis of results

3.2.1 Open porosity and resistance to freeze/thaw cycles

The air lime mortars with sands AGS 1/2 and FPS 120 did not show any clear trend, and it was observed that both, although with different values of open porosity, did not complete the 40 freeze/thaw cycles. The mortars with river sand, with intermediate values of open porosity, are the ones with the best behaviour to freeze/thaw cycles which suggests that in air lime mortars, other aspects than open porosity have a significant influence on the resistance to freeze/thaw cycles.

The porous structure and pore size distribution may explain the behaviour of the mortars with sands AGS 1/2 and FPS 120. AGS 1/2 is made of large particles that probably lead to wide drying/shrinkage cracks; therefore, as indicated by Lanas and Alvarez [9], the hardened material loses cohesion. Being a very fine sand, FPS 120 may create very small pores which decrease the resistance to freeze/thaw cycles. Powers, cited by Chatterji [10], confirms that finer pores adversely affect the resistance of mortars to freeze/thaw cycles.

In the case of the hydraulic lime mortars, there is a clear trend of lower resistance to freeze/thaw when the open porosity is higher. The mortars with this binder are those with a greater uniformity of behaviour in the relationship between porosity and resistance to freeze/thaw cycles. The porometry seems to have a key role in the behaviour of hydraulic lime mortars, since this type of mortar has presumably less shrinkage cracks when compared to lime mortars. With finer sands, porosity increases, but the smaller pore sizes could justify the behaviour of these mortars.

Lime+cement mortars show an opposite behaviour when compared to hydraulic lime mortars. The rate of degradation decreases with an increasing open porosity. Mortars with sand AGS 1/2 are those with a lower open porosity and increased degradation. It is with this mixture of binders that the best results were obtained. Mortars with sand FPS 120 are those that lose a smaller amount of material and have a higher value of porosity.

All air entrained mortars have a slightly higher open porosity than those without this agent. The mortars with air lime and an air entraining agent generally have a higher rate of degradation in all cycles.

3.2.2 Mechanical resistance and resistance to freeze/thaw cycles

Air lime and hydraulic lime mortars do not show any direct relationship between mechanical strength and the rate of degradation caused by freeze/thaw cycles.

Lime+cement mortars denote a tendency towards the increased resistance to freeze/thaw with a higher mechanical strength. Cement does increase the mechanical strength of mortars and therefore mortars do have a better mechanical resistance to freeze/thaw cycles.

The use of an air entraining agent showed different trends depending on each type of binder. In hydraulic lime mortars it appears that this component did not introduced significant changes. In the other compositions, this agent not only worsened the resistance to freeze/thaw cycles but also led to unexpected results in the compressive strength tests: air entrained mortars presented higher values.

4 Conclusions

In this work the test results of 12 mortar formulations are compared in order to assess their resistance to freeze/thaw cycles. Due to the specific nature of the mortars considered, it was necessary to develop a test protocol for the freeze/thaw evaluation.

The two hypotheses proposed: (i) the variation of the type of binder generates mechanical resistance of different orders of magnitude and conditions to freeze/thaw cycles; (ii) the variation in particle size distribution of the aggregate and the use of an air entraining agent modify the microstructure of the hardened material generating different reactions to the freeze/thaw cycles, initially serve as a starting point to establish the general conclusions presented here.

In air lime and hydraulic lime mortars the increase of mechanical strength is generally associated with a lower resistance to freeze/thaw cycles. Air lime+cement mortars show the opposite trend.

The increased open porosity in lime mortars (mostly influenced by a decrease in the grain size of sands), is most probably accompanied by a reduction in pore size. Thus, where there is a greater amount of pores with smaller dimensions the

behaviour of mortars to freeze/thaw cycles worsens. Air lime+cement mortars have an opposite trend in the relationship between pore size and freeze/thaw resistance. This behaviour indicates that, in the analyzed mortars, the effect of higher mechanical strength overlaps the pore structure characteristics.

The use of the air entraining agent led to unexpected results. The increase of open porosity (although slight) was not accompanied by the improvement of the behaviour of mortar in the freeze/thaw cycles.

Some surprising results justify the relevance of continuing this still incomplete research. The intention is to gain more knowledge regarding the introduction of air in lime mortars, determine the influence of application on site and to develop a better framework for this subject in consideration to the resistance of mortars to freeze/thaw cycles.

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II.02

Assessment of an Experimental Test Setup for Glazed Tiles by Finite Element Simulations

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Abstract The use of glazed tiles in façades is typical of urban 19th Century Portuguese architecture and an identity marc that has been the subject of studies and thesis denoting the fascination of this artistic expression, but also the complexity of the theme, that still lacks a deep study in order to support conservation and restoration interventions. Ceramic tiles cannot be studied without taking into account their architectonic support, to which they give special chromatics and luminosity. Despite the large cultural heritage represented by buildings with ceramic tile façades, conservation and restoration interventions have been made without a consistent basis. Conservation and restoration interventions need solid scientific knowledge of materials used in the old buildings in order to allow for the development of compatible materials and techniques. The characterization of tiles and mortars has been developed and although characterization schemes are currently applied with success in mortars, further development is needed in terms of tiles and of the mortar/tile system. Some of the main problems to be found in ceramic panels are cracking and detachment originated by differential volumetric variations of the different materials (masonry, mortar and tiles) originated by hydrothermal actions. Numeric modelling of these structural systems will allow for the identification of critical areas, that may need intervention and, above all, numerical experiments can be used to test solutions related with the experimental tests. This paper presents numerical simulation for the determination of mechanical behaviour of tiles that includes tension and shear parameters. The results of the numerical model are compared with results of laboratory tests. The model aims at being a tool to evaluate the compatibility of mortars for the re-adherence of ancient tiles.

1 Introduction

Although the use of ceramic glazed tiles in façades is widespread throughout Portugal, having reached its peak in the 19th Century, a considerable number of

buildings need intervention. Detachment, cracking, and loss of tiles are frequently noticeable in these façades, and the lack of a solution to these problems contributes to further degradation [1-2]. In order to establish a solid basis for the conservation of this particular heritage, a scientific approach comprising the study of materials and behaviour of the mortar/tile system is necessary. With the aim of studying the adhesion and shear between the elements present in the system, numerical modelling and laboratory tests were initiated to evaluate these parameters and their effect on the degradation/conservation of these systems.

2 Testing and modelling glazed tiles

The problem of modelling glazed tiles regarding mechanical actions is rather complex. In fact, at least three materials are involved: masonry (or other wall support); mortar (or other material used to bond the tiles to the wall); and the glazed tiles. Besides these materials, there are the interfaces between them: tile/mortar and mortar/brick. Therefore, an adequate modelling of the mechanical behaviour of glazed tiles in façades will imply the knowledge of the properties of three materials and of the bond between them.

Strength properties of bricks and mortars are commonly available or can be determined from standard tests, but there is usually little or no information for tiles. In addition, deformation properties (modulus of elasticity) of the materials are more difficult to obtain. Further difficulties arise when ancient constructions are being restored, because information regarding old materials is even less accessible.

Characterization of the interface behaviour between mortar, tiles, and bricks is difficult and involves several problems. Appropriate tests do exist, such as ASTM C 482 [3] to characterize the bond strength of ceramic tile to Portland cement paste or RILEM MR14 [4] for determination of the bond of renderings by shear tests. Although such tests are not completely adequate for the characterization of the tile/mortar/brick structure, they can be used as a basis for the development of new test.

In this work, a protocol is being developed to assess the tile/mortar/brick structure with a single test. Basically, the test is a double shear test in which two glazed tiles are bonded to one central brick. The whole specimen is then tested under a compressive load (see Fig. 1). The layout of the test is similar to that of RILEM MR14.

This test is aimed to characterize the type of failure that will occur due to shear actions at the interface of the materials. These actions may be caused by differential movements of the different materials as a result of moisture or temperature, for example, or by direct applied forces. With this layout it will be possible to identify the weakest point of the structure, since failure theoretically can occur in mortar, in the tile/mortar interface, or in the mortar/brick interface.

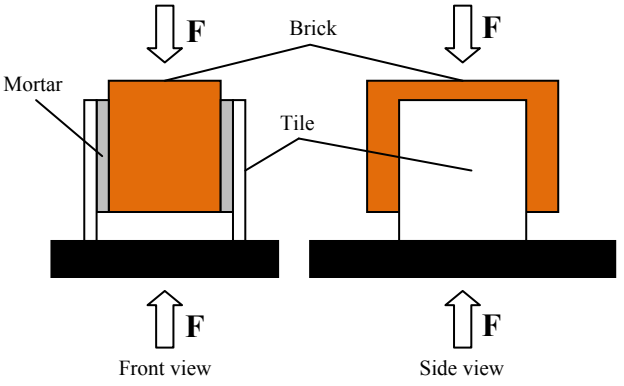

Fig. 1 Layout of the test

Because this type of test is not really a shear test, in the sense that shear stresses are not constant in the interface of the materials and that the tiles could bend, a series of numerical simulations has been performed to investigate the importance of the geometry in the performance of the structure. It is expected that the main mechanisms of the test will be identified with the numerical simulations.

The results, in terms of shear stress, τ, can be obtained by dividing the applied force, F, by the contact area of the two tiles, A_t, as:

$$\tau = \frac{F}{2A_t}. \tag{1}$$

3 Experimental results

A small preliminary series of tests was performed to assess the testing apparatus. In these tests, the geometry of the test specimens was as shown in Fig.1. The mortar used in these preliminary tests had a 1:4 cement to sand ratio and a water content of 20% of the cement weight. Tiles were placed as is usual in Portugal, by first placing a layer of mortar on the brick and on the tile back and then placing them together. The bending strength of mortar, measured in a standard 40 mm x 40 mm x 160 mm prism was 4.31 MPa. Tiles had a size of 150 mm x 150 mm x 5 mm, and the contact area of mortar with the tile was 140 mm x 150 mm. Brick thickness was 70 mm. A photo of the test specimen is shown in Fig. 2. To ensure an adequate contact surface between the tiles and brick with the testing machine plates, a 5 mm neoprene plate was introduced between the machine and the specimen. Tests were performed under displacement control at a rate of 0.01 mm/s.

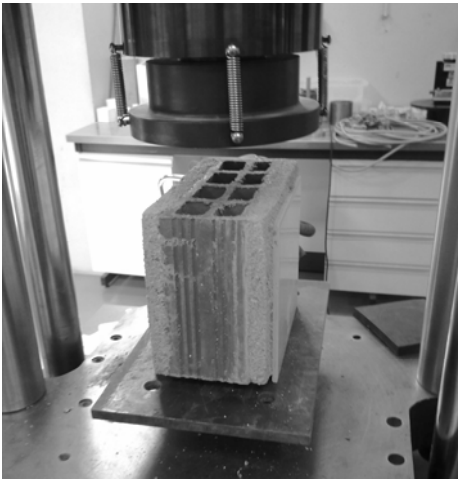

Fig. 2 example of specimen tested and load apparatus

All specimens broke, as expected, at the tile/mortar interface, indicating that the test setup is appropriate for characterization of that interface. The average force measured was 1.8 kN. The average shear stress as defined by equation (1) was τ = 85.7 kPa. A photo of typical tile and mortar surfaces after the test is shown in Fig. 3.

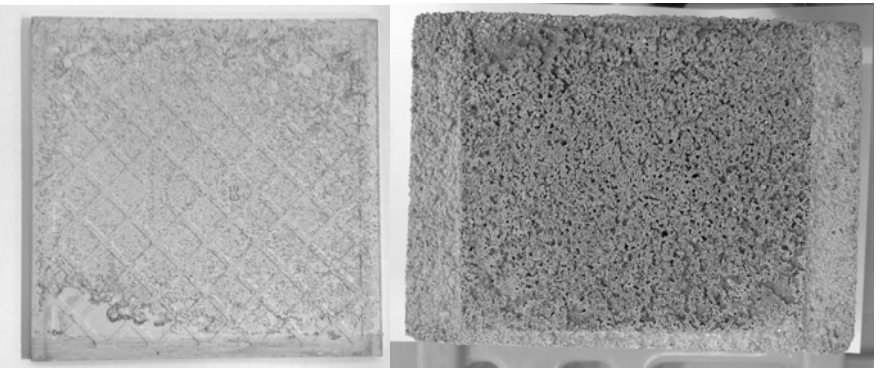

Fig. 3 Typical tile (left) and mortar (tight) surfaces after the test

4 Finite element model

A 2-D finite element model that uses plane and link elements was applied. The software used was SAP2000. Four-node plane finite elements were used to model

glazed ceramic tiles, mortar, and bricks. Linear-elastic behaviour was assumed for these elements. For the interfaces, two-node link elements were employed. These are the only finite elements of the model with non-linear behaviour. Two sets of properties were used for these elements in order to model tile/mortar and mortar/brick interfaces.

The material properties (Young modulus and Poisson coefficient) used for the brick, mortar, and tile are presented in Table 1.

Table 1 Material properties for finite element calculations

Name	E (N/mm2)	υ (-)
Brick	8000	0.30
Mortar	15000	0.20
Tile	150000	0.15

Regarding the stiffness of the links, a parametrical study was performed in which the properties of normal and tangential stiffness were changed. Because the links were used to simulate the bond between materials, their stiffness should be high so that a perfect bond between materials could be modelled. On the other hand, if it is too high some numerical errors could occur.

Table 2 List of numerical simulations

Designation	Mortar thickness (mm)	Type of mesh	Stiffness of spring (kN/m)	Horizontal displacement
15-5-rf	15	Refined	10^5	Free
15-6-rf	15	Refined	10^6	Free
15-7-rf	15	Refined	10^7	Free
15-6-rr	15	Refined	10^7	Restrained
15-6-cf	15	Coarse	10^6	Free
10-6-cf	10	Coarse	10^6	Free
20-6-cf	20	Coarse	10^6	Free

To investigate the effect of the size of the finite elements in the performance of the model, two finite element meshes were used where the maximum size of the shell elements is 0.125 and 0.250 mm. The finite element meshes used are shown in Fig. 3. Because the friction between the tile and the load plate could be important, a simulation considering the tile-restrained horizontal movement was also analysed. Different thicknesses for the mortar layer were also investigated (10 mm, 15 mm, and 20 mm), though 15 mm is the standard thickness. The different configurations used for numerical tests are shown in Table 2.

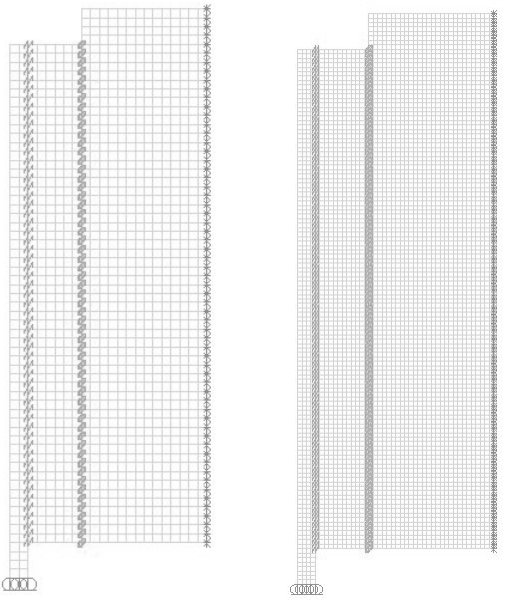

Fig. 4 Finite element meshes used in simulations

5 Results of the numerical analysis

In this section, a comparison of different models is performed to show the advantages and disadvantages of each test configuration. The results presented were obtained for the average load of 1.8 kN.

In Fig. 5 and Fig. 6 the normal and tangential stresses at tile/mortar and mortar/brick interfaces for different stiffness of the interface elements are plotted. Regarding normal stresses at the tile/mortar interface (see Fig. 5), it is evident that a peak tensile stress occurs near the bottom of the mortar. This peak tensile stress occurs approximately at the same location as the maximum tangential stress. This combination of stresses seems to indicate that failure at the tile/mortar interface occurs due to a combination of shear and tensile stresses. It also can be observed from the figures that the shear stress is not constant along the interface, indicating that the average stress defined in equation (1) is in fact only a conventional shear stress failure. The mortar/brick stresses observed in Fig. 6 indicate that if failure occurs at this interface it will start at the top of the brick, due also to a combination of shear and tension. The failure observed in the experimental tests indicates that the mortar/brick interface was stronger than tile/mortar interface.

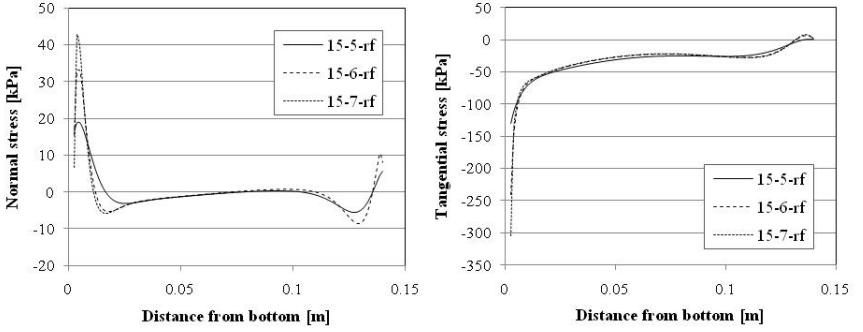

Fig. 5 Normal (left) and tangential (right) stresses at tile/mortar interface for comparison of link stiffness effect

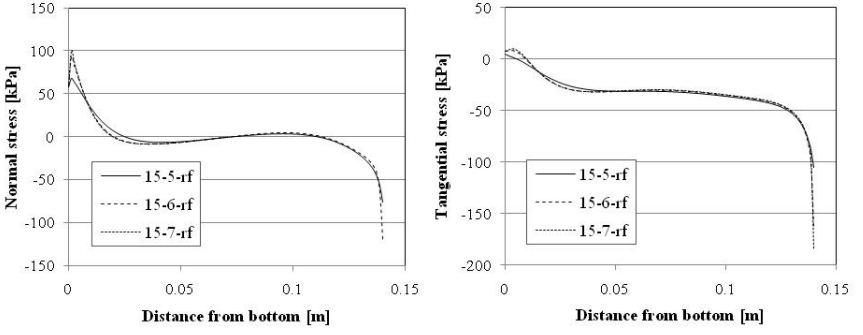

Fig. 6 Normal (left) and tangential (right) stresses at mortar/brick interface for comparison of link stiffness effect

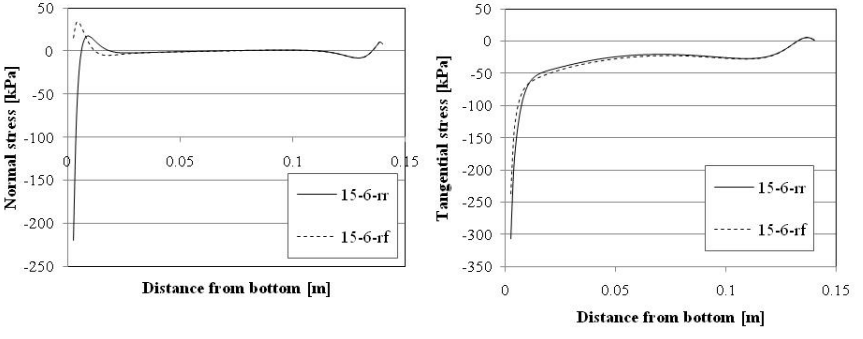

Fig. 7 Normal (left) and tangential (right) stresses at tile/mortar interface for comparison of horizontal restraint effect

In Fig. 7 the effect of the horizontal restraining in the tile/mortar interface stresses is shown. It can be seen that for a small perturbation at the bottom of mortar, the stress distribution along the interface is very similar.

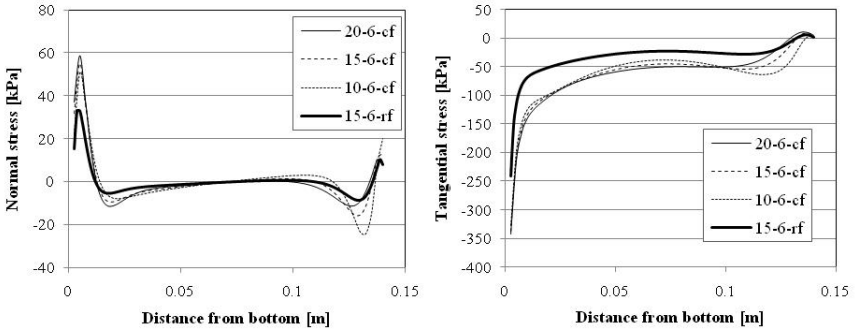

Fig. 8 Normal (left) and tangential (right) stresses at tile/mortar interface for comparison of mesh size and of the mortar thickness effect

The effects of the mesh size and mortar thickness in the tile/mortar interface stresses are shown in Fig. 8. Regarding the effect of mortar thickness, it is apparent that small variations in thickness cause no significant changes. However, it was observed that the size of elements used in the finite element mesh may have some influence in the calculation of the stresses, indicating that further analysis and comparison with experimental tests should be performed in order to obtain adequate meshes.

6 Conclusions

In this study a layout for the assessment of the behaviour of ceramic glazed tiles in façades has been investigated. Both experimental and numerical tests have been performed. The results and conclusions presented here represent only preliminary investigations on the subject. Nevertheless, some conclusions and guidelines for the continuation of the study can be drawn:

- Despite the fact that the failure modes obtained were in agreement with what was expected, it was not possible to conclude whether failure occurs by tangential or normal stresses in the tile/mortar interface. In fact, according to numerical results it is most likely that failure occurs by a combination of tangential and normal stresses.
- The numerical model adequately simulates the tests and is an important tool for the assessment of the experimental setup, given valuable indications regarding the points that must be taken under consideration.

Despite all the limitations and additional research work necessary to use this type of test, it seems that it can be used for the characterization of the behaviour of glazed ceramic tiles in façades.

7 Acknowledgements

Funding provided by the Portuguese Foundation for Science and Technology to the Research Units LABEST and GeoBioTec and to the Project PTDC/ECM/101000/2008 – AZULEJAR – Conservation of glazed ceramic tile façades is gratefully acknowledged.

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II.03

Lime Lump Development and Textural Alteration during the Production of Mortar

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Abstract Historic lime mortars are complex materials that are often seen to contain lime lumps. The origin of lime lumps is debated and at present no single cause of formation has been agreed upon. An experiment to analyse the production of lime lumps within the early life cycle of a mortar was formulated to clarify this problem. This article presents the background and the early results of the burning and slaking of four selected samples.

1 Introduction

Historic lime mortars, like any material derived from a geological source, are complex and diverse; however such mortars must always contain a lime rich binder and any combination of aggregates and admixtures. Within the binders of such mortars, it is common to find lime lumps, also referred to as lime inclusions, lime clots and binder related particles. These manifest as rounded particles between 10μm – 3cm in size which are primarily white – yellow in colour. They are seen to contain internal cracks and lack traces of aggregate; often they are found to contain relict limestone textures, are porous and consist of a fine grained sub-microscopic structure that predominantly consists of calcite crystals.

The most debated topic within the study of lime lumps is their mode of formation; several hypotheses exist but few have been proven. At present, most authors tend to fall into three schools of thought: those that believe the cause is related to the process of dry slaking, those that believe the cause is related to slaking, and those that are undecided. Dry slaking is at present the most popular theory within academic circles.

2 The experiment

A simple study has been formulated to examine the formation of lime lumps during the production of a lime mortar; starting from the production of quicklime through to the final mixing and hydration of the mortar's binder. This article presents an overview of the initial phase of this work which involves a study into the changes that limestone undergoes as it is calcined into quicklime and its effect on reactivity.

2.1 Samples

Four limestones were tested; three from Scotland and one from England.

Dornie: From the Ballachulish subgroup of the Dalradian rocks of the Highlands of Scotland, near Fort William. This is medium to coarsely crystalline metamorphosed limestone (strictly a marble) which commonly outcrops in beds of dark grey fine to medium crystalline limestone interbedded with thinner dark grey pelites [1]. It comprises of coarse equigranular calcite in a granoblastic low texture, with finely disseminated silicates in quantities of a few percent, quartz, sheet silicates, pyrite and some oxides. The stone has no porosity visible in thin section.

Parkmore: This limestone is also from the Dalradian supergroup, but is located within the Blair Atholl subgroup and Sandend group. A metamorphosed limestone, it appears to be lithologically similar to the Dornie limestone but contains veins of coarse white twinned calcite [2-4]. Accessory minerals within the limestone include quartz and muscovite; traces of MgO, Al_2O_3 and Fe_2O_3 have also been found during analysis [4].

Trearne: A biomicritic packstone from the Brigantian sedimentary succession of the Midland Valley. It is a sedimentary limestone containing abundant crinoid, coral and mollusc fragments and typically 50% mud [5] with minor inclusions of quartz, kaolinite and pyrite.

Ham Hill: This limestone is found as a lense within the Upper Yeovil Sands of Somerset. It is a shelly bioclastic sedimentary limestone, with a high porosity. It is famed for its honey brown colour which is caused by the presence of Goethite, an iron hydroxide; accessory minerals include limonite and quartz [6].

2.2 Calcination and reactivity testing methods

Each limestone was crushed into fragments 2-6 cm in length. Sample sets were then created which consisted of either 25 or 30 fragments (dependant of limestone sample); each weighing a total of 600g.

Using a programmable laboratory furnace each sample set was heated from room temperature at a rate of 40°C /min to 450°C to avoid shock calcination. This

temperature was maintained for one hour before the temperature was further increased at the same rate to 900°C (the disassociation temperature of calcite being 898°C [7]). The samples were each subjected to calcination for set time periods ranging from 2 hours to 5 hours at 30 minute intervals.

After the residence time for each sample had been achieved and a duration of at least an hour passed, the samples were removed from the furnace, weighed, and left at room temperature to cool. Once the samples had cooled, they were crushed and sieved through a 3.35mm sieve; 150g of the sample was then selected for testing. Following this the samples were tested for reactivity using the wet slaking test described in BS EN 459-2: 1994 combined with ASTM C110 – 04, where the 150g of quicklime was added to 600g of distilled water with a starting temperature of 26-28°C. The temperature rise was recorded every thirty seconds for a period of fifteen minutes, whilst the sample was stirred mechanically.

The results of temperature change versus time were recorded and plotted on a series of graphs. The percentage of weight loss that occurred during each burning, the rate of temperature rise in the first thirty seconds, and the temperature at which the reaction is 80% complete (Tu), was determined for each sample set. The Tu was calculated according to the following formula which is outlined within BS EN 459.2:1994.

$$Tu = (0.8 \times Tmax) + (0.2 \times To)$$

Where: Tmax = maximum temperature achieved during slaking
To = start temperature

3 Results and discussion

As seen in Table 1, the rate of temperature rise in the first thirty seconds of the reaction is generally constant amongst the limestones sampled and, as indicated by the low standard deviations, throughout the sample sets for each limestone. It is this period in the reaction that reflects the greatest reactivity due to the instant hydration of the CaO on the surface of the quicklime particles.

The Dornie limestone displays a higher rate of temperature rise than all other limestones tested (Fig. 1); reflecting a greater abundance of CaO available for an initial reaction, therefore indicating a potentially well calcined, pure limestone.

Fig. 2 displays the percentage weight loss for the Parkmore, Dornie and Trearne limestones. As it can be seen, only the Dornie and Ham Hill limestone samples achieved complete calcination (with losses averaging 40%), whereas the results of the Parkmore and Trearne samples indicate incomplete calcination with a weight loss closer to 30%. This is predominantly due to the impure nature of these two limestones when compared to the Dornie and Ham Hill samples.

Table 1 A comparison of the slaking characteristics of each sample

	Parkmore	Dornie	Dornie inc. Retest	Ham Hill	Ham Hill inc. Retest	Trearne
n	7	10	1	8	1	5
Average Rate of change in first 30 seconds (°C/second)	1.5	2.49	2.53	1.77	1.77	1.73
Standard Deviation	0.09	0.2	0.24	0.06	0.06	0.15
Average Tu (°C)	48.73	65.91	66.77	60.96	61.51	52.88
Standard Deviation	3.04	4.53	5.24	2.42	2.01	3.95
Average % Weight Loss	30.63	40.53	40.73	39.6	39.87	33.14
Standard Deviation	5.3	2.06	2.11	1.41	1.41	2.93
Maximum Temperature Reached (°C)	58.5	84		74		65
Residence time which produced most reactive quicklime (hours)	4.5	4		3.5		4
Average Time for reaction to Complete (seconds)	450	72		259		190
Standard Deviation	156.84	35.21		39.07		75.1

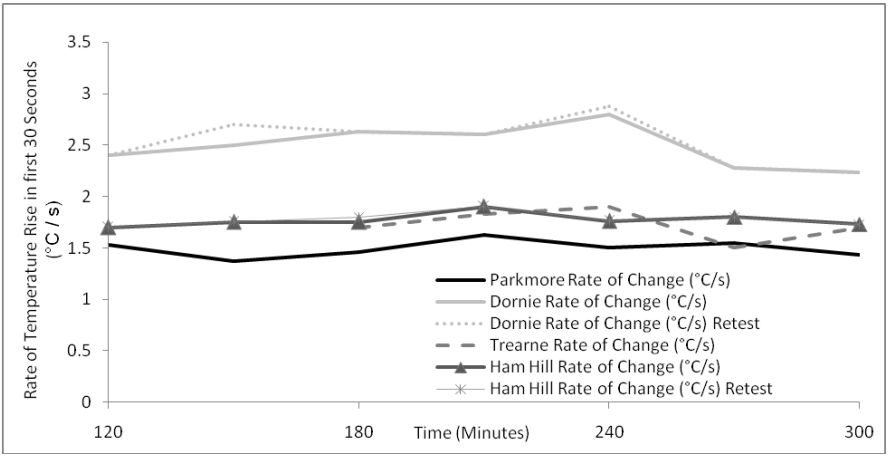

Fig. 1 A comparison of the rate of temperature rise during the slaking test in the first 30 seconds versus calcination time for each limestone.

The percentage weight loss across sample sets is quite consistent, as seen be low standard deviations (Table 1), therefore reflecting a homogeneity between all sample sets, bar the Parkmore limestone. The inconsistency between the Parkmore samples is due to the calcite veins present in some, but not all, of the fragments.

Fig. 2 shows that the Dornie, Trearne and Parkmore (and to a lesser degree Ham Hill) limestones display a common pattern in weight loss; between residence times of 2 – 3 hours the samples show a small rise in the percentage of weight lost, at which point the samples would be under burnt. At 3½ – 4 hours, the samples show a maximum percentage weight loss, reflecting a period of peak reactivity and therefore the period at which the samples undergo the most thorough calcination. Beyond this period, the percentage begins to drop as the samples become over burnt and weight loss is reduced due to increased residue left after the reaction has finished. This reduction is only noticeable in the Parkmore and Trearne limestones at this time; the Dornie limestone only displays a decline after 4 hours and the Ham Hill limestone only displays a very slight drop. Without further analysis this variability can not be easily explained; however such behaviour is possibly related to porosity as the Ham Hill limestone is very porous when compared to the Parkmore limestone.

The Parkmore limestone shows an interesting trait as after 4 hours the percentage weight increases; due to this being restricted to a crystalline limestone (a similar but slighter rise can be seen for the Dornie limestone) this is presumably due to an increase in density resulting from the agglomeration of crystals and the sintering of the limestone within the kiln [8].

As seen in Fig. 3, the Dornie limestone is the most reactive of those tested; this is confirmed by the rapid rate in which the hydration reaction is completed as well as the highest maximum temperature and Tu. The optimum residence time for the Dornie limestone is 4 hours; as is indicated by the attainment of the highest

maximum temperature during this period as well as the highest percentage weight loss and fastest rate of reactivity. The slaking curve of the optimum residence time can also be seen to exceed that of commercial quicklime (Fig. 3).

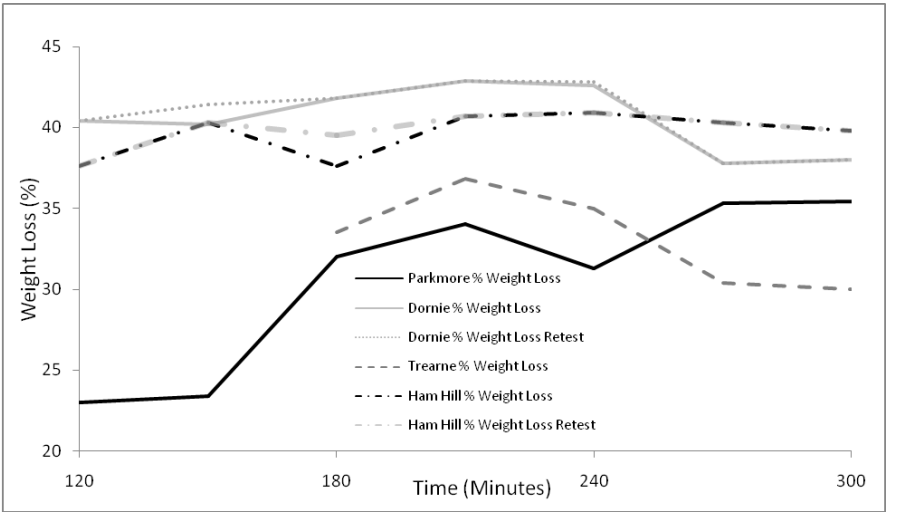

Fig. 2 A comparison of the percentage weight loss for the Dornie, Parkmore and Trearne Limestones

As it can be seen in the SEM images in Fig. 4, once calcined, the Dornie limestone displays a highly porous open texture due to the release of CO2 during calcination. This therefore produces highly reactive quicklime with a large specific area and a low density with an abundance of CaO available due to the low level of impurities present within the Dornie limestone.

The Ham Hill limestone is the second most reactive limestone, and in terms of reactivity, this limestone is most similar to the commercial quicklime tested (Fig.3).

Ham Hill differs from the others limestone samples by having a lower optimum residence time of 3½ hours; confirmed by the results of a residue analysis that was conducted on the Ham Hill and Parkmore sample sets. After the slaking test of each set had been completed, the residue was sieved through a series of graded sieves ranging from 2mm to 500μm – producing an overall analysis of residue ranging from 3.35mm to 500μm, the results of which are seen in Fig. 5. Fig. 5 shows that minimal residue was also produced for the 4 and 4½ hour residence times but temperature and therefore reactivity was not optimum for this period.

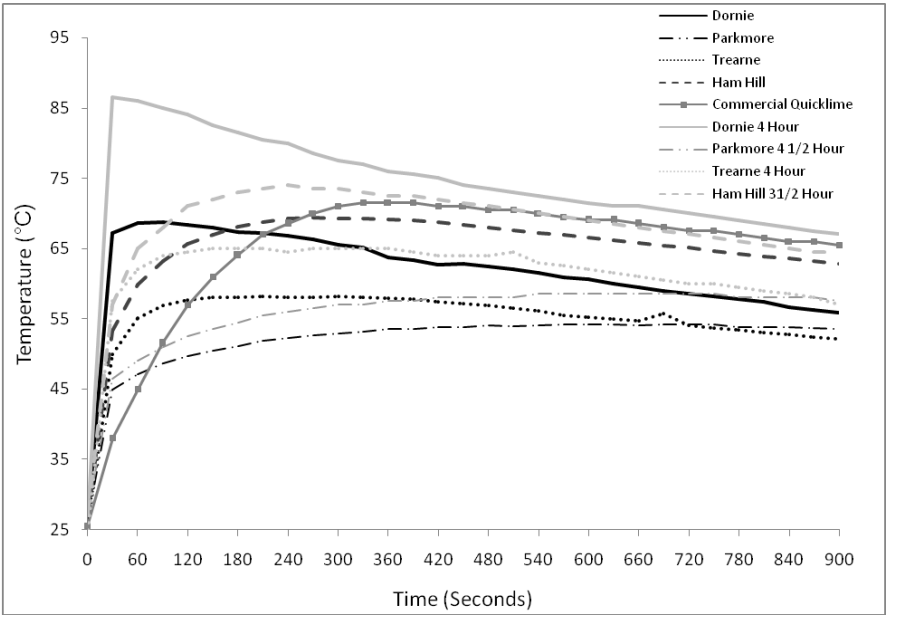

Fig. 3 A Comparison of the average reactivity (in black) and the maximum reactivity (in grey) of Each Limestone and non-hydraulic commercial quicklime.

Ham Hill is relatively reactive due to its high porosity and calcite content resulting from an abundance of bioclasts. The lower rate of reaction and maximum temperature would result from the inclusion of impurities within this limestone.

The Trearne limestone, the third most reactive, would also share an availability of pure calcite resulting from a bioclastic content; however the clay content of the limestone would impede the porosity as the fibrous clay particles tend to seal and existing pore spaces within the limestone [8], resulting in a denser limestone that is harder to calcine and is therefore less reactive.

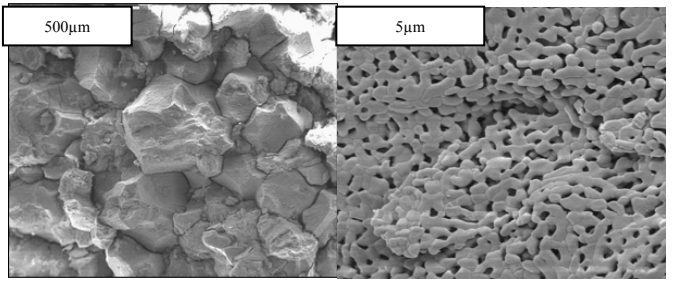

Fig. 4 SEM images of the Dornie limestone – Right: limestone before calcination, showing the granoblastic texture. Left: after calcination at 900°C for 3hrs.

The Parkmore limestone is the least reactive limestone tested; however the samples also display the most variability in terms of percentage weight loss and time to complete the hydration reaction. Such variability may be caused by the tendency for each sample set to maintain its optimum temperature for a period of at least 60 seconds; a trait not displayed by the other limestones.

The optimum residence time for the Parkmore limestone was 4 ½ hours, the highest of all the limestones. Again this can be confirmed by the results of the residue analysis seen in Fig. 5; this graph also demonstrates the variability of the samples.

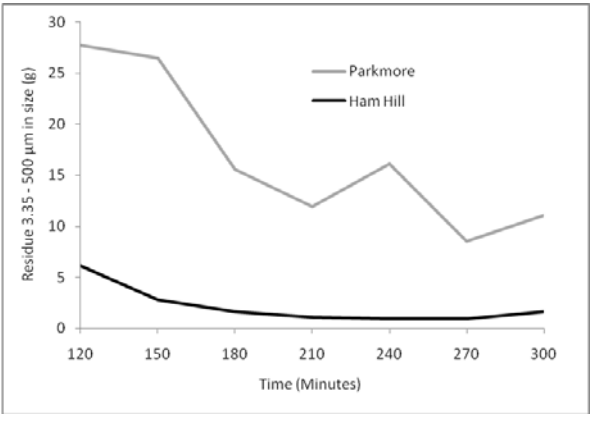

Fig. 5 The results of a residue analysis for the Parkmore and Ham Hill limestones

Parkmore, although texturally similar to Dornie is most likely to be the denser of the two. This density would impede the calcination of the limestone by preventing the progression of CO2 throughout the crystal lattice resulting in the incomplete calcination of samples (as seen by the percentage weight loss) [7]. The under burned nature of the quicklime would reduce the availability of calcite available for hydration resulting in a poor rate of reactivity.

4 Conclusion

As it can be seen the use of reactivity is a successful method for determining the peak calcination conditions for individual limestones; however none of the limestones used have yet to show the characteristic lag in reactivity that according to Boynton [7] is common is the lesser reactive limestones.

It is hoped that once the calcination experiments have been completed, the results can be combined with detailed petrographic and chemical examination to further understand each sample used within this experiment. Once this is done, it will be easier to notice changes in the structure of the limestones that are unusual and therefore possibly related to the early stages of lime lump development.

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II.04

Characterization of Mortars Using DRMS: Tests on Field Panels Samples

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Abstract Non-destructive or at least micro destructive *in situ* tests are very relevant on physical characterization of materials used in historical buildings. "Controlled penetration", "sphere shock" and "sonic methods" can be used to evaluate mechanical resistance of mortars and renders or to monitor the evolution of the surfaces after their application. Used to evaluate surface hardness, *micro-drilling* (DRMS) is a very sensitive technique and its use in this field is expected to contribute for more precise results. The diversity of the composition of the mortars and the systematic presence of abrasive components are limiting factors for the use of this method in this field. In this study, several mortars with different composition and hardness are compared, using drilling resistance as the comparative parameter. The mortars were applied on site aiming at their use in real situations and some samples were tested in laboratory, using conventional techniques complemented by others currently used for on site characterization of materials. The results also highlight the need of having an integrated perspective of laboratory and on site information.

1 In situ testing of mortars and renders. General aspects

The conservation of old renders and mortars requires a full characterization of the old materials as well as a very good knowledge of the new ones considered as the most adequate solutions for their replacement. In general, both laboratory and on-site characterizations are considered necessary, and the integration of these two types of information is required for a correct diagnosis and to reach the best solution during conservation or restoration.

Studies performed in laboratory conditions involving mortars and renders usually consider several parameters and are very well documented in the vast literature published in this domain [1-4]. Although the characterization of the

materials applied on-site is considered necessary, the few techniques are available and are considered inaccurate. The LNEC team has been using several methods to characterize old mortars on-site to evaluate the decay state and the properties of the old materials where they are still well-preserved. In some cases, to complement laboratory studies, experimental panels of new formulations have been prepared in order to predict their behaviour, to allow a better selection for the specific case [5-7], and to evaluate the compatibility with locally preserved old materials.

Quite often, the methods used *in situ* to determine specific parameters that are considered very relevant for a good performance. Such parameters include "the adhesion to background" and "degree of carbonation" (applicable to control the evolution of new formulations in time), as well as water properties, such as "water content" and "water permeability under low pressure." *In situ* techniques also can provide specific information about the type of salts present that can explain decay, and they can help control the expected behaviour of new formulations. Regarding the mechanical characterization, some relevant tests also can be done in order to indirectly evaluate the strength of the render, including 1) *"sphere impact"* and 2)*"controlled penetration,"* two tests that are able to evaluate a kind of resistance offered by the material when a physical object hits the surface. A sonic method, namely 3) *"Pulse wave velocity,"* is a very interesting non-destructive technique; when it is used to characterize a surface, the "indirect array" must be used, although, in this case, additional difficulties related to the interpretation of the results are introduced. "*Schmidt hammer test*" also could be used to evaluate rebound hardness [8], but its use on mortars is limited compared to its use in objects made of concrete. Actually, the integration of all the information provided by multiple tests is generally accepted as the best philosophy.

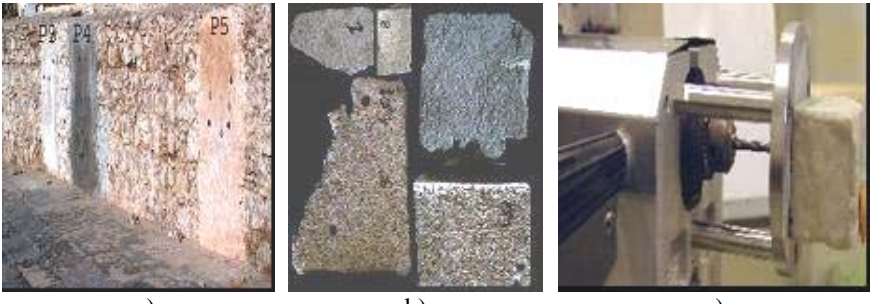
In addition to mortars and renders, on-site characterization of other types of materials and their decay state is a universal demand. *Non-destructive* or at least *micro-destructive* tests have been developed in the last years for better characterization of stone materials used in historical buildings. For example, the 4) "*micro-drilling technique (DRMS)*" was developed for stone characterization, not only in the laboratory but mainly for *in situ* analysis [9]. When applied to mortars, this technique needs to be properly evaluated, given the peculiar nature of these materials, specifically their high quartz content and high heterogeneity. A new instrument has been available and has been successively updated since about 2000 (SINT Technology, Italy), but its use for the characterization of mortars is still very limited.

This paper presents the results of drilling tests performed on samples collected from experimental panels prepared with several lime based mortars, applied in a fortress near Lisbon ("Forte dos Oitavos"). The original compositions of the old lime mortars present and compatibility criteria [7] were taken into account during sample selection.

2 Materials and methods

2.1 Samples

In this study, several compositions of mortars were considered. They include several binders: lime, hydraulic lime, natural pozzolan (from Cabo Verde), silica fume, metakaolin, and white cement. The panels were prepared according to a specific protocol [9], and the mortars were applied in two layers with different compositions, as is usually the case in traditional renders. The panels' compositions are described in Table 1. Fig.1 illustrates three zones of those experimental panels on the Fortress walls (a), the macroscopic aspect of the mortars (b), and the drilling equipment used (c).



a) b) c)

Fig. 1 The experimental panels (a), the macroscopic aspect of the mortars (b), and the DRMS front (c)

After *in situ* characterization, some samples were removed from the panels for laboratory testing (Fig. 1b). These samples are more heterogeneous than conventional laboratory specimens because they are composed of two different layers. Furthermore, they have been exposed to complex conditions, namely, submitted to suction of the substrate in fresh state, variable climatic conditions during the hardening period, and exposure to air over much of the surface. These external conditions produce changes in the mortars' microstructure not expected in the laboratory samples.

Table 1 Composition of mortars tested on the experimental panels

Main constituents	P1 Lime/Hydraulic lime	P2 Lime/White cement	P3 Lime/Pozzolan	P4 Lime/Silica fume	P5 Lime/Metakaolin
Volumetric dosage (*air lime: other binder :sand*)	1:1:6 (1st) 1:2:9 (2nd)	1:1:6 (1st) 1:2:9 (2nd)	1:0.5:2.5 (1st) 1:0.5:3 (2nd)	1:0.25:2.5 (1st) 1:0.25:3 (2nd)	1:0.5:2.5 (1st) 1:0.5:3 (2nd)

(1st) – first layer; (2nd) – second layer

2.2 Methods

This study will focus on the drilling test results obtained on samples indicated above. In addition to the DRMS data, ultrasonic and compressive strength results are used for comparative purposes. Other swift techniques used to characterize mortars on-site are also taken into account.

2.2.1 Micro-drilling technique (DRMS)

The test consists of drilling a hole and continuously measuring the penetration force with a load cell. During the test, the rotational speed and the penetration rate are kept constant. "Drilling resistance" or "surface hardness determined by drilling" are terms also used to express the value measured.

Several types of drill bits can be used; in this case a 5 ϕ mm of Fischer Extra produced by BOSCH was used. The initial conditions of testing were selected taking into account the expected low resistance of these lime-based materials. The rotation speed of 100 revolutions per minute and the penetration rate of 10 mm/min were selected ("100/10"). Moreover, higher values of rotation speed (until 1200 rpm) were also used in order to test the harder samples. This paper only presents results obtained with "400/10." To compare and control the wear effect of the drill bits, a very soft, non-abrasive, and homogeneous limestone (Ancã stone) was used.

The experience gathered by utilizing this method on several rock materials allowed us to take several aspects into account when interpreting the drilling data. The "packing effect" due to difficult removal of cuttings and the "abrasiveness" of the material on the drill bit are two examples of effects that can increase the measured values [11, 12].

2.2.2 Other techniques

The *Ultrasonic pulse velocity* (UPV) is calculated as the travel time of the longitudinal wave between two points located at a known distance in the material. An electro-acoustical transducer held in contact with the surface produces a pulse of longitudinal vibrations. After traversing the material, the pulse of vibrations is re-converted into an electrical signal by a second transducer placed at a known distance. Electronic timing circuits enable the transit time of the pulse to be measured. In laboratory conditions, the UPV was determined following the *direct mode* (transmission), by using exponential transducers of 45 kHz. In the field, the *indirect mode* (refraction) can also be used, although it usually leads to less accurate results.

The *Sphere impact test* consists of impacting a hard body with the energy of 3 joules, produced with a steel sphere of 50 mm in diameter. The impact resistance evaluated through the diameter of the concussion made by the sphere and the type of resulting damage allow the assessment of the mortar's deformability.

The *Controlled penetration test* consists of the penetration of a steel nail, guided by a device fixed to a Martinet Baronnie apparatus to guarantee that the stroke is perpendicular to the surface. Several impacts (typically, three impacts) with constant energy are produced and the respective penetration depths are registered. This test gives information on the mechanical resistance of the internal render coats, permitting the assessment of their performance [6, 7].

3 Results

3.1 Drilling tests

Drilling tests performed on mortars show very different characteristics in comparison with typical graphs obtained in homogeneous rocks such as Ançã (as it is shown on Fig.2, blue line in P2, on the left). Mortars are very heterogeneous materials, and the presence of quartz grains justifies the large variations of the registered forces.

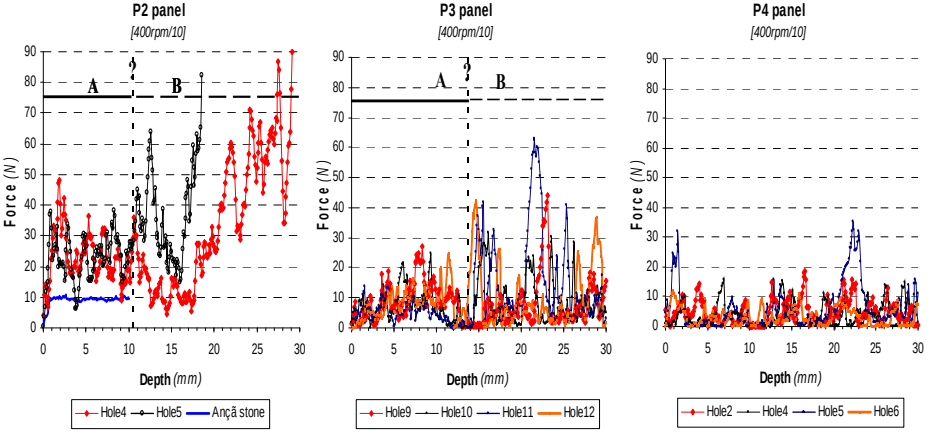


Fig. 2 Drilling graphs of panel samples. Note: A-"external layer", B-"internal layer"

Despite being so diverse and heterogeneous, the materials tested are clearly distinct. For instance, sample P4 shows lower values of drilling forces when compared to P3 and P2. P2 is the hardest of the tested materials. In two cases (P2 and P3), the graphs indicate the presence of two zones with different characteristics; the external layer (10-15 mm) is softer than the internal one, in which the values of forces are higher. This is explained by the application in two layers, with the internal layer designed to be harder than the external one. In the case of P2, the drilling of the "second layer" reaches the maximum limit imposed

by the load cell (100N), and even under extreme conditions (1200 rpm) it was not possible to drill this part of the sample. In this particular case, this is due to the presence of different layers in this sample, but without any information about the characteristics of the material, this effect could be misunderstood or attributed to the well known "packing effect" that results from dust accumulation inside the hole. In P3, the existence of two layers is also identified, but in this case the two zones are much more similar. On the contrary, the results for sample P4 do not differentiate the two layers as established in the preparation protocol.

A second handicap must be noted when the drilling technique is used to characterize mortars. In very weak materials, the resistance offered by the material is low. Fissures develop and propagate during the process, producing drill holes with irregular borders and increasing the variation of forces measured during the test. The indentation phase, well-recognized on a typical drilling graph, is not evident in the graphs obtained on mortars, as clearly seen on the examples. For all these reasons, the distributions of drilling forces obtained on heterogeneous materials have a pronounced range of values; the standard deviation is of the order of magnitude of the average values, and in these circumstances the results and conclusions must be taken with care. Even so, the method can also be used in these particular cases, especially if this information is properly integrated.

In this particular case, an evaluation of the mortars abrasiveness was taken into account when the drilling tests were planned. The results indicate that all the materials tested were able to wear the drill bit. In this context and for comparative purposes, the raw data without any correction are considered valid, and the discussion of this topic will be made in a future publication.

Table 2 presents the global average results of the drilling tests; in this context, these values include both layers, even when drilling tests can discriminate their presence.

Table 2 Drilling resistance measurements of mortars (average global values)

Panel Samples	P1	P2	P3	P4	P5
	Lime/Hydraulic lime	Lime/White cement	Lime/Pozzolan	Lime/Silica fume	Lime/Metakaolin
Force (N) *[400rpm/10]*	11.9	31.5	9.7	4.4	6.4

Each sample was tested with a different drill bit and about ten holes were drilled. The results are expressed as the mean value of the drilling forces along the total hole length. Of special note are the effect of the white cement in the resistance increase and the advantage of the addition of natural pozzolan in comparison with metakaolin or silica fume, which produces values similar to those obtained in a mixed formulation with hydraulic lime (P1).

The distribution of values is also meaningful and diagnostic, as evident in the histogram presented in Fig.3. P4 and P5 are considered "weak" mortars, identified by A in the graph. They are completely distinct from "strong" mortars identified as C, which in this particular case are characterized by a very wide range of

values, represented in this group by P2. B group represents intermediate characteristics of hardness and includes P1 and P3.

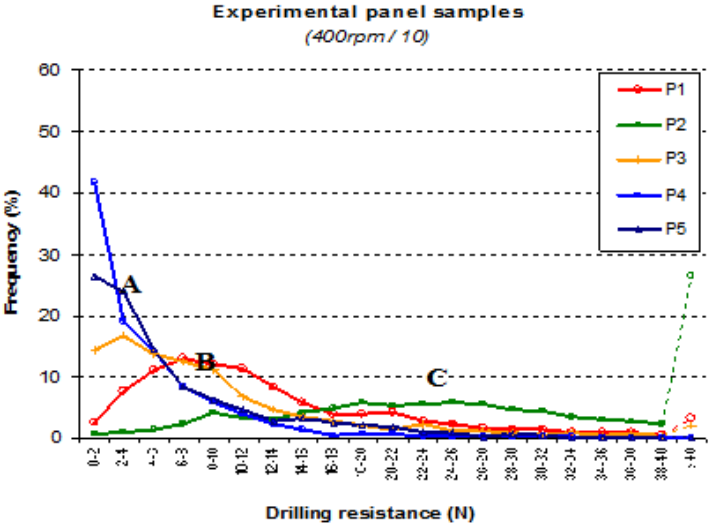


Fig. 3 Frequency distributions of drilling forces on mortar samples

3.2 Other resistance measurements

In different phases of the study, several data were obtained on the experimental panels; during the curing process, *sphere impact* and *controlled penetration* tests were performed. Later, samples were extracted and tested in the laboratory in different steps, the last one corresponding to the drilling and ultrasonic tests. For comparison, all data are presented in Table 3, and the graphs of Fig. 4 represent the most significant correlations.

Table 3 Drilling forces and other resistance measurements

Samples	P1 Lime/ Hydraulic lime	P2 Lime/ White cement	P3 Lime/ Pozzolan	P4 Lime/ Silica fume	P5 Lime/ Metakaolin
DR-Force (N) *[400rpm/10]*	11.9	31.5	9.7	4.4	6.4
Ultrasonic velocity (m/s)	1700	2900	1090	950	1530
Compressive strength (N/mm^2)	1.2	3.8	1.5	0.7	0.8
Sphere impact (ϕ, mm) *	15	12	11	15	11
Controlled penetration (mm)*[a]	11.7	7	6.6	10	9.7

[a] Σ three penetrations * Determined directly on panels after 14 weeks app.

Measured on-site, sphere impact and controlled penetration gave information about the evolution of the resistance in time, and the latter was able to discriminate the different mortar formulations. Nevertheless, as indicators of the final resistance of the surface, the interpretation must be considered with care.

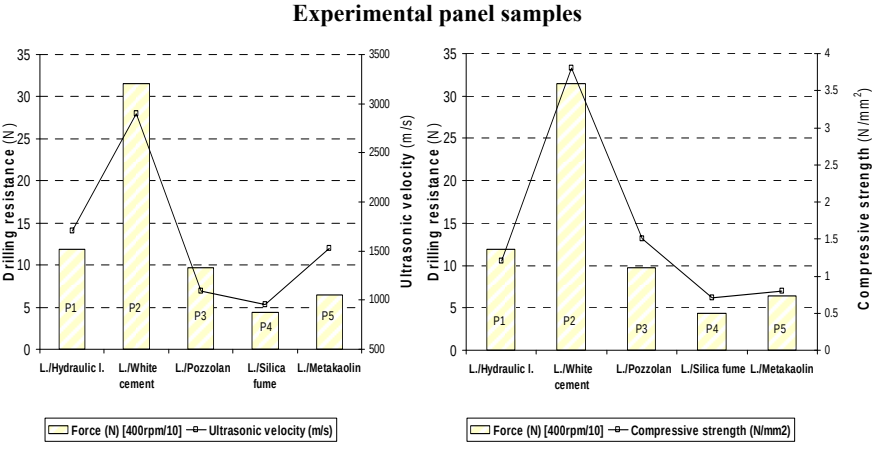


Fig. 4 "Drilling resistance" results versus "Ultrasonic velocity"/"Compressive strength"

The ultrasonic velocity is in good agreement with drilling results, although expressed by the average values of the distributions with great variations.

For hardness characterization, the drilling test should be performed on quite homogeneous samples, but these in situ samples are much more complex due to the application process by layers. In spite of this fact, the classic correlation of compressive strength to drilling hardness indicates the same behaviour, as is clear from the graphs presented here.

4 Conclusions

In this paper, non-destructive and micro-destructive techniques were used in the laboratory to characterize the mechanical resistance of mortars applied on experimental panels simulating real applications.

The ultrasonic velocity, measured in direct mode, is in good agreement with the drilling results. For hardness characterization purposes, drilling tests performed on very heterogeneous materials were able to discriminate different formulations of mortars, confirming the tendency indicated by the non-destructive method. The classic correlation of compressive strength to drilling hardness indicates a strong

correlation coefficient and must be considered an encouraging finding, but the low number of samples indicates a need for further research in this domain.

Further investigations should be conducted comparing laboratory samples with similar formulations prepared according to regular procedures used for laboratory testing. On-site characterization of mortars with similar formulations is also needed, not only because the methods must be applied in different conditions (as is the case of the sonic method), but also because the variability of local parameters can influence the final results obtained through on-site measurements.

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II.05

Influence of Mechanical Properties of Lime Mortar on the Strength of Masonry

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Abstract This paper aims at improving the quality of lime mortar masonry by understanding the mechanics of mortars and masonry and their interactions. It investigates how the mortar's compressive and flexural strengths and elastic moduli, impact the compressive and bond strength of clay brick masonry bound with calcium lime (CL) and natural hydraulic lime (NHL) mortars. It concludes that the strength of the bond, rather than the mortar's strength, determines the compressive strength of masonry, which increases proportionally to the strength of the bond with linear relationships up to 6 months. It was noted that low-strength-mortar masonry (CL90) with a good bond is stronger than that built with stronger mortar and a poorer bond. Finally, the mechanics of lime mortars and their masonry are similar. The predominantly elastic behaviour of the higher hydraulic strength mortars compares well with the elastic and brittle behaviour of their masonry, with either little (NHL2) or non existent plasticity (NHL3.5 and 5); in contrast, CL90 mortar and masonry exhibit a plastic behaviour.

1 Introduction

Mortar properties influence those of masonry to such a great extent, that a mortar can either enhance or adversely affect the durability of masonry. For example, deformations in the mortar have a greater effect on the behaviour of masonry structures than the strength/stiffness of the units [1]. It is widely accepted that historic mortars should be replaced with similar, compatible mixes. Research has focussed on specifying repair mortars based on the characteristics of the originals. Rather, this work proposes to understand the mechanical properties of mortar and masonry and their interactions in order to specify mortar repairs. It does not consider the properties of the original mortar but those of the new mortars, building units and resultant masonry. It investigates compressive and bond strength of masonry bound with lime mortars of diverse hydraulic strengths

(made with non hydraulic as well as feebly, moderately and eminently hydraulic limes) and thus different stiffness and deformability.

In relation to the mechanics of masonry in compression, it is generally accepted that the difference in elastic properties of the unit and the mortar is the precursor of failure ([2] referring to Hilsdorf 1969 and McNary and Abrams 1985). Uniaxial compression of masonry leads to a state of tri-axial compression in the mortar and of compression/biaxial tension in the unit: during compression lime mortars expand laterally more than bricks due to their lesser stiffness, however, within masonry, the mortar is laterally confined at the brick-mortar interface. As a result, shear stresses at the interface result in an internal state of stress which consists of triaxial compression in mortar and bilateral tension coupled with uniaxial compression in bricks. This state of stress initiates vertical splitting cracks in bricks that lead to prism failure ([3] referring to Atkinson and Nolan 1983 and Drysdale et al 1994). The properties of the units affect the mechanics of masonry in compression. The crushing strength of the weakest brick, rather than the interaction between brick and mortar, often determines masonry strength; and that this can mask the influence of the mortar's strength on the strength of the masonry [4]. In addition, masonry compressive strength is not sensitive to bond strength variations when the masonry unit is stiffer than the mortar [5].

The strength of the bond between mortar and units is essential, as it determines how the masonry transfers and resists stresses due to various applied loads. Water absorption has a significant influence on bond development and hence flexural strength [6, 7]. Mortars of different compressive strengths but similar bond strength result in similar masonry compressive strength; and both the bond strength and the masonry's compressive strength are not significantly impacted by the strength of the mortar [5, 8]. Current literature indicates that an increase in bond strength, while keeping the mortar strength constant, results in an increase in the compressive strength of the masonry [9]. The rate of brick absorption and the mortar moisture retention are essential to bond development, as they control moisture transport at the interface allowing formation of the hydrates that enable bond [10]. Results by [11] agree with these, stating that the main mortar parameter that influences bond strength of NHL-mortar masonry is water retention, followed by water content and, finally, hydraulic strength. The authors demonstrated that the strength of the bond is not determined by the hydraulic strength of the binder, but it increases with the mortar's water retention.

2 Materials and Methods

2.1 Materials

Mortars were made with CL90-s and three NHLs of hydraulic strengths 2, 3.5 and 5 MPa. A siliceous aggregate (particle size distribution ranging within the standard limits [12]) and moulded, frogged clay bricks (Table 1) were used. A binder: aggregate ratio of 1:3 by weight was kept constant.

2.2 Mixing and curing. Initial flow and workability

Water content is the main contributor to mortar workability and determines initial flow, a measurement that takes into account variables affecting workability, such as porosity, size/shape of aggregate, binder type and aggregate/binder [13]. A definite initial flow of 165±3mm was specified for all mortars to ensure adequate workability. Initial flow was measured [14], and the water content reported as the ratio of water to total mortar by mass. Mixing, curing and storage were in accordance with [14]. Wallettes were constructed in accordance with [15, 16, 17] for compressive, flexural and bond strength respectively.

Table 1 Brick Characteristics

Property (Testing standard: EN 771-1 :2003)	
Compressive Strength (N/mm^2)	≥ 12
Water absorption (%)	Max 15
Unit size (mm) / Size tolerance	215 x 102.5 x 65 /T2 - R1
Gross / net density (kg/m^3)	1630/ 1920
Initial rate of absorption (kg/m^2/minute)	1.0

2.3 Mechanical properties of mortar

Compressive (R_c,) and flexural (R_f,) strength were determined using equ.1 and 2 [12, 14]. Where: F_c is the max load at fracture (N); 6400 - area of the face (mm); F_f - load at fracture (N); b - prism section (mm); l - distance between supports (mm). The mortar's elastic modulus in both compression and flexion were determined from the stress strain curves. The modulus of elasticity in compression was found using eq.3. Where: ϵ_c is the strain; σ_c - stress; d_0 - original depth of the prism (mm) and d_i-d_0 - change in prism depth. Eq.3 was also used to determine the modulus of elasticity of masonry. The modulus of elasticity in flexure was found

using eq. 4. Where: σ_f is the flexural stress (N/mm^2); ε_f is the strain; m the slope of the linear stress-strain plot and D the deflection in mm.

$$R_c = \frac{F_c}{6400} \quad (\text{N/mm}^2) \tag{1}$$

$$R_f = \frac{1.5 \times F_f \times l}{b^3} \quad (\text{N/mm}^2) \tag{2}$$

$$E_c = \frac{\sigma_c}{\varepsilon_c} = \frac{\sigma_c}{\frac{d_i - d_0}{d_0}} \quad (\text{N/mm}^2) \tag{3}$$

$$E_f = \frac{\sigma_f}{\varepsilon_f} = \frac{\sigma_f}{6Dd/l^2} \frac{l^3 m}{4bd_0^3} \quad (\text{N/mm}^2) \tag{4}$$

2.4 Compressive and bond strength of masonry

Lateral variable displacement transducers recorded strain during compression [15]. Eq. 5 and 6 were used to determine the compressive (f_i) and characteristic compressive strength. Where: $F_{i,max}$ - max load (N); A - loaded cross-section (mm^2). The flexural bond strength was determined with the bond wrench test using five-brick-high bonded prism stacks [13, 17].

$$f_i = \frac{F_{i,\max}}{A_i} \quad (\text{N/mm}^2) \tag{5}$$

$$f_k = \frac{f}{1.2} \text{ or } f_k = f_{i,\min} \quad (\text{N/mm}^2) \text{ whichever is smaller} \tag{6}$$

3 Results and Discussion

3.1 Properties of lime mortars

As expected (Figs. 1, 2), the most hydraulic limes build strength faster and reach a higher ultimate strength. The NHL 3.5 and 5 mortars gain compressive strength at similar rates throughout curing while NHL2 mortar increases compressive strength by 18% between 1 and 2 months. The CL90 mortar increases flexural strength the fastest (by 64% between 1 and 2 months and by a factor of four between 2 and 6). Flexural strength of NHL3.5 mortar also increases substantially between 2 and 6 months (by a factor of three). Also as expected, the elastic moduli increase over time as mineral bonds appear in the paste and pores

and water lessen increasing stiffness (Figs. 3, 4). Except for NHL3.5 in flexion, both moduli increase with the hydraulic strength: the most hydraulic mortars being the stiffest. In compression, the NHL 5 and 3.5 mortars achieve 50% of their 6-month modulus at 1 month; the NHL 2 follows a similar trend (34% increase 1-2 months) while the CL90-s mortar takes 1.5 months to reach 50% of its 6-month modulus (reaching 70% at 2 months). In flexion, all mortars have gained over 50% of their 6-month modulus by 2 months (NHL5 has reached 80% while CL90 and NHL3.5 achieved 50% and 60%). The stress–strain results revealed that, in compression, the mortars of higher hydraulic strength exhibit a predominantly elastic behaviour whereas the NHL2 and CL90 mortars behave in a more plastic manner. Similarly, the results evidenced the plastic behaviour of the CL90 masonry (supporting small stress increases while progressively deforming and a short elastic region) against the elastic and brittle behaviour of the NHL masonry, with either little (NHL2) or non existent plasticity (NHL3.5 and 5). It was also evidenced that, in flexion, lime mortars display an elastic and brittle behaviour, straining linearly on stress application until sudden failure occurs with little or no plastic deformation. In flexion, CL90 mortars strain significantly more than NHL mortars, before failing at relatively lower stresses.

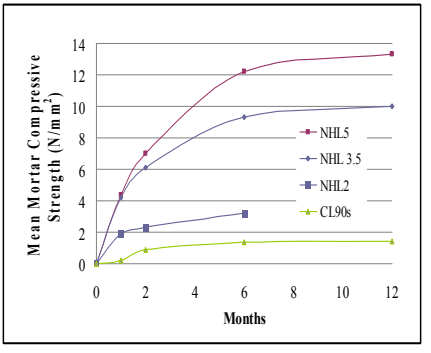

Fig. 1 Compressive strength of mortars.

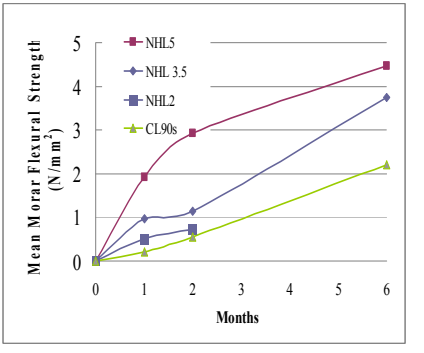

Fig. 2 Flexural strength of mortars.

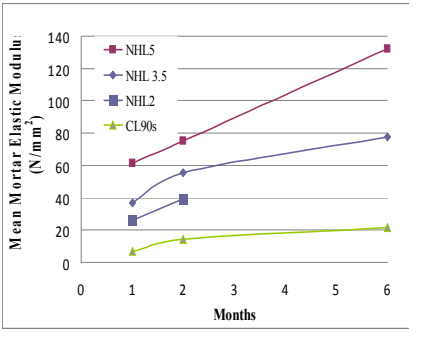

Fig. 3 Mortar elastic modulus-compression

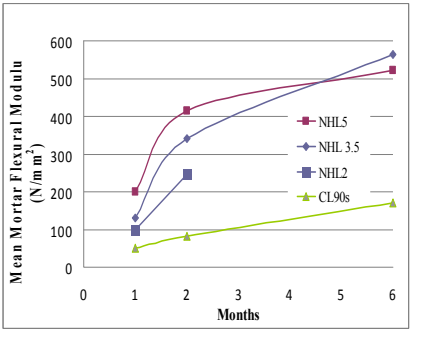

Fig. 4 Mortar elastic modulus-flexion

3.2 Properties of masonry

The compressive strength development of NHL5 and 3.5 masonry is similar (Fig. 5). Initially, they gain strength at the same rate, however, after 28 days the NHL3.5 gain becomes faster, becoming 6% stronger than the NHL5 masonry at 6 months and 5% at one year. The NHL5 and 3.5 masonry reach strength fast, at 56 days both have reached over 70% of their one year strength. NHL 2 shows a similar trend as significant gains occur in the first 28 days. In contrast, the largest gain of the CL90 masonry occurs between 2 and 6 months (at 150%), having gained over 90% of its one year strength at 6 months.

According to the results, 60-90% of the ultimate bond strength is achieved after 56 days (Fig. 6): at 2 months the CL90 masonry has reached 36% of its total one year bond strength, while NHL5 and 3.5 have reached 65%; the CL90 masonry bond strength at 6 months equals that of the NHL2 masonry at 2 months. However, the bond strength of the NHL3.5 masonry is greater than that of the NHL5 masonry (8% greater at six months).

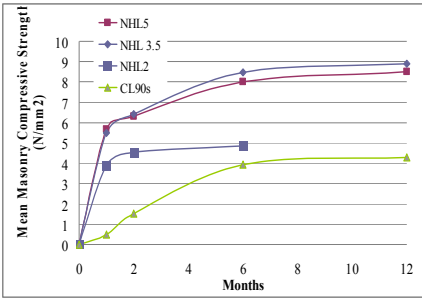

Fig. 5 Compressive strength of masonry

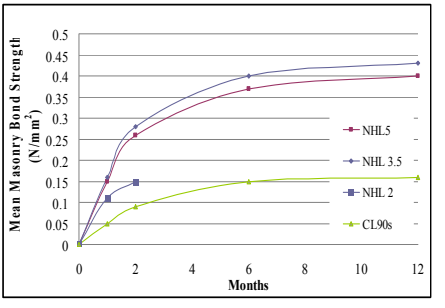

Fig. 6 Bond strength development over time.

The stress strain curves of masonry under compression at 56 days, evidenced the plastic behaviour of the CL90 masonry, supporting small stress increases while progressively deforming and displaying a small linear elastic region. In contrast, all the NHL masonry displays large elastic regions and either short (NHL2) or non existent plastic regions (NHL3.5 and 5). The results also showed that the NHL3.5 is stiffer than the NHL 5 masonry and deflects less under the same applied stress.

3.3 Influence of mortar properties on masonry strength

The results clearly evidenced that an increase in mortar compressive strength does not lead to an increase of masonry compressive strength (Fig. 7). Between 28 and 56 days, the compressive strength of the NHL5 mortar increases by 60% however, the corresponding masonry only increases by 11%. The same relationship is maintained between 2 and 6 months, where the mortar strength increases by 75% and the masonry's only by 30%. These results agree with

previous authors [6, 3] on that masonry compressive strength is not significantly impacted by mortar strength. According to the results, the mortars of higher hydraulic strengths (NHL5 and 3.5) are stronger than their corresponding masonry: after a year, the NHL 5 mortar is stronger in compression (12.21 N/mm^2) than its masonry (8.01 N/mm^2); and NHL 3.5 mortars follow the same trend (a 10 N/mm^2 mortar vs a 8.9 N/mm^{2}masonry). In contrast, NHL2 and CL90-s show the opposite trend: the mortars have a mean 56 day compressive strength of 2.29 and 1.39 N/mm^2 respectively while their corresponding masonry strengths are 4.54 and 4.3 N/mm^2 respectively. The hydraulic strength of the lime (thus mortar strength) and the bond strength of the resultant masonry tend to display an inverse relationship (Fig. 8).

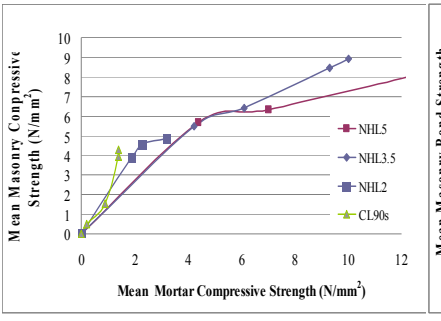

Fig. 7 Influence of mortar compressive strength on masonry compressive strength.

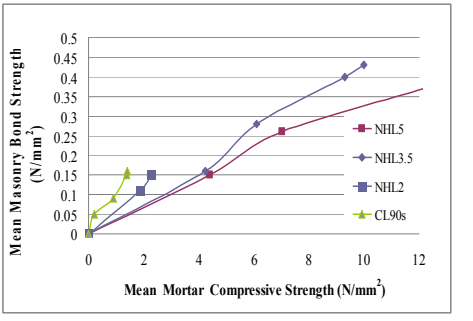

Fig. 8 Influence of mortar compressive strength on bond strength.

In relation to the influence of mortar flexural strength on the compressive and bond strength of masonry (Figs. 9 and 10), the strong raise in flexural strength of the CL90s mortar does not seem to impact the compressive and bond strength of the CL90 masonry, whereas for the NHL mortars, the bond and compressive masonry strength tend to increase proportionally to the flexural mortar strength.

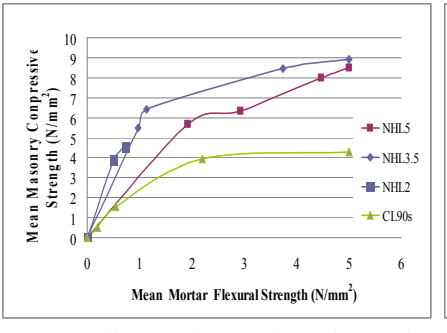

Fig. 9 Influence of mortar flexural strength on masonry compressive strength.

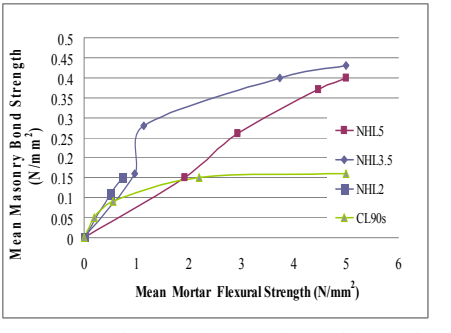

Fig. 10 Influence of mortar flexural strength on bond strength.

Bond strength has a much stronger correlation with the compressive strength of masonry than mortar strength (Fig. 11): the masonry compressive strength increases with the strength of the bond (linearly proportional relationships exist up to 6 months). The results also reveal that a low-strength mortar (CL90) with a good bond performs better than a strong mortar with a poorer bond: CL90 masonry with good bond (0.15 N/mm^2) will reach 4 N/mm^2 compressive strength whereas hydraulic mortar masonry with a poorer bond (0.1 N/mm^{2}or under) will not reach this value. This indicates that bond strength strongly impacts the compressive strength of masonry agreeing with previous authors [7]. There appears to be correlation between the elastic modulus of the mortar and the bond and compressive strength of the masonry. However, further analysis is required to determine the exact nature and fit of this relationship.

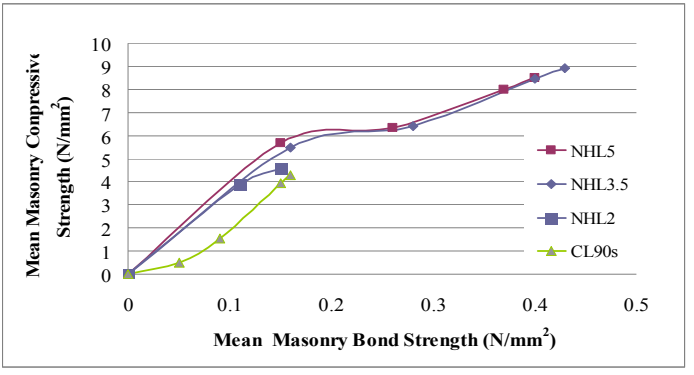

Fig. 11 Influence of bond strength on masonry compressive strength.

4 Conclusion

The mechanics of lime mortar and lime mortar masonry are similar in compression: the mortars of higher hydraulic strength exhibit a predominantly elastic behaviour whereas the NHL2 and CL90 mortars behave in a more plastic manner. Similarly, the results evidenced the plastic behaviour of the CL90 masonry (with a short elastic region) against the elastic and brittle behaviour of the NHL masonry, with either little (NHL2) or non existent plasticity (NHL3.5/5).

It seems from the results that, in flexion, lime mortars display an elastic and brittle behaviour, straining linearly on stress application until sudden failure occurs with little or no plastic deformation.

According to the results, the compressive strength of the masonry is not significantly impacted by the mortar's compressive strength:

- increasing mortar strength does not significantly increase masonry strength: the compressive strength of NHL5 mortar and masonry increase by 60% and 11% respectively between 1 and 2 months; 75% and 30% between 2 and 6.
- the compressive and bond strengths of NHL3.5 masonry are greater than those of NHL5 masonry, while the compressive and flexural strengths of the NHL3.5 mortar are lower than those of the NHL5 mortar.

In contrast, bond strength strongly impacts the compressive strength of masonry:

- the masonry's compressive strength increases with the strength of the bond (linearly proportional relationships exist up to 6 months).
- a low-strength mortar (CL90) with a good bond performs better than a stronger mortar with a poorer bond.

The CL90s mortar increases its flexural strength at a faster rate than any of the other mortars; however, this does not seem to impact the CL90 masonry properties while, in contrast, the bond and compressive strength of the NHL masonry increase proportionally to the flexural strength of the NHL mortars.

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II.06

Non-Standard Testing in Characterisation and Consolidation Assessment of Historic Mortars

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Abstract Non-standard tests are carried out on specimens made of materials extracted from historical objects, and they typically have non standard dimensions. Assessments of strengthening effects are also usually studied on non-standard specimens purposely designed and made of materials modelling the historic materials. The tests themselves are destructive, as engineers prefer destructive tests on a real material for a better understanding of the real material behaviour. Destructive tests provide a better opportunity to acquire data for numerical modelling and for following the gradients of qualities, namely after consolidation interventions. The tests include compression tests, bending tests, shear tests, and a series of tests on specific specimens designed for studies of consolidation effects.

1 Introduction

Conservation policy requirements and a wide range of problems in the field of preservation and protection of historic materials and monuments call for the development and application of testing methods and procedures that are tailored for specific tasks and have not been standardized. Although a certain degree of creativity is indispensable here, the techniques, procedures and protocols that are adopted should be verified and must reliably provide reproducible results or data. The most severe limitation stems from the fact that material samples can typically be extracted only in small amounts and with limited dimensions. It was therefore necessary to develop methods that enable tests on specimens of non-standard shapes and dimensions, and methods for evaluating the measured data and for assessing its probable relation to equivalent standard values.

This paper discusses direct non-standard methods for measuring mechanical characteristics. Only sampling tests that are destructive in a minor and considerate manner – in terms of conserving the object – are presented here. They are carried out on specimens made of materials extracted from historical objects, and their

dimensions are typically non-standard, because it is usually possible to extract pieces of joint mortar or plaster only about 20 mm in thickness. Strengthening effects are typically tested on specially-designed non-standard specimens made of materials that model historic materials. All reported tests are destructive, but the acquired data must be appropriately interpreted in relation to existing standard test results.

2 Non-standard testing of historic mortars

Although quite reliable methods for testing historic mortars have been developed and verified, the problem of the representativeness of the real material samples remains, since it is not possible in practice to extract quantities of original material that are sufficient for statistically significant series of specimens. For this reason, the tests described below must be understood as study tests providing only indicative characteristics or data. Nevertheless, such data is valuable for designing compatible repair mortars and/or for assessing the safety and reliability of historic masonry structures, or for retrofitting them.

2.1 Compression tests

The size and shape of specimens for use in determining the compressive strength of materials have been studied for more than a century. It has been known since the 19th century that the size of a testing specimen has a significant influence on the measured strength, and numerous forms have been proposed for transferring the attained characteristics of concrete and cement mortars to standard values. The correction functions depend mainly on the length of the specimen base edge, on the slenderness or the height-to-base edge length ratio, and on the quality (compression strength) of the mortar. Tests on small specimens are further influenced by other factors. Manufacturing the specimen for a compression test (cutting a cube) has a significant influence on the properties of the sample, as it basically disturbs the surface strata and reduces the strength. In most cases, the compressed surfaces need to be supplemented by a leveling layer. For this reason, specimens in the shape of irregular mortar “cakes” from the masonry joint have also been suggested or applied for compression tests in recent times, e.g. [1].

The strength attained on non-standard samples is always higher than the strength measured on standard specimens. A review of results of tests on cement mortars, based on a literature survey supplemented by a series of tests on a cement mortar [2], was published in [3], where the author presents correction coefficients applicable for assessing the equivalent standard compression strength from tests on non-standard specimens.

For lime mortars of very low standard strength of about 0.365 MPa, corresponding to degraded historic mortars, the experimentally measured strength of specimens with low slenderness can be corrected with the use of equation (1)

$$f_c = f_e / (h/a)^{-1,9} \qquad (1)$$

where f_c denotes the computed equivalent standard compression strength, f_e is the experimentally attained compression strength, and h/a is the slenderness of the specimen. The formula is valid for specimens with length a of the base side of about 40 mm and with low strength (the lime:sand mixture was only 1:9 (vol.)). Further series of tests showed that the experimentally attained differences in the exponent in equation (1) are not very severe for lime mortars of various strengths, even if they are modified with pozzolana additives [4]. Form (1) is therefore recommended for an approximate assessment of the standard equivalent historic lime mortar qualities (compressive strength) applicable in standard redesign processes, Fig. 1.

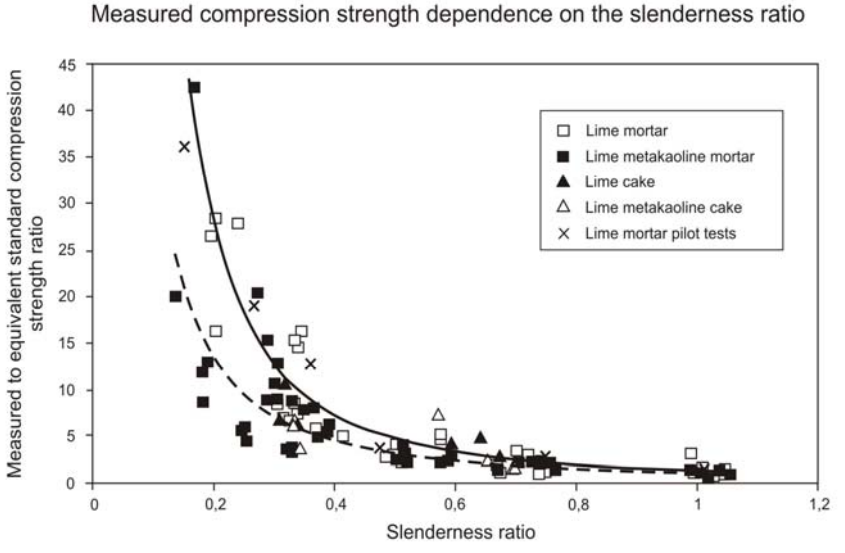

Fig. 1 Results of compression tests on specimens of various mixture and base side dimension (squares of 20 mm, 40 mm, 60 mm and discs 60 mm in diameter). The full line corresponds to equation (1), the dashed line represents a trend line for lime metakaoline mortars.

The circular plates with diameter larger than the punching steel plates, Fig. 2, exhibit approximately the same average strength as the square regular shapes, see Fig. 1. Therefore the same reduction corrections are applicable.

Recent research has confirmed that the behaviour of non-standard mortar specimens can be predicted numerically with reasonable accuracy, making use of a description of the material behaviour by an elasto-plastic Mohr-Coulomb constitutive model [4].

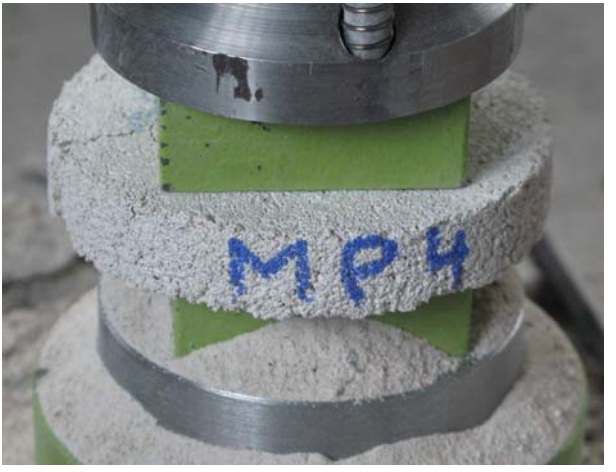

Fig. 2 Compression test on circular discs.

For material models the deformation characteristics are needed. They can be acquired iteratively by approximation of the known load-deformation diagrams, as applied in the above-mentioned Mohr-Coulomb constitutive modelling. Strains can be measured directly on the surface of small specimens, using optical methods, namely the digital image correlation. Here the sand grains on the surface create a sufficiently characteristic pattern, which may be used to follow up the deformation path in the course of loading [5]. However, the attained strain distribution field reflects the overall 3D deformation (substantially constrained on the contacts between the loading plates and the specimen) of the tested specimen, and the assessment of the modulus of elasticity must take this fact into account. For deformation measurements, the most satisfactory results are still obtained from bending tests.

2.2 Bending tests

The extracted sample size of mortars is usually too small for flexural tests. The author therefore devised and has been using a sample extension with another material in the form of so-called "prostheses". The method was developed at ITAM in 1998 and has been used, among other things, for analysing various types of historic mortars [2], and also lime mortars reinforced with organic fibres [6]. In the course of "prosthesization", the sample of material taken from the structure is supplemented symmetrically on both ends to the required length, with two "prostheses", in order to satisfy Navier's assumption of linear stress distribution along the cross section in flexure. Wood has been found to be a suitable material for mortar prosthesization. The tested material is placed at the centre of the test specimen, Fig. 3.

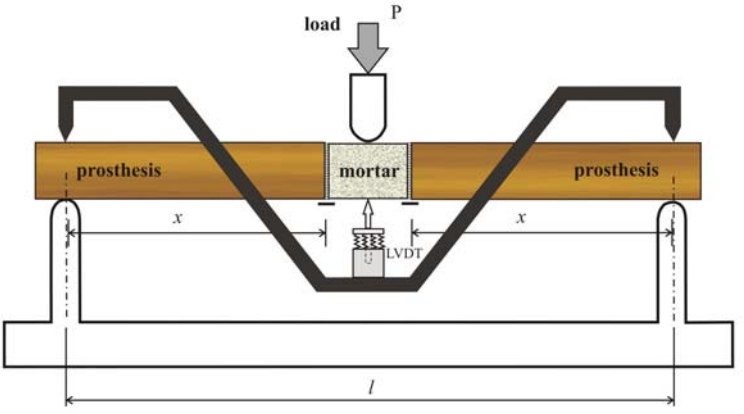

Fig. 3 Bending test rig with a prosthesized mortar specimen.

According to the results of tests comparing the flexural strength of pure mortar beams with the strength ascertained on prosthesized identical material, the influence of prosthesization is negligible. The values for the ratio of the strength of the prosthesized sample to that of "standard" all-mortar specimens were between 0.98 and 1.02 if the specimen broke in its central part (undisturbed mortar). The effect of size on bending strength was also evaluated from these tests. Again, higher strengths than the standard values are measured on the small size specimens, and the necessary reduction tendency can be assessed by an approximate equation (2):

$$f_b = f_e / (1 + C_{ssb} - C_{ssb}\, h/h_s) \qquad (2)$$

where f_b denotes the computed standard flexural strength, f_e the experimentally-attained flexural strength, h/h_s the cross-sectional height of the specimen to the standard $h_s = 40\ mm$ ratio, and the small size bending correction coefficient C_{ssb} varies on an average around 0.47 for lime mortar specimens between 20-40 mm in height, (the measured C_{ssb} varied from 0.36 to 0.58 and apparently depends on the technological parameters, e.g. compacting and treatment).

The modulus of elasticity can be estimated from the measured deflection of the beam during the course of loading. To calculate the modulus of elasticity in the case of three-point bending we exploit formula (3), developed with the use of Mohr's methodology for calculating the deflection as a moment on the so-called dual beam loaded by a reduced moment diagram. This gives the following form for the Young's modulus of mortar E

$$E = P (l - x) E J ((l - x)^2 + 6 (l - x) x + 12x^2) / 8 (6 y J E_1J_1 - P J x^3) \qquad (3)$$

where P denotes the acting force, l the span of the composite beam, E_1, J_1 the modulus of elasticity and the cross-sectional moment of inertia of the prosthesis material (usually wood), $J = b\ h^3 / 12$ (b being the width of the mortar beam and h its height), y the measured central deflection, and x denotes the length of the prosthesis on the beam between the supports, which is equal to *0.5 (span l - length of the mortar specimen)*.

2.3 Shear tests

The broken parts from the bending tests can be advantageously re-used in shear tests derived from the methodology for shear testing of soils. For tests of this type, a specimen of any convex shape is embedded into a block of stiff material, e.g., epoxy resin divided into halves. The dividing plane is provided with a separation and a sliding layer. Then the block is tested in a simple shear box and the measured normal and shear stress is evaluated using the standard soil mechanics methodology.

3 Non-standard testing of the effects of consolidation on model mortars

Difficulties connected with the on site extracting real degraded mortar samples from existing buildings or structures, on the one hand and, in some cases, a need to measure very subtle strengthening effects, on the other, call for the development and application of test procedures which use model materials and specifically shaped testing specimens. Compacted crushed old mortars or sand are used for modelling the disintegrated mortars and lean mortars that typically substitute degraded mortars. As concerns the mode of testing and the shape of the tested specimens, creative approaches according to the problem under study give the most satisfactory results. Examples developed for testing the effects of lime water treatment on mortars are presented below.

3.1 Test specimens

The specimens were designed on the basis of a thorough literature survey, which indicated very slight effects, as regards both penetration and strengthening, of repeatedly wetting historic mortars or stone with lime water. Specific test specimens in the form of short and rather thin-walled tubes for compression tests and plates for tension tests were therefore applied, Fig. 4. The specimens were fabricated from a very weak lime mixture, cast in stainless formwork, with no separation and well compacted, which enabled them to be pushed out from the formwork immediately after casting, and prevented the origination of shrinkage

cracks. The thin-wall forms increased the surface-to-cross-section area ratio and intensified the measurable strengthening effect. It also improved the agent penetration and the maturing conditions.

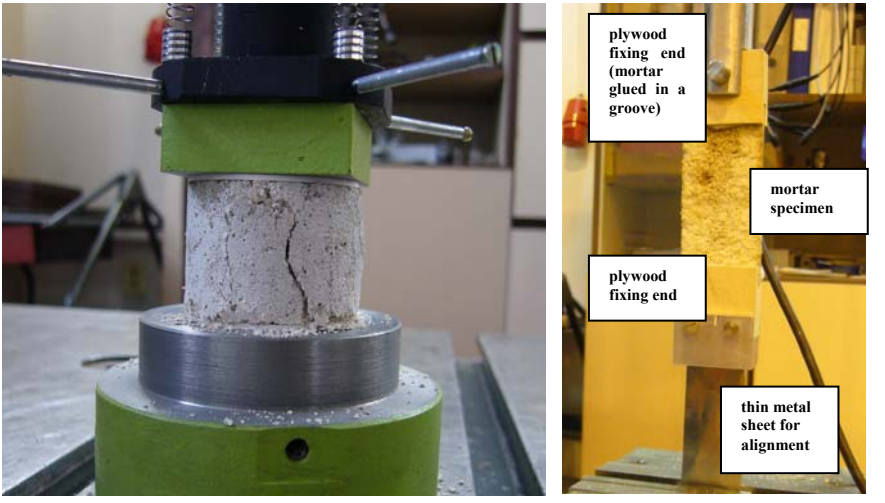

Fig. 4 Arrangement of compression tests of thin-walled mortar tubes and tension tests of thin mortar plates.

The plates for the tension tests were provided with wooden (plywood) heads to enable them to be fixed into the special flexible loading grips, ensuring the correct alignment without disturbing bending and without eccentricity, Fig. 4. This mode was more effective than the use of special tension grips, which were also developed. It is beyond the scope of this paper to go into a more profound discussion. The reader may find details e.g. in [7].

3.2 In situ testing of consolidation or strengthening effects

It is very difficult to make in situ tests for subtle changes in the surface characteristics of consolidated mortars. One method relies on peeling off the surface material by sticking some scotch tape on and then rapidly removing it. Though the results do not fully correlate with the mechanical characteristics of the material, this test can be used for a very rough check on the consolidation effect. It is only necessary to keep to the recommended procedure, which consists of repeating the test on the same surface area several times (a minimum of 5 times) before applying the treatment, and doing the same again after the treatment. Then the results give reasonably objective data for a relative or comparative assessment of the consolidation or strengthening efficiency. More detailed information is given in [7] or on the website of the EC 7th FP project STONECORE www.stonecore-europe.eu.

4 Conclusion

Our nonstandard methodology for testing historic mortars provides engineers with a reliable tool for assessing the realistic material characteristics of historic masonry. It further enables a study of various correlations among different characteristics of historic mortars, providing interesting results and a new insight into the composition of the mortar and the historic mixture preparation technology.

The methodology of prosthesization also plays an important role in the development of new mortars. Here, usual standard mortar test specimens with dimensions 40 x 40 x 160 mm are tested in bending, and their broken halves after the tests can be used for compression tests and fracture bending tests on prosthesized beams with an artificial notch. In this way, we obtain data on several basic material characteristics acquired on identical specimens by means of destructive tests. This is an additional and substantial advantage of our technique.

5 Acknowledgement

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II.07

In Situ Techniques for the Characterization of Rendering Mortars

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Abstract In this paper, compressive strength, porosity and two "*in situ*" techniques (ultrasonic velocity and rebound hardness test) are used for the characterisation of mortars. Several aerial and hydraulic lime-based mortars were tested. Prismatic specimens and mortars applied as brick render were used for the characterisation of the mortars. A comparative analysis of the "*in situ*" results and compressive strength is performed and the relationship between porosity and ultrasound velocity is analysed. A satisfactory relationship between the porosity and ultrasound velocity values was found and this indicates the possibility of estimating porosity from ultrasound velocity. The good relationship between compressive strength, ultrasound velocity and rebound values emphasizes the potential of the "*in situ*" test methods for mechanical characterization of mortars.

1 Introduction

Renders are the most common external wall covering of the world's built heritage. They are particularly exposed to aggressive physical and mechanical actions and often need conservation operations to prevent further degradation. For the characterisation of renders and the assessment of their degradation forms and processes, several characterization tests methods need to be used [1]. However, sampling is not always feasible and even if it is, the number of samples that can be taken is often limited and the testing methods that can be used in the laboratory for their characterisation are limited due to their shape and size diversity [2]. The solution is, therefore, to complement the information that can be achieved with the characterisation of collected samples with the use of "*in situ*" techniques, for assessment of the render's properties on site [3].

"*In situ*" tests are specially designed to be applied on site and are usually easy to carry out, economical and non-destructive or semi-destructive, and the results are quickly available. However, the analysis of the results achieved with "*in situ*"

test methods is not always straightforward. The long experience of using laboratorial test methods for mortar characterisation and the interest in doing it by means of "*in situ*" tests justify the importance of seeing how possible it is to estimate some of the physical and mechanical properties of rendering mortars through "*in situ*" characterization test methodologies [3,4].

The purpose of this paper is to compare results and to establish relations between data provided by current laboratory test methods (compressive strength and porosity) and "*in situ*" test methods (ultrasonic velocity and rebound hardness), so that the long experience and knowledge reached with the first could be transposed to the latter and, hence, make the "*in situ*" tests more trustworthy for dissemination through the scientific and technical community.

2 Mortars and materials

To achieve the proposed aims, 25 mortar formulations (see Table 1) were tested in order to have a wide range of mechanical and physical properties. This range was obtained with different binders, water/binder ratios, aggregates, curing ages, consistencies and curing conditions.

Most of the tested mortars have a volumetric binder/aggregate ratio of 1:3. Three different siliceous sands – yellow sand (Y), river sand (R) and fine sand (F) – were used, combined in different proportions or alone, and this provided six different aggregate mixtures with fineness modulus (FM) comprised between 1.5 and 3.0, Table 1. The maximum aggregate size (D) of the sands are: 2.38mm (Y, R) and 0.59 (F). The fineness modulus was calculated as the sum of the cumulative percentages by mass retained on the sieves (4.76, 2.38, 1.19, 0.59, 0.297 and 0.149 [mm]) divided by 100 [based on prEN13139:1998]. The maximum aggregate size (D) was defined by the smallest sieve opening through which passes 90% or more of the aggregate sample.

Four binders were used: a commercial hydrated lime CL90 [EN459-1:2002]; a lime putty slaked in a laboratory from a CL90 commercial powdered lime; a commercial NHL5 [EN459-1:2002]; and a CEM II/B - L 32.5 N [EN197-1:2000]. The water/binder ratios of the mortars were what was required to achieve a consistency of 165±5 mm [5] given by the flow table test [EN1015-3:1999], with the exception of C10 (130±3mm) and C11 (210±1mm). The most important factors that influenced the water-binder ratio were: type of binder, aggregate granulometry and binder/aggregate ratio. The consistency of 165±5 mm was achieved with water/binder ratios ranging from 0.5 to 0.95 for the hydraulic mortars and from 1.44 to 1.73 for the aerial lime based mortars.

Mortar production was based on EN1015-2:1998 recommendations. The mortar characterisation was performed on prismatic specimens (4cmx4cmx16cm) and on mortars applied as brick coat (2cm thickness) simulating a render. Mortars were cast into prismatic moulds (4cmx4cmx16cm) and the specimens were stored in a

laboratory room at 20±2ºC and 50±5% of relative humidity until their characterisation. Hydraulic and lime mortar specimens were removed from the moulds after 2 and 7 days, respectively. The mortars H6, H7 C2 and C3 were cured under wet conditions (20±2ºC and 95±5% of relative humidity).

Table 1 Tested mortars. Binder, aggregate or aggregate mixture, binder/aggregate ratio [6-13]

Aerial lime (CL90) 1:3				Hydraulic lime (NHL5) 1:3				Cement (CEM II/B-L 32.5N) 1:3; 1:2.5; 1:3.5			
Mortar	Aggregate			Mortar	Aggregate			Mortar	Aggregate		
	Comp[2].	FM[3]	D[4]		Comp.	FM	D		Comp.	FM	D
A1	½ Y + ½ R	2.8	2.38	H1	½ Y + ½ R	2.8	2.38	C1, C2, C3	½ Y + ½ R	2.8	2.38
A2[1]	½ Y + ½ R	2.8	2.38	H2	Y	3.0	2.38	C4 (1:2.5)	½ Y + ½ R	2.8	2.38
A3	½ Y + ½ R	2.8	2.38	H3	F	1.5	0.59	C5 (1:3.5)	½ Y + ½ R	2.8	2.38
A4	Y	3.0	2.38	H4	½ Y + ½ F	2.3	2.38	C6	Y	3.0	2.38
A5	R	2.6	2.38	H5	⅔ Y + ⅓ F	2.3	2.38	C7	F	1.5	0.59
A6	½ Y + ½ F	2.3	2.38	H6	½ Y + ½ R	2.8	2.38	C8	½ Y + ½ F	2.3	2.38
A7	⅔ Y + ⅓ F	2.3	2.38	H7	½ Y + ½ R	2.8	2.38	C9	⅔ Y + ⅓ F	2.3	2.38
								C10 (1:2.5)	½ Y + ½ R	2.8	2.38
								C11 (1:3.5)	½ Y + ½ R	2.8	2.38

[1] Lime putty; [2] Comp.: Composition of the aggregate mixtures; [3] FM: Fineness modulus
[4] D: maximum aggregate size [mm]

The characterisation of the aerial lime was performed after curing times of 60 and 90 days and the hydraulic mortars with a curing time of 28 days. Some mortars were also tested at younger ages. The mortars A1, A2 and A7 were tested after curing times of 14, 21 and 28 days. The mortars H1, C1, C10 and C11 were tested at some of the following ages: 3, 7, 14, 21, 60 and 90 days. The porosity and ultrasound velocity of all the mortars after 2 years of curing time were also measured.

3 Test methods

The flexural and compression strength tests performed were based on EN1015-11:1999 and carried out using a Form test - Sneider universal machine, model D-7940. For all the tested mortars and curing times, the flexural strength and the velocity of ultrasound were assessed on 3 prismatic specimens. The ultrasonic test was performed using PUNDIT equipment (Portable Ultrasonic Non-destructive Digital Indicator Tester), by CNS Electronics, comprising an ultrasonic pulse generating unit and two cylindrical transducers of 5cm diameter and a frequency of 54 kHz. The measurements of the ultrasound velocity were performed under direct transmission mode on prismatic specimens. Compression strength tests were

performed on the fragments of each specimen resulting from the flexural test. The superficial hardness of the mortars applied as brick coat was assessed using a Schmidt pendulum hammer type PT [14]. The presented results were obtained from at least 6 measurements performed on each mortar applied as brick coat.

The porosity of all tested mortars was assessed on 3 prismatic specimens following RILEM I.1 [15] recommendations.

4 Results and discussion

Table 2 presents the average and standard deviation values of the porosity, compressive strength, velocity of ultrasound and rebound for all the tested mortars stored under dry curing conditions and formulated with each tested binder type.

All the tested methods made it possible to distinguish the mechanical properties of the studied mortars and reveal the influence of the binder type.

Table 2 Properties of the tested mortars

Mortars (curing ages)	Porosity [%]	Compressive strength [MPa]	Ultrasound velocity [m/s]	Rebound
Aerial lime (60days)	29.5 ± 2.0	0.83 ± 0.11	1500 ± 80	23 ± 2
Hydraulic lime (28days)	24.2 ± 2.5	2.30 ± 0.49	1790 ± 270	29 ± 4
Cement (28days)	21.6 ± 1.9	13.3 ± 3.2	3140 ± 240	55 ± 6

The linear trend-lines between the porosity and velocity of ultrasound values and the correspondent coefficients of determination are presented in Fig. 1 (left and right graphs) for each binder type mortar, with a consistency of 165mm and cured under dry conditions. The satisfactory relationship achieved between the porosity and ultrasound velocity confirmed by the coefficients of determination obtained for the aerial (0.74), hydraulic lime (0.96) and cement mortars (0.89) point to the possibility of estimating porosity from ultrasound velocity values.

The influence of the curing conditions on the above relationships was analysed, and is shown in Fig. 2, on hydraulic lime and cement mortars with a consistency of 165mm cured under dry and wet conditions. The porosity and ultrasound velocity measured on cement mortars seemed not to be influenced by curing condition (Fig. 2 left graph). However, the values of velocity of ultrasound measured on hydraulic lime mortars cured under wet conditions were higher than the values for mortars cured under dry condition (Fig. 2 right graph). The increase in the ultrasound velocity values in this case was not followed by porosity (Fig. 2 right graph). These results indicate that similar mortars cured under different conditions might have similar values of porosity, although differences in their pore structure may influence the velocity values measured under dry and wet conditions.

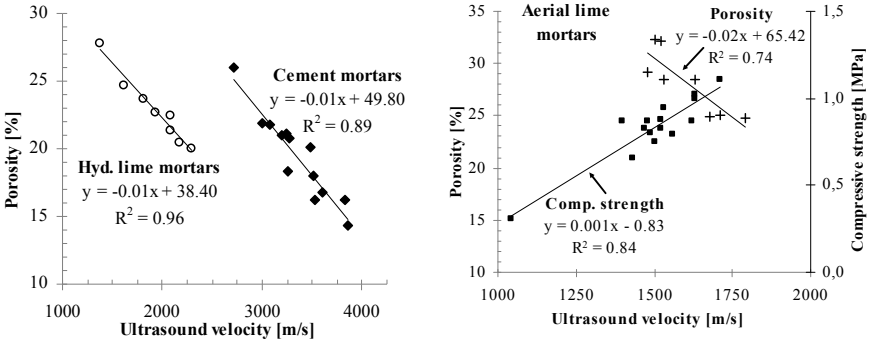

Fig. 1 Hydraulic and aerial lime mortars with a consistency of 165mm cured under dry conditions. Left graph - Relation between porosity and ultrasound velocity values for hydraulic mortars. Right graph – Relation between porosity and ultrasound velocity values, and compressive strength and ultrasound velocity values, for aerial lime mortars

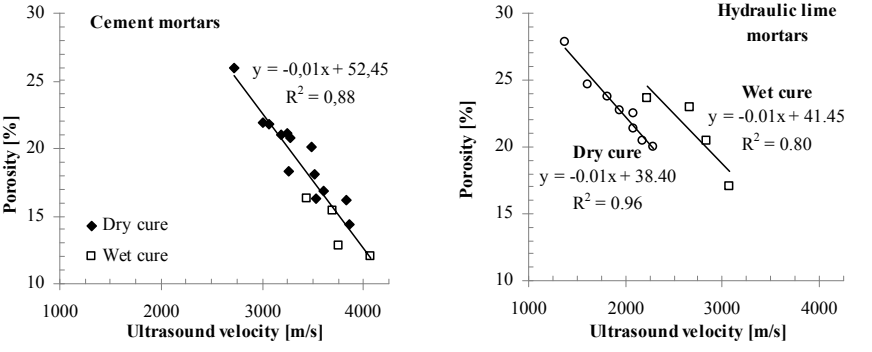

Fig. 2 Hydraulic mortars cured and tested under dry and wet conditions – Influence of the curing conditions on the relation between porosity and ultrasound velocity values. Left graph – Cement mortars. Right graph – Hydraulic lime mortars

Fig. 1 (right graph) and Fig. 3 (left graph) present the relation between the compressive strength and the ultrasound velocity values assessed on prismatic specimens. Satisfactory coefficients of determination were obtained for the different tested binder mortars formulated with the same consistency and cured under dry conditions (R^2=0.84 - aerial lime mortars, Fig. 1 (right graph); R^2=0.67 - hydraulic lime mortars and R^2=0.82 - cement mortars, Fig. 3 (left graph)).

The linear trend-lines present on Fig. 3 (right graph) considered all the tested hydraulic mortars, even those with different consistency (C10 and C11 – consistencies of 130mm and 210mm, respectively) and wet curing conditions (H6, H7, C2 and C3). For both hydraulic mortars, the relation between compressive strength and ultrasound velocity was not significantly modified due to the inclusion of some values assessed on mortars with several consistencies and both

tested curing conditions (Fig. 3 right graph), although coefficients of correlation were different (R^2=0.85 on hydraulic lime mortars and R^2=0.75 on cement mortars). Analysis of the two factors taken separately – curing conditions and consistencies – led to the following conclusions: i) R^2 became higher when considering only the results of the mortars with a consistency of 165mm cured under both conditions (R^2=0.85 - hydraulic lime mortars, Fig. 3 (right graph) and R^2=0.86 - cement mortars, not shown separately in a graph) than those achieved when only dry conditions are considered (R^2=0.67 - hydraulic lime mortars and R^2=0.82 - cement mortar, Fig. 3 (left graph)); ii) R^2 became lower when considering mortars with several consistencies cured under dry condition (R^2=0.64 on cement mortars, not shown separately in a graph; no different consistency hydraulic mortars were tested). The increase of the dispersion of the results when considering different consistency mortars points towards a need to develop further research on this issue.

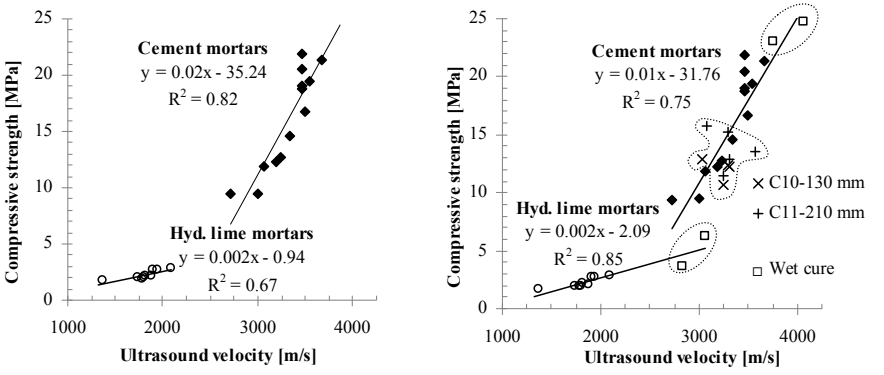

Fig. 3 Hydraulic mortars - Relation between compressive strength and ultrasound velocity values. Left graph –the results of the mortars with a consistency of 165mm cured under dry conditions. Right graph - the results of all hydraulic mortars tested (different consistencies and curing conditions)

Satisfactory coefficients of correlation between the compressive strength and rebound values were obtained, Fig. 4, (R^2 ranging from 0.79 to 0.92). The influence of the consistency and curing conditions were also assessed for the rebound values and led to the conclusion that the relation between compressive strength and rebound values was not significantly altered.

Fig. 5 presents the power functions between compressive strength and ultrasound velocity values, and compressive strength and rebound values, when all the tested formulations are considered, even those with different consistencies and curing conditions. In both cases good relations were achieved (R^2=0.95 - rebound and R^2=0.96 - ultrasound velocity), a fact which points to the potential of the studied "*in situ*" techniques for estimating the compressive strength of mortars.

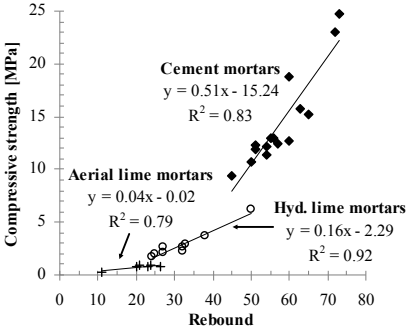

Fig. 4 Aerial, hydraulic lime and cement mortars - Relations between compressive strength and rebound values considering all tested consistencies and curing conditions

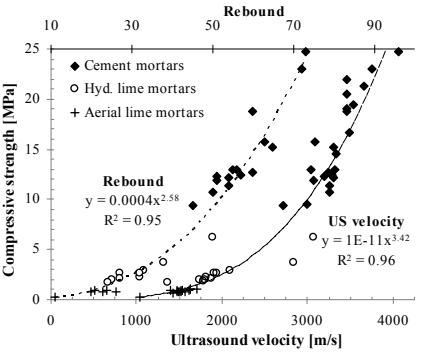

Fig. 5 All tested mortars – Relation between compressive strength and ultrasound velocity and rebound values considering all tested consistencies and curing conditions

5 Conclusions

Tests were undertaken on several mortars with quite diverse physical and mechanical properties (porosity: 10-30%, compressive strength: 0.6-25 MPa), with the objective of assessing the possibility of estimating compressive strength and porosity through ultrasound velocity and rebound hardness measurements. Different binder types, water/binder ratios, aggregates and consistencies were used for the formulation of the tested mortars, and the assessment of their properties with different curing periods and conditions was also tested.

A satisfactory relationship between the porosity and ultrasound velocity values was achieved, which points to the possibility of estimating porosity from ultrasound velocity. The results also demonstrate the potential of both "*in situ*" test techniques to estimate the compressive strength of mortars with unknown formulation or when destructive tests are not possible. Among the interesting findings is the value of using the rebound test for onsite characterisation of rendering mortars.

The good relationship between compressive strength and ultrasound velocity assessed on prismatic specimens enhances the interest in developing future research, already in progress, to study the behaviour of this feature when measured under indirect transmission mode over mortars simulating rendering coats.

6 Acknowledgments

The authors would like to thank the Foundation for Science and Technology through the funding allocated to ICIST, Institute of Structural Engineering, Planning and Construction. They are also grateful to C. Agostinho, I. Santos, A. Fernandes, B. Mendonça, A. Martins, N. Cruz and P. Lima for their collaboration in the experimental work within the scope of their MSc dissertations.

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II.08

The Role of Mortars in Ancient Brick Masonries' Decay: a Study in the Pio Palace at Carpi (Italy)

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Abstract The use of cement-based mortars for the repair of ancient masonry joints was quite common in the past and can account for a significant role in masonry decay, especially when highly porous building materials are present (bricks, sandstone, etc.). Mortar-induced degradation mechanisms in ancient masonry walls are quite complex and worthy of investigation, in order to properly assess the decay causes and to select suitable conservation strategies (removal, cleaning, substitution with compatible repair mortars, etc.). In the present paper, the case of the 17th century main portal of the Pio Palace in Carpi (Modena, Italy), where an outstanding differential decay between mortars and bricks is present, is discussed. Both bricks and mortars were characterized and the actual decay causes were detected, also in connection with the analysis of the environment surrounding the building and the historical evolution of the palace. The different microstructure of the original and repair materials was found to be responsible not only for different mechanical behaviour, but also for a different response to salt crystallisation, particularly intense in the palace due to the capillary rise of underground polluted water.

1 Introduction

The Pio Palace at Carpi (Fig. 1) developed quite randomly since the 14th century, through the addition of later parts to an original building nucleus [1]. In the 17th century the palace was rearranged by the addition of a Renaissance façade, overlooking the main town square and giving the palace a unitary appearance; the main entrance was enriched by a clock tower (Fig. 1, right), built between 1625 and 1637 [2].

The ashlar-worked brick portal in the clock tower presently suffers from outstanding decay (Fig. 2), with no similarity in any other part of the palace.

In a previous work [3], the environmental aggression towards the palace and the historical evolution of the portal were investigated and the following main critical aspects detected:

- the bricks are low quality, due to their likely provenance from a temporary kiln built for the construction of the near cathedral (Fig. 1, left) and, hence, due to their handmade technology and low firing temperature;
- the removal of the frescoed plaster from the portal during the late XIX cent. maintenance works left the bricks unsheltered from environmental aggression;
- the intense vehicular traffic in the square implied some chemical attack to the detriment of the portal materials in the period 1950-1980;
- no significant wind action seems involved in the portal decay, despite the wideness of the square (about 50x250 m);
- the portal is subject to an intense capillary rising damp from the ancient moat running under the clock tower, now covered and integrated in the town sewer network. Moisture is responsible for freeze-thaw cycles and salt crystallisation within the material pores (as the rising water is polluted).

It is noteworthy that a differential alteration between bricks and mortars occurs (Figs. 2 and 3): the brick degradation is several centimetres deep, while the contiguous embedding mortars are in some cases perfectly conserved. In this paper, a possible direct role of embedding mortars (supposedly cement-based, applied during some not-documented 20th century maintenance work) into brick decay is investigated; for this purpose, mortars and brick samples were withdrawn from the portal and characterised.

Fig. 1 The Pio Palace (left) and the portal in the clock tower (right)

2 Materials and Methods

2.1 Samples

Some significant embedding mortar and brick samples were withdrawn from the portal: the sampling areas are shown in Fig. 3, while a brief description of the samples is given in Table 1.

Fig. 2 Details of the materials' decay in the portal

Fig. 3 Position of sampling points 5-6 (left) and 10-12 (right)

Table 1 Identification of the samples

Sample	Sampling point (Fig. 3)	Description of the sample
5M	South front (height ≈ 1.5 m)	Rose surface joints mortar
6M	South front (height ≈ 1.5 m)	Grey embedding mortar underlying sample 5
10M	Portal intrados (height ≈ 2 m)	Grey embedding mortar
10B	Portal intrados (height ≈ 2 m)	Brick adjoining 10M
12M	Portal intrados (height ≈ 2 m)	Grey embedding mortar
12B	Portal intrados (height ≈ 2 m)	Brick adjoining 12M

2.2 Samples characterisation

The samples' composition was determined, after grinding to a fineness <0.075mm, by X-ray diffraction (Philips Diffractometer PW 1840, 40kV/20mA, Cu Kα anode), Dietrich-Frühling method (expressing the carbonates content as $CaCO_3$ wt%) and thermal-gravimetric analysis (TA Instruments Q50; nitrogen flux 40ml/min; temperature increase 30°C/min).

Microstructural characterisation by mercury intrusion porosimetry, MIP (Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba) was carried out on the samples. For the brick samples (10B and 12B), in order to appraise possible heterogeneity even within the same brick, the MIP was performed separately on both internal and surface fragments (the latter just in adhesion with the relevant embedding mortar): thus the brick samples analysed by MIP are named 10B-centre, 10B-adhesion, 12B-centre and 12B- adhesion respectively.

The nature of the soluble salts and their amount, in terms of anions, were investigated (after samples grinding, salt extraction in distilled boiling water and filtration) by ion chromatography (Dionex ICS 1000). For the brick samples, the inner part, the external surface part and the part in adhesion with the relevant mortar were analysed separately.

3 Results and discussion

X-ray diffraction (not reported for brevity sake) shows that all the investigated mortars are made of calcite and quartz, with traces of feldspar. The carbonate content of the mortar and brick samples is reported in Table 2, while the TGA results for mortars are plotted in Fig. 4.

All the mortars are quite similar in composition. Calcite-quartz-feldspar aggregates seem to be present, together with a cement or, at least, an eminently hydraulic lime binder: as a matter of fact, the weight loss around 600-650°C in the samples (Fig. 4) is ascribable to hydraulic compounds [4]. In Fig. 4, mortars 5M and 6M exhibit a great similarity and, hence, they are probably coeval, although they have a quite different appearance (Table 1): 5M contains ground bricks or

potsherd (the Italian *cocciopesto*), giving the final material its rose colour, while 6M is a grey mortar with no specific intentional aesthetic value. Hence, the ground brick was probably not used in 5M mortar as a pozzolanic addition (traditionally used for slaked lime mortars [5]), but for a simply aesthetical purpose, i. e. for giving the wall a quite uniform final brick-colour (as in the Italian traditional *sagramatura* finishing [6]). Some organic admixture too seems to be present in mortar 5M (weight loss in the range 250-550°C, Fig. 4), improving its resistance to the outdoor environment.

The high calcium carbonate content of the bricks used in the portal (Table 2) confirmed their low firing temperature, as mentioned above.

The pore size distribution curves are reported in Fig. 5 and the following remarks can be made:

- the pore size distribution of the two bricks is quite similar; moreover, no systematic difference between the brick's inner part and the fragment adjoining the mortars can be detected, hence the differential decay of the bricks in the portal (Fig. 2) can't be ascribed to each brick's internal heterogeneity;
- the investigated mortars 6M, 10M and 12M are quite similar and exhibit a remarkably lower porosity and a slightly larger pores mean radius than the bricks; mortar 5M, containing organic admixtures too, shows a much lower porosity and a definitely finer porosity.

Table 2 Carbonate content of the mortars (left) and bricks (right) samples

Sample	$CaCO_3$, wt%
5M	31.9
6M	36.3
10M	40.5
12M	41.9

Sample	$CaCO_3$, wt%
10B	7.6
12B	9.1

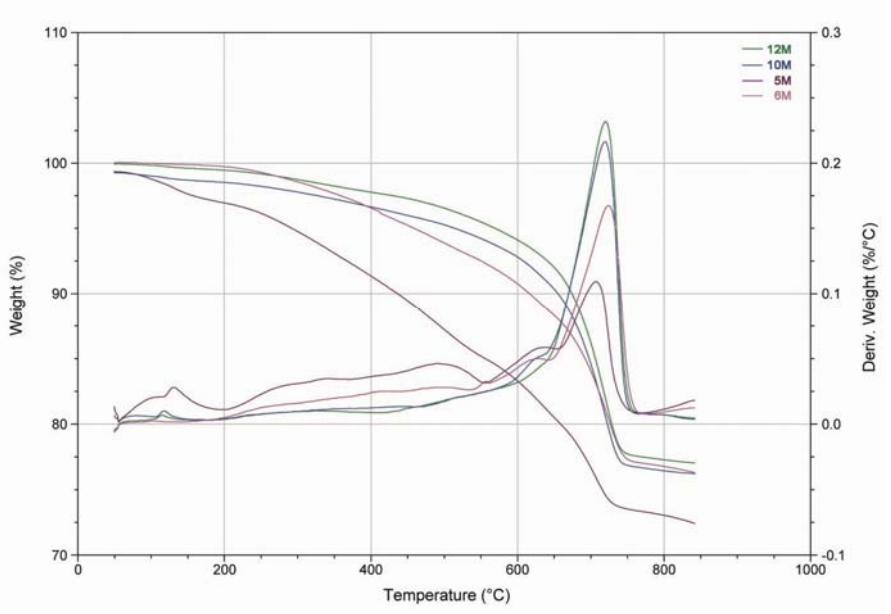

Fig. 4 TGA results for the mortars samples

The compact mortar's microstructure might result in a possible lack of compatibility with the bricks. For the external joints mortar (5M) this incompatibility is more evident: its low porosity caused a wide detachment from the underlying mortar (Fig. 3), under the action of freeze-thaw cycles and salts crystallisation driven by rising water. However, the SOM observations of mortars 10M and 12M evidenced a good adhesion with brick, hence the differential decay can't be due to a simple mechanical incompatibility (Young's modulus, thermal expansion, etc.) and some further mechanism must be involved.

In order to evaluate the role of soluble salts in material degradation, the anion content of the samples was determined (Table 3). The very high nitrates and chlorides percentages are due to the polluted water rising from the channel under the clock tower, as quoted above. Mortars 10M and 12M exhibit a lower anion content than the adjoining bricks, suggesting that the salts driven by rising water (usually following quite unpredictable paths, according to the materials' microstructure) tend to crystallise in correspondence to the more porous material, i.e. brick in this case, rather than in the mortar. As a matter of fact, the propensity of salts to form efflorescence/subflorescence in correspondence to the most porous materials can be often observed in historic brick masonries, as in the examples of Fig. 6, where the decay by salts is prevalent in a highly porous brick (left) or in the mortars (right).

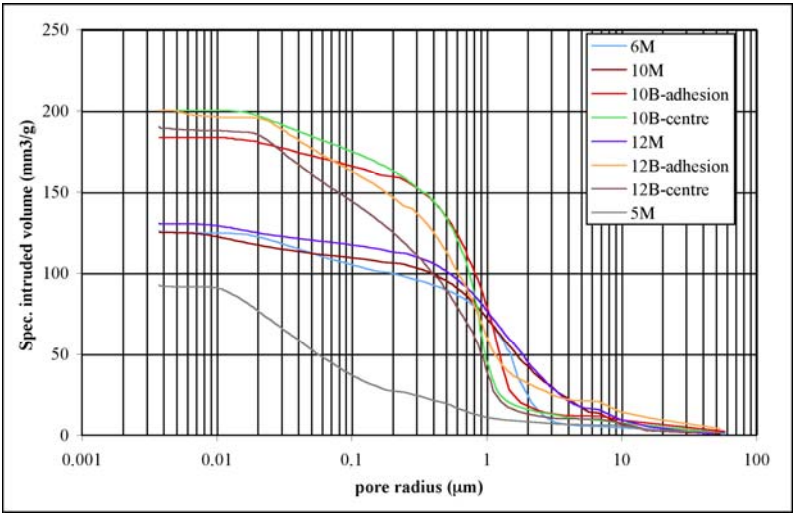

Fig. 5 Pore size distribution of the samples

Table 3 Results of ion chromatography (wt%)

Sample		SO_4^{2-}	NO_3^-	Cl^-
5M		0.5	4.0	1.3
6M		0.7	2.4	0.8
10M		0.2	1.2	0.5
10B	External surface	8.0	0.6	0.3
	Adhesion surface	1.2	1.4	0.7
	Internal part	0.3	1.9	1.6
12M		0.2	1.0	0.4
12B	External surface	3.3	2.2	0.7
	Adhesion surface	1.0	2.3	1.0

Fig. 6 Differential efflorescence in the bricks (left) and salt decay in correspondence to the mortars (St. Lazarus church in Modena, Italy, XII-XVII cent.)

4 Conclusions

Repair mortars and original bricks from the portal of the Pio Palace at Carpi were characterised and their main decay causes and mechanisms detected. A significant role or repair mortars into bricks decay has been assessed, suggesting that the removal of such mortars is compulsory for the masonry preservation, along with rehabilitation works stopping the rising dampness. The present results also stress the importance of the repair mortars' design (in terms of both formulation and microstructure) for ancient unplastered masonry durability.

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II.09

Historical Busts Made of Cement Mortar – Methods of Examination and Causes of Corrosion

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Abstract The aim of the project was to define the causes of damages done to two of thirteen busts made by Jerzy Sobocinski in 1971. The collection belongs to The National Museum in Szreniawa and represents important figures of Polish history, such as Stanislaw Staszic, Marian Czapski and Tadeusz Kosciuszko. The busts are made of cement mortar, which imitates natural stone. The basic damages of the busts are cracks, cavities, joints' defects and leakages of white calcium compounds. The study describes the investigation of properties and structure of artificial stone. Material for analysis was taken by means of chisels and in the form of borehole cores. The steel rods embedded in mortar were localised using electromagnetic induction, gamma-ray and X-ray photographs. Research with the help of active infrared thermography was executed to locate cracks and defects. The laboratory tests included: X-ray fluorescence, IR spectroscopy, X-ray diffraction, DTA, petrographic examination, pH, density, water absorption capacity, capillary suction, open porosity, content of soluble salts such as: chloride, sulphate, magnesium, ammonium and nitrate ions.

1 Introduction

The entire collection consists of thirteen busts. All of them are exhibited in a beautiful park in The National Museum of Agriculture and Agricultural-Food Industry in Szreniawa (Fig. 1). The sculptures were designed and made by the famous sculptor Jerzy Sobocinski in 1971. This collection represents important activists, writers, poets, such as Tadeusz Kosciuszko, Stanislaw Staszic, Michal Drzymala, Bartosz Glowacki, Jan Dzierzon and Marian Czapski. All the busts are larger than life-size, about 73-80 cm in height and placed on stone pedestals. Low

relief plates with the names of portrayed people are attached to the front side of the pedestals and are cast in the same cement mortar as the busts.

Fig. 1 The bust of Tadeusz Kosciuszko in The National Museum in Szreniawa

Fig. 2 Many busts have numerous cracks and cavities with visible corroded rods under a thin and porous mortar layer

2 Technology used

Unfortunately, no photographic documentation of the sculpturing project remains. The most valuable information about the creative process was obtained from the artist's son Robert Sobocinski, who is also a very active sculptor in Poland and France [1].

All the sculptures were made using the same technology and the same material - cement mortar with the addition of natural pigment - ochre. The identification of the pigment was carried out using X-ray fluorescence and micro-chemical reactions. Results of these analyses showed the presence of iron compounds.

In the preliminary work stage, Jerzy Sobocinski sculptured all portraits in clay in his workshop in Poznan. Then he prepared a three-part gypsum split mould. At the end he cast the busts in mortar. The busts have a two layer construction - the outer layer is based on white Portland cement, the inner layer on blast furnace slag cement. The sculptures are empty inside. The thickness of these two layers is various in different places and ranges from 5 to 11 cm.

Many steel rebars with a diameter of 7 mm are placed inside the concrete to keep the crack width at an acceptable level.

In some parts of the busts, marks of the mould joints were invisible, whilst in others places, crevices appeared. The sculptor glued these crevices using styrene-polyester resin, probably Polimal 108. The identification of this resin was performed using infrared absorption spectroscopy.

The busts had a quite porous surface, therefore they were painted with coloured cement slurry (the thickness of the slurry was about 1.5mm).

3 Condition

Despite their great importance as elements of the cultured landscape, unfortunately they are in a bad condition. Most of the busts have numerous cracks, defects and cavities as visible in Fig. 2. Others are in a better condition. It depends mainly on the location. Some of the busts are especially exposed to the rain (alternating cycles of wetting and drying), while others are under the shelter of trees. In addition, some busts are regularly wetted by garden sprinklers.

Many sculptures, e.g. Dezydery Chlapowski's bust, have a network of cracks. The smallest cracks are 0.05 mm wide, the largest 1 mm. After rainfall and snowfall the cracks remain wet for a long time. Technological faults are apparent in some busts. In many places rods were placed too close to the surface (even at the depth of 2 mm). Some rods were not covered with cement mortar, especially inside. In these places the rods are highly corroded.

Further repairs of crevices are visible in the form of dark cement fillers.

Originally, the busts had an intense purple colour, as shown in Fig. 3. A surface layer of mortar with the pigment has been leached out and currently the busts have a grey colour.

Fig. 3 The original purple colour of busts

Fig. 4 White calcium carbonate efflorescences leached out from cracks

The concrete surface is very porous, covered with grime, lichens and moss colonies. Some connections between three technological parts are leaky; the width of the crevices varies from 0.1 to 3 mm. There is especially a lot of moss in these places. The soluble components of the concrete, visible as white calcium carbonate efflorescences**,** were leached out by water, as shown in Fig. 4 [2].

4 Methodology of examination and results

4.1 Examination of material

The previous information about the technology and condition concerned the all collection, but examinations were performed on two sculptures: Daniel Janasz's and Dezydery Chlapowski's busts.

Samples of mortar in the form of bore holes (Ø10 mm) were taken from cavities from the aforementioned busts for the determination of pH (water extract).

The pH of tested material has a value of 11.66 to 12.38, depending on the depth. It is well known that the loss of the passivity of the steel rods begins at a pH value about 11.80, so some of the rods placed close to the external and internal surface (at 2-4 cm depth) began to corrode.

A major threat to concrete durability is the high content of chloride, sulphate, magnesium, ammonium and nitrate ions. Total chloride content in this concrete is very low within a range of 0.03-0.05% in relation to cement [3, 4]. The amount of sulphate is also low in the range of 0.04-0.09% of the weight of concrete. The contents of ammonium and nitrate ions are about 0.01% in relation to concrete. Analysis did not show a presence of magnesium ions.

Chemical analysis revealed that the amount of insoluble parts in hydrochloric acid constitutes about 64.68% of the cement mortar sample, of which the largest number i.e. 24.46% comprises aggregate of fraction 0.5-1.25 mm. Fraction below 0.05 mm represents silica from the decomposition of calcium silicate cement and pigment (Table 1).

Table 1 Sieve analysis of tested mortar

Aggregate fraction [mm]	> 2.5	1.25–2.5	0.5–1.25	0.315–0.5	0.25–0.315	0.2–0.25	0.1–0.2	0.05–0.1	< 0.05
[%] of cement mortar	1.05	6.86	24.46	0.50	6.12	16.88	3.79	1.94	2.48

The next stage of examination was the determination of water absorption by capillarity. Capillary suction is the process by which water travels through pores due to tension forces developed between the solid particles and the water molecules. The dry samples were immersed to a depth of 10 mm. They were weighed at specific time intervals. The water movement by capillary suction in tested concrete is fast - up to a height of 4cm in 4 hours, up to a height of 6 cm within 24 hours, and up to a height of 10 cm within 3 days.

Water absorption capacity is very high 9.25%, open porosity 20.37% and volumetric density 2.20 g/cm^3. Results of these analyses are especially important during restoration works in order to prepare cement mass for filling cavities with similar composition and properties.

Differential Thermal Analysis (DTA) of nine concrete samples revealed the presence of calcium hydroxide within a range of 2.30-4.47% and calcium carbonate within a range of 10.80-15.48%. The amount of the residue which has not been decomposed in the terms of the analysis varied from 76.16 to 81.80%.

DTA of white calcium carbonate efflorescence showed mainly the presence of calcium carbonate (58.62-81.10%) and calcium hydroxide (5.80-11.0 %).

The cement slurry, prepared by mechanical segregation of visible aggregate was subjected to X-ray diffraction. Results showed mainly quartz, calcium carbonate, a small amount of calcium magnesium carbonate, allophane (a hydrous aluminium silicate clay mineral), albite (a plagioclase feldspar mineral) and nepheline mineral (sodium potassium aluminium silicate).

The next stage of the research was a petrographic examination. This investigation was carried out in order to confirm that the outer layer of concrete is based on white Portland cement and the inner layer on blast furnace slag cement. The examination confirmed this hypothesis and gave precise information about

composition, the type and fraction of aggregate and the volumetric ratio between ingredients. The results showed that the cement binder in Portland cement mortar was homogeneous, in contrary to the blast furnace slag cement mortar with a more heterogeneous binder. Grain frame in both materials was the same, predominated by detrital quartz. Feldspars, especially plagioclase and microcline-perthite, glauconite, fragments of rocks: granitoids, limestones and very rarely argillaceous sandstones belonged to minor components. The marginal aggregate was exemplified by grains of amphibole and biotite. Most of the aggregate had rounded corners and did not exceed 1 mm. Large grains measuring 2-3.5 mm occurred very rarely. Individual grains did not have contact with each other, forming a diffuse grain frame.

Approximate volumetric ratios of concrete ingredients were: binding agent (cement) ca. 39%, quartz ca. 36%, feldspars ca. 4%, fragments of rocks ca. 12% and pores ca. 8% [5].

The next significant part of the research was a microbiological test. This examination was performed to determine the species of lichen. The study showed the presence of three lichens: *Lecanora sp.*, *Caloplaca sp.* and *Physcia sp.*

4.2 Construction examination – location of rebars and cracks, assessment of lagging thickness

A non-destructive examination using electromagnetic induction, x-ray and gamma-ray photographs was carried out in order to locate the rebars and to specify the thickness of lagging [6]. Figs. 5 and 6 show location of rods in Chlapowski's bust and the width of the crevices. The rods lying in the closest position to the surface and directly under the cracks are situated at a depth of 2, 3, 4 and 5 cm.

The last stage of the research was an examination with the help of Infrared thermography (IRT) camera. IRT mapping showed temperature variation on the bust's surface and the occurrence of deep crevices. Discontinuities interrupted thermal conduction of concrete. As a result of the occurring defects, the temperature over the crevices was higher (during heating) than in the rest of the concrete. This allowed specification of the area of cracks, as presented in Fig. 7.

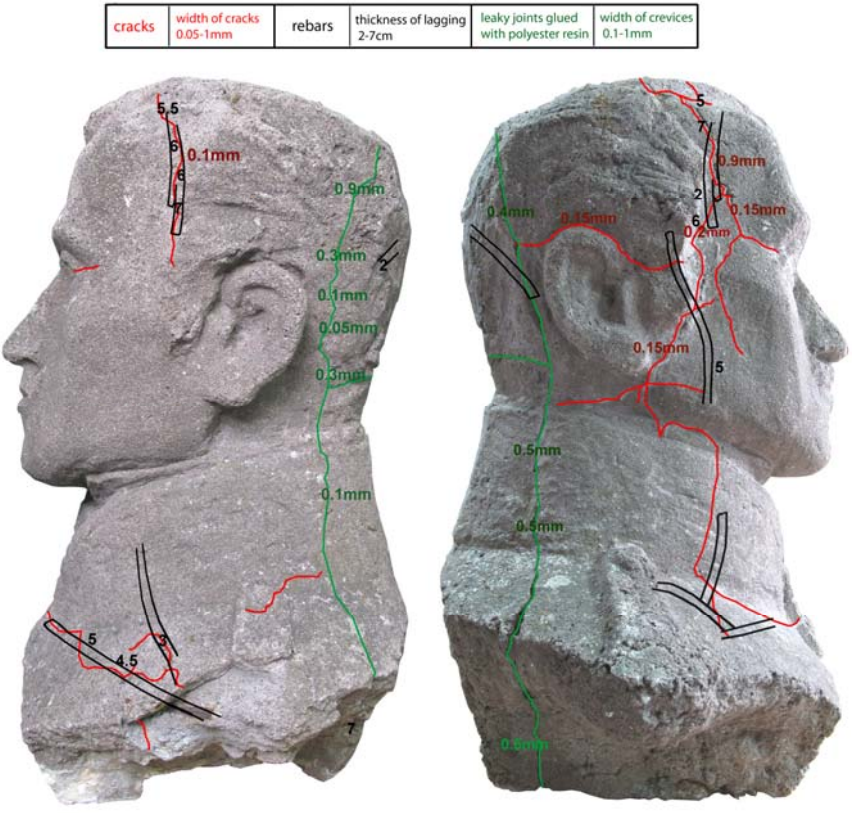

Fig. 5 The bust of Dezydery Chlapowski - view from the left and right side. The location of rods, thickness of lagging, the width of the cracks and crevices

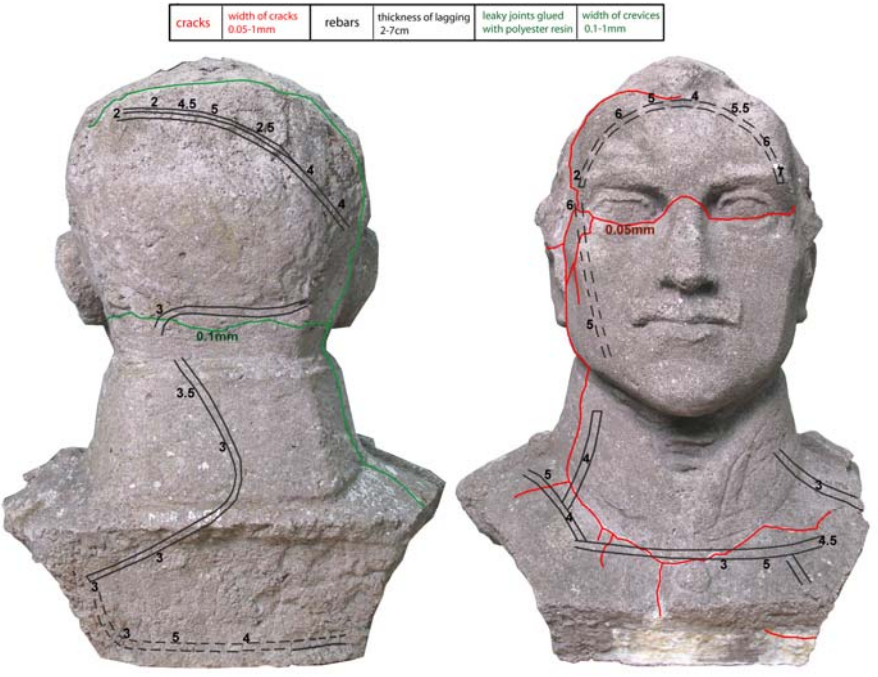

Fig. 6 The bust of Dezydery Chlapowski - view from the front and back. Location of rods, thickness of lagging, the width of the cracks and crevices

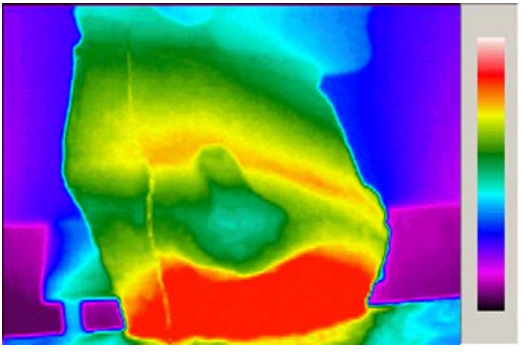

Fig. 7 Infrared mapping showed the occurrence of deep crevice

5 Conclusions

All the investigations performed on the historical busts have shown very interesting results and helped to find the causes of damage.

Rebars inside the sculptures were found to be not the traditional reinforcement, but loose steel rods, not joined to one another. In some places of the sculptures, rods remained bare, uncovered by cement mortar; in others they were placed too close to the surface. This technological fault caused that, directly after their erection in this location, an atmospheric corrosion of steel commenced, accelerating steel corrosion in the interior of the busts. Expansive rust produced by the rebars has caused visible cracking, spalling, delamination of the concrete cover and cavities.

High water absorption and open porosity facilitated water penetration, leaching, and entrance of air polluted by acid oxides, especially carbon dioxide, which significantly speeded up carbonation [7]. Leaching of calcium hydroxide contributed to a decrease in pH and accelerated steel corrosion.

Crevices between technological joints, in the beginning very narrow, were constantly expanded by frozen water and the roots of moss. This resulted in cavities and lagging exfoliation.

The development of lichen and moss contributed to the slow destruction of busts by: in-growth and mechanical blasting, secretion of organic acids and hindering water evaporation. In the long term, effects of their development caused etching of the surface layer, its weakness and the formation of cracks and cavities [8].

6 Acknowledgements

Authors would like to thank Dr. Jan Mackowiak - the Director of The National Museum of Agriculture and Agricultural-Food Industry in Szreniawa, Dr. Joanna Karbowska-Berent, Mr Adam Cupa, Dr. Wojciech Bartz, Mrs Wioleta Oberta, Ms Teresa Kurkiewicz, Mr Michal Gorski and Mr Krzysztof Lisek for their valuable help in this study.

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II.10

Deterioration of Cement-Rendered Brick Masonry Buildings: Case Study of a World War II Airfield in East Lothian, Scotland

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Abstract This paper investigates the deterioration of cementitious renders, with reference to the buildings on a World War II Airfield, now the Museum of Flight, in East Lothian, Scotland. Most of the buildings are brick masonry with a thin cementitious render, and on several of them the surface of the render is blistering, flaking and eventually being lost altogether. The blistering was investigated using non-destructive techniques such as infrared thermography, electrical resistivity measurements and rebound hardness testing; and with analytical methods such as X-ray diffraction, scanning electron microscopy and ions analysis of aqueous extracts. The results show that the deterioration is active and ongoing, and suggest that it may involve the movement of moisture, may be linked to the presence of certain aggregates within the render and may be salt-related.

1 Introduction

1.1 The deterioration and conservation of concrete and cement

Buildings and structures constructed using concrete and cement constitute an important part of our tangible cultural heritage from the late nineteenth and twentieth centuries. However, the significance of these buildings has only recently begun to be recognised, and so less research has been undertaken to understand how and why they deteriorate than for traditional buildings. The development of conservation methods and techniques is also at a less advanced stage than for traditional buildings, and most of the literature relating to concrete repair is directed towards modern reinforced concrete, rather than historic concrete and

cement. A further issue is the difficulty of applying the usual principles of building conservation to concrete and cement, 'particularly in relation to the aims of minimum intervention, retention of authenticity and reversibility' [1].

1.2 The museum of flight, East Fortune

A Royal Naval Air Station was built at East Fortune, in East Lothian, Scotland, in 1915, to house both airships and aircraft. It was and still is a rural location, approximately 5 miles from the North Sea. The station was used for military purposes again during the Second World War, and many new buildings were constructed very quickly. After the war finished the station was gradually wound down, until 1975 when the Second World War buildings were opened as a Museum of Flight by National Museums Scotland. In 1990 the site was designated as a Scheduled Ancient Monument and 8 of the most significant buildings were given a category B listing.

The Museum of Flight includes around 23 brick buildings with cementitious renders. They are simple rectangular structures, with protruding piers on the outsides for extra structural stability, and although they may appear to have little architectural merit in themselves, they are significant because they help to make the site 'probably the most complete Second World War temporary airfield in Britain' [2]. In order to preserve this completeness, the original fabric of the buildings needs to be preserved as far as is possible.

Fig. 1 The Crash Tender (Building 38), an example of the cement-rendered brick masonry buildings

1.3 Types of deterioration

Considering their age and the circumstances of their construction, the buildings are in fair condition. Many still have their original asbestos roofs, still functioning, and most of the cementitious render is original. Only a few of the most severely deteriorated bricks have been replaced. However, some deterioration has occurred, due to a combination of the way the buildings were designed and constructed, and the environmental conditions at the site. The deterioration includes breaking and crumbling of the unrendered bricks just above the ground; salt efflorescences forming on the inside walls of the buildings; cracking and delamination of the render; and blistering and flaking of the render. This paper will focus upon the work that has been undertaken to investigate the blistering render and identify possible causes for it.

Fig. 2 The blistering render on Building 47 (Spare Parts Store)

2 Method

2.1 Surveys to investigate the patterns of deterioration

A condition survey found blistering and flaking on only 3 of the brick masonry buildings with a cementitious render: the Main Stores Office (Building 26), a small Latrine block (Building 46) and the Spare Parts Store (Building 47). Infrared thermography was employed as an additional method for mapping the areas of blistering render, in the hopes that it might identify areas where the blistering was at a very early stage. The Flir B400 camera that was used was able to measure the temperature of all the surfaces in the field of view and produce a false coloured image to facilitate the interpretation of the thermal patterns.

2.2 Moisture movement through the render

In order to understand the movement of moisture through the render, the sorptivity of the render was measured and compared to the values obtained for the bricks used at the site. Sorptivity characterises the ability of materials to absorb and transmit water by capillarity and was measured using a standard procedure [3].

The pattern of moisture movement through the render was initially investigated simply through visual observation of the buildings in different weather conditions, since the render appears darker when it is wet. The moisture contents of the bricks and the render were then investigated non-destructively using infrared thermography and moisture resistivity measurements, and direct analysis of the moisture content of the bricks and the render was also undertaken where possible, by sampling small pieces of delaminating material still in contact with sound material. The results were compared to values for the moisture content at saturation for the material type, obtained during experiments to measure the porosity of samples.

2.3 Surface properties of the render

The surface properties of the blistering render were investigated non-destructively using a rebound hammer, also known as a Schmidt hammer, which measures the rebound hardness of a material. Hardness testing may be considered equivalent to performing a compression test on a small volume of the material's surface, and a correlation between hardness and yield stress may therefore be expected, and has been demonstrated experimentally [4].

In order to compare the appearance of the render at the surface and in-depth, core samples were taken in a blistering area and a non-blistering area on Building 46, and examined with the naked eye and at low magnification.

2.4 Analysis of the cementitious component of the render

X-ray diffraction was carried out on finely ground samples of the cementitious part of the render, from which as much aggregate as possible had been separated either manually or by sieving. Aqueous extractions were then prepared from the bricks and from the cementitious parts of the mortars and renders, and were analysed using Ion Chromatography to obtain concentrations of chloride, nitrate, phosphate and sulphate; and with ICP-OES to obtain concentrations of calcium, magnesium, sodium, potassium and aluminium. The percentage by weight of each ion extracted from the sample was calculated.

2.5 Analysis of the aggregate component of the render

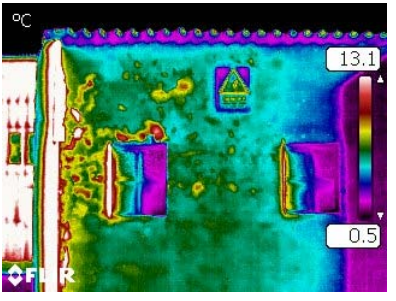
The render composition varies from building to building: some render contains almost no aggregate except fine sand and some is very rich in pebbly aggregate. The blistering only occurs in the latter type of render, suggesting that the pebbly aggregate may be a relevant factor. Blistering pieces of render were sampled and inspected, and specific aggregate particles were then examined using an optical microscope and a Scanning Electron Microscope (SEM), and were analysed with the SEM and with X-ray diffraction.

3 Results and discussion

3.1 Surveys to investigate the patterns of deterioration

The visual survey demonstrated that for the 3 affected buildings, the blistering occurred more frequently on south-facing walls, but also on north-facing walls. It was found in patches all over, but seemed to be concentrated on the piers and on the flat areas of wall just adjacent to the piers. On Buildings 46 and 47 it was found immediately to the right of the piers, on the south east side.

The infrared thermography survey was undertaken on a day when the walls of Building 46 were heated up by the sun, and the blistering areas appeared warmer. This was because there are air pockets within the blistered render, creating a thermal break and resulting in the render heating up more readily than elsewhere. Furthermore, the infrared thermography showed large areas adjacent to the visible blistering which looked sound to the naked eye, but where hollow patches had begun to form below the surface. This was confirmed by tapping. For example, the area between the 2 windows on the NW side of the SW wall on Building 46 looked fine, but the infrared thermogram showed that it was beginning to blister.



Figs. 3, 4 Infrared thermogram of the SW wall of Building 46, with a digital image for comparison (Images: Maureen Young)

3.2 Moisture movement through the render

Table 1 Sorptivity of the cementitious render and bricks from the Museum of Flight

	Render from Building 24	bricks type 1 (Niddrie)	bricks type 2 (Edinburgh)	bricks type 3 (White Hill)	bricks type 4 (Prestongrange)
Sorptivity in $mm/min^{1/2}$	0.10	0.51	0.58	0.67	1.79

The render was found to have low sorptivity in comparison to the bricks, meaning that the absorption and desorption of moisture by the render occur fairly slowly.

It was observed that many buildings appear to have a zone of rising damp at the base of the walls, extending up to 1 m from the ground. When it rains the entire wall surface is wetted, and because the piers are the most exposed parts of the walls, they become wet most quickly, and take longest to dry out. These observations were substantiated by the moisture content data in combination with the non-destructive testing, which showed that the bricks and mortar close to the ground are very wet, and that the render at this level is also wet or at least damp. The driest areas of render are found at heights above 1 m on the flat walls, and the render on the piers tends to be slightly damp even on dry days.

Table 2 Moisture content of the cementitious render and bricks from the Museum of Flight

	Unrendered bricks just above the ground	Mortar from joint in bricks close to ground	Render from close to the ground	Render on piers at various heights, on wet and dry days	Render from above 1.5 m on flat walls on dry days
Moisture content (% weight)	10.3 - 14.8	13.4	7.6 – 13.1	4.4 – 6.8	1.3 – 2.1
Moisture content at saturation for similar material (% weight)	12.9 - 16.4	14.9	17.3	17.3	17.3

3.3 Surface properties of the render

The rebound hammer testing on Building 47 showed that the reading in blistering areas was usually the same as in adjacent sound areas, suggesting that the blistering is not indicative of significantly weakened render. Additionally, although the surface of the core from the blistering area broke off in a thin sheet

approximately 2 mm thick, the samples were otherwise visually very similar. The core from the blistering area did not appear to be disintegrating throughout.

3.4 Analysis of the cementitious component of the render

The most useful results to date have been obtained from the analysis of aqueous extracts.

Table 3 Percentage of selected anions and cations extracted from render samples

	% Cl^-	% SO_4^{2-}	% Ca^{2+}	% Na^+	% Al^{3+}
Building 23	0.0006	0.0154	0.1158	0.0082	0.0002
Building 24	0.0015	0.1831	0.1433	0.0118	0.0002
Building 23 (1992 render)	0.0012	0.1106	0.0409	0.0046	0.0001
Building 26: blistering area	0.0039	0.0245	0.1580	0.0135	0.0593
Building 26: no visible blistering	0.0009	0.0341	0.0559	0.0087	0.0219
Building 46: blistering area	0.0158	0.4876	0.2106	0.0187	0.0179
Building 46: no visible blistering	0.0045	0.0916	0.1373	0.0092	0.0103

The results have been given for the historic render and a more modern render on 2 buildings where there is no sign of blistering (Buildings 23 and 24), and for the blistering and non-blistering areas on Buildings 26 and 46. Figures have only been quoted for those ions which were detected in reasonably high concentrations. More comprehensive ions analysis is required, but these initial results show that the 3 highest concentrations of chloride ions and the highest concentration of sulfate ions came from buildings where the render is blistering. Also, the concentrations of aluminium ions, although low, were over 10 times greater for the buildings with blistering render than for the buildings with no blistering.

3.5 Analysis of the aggregate component of the render

It was found that blisters often seem to form above certain types of aggregate, including a greyish flaky material, a soft orange-yellow material, and little pods of fibrous material, which may be of plant origin. Examination with the SEM showed that the small pods are composed of long tangled fibres. The greyish material has a fairly smooth appearance, and the soft yellow material is rough and granular. Preliminary X-ray diffraction results have identified lots of carbon in the greyish material, suggesting it may be charcoal, and quartz in the yellow material, suggesting it may be sandstone. These aggregates are all very soft, and are probably quite porous.

Fig. 5 A blistering piece of render on Building 47, with a large grey particle underneath

4 Conclusions

The blistering of the render on some of the buildings at the Museum of Flight is concerning because original render is being irreversibly lost, and the deterioration is active and ongoing. Condition surveys show that the blistering seems to be concentrated on and around the piers, which are the parts of the buildings undergoing frequent cycles of wetting and drying. This suggests that moisture may play a part in the deterioration mechanism.

Examination of core samples and rebound hardness readings indicate that the blistering is largely a surface effect which does not occur through the depth of the render, and that the blistering areas are not significantly weakened.

The ions analysis results are not fully comprehensive, but suggest that the blistering may be linked to higher concentrations of chlorides, sulfates and aluminium than those found elsewhere. It is possible that gypsum ($CaSO_4.H_2O$) and/or ettringite ($[Ca_3Al(OH)_6.12H_2O]_2.(SO_4)_3.2H_2O$) is crystallising within the render, but this requires further investigation.

Finally, the blistering seems to be related to the presence of pebbly aggregate. The presence of plant material shows that the aggregate was not particularly clean, so it is possible that it was contaminated with soluble salts. It may also be that the chemistry of individual particles is relevant, as the blisters often seem to form above certain types of aggregate. There may be some physical effect connected to the absorption and desorption of moisture from the aggregate particles, with associated dimensional changes, or even a chemical effect due to concentrated areas of soluble salts forming around the aggregate particles, and subsequently crystallising, perhaps as less soluble compounds.

If the blistering is related to the chemical composition of the render, there is little that can be done to prevent it. The buildings where blistering is occurring need to be recorded thoroughly before the render is lost, and techniques to

conserve the render need to be investigated. If replacement of areas of the render becomes unavoidable, this should be undertaken as sympathetically as possible.

5 Acknowledgements

I am grateful for the assistance of Maureen Young at Historic Scotland with infrared thermography; Lorna Eades, Peter Anderson and Henry Hercock at the University at Edinburgh for ICP-OES, Ion Chromatography and rebound hardness testing respectively; and Susannah Kirk at National Museums Scotland for scanning electron microscopy. I also thank Christopher Hall at the University of Edinburgh for help with writing this paper and AHRC UK for financial support.

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II.11

The Influence of Calcium Hydroxide on the Plasticity of Lime Putties

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Abstract It is well-known that different slaked limes (calcium hydroxide) influence the plastic properties of fresh mortar differently. There is not sufficient scientific literature that describes the characteristics of calcium hydroxide that influence the plasticity in lime-based mortar systems. Therefore, the building industry increasingly uses chemical additives combined with hydraulic binders to achieve the required plasticity (workability) of a mortar. In order to exploit the positive environmental and plastic working properties of lime-based mortars investigating the mechanism of hydrated lime on the plasticity of mortar systems is necessary.

1 Analysed materials

The analysed materials are ten calcium limes (CL) from ten different regions and manufacturers. The value for CaO + MgO is between 75% (CL 70) and 98% (CL 90). Each lime has been analysed as dry hydrate and as the corresponding quicklime. Due to the complexity of this topic this article is focused on lime putties produced from dry hydrated lime.

Table 1 Analysed materials

Sample	CL90-1	CL90-2	CL90-3	CL90-4	CL90-5	CL80-6	CL70-7	CL90-8	CL80-9	CL90-10
water/binder	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Emley 24 h	206	189	364	162	206	131	117	176	237	166
water/binder while soaking	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
water/binder at measuring	0.67	0.72	0.72	1.14	0.56	0.81	0.90	0.63	0.68	0.95
Emley 28 d	326	202	307	321	251	135		219	206	260
water/binder while soaking	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
water/binder at measuring	0.84	0.82	0.86	0.87	0.74	0.61	0.75	0.70	0.88	0.93
Emley 28 d	321	189	423	355	206	125	119	180	189	210

2 Analysed parameters

In addition to the physical-mechanical properties of hardened mortar such as density, porosity or durability that hydrated lime provides to mortar, it also provides plasticity to the fresh mortar. This parameter contributes to flexibility, yield, machinability (mixing) and water retention of the mortar.

The factors responsible for the development of plasticity in hydrated lime are investigated using several calcium hydroxides of different manufacturers and their corresponding quicklimes. The results are evaluated by correlating objective plasticity values with subjective workability data by judging of an experienced craftsman in pilot plant experiments with defined lime mortars. The resulting material parameters responsible for plasticity will then be pointed out. The analysis included characterization of raw materials and detailed investigations of different slaked lime and lime putty. The determination of plasticity occurred accordingly to a technique by W. Emley [1].

The Emley Test method for plasticity takes into account the force required to lift a weight due to friction of lime putty against a platen. At the same time the puttywater is being suctioned into a gypsum base plate and the time it takes to reach failure is being recorded. The starting materials for Emley plasticity measurement are lime putties of the same consistency slaked directly from quick lime or from putty made from dry hydrated lime [1, 2].

Fig. 1 Emley plasticimeter

Experience and comparison of the rheological properties of other mineral systems indicate that particle size distribution and particle shape as well as formation of the surface are of primary importance [3]. It is known that the rheology of lime-water suspensions (lime putty) is affected by the amount and the form of available fines of calcium hydroxide [3]. The plasticity also results from the interaction of the liquid phase with the particles of calcium hydroxide and therefore depends on the specific surface. The specific surface of the dry (unsoaked) calcium hydroxide samples was determined via gas adsorption as single-point method according to Brunauer, Emmett and Teller [5]. The samples have been dried at 110°C and rinsed with dried N_2 gas at 120°C for 2 hours. The sample weight has been determined after desorption. An increasing plasticity value shows some correlation with increasing specific surface area (SSA) (Fig. 2).

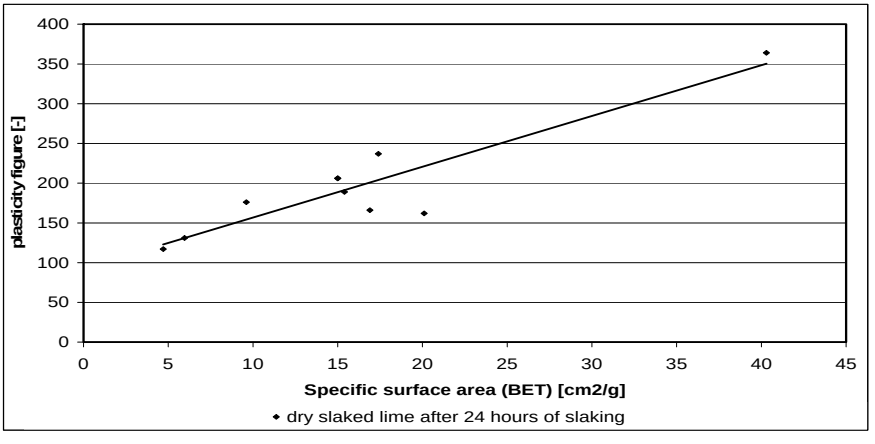

Fig. 2 Scattergram of SSA versus Emley plasticity value

Coarse particles (> 1 μm) of calcium hydroxide, which consist of agglomerates, time-dependently form fines of calcium hydroxide and decisively influence the plasticity. This process is founded in crystal habit and morphology of the lime particles. The micrographs of the scanning electron microscope (Figs. 3 and 4) illustrate the result of the process of "refinement".

The degree of "refinement" is different with each hydrate and, as is suggested, related to the development of plasticity. The available foreign ions such as Al [6] and structural defects in the $Ca(OH)_2$ crystal can be divided into those appearing as "notches" that lead to division and refinement causing increased plasticity, and others appearing as "stick points" that avoid such a division, or even lead to a coarsening (see Fig. 3 to Fig. 8) [3].

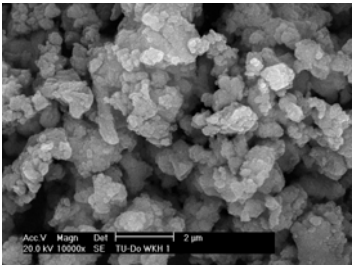

Fig. 3 Calcium hydroxide - sample CL 90-1

extended soaking-time → in excess of water

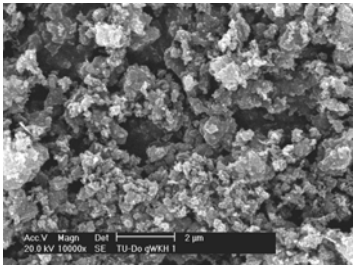

Fig. 4 Calcium hydroxide after 28 days of soaking - sample CL 90-1

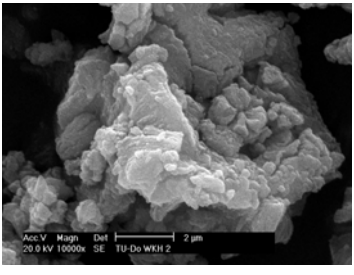

Fig. 5 Calcium hydroxide - sample CL 90-2

extended soaking-time → in excess of water

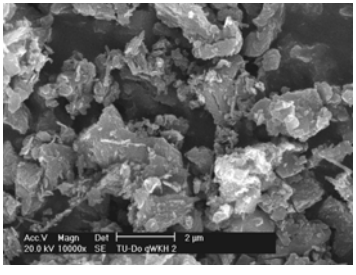

Fig. 6 Calcium hydroxide after 28 days of soaking - sample CL 90-2

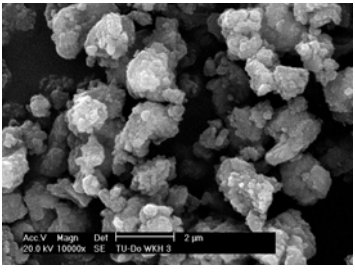

Fig. 7 Calcium hydroxide - sample CL 90-3

extended soaking-time → in excess of water

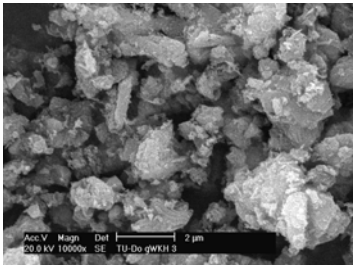

Fig. 8 Calcium hydroxide after 28 days of soaking -sample CL 90-3

Based on the Figures 9 and 10 the temporal influence of soaking time and the process of refinement are visible. The duration of workability and thus the plasticity figure of different samples of slaked lime increase after 28 days of soaking. Especially sample CL 90-1, which shows a distinctive refinement (Figs. 3 and 4) also shows a clear rise of the plasticity. Other samples such as sample CL 90-3 (see Figs. 7 and 8) remain virtually unchanged.

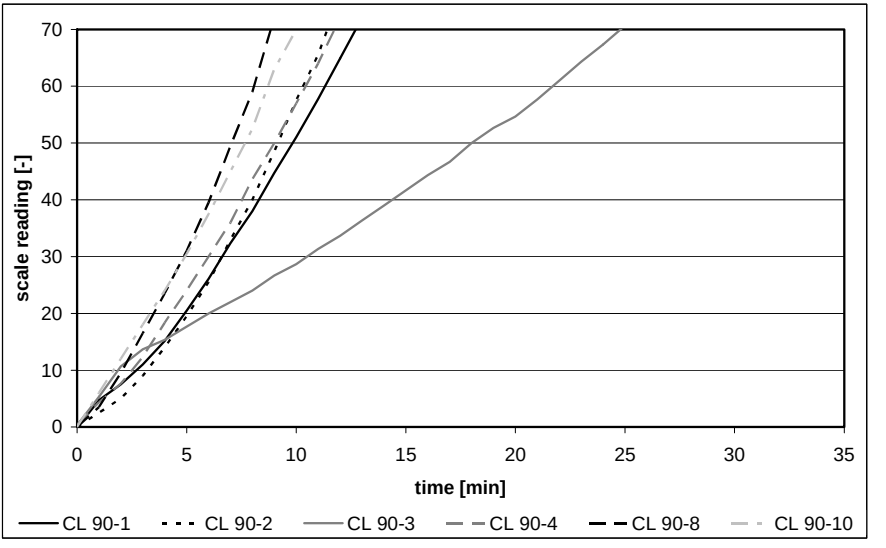

Fig. 9 Development of plasticity in correlation with time - after 24 hours of soaking

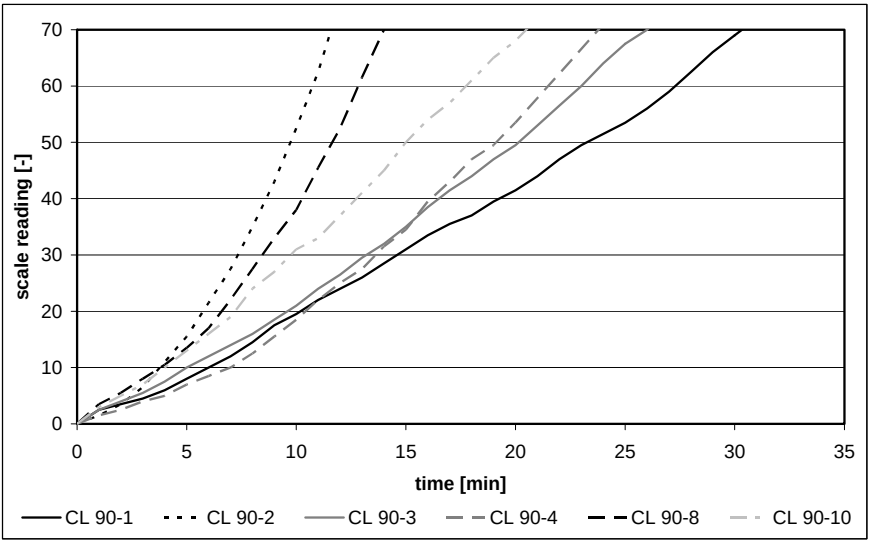

Fig. 10 Development of plasticity in correlation with time - after 28 days of soaking

The 28 day soaked hydrated limes are in a surplus of water with different water/binder ratios (w/b 0.8 and w/b 1.5). Before the measurement all putties were dried at 40°C to a standard consistency. In many cases, the samples that initially soaked in a larger amount of water possess higher plasticity values (see Fig. 11). This observation leads to the conclusion that the amount of available water affects the development and refinement of the hydrated lime particles.

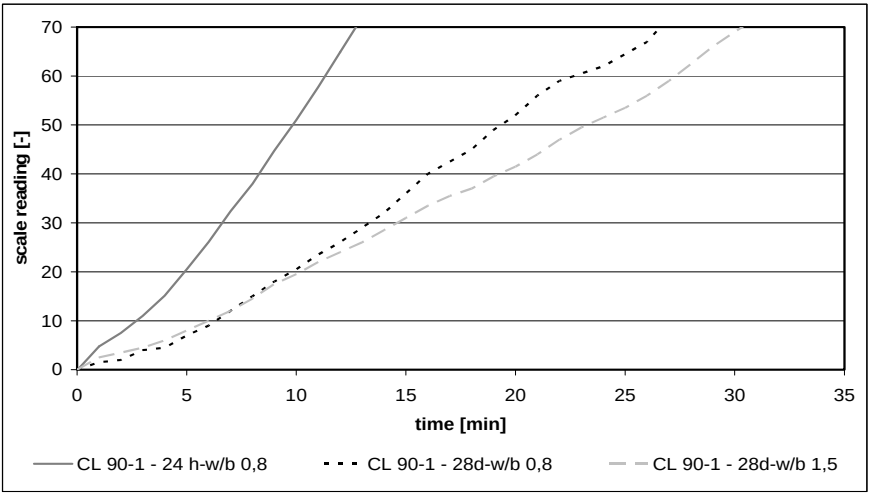

Fig. 11 Plasticity figures after 28 days of soaking in different lime-water proportions compared to the measurement after 24 hours

The process of refinement is also indicated with analysis of particle sizes at different times using He/Ne-Laser granulometry. The samples have been measured as slurry in isopropanol at 50 mm focal width, 30 seconds ultrasonic exposure and 60 seconds ultrasonic pause. The maximum percent of the particle size distribution of those samples that increase their plasticity with time of soaking moves to the area of the finer particle sizes (Fig. 12 - sample CL90-1). Samples which show slightly increased plasticity figures also only show small changes in the curves (see Fig. 12 - sample CL90-3). Several curves become significantly steeper, which indicates rather an accumulation of particles of equal size than a refinement. For these samples increasing plasticity figures can not be recorded (see Fig. 12 - sample CL90-2).

Since the curves of three samples with different plasticity development and different plasticity figures look similar after soaking, conclusions about the plasticity can not be drawn just according to particle size and size distribution, whereas changes due to soaking within one sample can be identified.

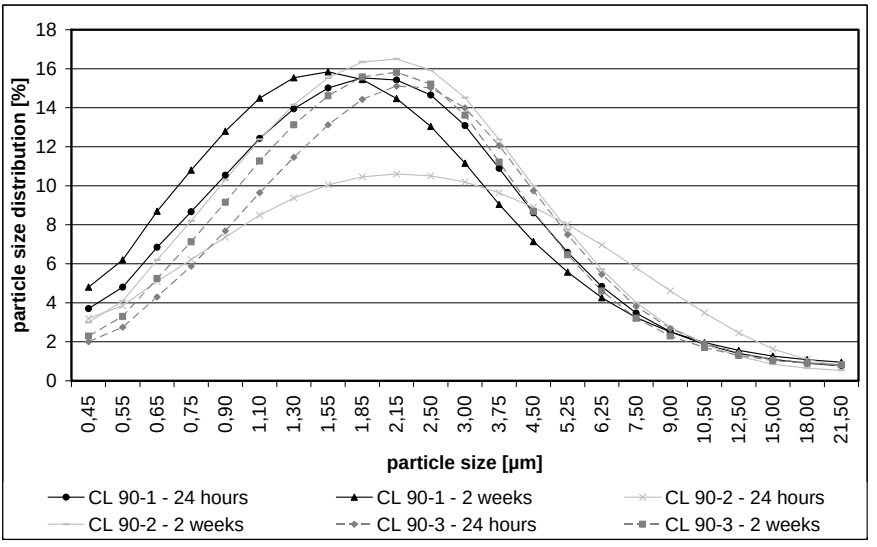

Fig. 12 Particle size distribution at different times of soaking

3 Conclusion

The test method developed by Emley for measuring plasticity is an adequate test method for measuring the workability of lime putties and mortars. It provides objective data and reveals the evolution of plasticity over time.

Plasticity development relies on different parameters. In general it can be said that plasticity values increase with increasing soaking time. Due to crystal habit and morphology coarse particles (> 1 µm) of calcium hydroxide consisting of agglomerates time-dependently decrease in particle size when left in water.

Plasticity is influenced by the particle size distribution of the lime, i.e. plasticity increases with decreasing particle sizes. In mortar systems the plasticity is also mainly influenced by the particle size distribution, the particle shape and the amount of used aggregates. It is obvious that the higher the amount of aggregates the lower is the influence of the lime.

Nevertheless, the investigations have shown that because of their fines lime based mortars have a much better workability than mortars with different inorganic binders.

4 Acknowledgments

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II.12

Influence of Interfacial Material Pore Structure on the Strength of the Brick/Lime Mortar Bond

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Abstract This paper builds on previous work investigating the flexural bond strength, initial shear strength and compressive strength of fired clay brickwork built using hydraulic lime mortars. It has been shown that whilst flexural bond strength and initial shear strength of the brickwork generally increased with mortar strength, flexural bond strength was significantly impaired by both low and high brick water absorption. This paper describes a study of the pore size distribution of the surfaces of brick and mortar at the brick/mortar interface using Mercury Intrusion Porosimetry. The paper identifies critical pore sizes at the brick surface which would appear to govern resultant bond strength.

1 Introduction

Lime has been used as a binder in construction for thousands of years. Examples of its use have been found in Palestine and Turkey dating from 12000 BC [1]. Lime mortars were widely used by the Romans, and techniques for its manufacture and the design of mortars to different performance criteria were well understood. Vitruvius [2] in 30 BC described the manufacture of lime mortars and the key criteria to be considered in order to manufacture a good quality mortar. In 1837 an English translation of Vicat's 1828 publication gave a comprehensive analysis of the state of the art [3]. Practical formulations and application techniques were given in the form of a textbook for students of Building Materials published by Rivington's in 1875 [4], and detailed specifications were published by the Building Research Establishment in 1927 [5]. Since the end of the 2nd World War, lime has displaced by the faster acting, stronger, cement based mortars. Much expertise and understanding of lime based mortars has been lost, and there is very little guidance and performance data available to support structural design codes.

In recent years some research has been completed investigating the properties of hydraulic lime mortars [6, 7], but there is a general scarcity of data on the mechanical properties of lime mortared masonry.

Previous work [8] has investigated flexural bond strengths of a range of brick types constructed with different hydraulic lime mortars varying from NHL2 to NHL5 at varying concentrations. It was found that brick water absorption characteristics had a significant influence on bond development of brickwork. Both high and low absorption bricks developed lower bond strengths than medium absorption bricks.

The results presented herein are a re-analysis of these data taking into account the pore size distribution of the surface of the bricks in an attempt to identify critical pore sizes involved in the mortar : brick bond.

2 Experimental programme

The hypothesis of this investigation is that the pore size distribution of the brick at the mortar : brick interface is modified by mortar products penetrating into its pore structure. The experimental programme investigated the relationship between the pore size distribution of a ~2 mm thick section of the top surface of a fresh brick, the pore size distribution of a ~2 mm thick section of the top surface of a mortared brick from which the mortar has been removed, and the bond strength characteristics of the brick : mortar combination.

2.1 Materials

Table 1 Brick characteristics

	Initial Rate of Absorption ($kg.m^{-2}.min^{-1}$)		24 hr water absorption (%)		Sorptivity ($mm.min^{-1}$)	
Brick No. & Name	Average	CV%	Average	CV (%)	Average	CV (%)
15. Cheddar Brown	0.5	14.4	4.5	13.5	0.17	30.6
7. Surrey Orange	0.6	27.1	7.2	16.2	0.42	28.9
2. Ruskin Red 73	0.7	6.3	6.1	4.4	0.48	15.4
4. Tradesman Antique	0.9	6.7	6.7	2.5	0.37	12.6
1. Red Multi	1.7	15.7	8.0	10.1	1.12	20.0
29. West Hoathly	1.9	25.6	7.4	6.3	0.45	36.4
12. Dorset Red Stock	2.1	4.6	12.7	1.2	1.31	11.1

Seven types of standard size (nominal dimensions 15 x 102.5 x 65 mm) wire cut, extruded fired clay bricks were selected for this study, chosen out of the 30 bricks in the earlier study. The bricks were selected to be broadly representative of a typical range of water absorption characteristics in the UK. Brick properties, including 24h immersion water absorption and initial rate of water absorption described elsewhere [8] are summarised in Table 1.

Castle Cement Ltd NHL was used with a well-graded blended mortar sand (Binnegar sand) for the mortar mix. The sand grading curve is shown in Fig. 1. The mortar used was 1 part NHL3.5 to 2.25 parts Binnegar sand by volume; equivalent to 1 part NHL3.5 to 6.62 parts sand by mass. The water/lime ratio was 1.40 and the flow value was 160.

2.2 Manufacture, curing and testing of specimens

All bricks were dried under controlled (20ºC, 65% relative humidity) laboratory conditions prior to construction. Dry binder and sand were initially thoroughly mixed in a drum mixer and thereafter water was added gradually and mixing continued for 10 min in total. The mortar was left to stand (under cover to prevent evaporative moisture loss) for 50 min before briefly re-mixing and use. This stand time, following common site practice, is believed to improve workability. In order to control materials the bricks were not wetted by the bricklayer during construction to adjust suction.

All masonry specimens and mortar specimens were covered with plastic after fabrication for 1 week, to prevent initial rapid drying in laboratory conditions, and afterwards uncovered and stored in a climate room, maintained at 20 ± 2ºC and relative humidity 65 ± 5% with ambient CO_2 levels, until testing. Masonry and mortar were tested at 91 days. Full details of the flexural strength tests are reported elsewhere [8]. Bond strength data are shown in Table 2. The flexural strength of the mortar at 91 days was 0.45 $N.mm^{-2}$ with a coefficient of variation (CV) of 27%; the compressive strength at 91 days was 1.0 $N.mm^{-2}$ with a CV of 12%.

After testing, bricks with one mortared face were sampled for porosimetry testing. For each brick the mortared face was gently scraped clean of mortar, taking care not to abrade the surface of the brick. A 2-3mm slice was cut from opposite faces of the brick producing specimens of ~10 x 20 x 2 mm as shown in Fig. 2

Specimens were tested using Mercury Intrusion Porosimetry (MIP) using a Micromeritics Autopore III. Approximately 1 g of material was tested in each case and intrusion pressures were increased in steps up to 400 MPa, which allowed intrusions into pores as small as 40 nm. The pore size distribution of the clean face of the surface of each brick was established and mapped against the bond strength. In addition, the pore size distribution of an un-mortared face was subtracted from the pore size distribution of a mortared face in order to identify changes in pore

size distribution induced by the mortar. These changes were also mapped against bond strength.

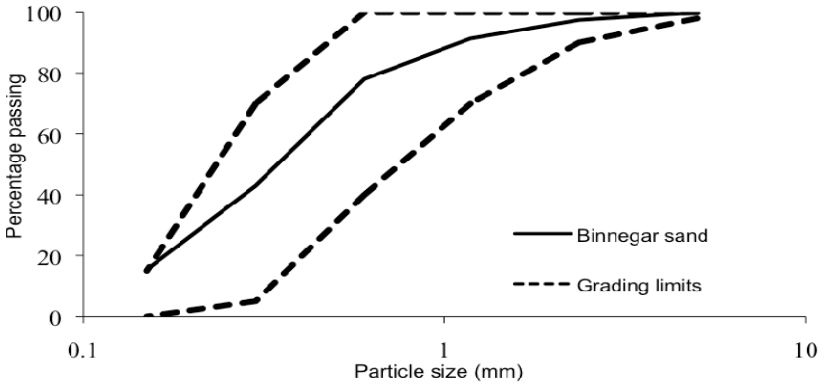

Fig. 1 Sand Grading

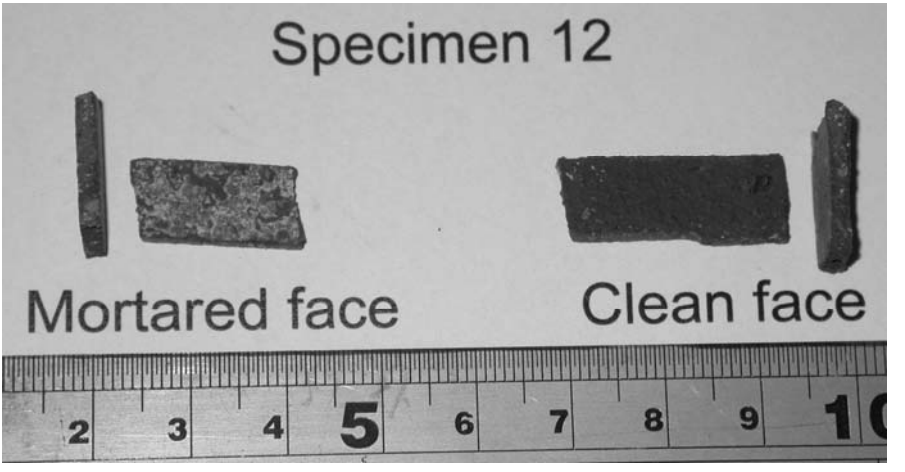

Fig. 2 Specimens for porosimetry testing

It should be noted that MIP produces a pore size distribution of pores that are accessible to intrusion (open pores). Closed pores will only be accessed when pore walls collapse under external pressure, which will only occur at high pressures, and small apparent pore sizes. Fig. 3 shows a small peak at ~0.01μm which is likely to have been produced by this collapse of pore walls. These closed pores would not be accessible to mortar products and therefore would not be involved in mortar bonding. In addition, the volume of pores smaller than 0.01μm (which would include all closed pores) is less than 7.5% of total pore volume in all cases, and therefore would not affect the conclusions drawn here.

Table 2 Bond strength data compared with pore size distribution

Brick No. & Name	Type & Texture	Mean Bond Strength ($N.mm^{-2}$)	Characteristic Bond Strength ($N.mm^{-2}$)	Initial Rate of Absorption ($kg.m^{-2}.min^{-1}$)	% pores greater than 1 µm
29. West Hoathly	Handmade	0.28	0.18	1.9	59.2
1. Red Multi	Wire	0.29	0.08	1.7	67.8
12. Dorset Red Stock	Stock	0.34	0.21	2.1	70.2
7. Surrey Orange	Wire-rolled	0.40	0.23	0.6	43.5
4. Tradesman Antique	Wire-rolled	0.46	0.32	0.9	36.2
2. Ruskin Red 73	Wire-smooth	0.52	0.35	0.7	36.5
15. Cheddar Brown	Wire-rolled	0.53	0.26	0.5	34.1

3 Porosimetry analysis

Fig. 3 shows the relative pore size distribution of the surface of the individual bricks.

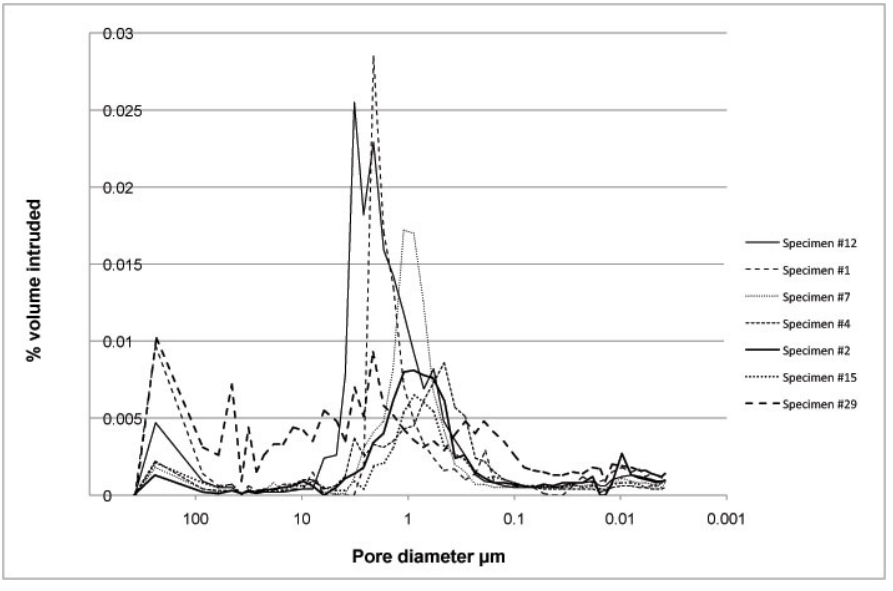

Fig. 3 Pore size distribution of clean brick surface

It can be seen that the majority of pore sizes in all bricks can be found between 10μm and 0.1μm, and in most cases the peak concentration of pores is around 1μm.

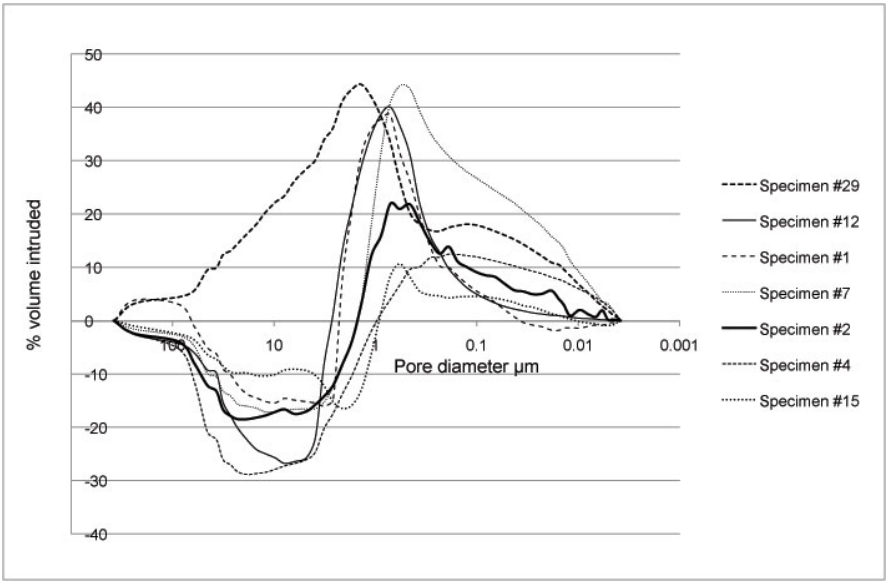

Fig. 4 Pore size distribution comparison of clean and mortared brick surfaces

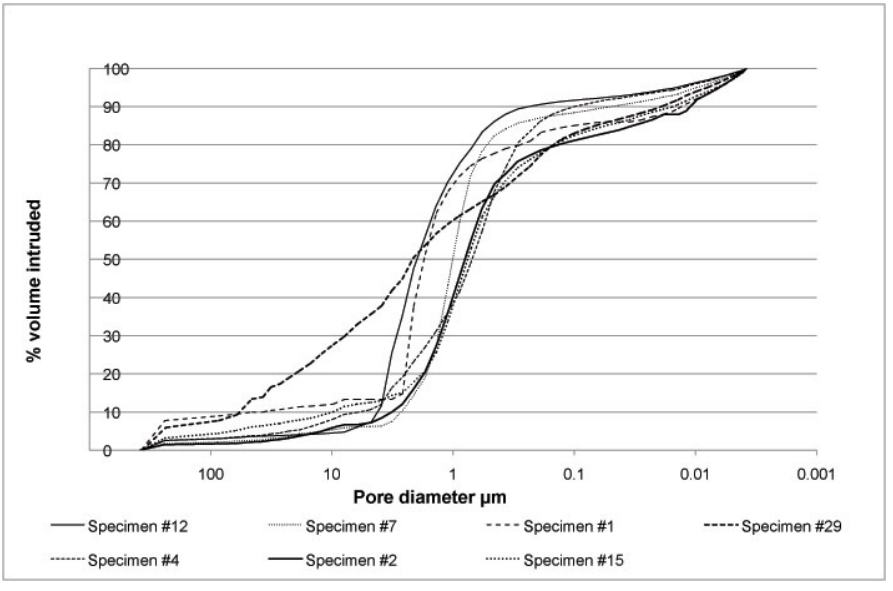

Fig. 5 Cumulative pore size distribution for brick surfaces

Some bricks have large pores, between 50 and 500µm, and there is also a small peak of pores at around 0.01µm, which includes the volume of larger closed pores as explained above.

In general, once mortared, there is a reduction in pores between 100 and 10 µm towards pores between 1 and 0.1 µm. This trend can be seen in Fig. 4 which shows a subtraction of pore size distribution between clean surfaces and mortared surfaces. With the exception of Specimen #29 where there is no reduction in large pore sizes, all specimens show the same trend. This is likely to be due to the fact that this brick has a high percentage of pores greater than 100µm compared with the pore size distribution between 100 and 10 µm. These larger pores would not be blocked by mortar. An examination of the cumulative intrusion curves shown in Fig. 5 shows a group of four specimens where the percentage of pores intruded increases rapidly as pore size reduces to below 1 µm. These were specimens 12, 7, 1 and 29, where the bond strengths were all below 0.4 N.mm^{-2}.

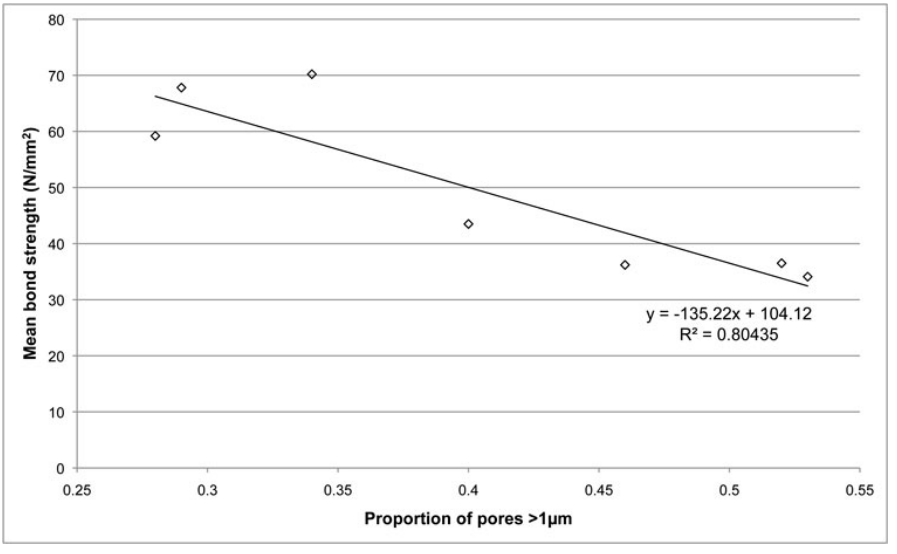

Fig. 6 Relationship between mean bond strength and the proportion of pore volume >1 µm

The other three specimens, numbers 4, 12, and 15 have similar cumulative pore size distributions, and their bond strengths are also similar and in excess of 0.46 N.mm^{-2}. Fig. 6 maps the bond strengths against the proportion of pore volume on the surface of the brick which is taken up by pores that are larger than 1 µm. There appears to be a linear relationship, with bond strength reducing as the proportion of pore volume that is greater than 1 µm increases.

4 Conclusions

Portlandite (calcium hydroxide) crystals range in size between 1 and 10 μm, and calcite (carbonated Portlandite) crystals range between 0.1 and 1 μm [9]. The shift in pore size distribution seen in figure 4 suggest that the pore sizes of the brick surface between 1 and 10 μm allow Portlandite to penetrate the pores and crystallise within them, thereby reducing the size of those pores. Calcium silicate hydrates have smaller crystals which range from 0.1 to 0.001 μm in size [10]. Since these hydraulic elements form a stronger bond than the Portlandite, and they are able to penetrate smaller pores, this would tend to explain the better bond strengths seen in bricks where a greater proportion of the pore volume is below 1 μm.

The general trend, therefore, is that the greater the percentage of pore volume on the surface of the brick that is represented by pores with sizes below 1μm, the better the bond strength with hydraulic lime mortars. Where bricks are known to have a higher than normal percentage of pore volume represented by pores larger than 1μm, designers might want to consider increasing the strength of the mortar in order to achieve a satisfactory bond strength. This could be done either by increasing the proportion of lime in the mortar, or changing from NHL3.5 to NHL5.

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II.13

Analytical Diagnosis Protocol to Assess the Impacts of Environmental Stressors on Historical Mortars Acting as the Support of Wall Paintings

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Abstract This work describes a new analytical diagnosis protocol to assess the environmental impacts on historical mortars acting as supports of wall paintings. The adequate assessment of such impacts requires not only the identification of the original and decaying products but also clarify the mechanisms (chemical reactions between original materials and environmental stressors) that promote the decaying. The proposed protocol is divided in four steps: (1) Analytical (both elemental and molecular) characterization by means of portable non-destructive spectroscopic and micro-destructive analytical techniques to identify the original and decaying compounds of the mortars, (2) Chemometric analysis on quantitative data of soluble salts, (3) Chemical simulations (MEDUSA, RUNSALT…) to explain the reactions between mortar components and environmental stressors and (4) Validation of the decaying reaction taking into account the agreement between the spectroscopic information and the chemometric calculation + chemical simulation results. The possibilities offered by this diagnosis protocol are described on two case studies: (a) mortars from medieval wall painting affected by ammonium nitrate rich infiltration waters and (b) Pompeian mortars of wall paintings exposed outdoors from the last 150 years after its excavations.

1 Introduction

A mural or wall painting is the general term for a painting applied directly to a wall. The mortar of a wall painting is composed of two layers, the *arriccio* layer

(the inner one composed mainly of slaked lime, sand, and/or brick dust and organic matter) and the *intonaco* layer (a much finer layer intended for painting). Mortars and pigments included in wall paintings can be affected by different factors (i.e., humidity, light, etc.). Some of these are the environmental stressors, such as infiltration waters, the impact of atmospheric pollutants, and the biodeterioration processes [1-5], which promote decay (different kind of efflorescence, black crusts, loses of binding strength, etc.). These affect the integrity of the wall painting, impacting first the painting layer; this layer can act as a protection for the plaster underneath, but sometimes the pigmented layer is not enough to prevent the external aggressions inside the mortars. In fact, deterioration in plasters of wall paintings is a well-known topic.

Many efforts have been carried out in recent years to investigate the nature of those decay products and the formation process of these salts, both of which promote the decay, including the enhancement effects between several stressors. Research also has been focussed on the development of innovative methods to remove these salt crusts [6]. The complexity of the problem requires a sound analytical protocol to assess the nature of the decaying salts (in the mortar of the wall painting, but sometimes also in the pigment layer) promoted by the effect of environmental stressors.

In this work, such a new analytical methodology is presented and discussed.. The protocol is composed of a combination of spectroscopic techniques to identify the molecular composition of the products, including infrared spectroscopy, Raman spectroscopy, and μ-x-ray fluorescence, in addition to quantitative analysis (ionic chromatography) on the solubilised ions coming from those salts. The structural and quantitative data are treated by chemometric tools (correlation analysis and principal component analysis) and by chemical simulation (thermodynamic models to predict the formation of salts under specific conditions) to ascertain the possible decay reactions resulting from environmental stressors on the original materials.

To exemplify how to apply this methodology, two case studies are presented: (a) mortars from a medieval wall painting affected by infiltration waters and (b) mortars from wall paintings from a Pompeian house excavated 150 years ago and exposed since then outdoors.

2 Experimental

2.1 Samples

Mortar samples (*intonaco* or plaster and arriccio layer) were taken from two locations with different environmental conditions. Nine mortar fragments (with remains of red pigment) were taken from a 12 m^2 medieval wall painting of a

church (Bay of Biscay coast, north of Spain) affected by ammonium nitrate rich infiltration waters. Three mortar fragments were taken from the upper part (left-middle-right part of the painting, A1-B1-C1), three from the middle part (left-middle-right, A2-B2-C2), and three more from the lower part (left-middle-right, A3-B3-C3) [see sample distribution in Fig. 3]. A wall crack is observed down A2 till C1. Additionally, two mortar fragments with red pigment remains (hematite) from a wall, as well as six mortar samples with pigment layer remains coming from wall paintings, were collected from the House of Marcus Lucretius in Pompeii (Insula IX 3,5/24) for analysis. This house was first excavated more or less 150 years ago, and since that time it has been exposed to the open air. These last samples were collected during the excavation works performed by the Finnish EPHU project (Expeditio Pompeiana Univeristatis Helsingiensis) from 2002 to 2007.

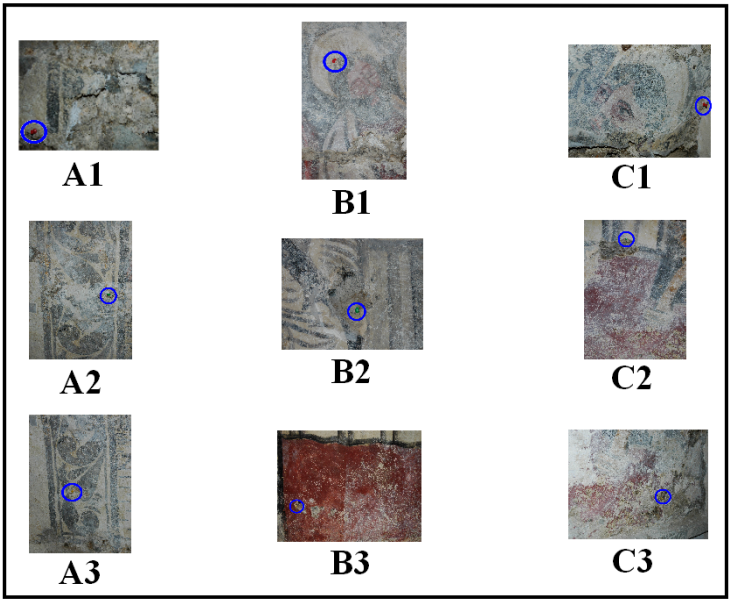

Fig. 1 Details of the location of the nine mortar fragments taken from the medieval wall painting from a church place in the Bay of Ciscay coast (north of Spain).

2.2 Analytical diagnosis protocol

The analytical diagnosis protocol is divided into four steps. First, several non-destructive spectroscopic and micro-destructive analytical techniques are used to perform the mineralogical characterization (molecular and elemental) of the bulk sample. The elemental analysis is conducted with a portable μ-ED-XRF

equipment provided with a molybdenum X-ray tube of 50 KeV and 800 mA intensity. The molecular analysis is done with a combination of Raman spectroscopy and FT-infrared spectroscopy [Diffuse Reflectance Infrared Transmission (DRIFT) mode]; Raman measurements were performed using a Renishaw RA100 portable Raman microprobe (785 nm diode laser) and a Renishaw inVia Raman microspectrometer mounted on a DMLM Leica microscope (785 and 514 lasers). Long-range objectives of 20x and 40x (for the first one) and 50x and 100x (for the second one) were used to analyse the samples without damage. The FTIR (DRIFT mode) analysis was performed using a SensIR (Smiths Detections) IlluminatIR FT-infrared spectrometer with nitrogen cooled MCT detector and mounted on an Olympus BX51 microscope. The interpretation of the spectra was carried out by comparison with the collected Infrared and Raman spectra of pure standard compounds in two databases [7, 8].

Then, a micro-destructive analysis is carried out to quantify the soluble anions and cations in the mortar samples (the soluble salts are extracted using an ultrasonic method developed as an alternative to the NORMAL method [9]) using a Dionex ICS 2500 suppressed ion chromatograph with a ED50 conductivity detector. The quantification of soluble salts is performed for both external and internal areas.

In a second step, chemometric tools are applied to treat the quantitative results. For this purpose, the Unscrambler ® 7.6 software is used. First, correlation analysis between the anions and cations (concentrations in milliequivalents Kg^{-1} units, balancing the charge of the different ions) is carried out, followed by Principal Component Analysis (PCA) to observe different groupings among data (according to sample type, external-internal areas, sample position, etc.).

In a third step, thermodynamic chemical simulation calculations are performed. These calculations are intended to explain the reactivity (the decaying mechanisms) between the original porous compounds and the environmental stressors (SO_x, NO_x, excretions of biological nature, etc.). Software packages such as MEDUSA and RUNSALT were used.

Finally in the fourth step, the analytical results (mineralogical and quantitative results) are compared with the predictions from the chemometric calculations and thermodynamic simulations, in an attempt to diagnose the possible decaying pathways to explain the experimentally observed decay compounds.

3 Results and discussion

3.1 Mortars from a medieval wall painting located in a Romanic church (13th century) in the North of Spain

The spectroscopic analysis of the unexposed areas of the mortars to the inner infiltration waters showed calcite ($CaCO_3$), quartz (SiO_2), and iron oxide (hematite type, Fe_2O_3) as the original components in the *intonaco* layer. These results were obtained with both Raman and infrared spectroscopy. Also carbon black (C) was detected and could be attributed to the soot promoted after the firing of the candles of the church. The elemental analysis performed with μ-x-Ray-fluorescence revealed K, Ca, Sr, Fe, and Mn as major components of the mortars; traces of Ba, Mg, Zn, and Cu also were identified in some samples. No additional elements that could be attributable to impacts of environmental stressors were detected.

The most surprising finding in the mortar fragments was the presence of a wide variety of nitrates [i.e., $Mg(NO_3)_2{\cdot}6H_2O$, KNO_3], with $Ca(NO_3)_2{\cdot}4H_2O$ or nitrocalcite and NH_4NO_3 the nitrate salts appearing most frequently (see Figure 3 A). The presence of both nitrates in a higher percentage could be explained if we consider the impact of infiltration waters, rich in ammonium nitrate [10], which react with calcite to produce the corresponding nitrocalcite and the other nitrate compounds.

Apart from the presence of nitrate salts, signs of biodeterioration were also identified. For example, traces of calcium oxalate dihydrate (weddellite) were identified with Raman spectroscopy (see Fig. 3B). These compounds are formed in the mortar as a consequence of a reaction between the oxalic acid excreted by the microorganisms with the calcium carbonate of the mortar.

The quantification of soluble cations and anions present in the *intonaco* and *arricio* layers revealed nitrate and chlorides as the highest concentration among anions. The highest values for nitrate (till 16.2 mg/g sample) in the *intonaco* layers belong to samples labelled with A and B. These samples are closer to the crack from which the infiltration water could enter. The concentrations in the *arriccio* layers were a little higher than those found in the *intonaco* ones, which means waters should came from outside the walls to the inner parts of the church.

The chemometric analysis on the concentrations of soluble salts gave a high correlation between nitrates and both ammonium (0.712 as the correlation coefficient) and calcium (0.810 as the correlation coefficient). Both correlations agree with the spectroscopic results, since calcium and ammonium nitrates were found by means of Raman spectroscopy.

After Correlation Analysis, Principal Component Analysis (PCA) was applied to the data from samples of *intonaco* and *arriccio* layers. With this mathematical procedure it is possible to obtain associations of samples according to specific variables. Taking into account the score representation of the PCA, samples A1,

A2, A3, B1, and B2 are highly clustered, and the rest of the samples are clustered apart. Moreover, the first group (A1-A2-A3-B1-B2) is closer to the nitrates if the scores are compared with the loadings representation (see Fig. 2). Quantitatively, these samples have higher nitrate salt concentrations.

These chemometric results (Correlation Analysis and PCA) agree with the spectroscopic and quantitative results, and they reveal that the samples taken near the crack (A1, A2, B1 and B2) have a greater abundance of salts (especially nitrates). Therefore, it appears that the crack is favouring the entrance of the dissolved salts.

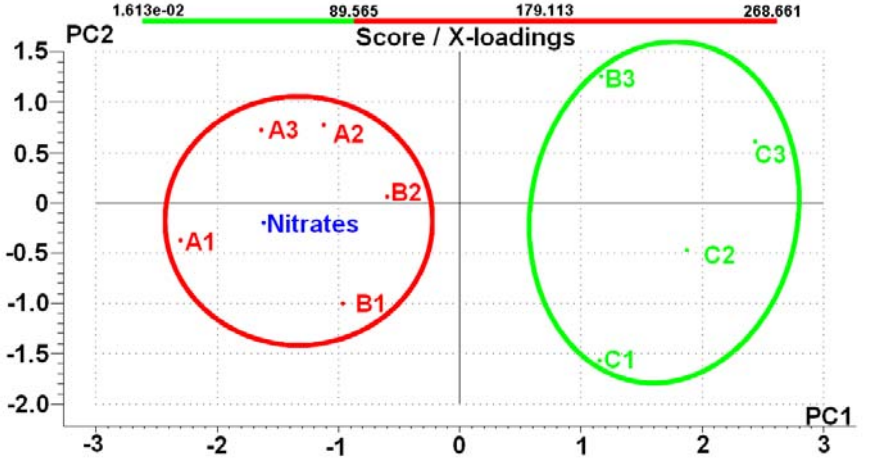

Fig. 2 PCA representation (scores and loadings) of the arriccio layers of medieval mortars (71% of the total variance explained).

3.2 Mortars from wall and wall paintings from the House of Marcus Lucretius (Pompeii, Italy)

The mortar samples were taken from areas with clear aesthetic damage such as cracks, fissures, etc., exposed to the open air for the 150 years since its first excavation. The typical infrared and Raman features of calcite and also small amounts of quartz were observed as the original composition of the mortars. A micro-spectroscopic FT-IR and Raman screening on the surface of the plaster showed a high variety of sulphate salts such as gypsum, mirabilite ($Na_2SO_4 \cdot 10H_2O$) [see Fig. 3 D], and epsomite ($MgSO_4 \cdot 7H_2O$). These sulphate salts were only detected in the first 40-50 μm with a decreasing profile when moving inwards, thus it was possible to rule out the intentional application of a layer of gypsum over the calcite mortar previous to the application of pigments. Therefore, the most logical explanation for the presence of sulphate salts is the

impact of atmospheric SO_2 (probably wet deposition of H_2SO_3 or H_2SO_4) on the carbonate mortar, giving as a result the correspondent sulphate. Apart from sulphate salts, nitrate traces also were detected [i.e., $Ca(NO_3)_2 \cdot 4H_2O$], thus a probable impact of atmospheric NO_x has taken place only on the surface of the mortars, as nitrates were not identified in the inner parts.

The soluble salt test (water extraction assisted by ultrasound energy) on these mortar samples was essential to attribute the sulphate and nitrate presence to environmental impacts. The quantitative analysis by ionic chromatography clearly agreed with the spectroscopic evidences, since the concentration of sulphates was the highest one (see Table 1). Also, important concentrations of nitrates were quantified (see Table 1). Chlorides and fluorides were present in the samples, but these last were almost always near the detection limit (see Table 1). Moreover, the highest value of soluble cations belongs to calcium (see Table 2)

Table 1 Concentrations of anions in milligrams/kilograms of extracted mortar sample

ANIONS (mg/g)	F^-	Cl^-	NO_3^-	$C_2O_4^{2-}$	SO_4^{2-}
W-1- *intonaco*	0.8 ± 0.1	3.2 ± 0.4	5.9 ± 0.5	*< D.L	107 ± 1.2
W-1- *arriccio*	0.1 ± 0.1	2.2 ± 0.3	2.8 ± 0.3	No peak	10 ± 0.3
W-2- *intonaco*	0.6 ± 0.1	4.7 ± 0.4	8.9 ± 0.4	*< D.L	178.4 ± 1.8
W-2- *arriccio*	0.3 ± 0.1	4.3 ± 0.3	6.2 ± 0.3	No peak	7.4 ± 0.6
W-2- *arriccio*-sand	0.3 ± 0.1	4.5 ± 0.7	7.5 ± 0.8	No peak	15.8 ± 0.4

Table 2 Concentrations of cations in milligrams/kilograms of extracted mortar sample

ANIONS (mg/g)	F^-	Cl^-	NO_3^-	$C_2O_4^{2-}$	SO_4^{2-}
W-1- *intonaco*	0.8 ± 0.1	3.2 ± 0.4	5.9 ± 0.5	*< D.L	107 ± 1.2
W-1- *arriccio*	0.1 ± 0.1	2.2 ± 0.3	2.8 ± 0.3	No peak	10 ± 0.3
W-2- *intonaco*	0.6 ± 0.1	4.7 ± 0.4	8.9 ± 0.4	*< D.L	178.4 ± 1.8
W-2- *arriccio*	0.3 ± 0.1	4.3 ± 0.3	6.2 ± 0.3	No peak	7.4 ± 0.6
W-2- *arriccio*-sand	0.3 ± 0.1	4.5 ± 0.7	7.5 ± 0.8	No peak	15.8 ± 0.4

According to these results, the soluble salts (mainly sulphates and nitrates) are distributed in the outer parts of the mortar. This evidence reinforced the hypothesis that the superficial impact of atmospheric acid aerosols (SO_2 and NO_x) is the source of the decaying in the calcite.

The Correlation Analysis on the quantitative data gave the highest correlation coefficient between calcium and sulphates (0.949) among all the ions considered. This high correlation means that both ions must necessarily came from the same soluble compound, i.e. gypsum. Moreover, the application of Principal Component Analysis (PCA) showed a clustering of the *intonaco* samples (outer area) in the Scores representation; these samples are close to sulphate and calcium, which are also near in the Loading representation of the PCA (64% of the total

variance was explained). Once again, the chemometric results (Correlation and PCA analysis) agreed with the spectroscopic data.

Apart from the impact of atmospheric pollutants, clear evidence of biodeterioration was observed in the mortar samples. As in the medieval mortars from the North of Spain, traces of calcium oxalate dihydrate (weddellite) were identified with Raman spectroscopy. Moreover, brown-orange patina was identified in some samples and analyzed. Spectroscopic analysis revealed that they belonged to deposits of carotenoids. Given the Raman results, it could be concluded that the carotenoids present are those composed of 9 C=C bonds linearly conjugated. Considering the Raman bands at 1521, 1180, 1156, 1004, and 963 cm^{-1}, it could be attributable to zeaxanthin carotenoid [11], but other carotenoids such as β-carotene or lutein cannot be ruled out (see Fig. 3C). The presence of carotenoids in the mortars could be attributable to excretion products of some microorganisms such as lichens, cyanobacteria, moss, etc. These biodeterioration signs should be studied further, thus new sampling and additional analysis will be carried out, focused on the investigation of the biodeterioration of Pompeian mortars from walls and wall paintings in the House of Marcus Lucretius.

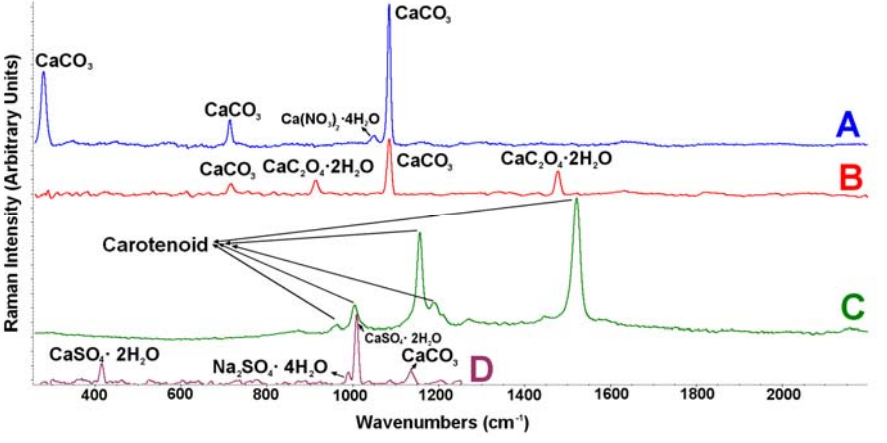

Fig. 3 Raman spectra of *intonaco* of medieval mortars (A, B) and brown-orange patina (C) and *intonaco* (D) of Pompeian mortars.

4 Conclusions

The proposed analytical diagnosis protocol was used to analyse two kinds of mortars exposed to different environments: a rural non-polluted area with infiltration water processes (medieval mortars) and a moderately polluted

atmosphere impacting mortars for roughly 150 years (Pompeian mortars). In both cases the analytical protocol was successfully applied, since not only the original and decaying compounds were identified, but it was also possible to identify the probable causes of the decay and the most probable decaying mechanisms:

The chemical simulations gave this reaction

$$CaCO_3 + 2NH_4NO_3 + 4H_2O \rightarrow Ca(NO_3)_2 \cdot 4H_2O + HCO_3^- + NH_4^+ + NH_3 \quad (1)$$

as the most probable explanation of the decay in the Mediaeval wall painting. However, the reactivity for the Pompeian mortars can be expressed by:

$$SO_2 \rightarrow SO_3 \text{ [Oxidation]} \rightarrow H_2SO_4 \text{ [Inclusion in the rain water]} \quad (2)$$
$$NO \rightarrow N_2O_5 \text{ [Oxidation]} \rightarrow HNO_3 \text{ [Inclusion in the rain water]} \quad (3)$$
$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2\,H_2O + CO_2 \quad (4)$$
$$CaCO_3 + 2HNO_3 + 4H_2O \rightarrow Ca(NO_3)_2.4H_2O + CO_2 + H_2O \quad (5)$$

It must be taken into account that Pompeii is near Naples, a city with a middle-high polluted atmosphere due to the traffic and the industrial harbour.

Both case studies illustrate how it is possible to use this procedure to identify decay processes promoted by the effect of different environmental stressors like infiltration waters, atmospheric acid pollutants, and even biodeterioration.

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II.14

Problems in the Assessment of the Stress-Strain Relationship of Masonry

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Abstract In restoration or repair of old buildings the correct estimation of the stress-strain-relationship of the existing structure is an important task. Masonry stiffness is crucial for the load bearing behaviour of a structure. It is common practise to evaluate the masonry stiffness from the compressive strength in lack of detailed investigations. This paper illustrates the danger of this approach in two case studies. The first example is a stone bridge upon the main. The thickness of the mortar joints in this construction allowed sampling of mortars suitable for direct testing of the stress-strain-relationship under uniaxial compression. Thus it was possible to calculate the masonry stiffness from the measured elastic modulus of stone and mortar. It became evident, that a first rough estimation according to the building standard would not have been safe. In a second case study dealing with masonry pillars it is shown that the quality of mortar samples is influenced by the situation of the specimen in the section.

1 Introduction

Refurbishment often implies the occurrence of a change of load. Constructions built with slim pillars and old stone bridges subjected to dynamic loads are very susceptible to modifications of this kind. Stiffer parts of the building attract stresses and therefore underestimation of stiffness can be harmful. Medieval or baroque masonry with small units of different stone is often too heterogeneous for in-situ tests by flat jacks or by sonic tests [1]. The elastic modulus is then evaluated from the moduli of stone and mortar prisms. The modulus of mortar can be derived either from the ultrasonic pulse velocity or from cube strength if suitable mortar prisms for direct determination of stress-strain-curves cannot be obtained in sufficient number. Another reliable method for the indirect testing of masonry strength is the method of bed joint drill cores. The ratio of the splitting tensile strength of bed joint drill cores and homogeneous stone cores is

approximately equal to the ratio of stone crushing strength and masonry strength [2]. Thus the influence of the mortar joint is taken into account.

Combining these methods the elastic modulus of historic masonry can be assessed with sufficient accuracy for most cases of restoration work, provided that the correlations between the investigated parameters are clearly understood.

2 Case study: stone bridge

The remaining piers and vaults of the medieval stone bridge upon the Main at Ochsenfurth (Southern Germany) date from three different building periods, the Middle Ages, Baroque and 19th century. The arches span is between 13 and 16 meters. Although the parts in the waterway are missing today, this bridge preserves important information for building history and therefore is protected as a historic monument. Plans to reuse the old structure and rebuild a carriageway raised the question of their strength and deformation properties. Due to the heterogeneity of this masonry and the multitude of stone varieties used, investigations by non destructive testing methods appeared not to be promising [1]. It was decided to refer to mechanical tests on stone and mortar. These investigations were carried out at the Institute of load bearing structures at the Karlsruhe Institute of Technology (KIT).

2.1 Sampling

Samples were taken as drill cores with diameters of 93 millimetres. The relatively large size was chosen in order to gain bed joint drill cores.

The sampling locations were chosen after diligent visual examination from places which from their exposure were most suspected of being damaged [3]. Reference samples from "healthy" masonry served to understand and calibrate the results.

The oldest parts of the bridge, three vaults on the southern side of the river, date back to the 12th and 15th centuries. Various sizes of roughly carved or chopped stone (average 30x25x50cm³) are still assembled in a good and regular rubble bond. The mortar and limestone has suffered from freeze/thaw and salt degradation due to a dense cement rendering. Endoscope investigation of boreholes however proved that the bed joints were thoroughly filled and that the mortar in the interior of the piers was well preserved. The drill cores contained large pieces of mortar with a good bond to the limestone and surprising strength. The thickness of the mortar joints permitted sampling of mortar for direct mechanical tests.

On the northern side of the river two vaults from the baroque period and three arches from the 19th century are preserved (Fig. 1). The baroque arches were built with small rubble material (25x15x30 cm³) and were in a poor condition. Similar

to the medieval vaults, mortar was severely damaged at the surface and large parts of the vault had been repaired with brick masonry fillings. The drill cores contained pieces of mortar that were extremely hard and very irregularly shaped. Most of these samples could not be cut into cubes or prisms for mechanical tests. Strength and modulus values were therefore assessed using ultrasonic pulse velocity (Fig. 2).

Fig. 1 Northern vaults of the bridge

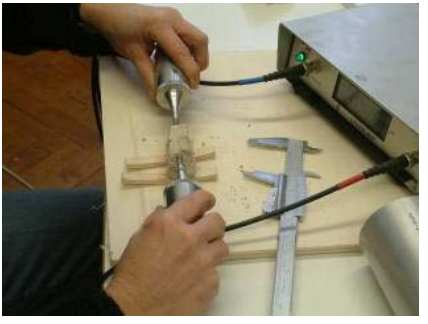

Fig. 2 P-wave velocity measurement on mortar

The vaults erected in the 19th century consist of massive limestone ashlars (30x48x60-80 cm³) with thin bed joints. Some of the cores presented a very hard mortar up to a depth of 5-10 centimetres while the material behind was completely frozen (Fig. 3). The loose mortar material was washed out during drilling. Mortar deterioration here was induced by a dense repointing mortar (20th century repair) which retained water in the inner section. Cutting mortar prisms or cubes was not possible in this case but the regular shape of the ashlars allowed the assessment of masonry strength by the bed joint drill core method (Fig.4).

The amount of mortar, its state of conservation and the composition varied not only with the construction phase but also within the same section. A repair mortar that could chemically and mechanically match with the original mortar inside the pillars was needed; as was the identification of the mechanical properties of the existing mortar in order to determine its elasticity.

Fig. 3 Drill core with various mortar types

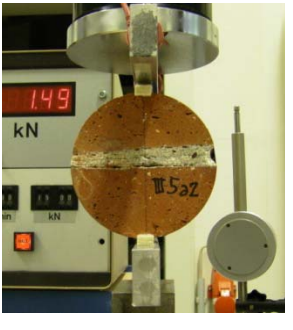

Fig. 4 Bed joint drill core (brick repair)

2.2 Mechanical tests

The mortars from the drill cores were cut into regular cubes and prisms (thickness between 3cm and 5cm) whenever possible. Although the mortars were of good quality, many of the specimens cracked during cutting. A total of 9 prisms and 30 cubes were obtained. After drying, the prisms were tested under uniaxial compression. Load was applied and displacement controlled with a speed of 0.1 mm/min (fig. 5). Fig. 6 shows the stress strain curves of each kind of mortar.

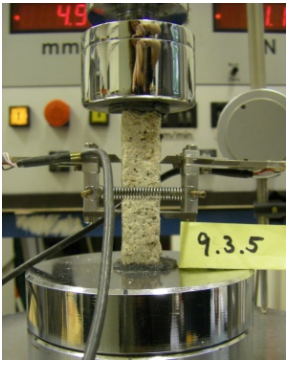

Fig. 5 Displacement transducers at mid height of the prism on opposite faces; Sample size approximately 20 to 20 to 80 mm³.

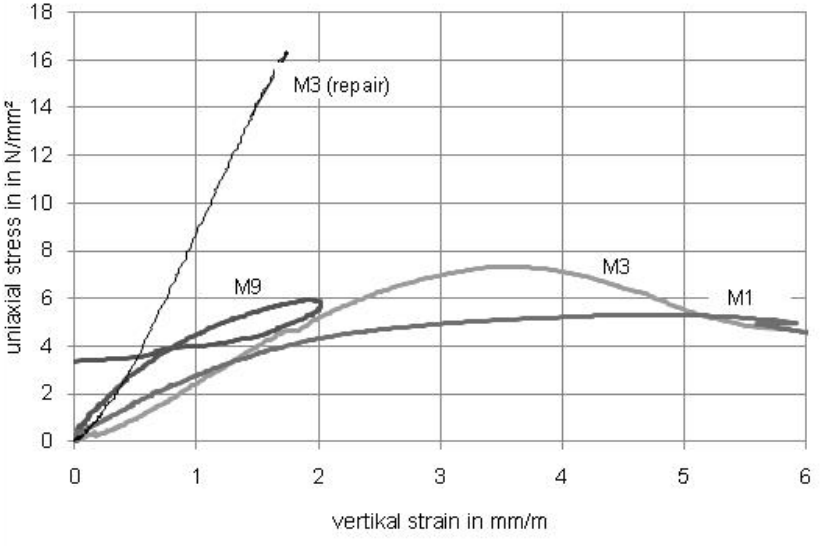

Fig. 6 Stress-strain-relationship of medieval (M1, M3) and 19th century mortars (M9) compared to a pure cement 20th century repair mortar.

Typical for the old lime mortars, in M1 and M3, is the concave shape or the rising branch and a long yielding plateau after reaching the crushing strength. Compared to line M3 (repair), which was a brittle cement repair mortar, the old lime mortars are significantly more ductile. In spite of the low modulus, they present an astonishing uniaxial compressive strength of more than 5 N/mm².

The 19th century mortars (example M9) equally showed a concave rise of strain, but once they reached the crushing strength there was complete rupture.

2.3 Ultrasonic tests

Since no direct measurement was possible on the mortar from the baroque masonry, the modulus was obtained by ultrasonic tests. From the ultrasonic pulse velocity **v** the dynamic modulus, or P-wave modulus, is calculated with the density ρ as

$$E_{dyn} = \rho . v^2 \quad (1)$$

Table 1 compares moduli obtained by direct testing to those calculated from the pulse velocity. For concrete or cement mortar the dynamic modulus is about 30% higher than the static modulus. Here the difference seems to be larger; 50% were measured in this series but the coefficient of variation is too important to permit a generalisation; however it was shown qualitatively that the baroque mortars behave similar to those of the older part of this building (Table 2). Chemical and mineralogical investigations confirmed that mortars of both building periods were very similar.

Table 1 Relation between dynamic and static modulus E_{dyn} / E_{stat}

sample	E_{dyn} [N/mm²]	E_{stat} [N/mm²]	E_{dyn}/E_{stat} [N/mm²]
M1.1.2	4640	2443	1.90
M3.2.7	6698	3225	2.08
M3.5.1	9924	8021	1.24
M9.3.3	4694	3548	1.32
M9.3.4	5705	2260	2.52
M9.3.5	6577	5768	1.14
M9.3.6	7492	5785	1.30
M9.3.7	8026	6819	1.18
M11.12	5678	6819	0.83
		Average	1.50
		Standard deviation	0.51
		Coefficient of variation [%]	34

Table 2 Evaluation of E_{dyn} (P-wave modulus) for the main building periods

sample			building period		
	n	E_{dyn}^{1} [N/mm²]	n^1	n^2	E_{dyn}^{1} [N/mm²]
1.1	8	4403		middle ages	
2	2	5354			
3.2	6	5816	16	3	5052
3.5	3	10204		repair mortar	
9.2	5	4960		19th century	
9.3	7	6358			
11.1	8	7519	20	3	6473
12.3	7	5772		baroque	
12.1*	2	2883	9	2	5130
n^1	number of samples				
n^2	number of sampling locations				
E_{dyn}^{1}	average value				

Ultrasonic tests could also be adopted to assess the compressive strength if a reliable correlation between the dynamic modulus and strength was known. In Fig. 7 the elastic modulus is compared to the compressive strength measured in direct compression tests on cubes (edge length between 15 an 35 mm) of medieval mortars and on samples from the 19th century masonry. This is plotted against the empirical relation that was established for new masonry mortars by Schubert [7].

$$E_m = 2100.f_m^{0.7} \tag{2}$$

It becomes evident, that the behaviour of old mortar cannot be determined from property relations found in modern material without adaption. A similar problem has been observed in trying to establish shape factors for compression tests on weak mortars with different lime binders [5]. Test methods need individual calibration.

After investigation of the stone properties and the geometric parameters the masonry strength was calculated using the following: the German national standard (DIN 1053) method of bed joint drill cores, and through analytical models [6]. While allowable stresses according to the design standard would have been between 1.7 N/mm² for the weaker masonry bond and 2.3 N/mm³ for the ashlar masonry, stresses from of 3.1 to 3.9 N/mm² could be allowed according to the results of the analytical approach. Bed joint drill cores proved that these values are sufficiently safe.

In masonry design the elastic modulus E_{ma} is evaluated from the design strength f_d as:

$$E_{ma} = 3500.f_d \tag{3}$$

For the older parts of the bridge this would have given a value of 6000 N/mm² and 8000 N/mm² for the ashlar masonry. It is clear that the 19th century masonry built with large blocks of limestone must be more rigid; however the modulus of the older parts was underestimated by this approach, in spite of the important amount of mortar in these piers. Calculated from the material properties using the elastic models described by Anzani et al. [8], values of 15000 N/mm² for the rubble masonry and 23000 N/mm² for the ashlar bond were obtained.

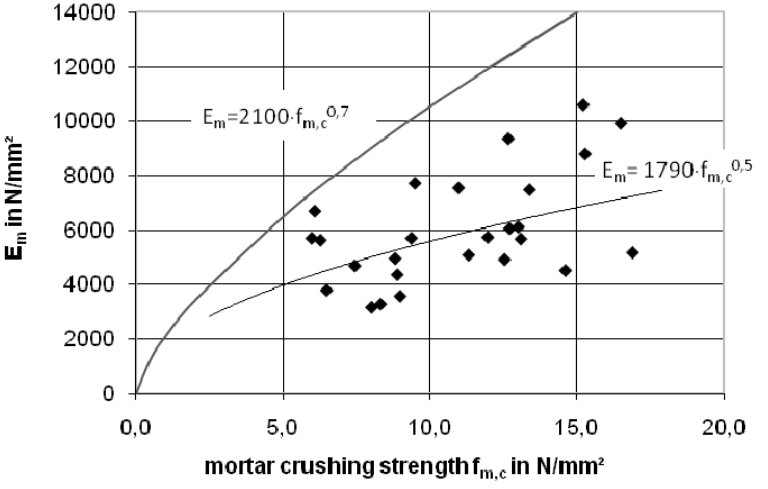

Fig. 7 Relationship of mortar strength and elastic modulus

3 Case study: baroque masonry pillars

In refurbishing the Historic Museum in Frankfurt the architects intend to increase the load on the pillars of a three storey baroque facade (Fig. 8). A first rough estimation, according to the German masonry standard, indicated that already the existing load exceeded the allowable stresses at least twice. Nevertheless the pillars showed neither cracks nor crushed joints nor any other signs of overloading. A more precise analysis based on material tests and the recalculation of masonry strength using more accurate material models indicated that the higher loads could be allowed for under the condition that the slots and voids discovered in the piers were repaired to allow the section to act as one

material. It was therefore vital that the repair masonry must have the identical deformation properties as the original masonry.

Investigations of the material properties here served to assess masonry strength and stiffness in as accurate a manner as possible and to determine the stone and mortar properties necessary for appropriate materials for repair. Initially the thickness of the joints seemed large enough to allow the removal of mortar prisms with a hammer and chisel. It was then observed that the mortar samples close to the surface showed poor cohesion whereas the bed joints in the inner section showed no decay (Fig. 9). Inside of the building this could not be explained by the effects of weathering. On mortar cubes from the inner section of the pillars an average compressive strength of 1.85 N/mm² was measured. The strength, as determined by ultrasonic tests, corresponded very well with this result (1.90 N/mm²). Mineralogical analyses confirmed that the mortars were pure lime mortars without hydraulic additives. From earlier research it is known that these mortars plastify at the outer rims of a masonry section at a rather low stress level, up to a depth of some centimetres [4]. The sections of the masonry pillars in this case are large in relation to the plastification zone. Masonry stiffness therefore is not influenced but mortar sampling here needs drill cores.

Fig. 8 Baroque masonry pillars

Fig. 9 Mortar samples–inner section

The stone and masonry bond differed throughout the different pillars; tests on stone and mortar lead to an estimation of the masonry strength between 1.1 and 2.3 N/mm², depending on the bond. The elastic modulus calculated from stone and mortar properties and the geometric relations again exceeded the first estimations with values between 8000 and 9500 N/mm² being determined.

4 Conclusions

When assessing the elastic behaviour of old lime mortar masonry the correlations determined empirically on modern material should be handled with care.

- Strength of existing masonry is usually underestimated for reasons of safety. Evaluating the elastic modulus from this value leads to an underestimation of stiffness.
- The better the properties of stone and mortar investigated, the more accurate the assessment of the load bearing behaviour of old masonry is. Combining direct tests on stone and mortar prisms or on bed joint drill cores allow the calibration of ultrasonic measurements. Masonry properties can then be calculated from analytical models.
- Stress distribution in masonry with very strong stone units and weak joints is not uniform. The quality of mortar samples is influenced by the situation of the specimen in the section. This observation is not to be neglected when choosing representative sampling points.
- In calculating the modulus of thin masonry sections from the elastic properties of stone and mortar under uniaxial compression, the plastification of mortar has to be taken into account.
- Due to weathering, salts, inappropriate repointing or dense renderings bed joint mortars frequently show signs of deterioration. The depth of deterioration influences the masonry's strength and elastic properties. Careful visual investigations in some cases are even more important for a correct assessment of the mechanical behaviour of masonry than sophisticated material models.

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II.15

Application of ^{1}H NMR in the Hydration Monitoring of Lime-Pozzolan Mortars

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Abstract The micro-structural evolution of a lime - pozzolan system, during hydration, was studied by ^{1}H Nuclear Magnetic Resonance (NMR). The hydration process was monitored for a period of one year by ^{1}H NMR spin-lattice relaxation measurements, performed in a portable magnet. The development of the hydration was also examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), mercury intrusion porosimetry (MIP), infrared spectroscopy (FT-IR) and thermal analysis (DTA/TG) and compared with the NMR results. The results indicated that ^{1}H NMR provides valuable information on the hydration process of lime-pozzolan mortars in a non-invasive way, as it was possible to monitor the development of the hydration phases through the resulted microstructure, in real-time.

1 Introduction

Lime-pozzolan mortars face, nowadays, an increased preference in the restoration of architectural monuments and also in the construction of buildings. This is mainly due to their enhanced chemical, physical and structural/ mechanical compatibility with both archaeological and historical building materials (stones, bricks and mortars). On the contrary, the application of cement mixtures as restoration materials have proved to be problematic, due to disadvantages related to incompatibility matters, high salt content, limited elasticity etc. [1]. Moreover, lime-pozzolan mortars are more environmentally friendly materials, compared to

cement mortars, when issues such as reduced energy consumption [2, 3], reduced CO_2 and particulate matter emissions are considered [4].

The study of the hydration process of lime - pozzolan mortars, through the monitoring of the C-S-H and C-A-H formation and the consequent changes of microstructure [5], is essential in order to evaluate the performance characteristics of the mortar, in terms of physical and mechanical properties, which are also interrelated with the longevity of the mortar.

In this context, the aim of this work was to study the micro-structural evolution of lime - pozzolan systems, during hydration, by ^{1}H Nuclear Magnetic Resonance (NMR), using NMR spin –lattice relaxation measurements [6-10]. ^{1}H NMR is a fast, powerful experimental technique that can be used to monitor in a non-invasive way the micro-structural evolution of the paste continuously and in real time, providing information on both the development of the hydration phases and the resulted microstructure changes of the binary paste. Contrary to conventional methods, such as XRD, DTA/TG, FT-IR and MIP, NMR does not require a drying process before the analysis. The hydration process is monitored by measuring the proton spin-lattice relaxation time T_1, where the relationship between the T_1 and the pore size is based on the fast-exchange relaxation theory [11].

In principle, the T_1 of a fluid (typically water) confined within a pore can be used to determine the pore diameter (actually, the ratio of pore volume to surface area). The presence of the pore wall increases the relaxation rate and thus, for a given material, T_1 will decrease as the pore size decreases [7, 12]. As a consequence, in complex porous materials such as lime-pozzolan systems, with pore sizes extending from nanometres to micrometers, T_1 spreads over a wide distribution of relaxation times, which directly reflects the complicated pore microstructure and the interaction strength between the adsorbed water molecules and the pore surface [13]. Specifically, during the mortar hydration the nuclear magnetization in a saturation recovery experiment can be expressed as [13]:

$$R(t) = \frac{M_0 - M(t)}{M_0} = \int_0^\infty g(T_1)\exp(-t/T_1)dT_1 \quad (1)$$

where, $R(t)$ is the proton magnetization recovery function, M_0 is the magnitude of the magnetization at equilibrium, $M(t)$ is the observed magnetization as a function of time t and $g(T_1)$ is the spin-lattice relaxation time T_1 distribution function, which can be resolved by means of an inverse Laplace transform, [14] unveiling important information about the porous microstructure in the hardened material.

In this work, we present a detailed study of ^{1}H NMR T_1 distribution profiles, attributed to mobile water molecules in a lime-pozzolan paste, as a function of hydration time, by excluding the undesirable NMR signal components (spin grouping method) [15] and keeping only those corresponding to pore (free) water. The T_1 distribution profiles clearly demonstrated the evolution of porosity and

particularly the formation of two distinct pore reservoirs. In addition, the hydration process was also examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), infrared spectroscopy (FT-IR), thermal analysis (DTA/TG) and mercury intrusion porosimetry (MIP).

2 Experimental

The hydration process was monitored for a period of one year, (under standard humidity conditions), on a lime - pozzolan mixture. The mixture consisted of equal parts of lime powder ($Ca(OH)_2$) (Merck, Germany) and a natural pozzolan powder of volcanic origin, a commercial, finely ground product with particle size below 75 μm, namely Lava Antica (LA), supplied by AGET, Greece.

The water to binder ratio was set to 0.7 and satisfied the requirement for optimum flow characteristics [16], while the mixture presented a flow value of 190 mm. The paste was prepared according to the procedure described in the EN 196-1 [17] standard. After mixing, the sample was sealed into NMR glass tube using Parafilm® membrane to avoid moisture loss and drying and then, immediately placed into the spectrometer. The sample dimensions were 9 mm in diameter and 30 mm in height. An additional amount of the above mixture was moulded in prismatic moulds, with dimension of 20 × 20 × 80 mm, and then placed in a curing chamber for setting, at RH = 95 ± 3% and T = 20 ± 2°C.

^{1}H NMR spin-lattice T_1 relaxation experiments were conducted using a circular Halbach array magnet, capable for low-field NMR measurements [18]. The field at the magnet centre was 0.29 T, corresponding to a proton resonance frequency of 12.1718 MHz, and a magnetic field gradient (G) equal to 1.03 T m^{-1}. The spin-lattice relaxation time, T_1 was measured using a standard saturation recovery technique [$(\pi/2)$ - t - $(\pi/2)$ - τ - (π)] with interpulse delay, t, ranging from 100 ms to 6 s. The signal was detected by the common Hahn echo pulse sequence. The experiment was performed at room temperature and the hydration process was monitored on the same sample for up to 12 months. The time intervals between successive experiments ranging were from minutes to several hours, without requirement for prior hydration stop.

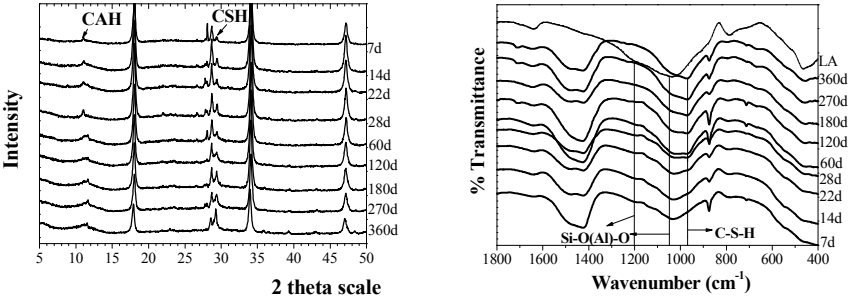
The setting process of the paste was interrupted at preset time periods, of 7, 21, 28, 60, 120, 180, 270 and 360 days (except MIP measurements that were carried out on specimens cured for 7, 28 and 60 days) according to a hydration stop procedure, which involved the immersion of the sample in two stop-bath solutions (acetone and diethyl-ether) for 60 min each, and then drying at 70°C for 22 h.

The setting mechanism was studied then, using the following analytical setup: X-ray diffraction analysis was performed in powder samples with a Siemens D-500 diffractometer (40KV/35mA). The spectra were collected between 5° and 60° 2θ scale, with a step of 0.03° / 5s. SEM examination was carried out in fractured surfaces, using a FEI Quanta Inspect scanning electron microscope. DTA/TG was

operated with a Perkin-Elmer Pyris 3000 Thermal Analyser; in static air atmosphere up to 1000°C at a rate of 10°C / min. FT-IR analysis was operated in a Bruker, Equinox 55/S spectrometer. Transmittance spectra were collected in the region of 4,000 to 400 cm^{-1}, with 4 cm^{-1} resolution. The samples were mixed with KBr and scanned 30 times, in order to reduce the signal to noise ratio. MIP measurements were recorded using a Quantachrome Autoscan 60 porosimeter, in the range of 2 – 4.000 nm.

3 Results and discussion

Although the pozzolan presented an amorphous matrix, some faint peaks of kaolinite, albite, anorthite and quartz were identified in diffraction patterns. During hydration, the pozzolan particles are corroded, resulting in the leaching of sodium and potassium alkalis in the pore solution. Consequently, Ca^{2+} ions take their place on the pozzolan surface and react with the free OH-, Si-O- and Al-O- radicals. This dissolution-precipitation mechanism inside pores, leads to the formation of calcium-aluminum and calcium-silicon hydrates (C-A-H, C-S-H), depicted on the XRD patterns (Fig. 1(a)). Moreover, FT-IR spectra (Fig. 1(b)) and DTA-TG analysis (Fig. 2(a)) provide a qualitative and quantitative respectively identification of the hydrates formation.

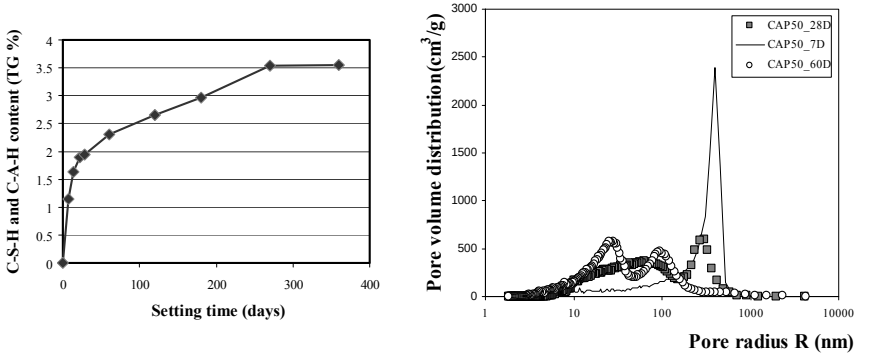


(a) (b)

Fig. 1 (a)X-Ray diffraction patterns exhibit the formation of C-A-H and C-S-H phases as hydration proceeds; (b) FT-IR spectra of the lime-pozzolan mortar at different hydration ages and of the raw pozzolan (LA)

On the FT-IR spectra (Fig. 1(b)) it is evident that the transmittance peak at 970 cm^{-1}, attributed to C-S-H, makes its appearance around the 28th day of hydration and increases as the hydration proceeds. The peaks at 1185-1200 and 1022-1140 cm^{-1} attributed to amorphous Si-O-(Al)-O polymerized bonds are present on both the spectra of the pozzolan and the paste, and decrease as the hydration proceeds [19, 20]. The thermogravimetric analysis, has detected the increasing formation of

C-A-H and C-S-H content over the hydration process, by measuring the weight loss in the temperature range of about 90 - 260°C [21].



(a) (b)

Fig. 2 (a) The C-S-H and C-A-H content vs. hydration time, measured by thermal analysis; (b) MIP pore distributions vs. pore radius at 7, 28 and 60 days of hydration

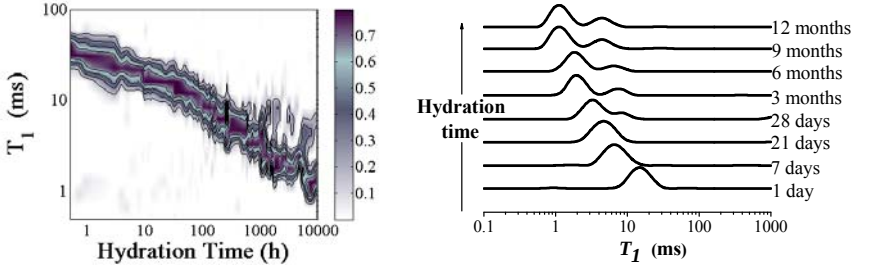


Fig. 3 T_1 contour plot (left) and T_1 distribution profiles (right) vs. hydration time

On the T_1 contour plot and T_1 distribution profiles (Fig. 3), resulted from the ^{1}H NMR relaxometry, we can see that during the early hours of hydration, the T_1 is slightly decreasing, which can be attributed to the initiation of the hydration process and the formation of small amounts of hydrated phases. At this stage, all protons magnetization relaxes with common T_1, due to the fast exchange between water spins in the various environments [22].

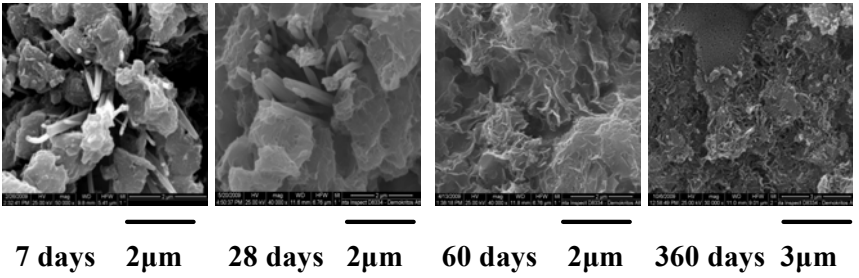


Fig. 4 SEM photomicrographs exhibit the development of hydrated phases: C-A-H and C-S-H are depicted in the form of needle – like fibres (7 days) and as a hydrous amorphous gel respectively; C-S-H gel is appearing denser as the setting time increases, resulting in the filling of micro and macro pores of the paste (360 days)

Up to 28 days of hydration, when the initial hydration products are formed (Fig. 4, 7 and 28 days), the T_1 relaxometry data are characterized by a single relaxation time. The hydrates content formed up to this period (28th day) corresponds to the 50% of the total hydrates content formed over a year, according to DTA-TG plot (Fig. 2(a)). After a hydration period of 28 days the T_1 relaxation mechanism deviates from a single exponential function and a multi-exponential behaviour is observed, which is resolved by means of an inverse Laplace transform, using a modified CONTIN algorithm [23]. In this period, there is a massive growth of the hydrated phases (Fig. 4, 28 and 60 days), and the formation of a second pore population with smaller pore radius, around 50 nm, as detected at 28 days by MIP (Fig. 2(b)). At this point the T_1 distribution profiles (Fig. 3) splits in two components similarly to MIP plots (Fig. 2(b)), which remain almost invariant with hydration time. The rise of the second peak, corresponding to the smaller pores, is indicative of the microstructure evolution of the paste as the setting time increases. The further reduction of T_1 can be explained by the growing dense network of amorphous hydrated phases that fill the majority of pore spaces (Fig. 4, 60 days). The two peaks clearly demonstrate the presence of two distinct pore reservoirs in the paste: one, with short $T_1 \approx 4.5$ ms attributed to small pore sizes and assigned to small capillary pores; and a second, with longer $T_1 \approx 11$ ms, corresponding to bigger pores and assigned to medium capillary pores in the paste (Fig. 4, 360 days).

4 Conclusions

The hydration process of lime-pozzolan paste was successfully monitored by measuring the proton spin-lattice relaxation time T_1 using a portable magnet. The method proved to be a sensitive tool to probe the development of capillary pores, formed during hydration of lime-pozzolan mixtures. It was therefore possible to

asses in real time the resulted microstructure changes in a consistent way and, to provide information that was in accordance with the results of the XRD, FT-IR, SEM, DTA-TG and MIP techniques

Specifically, T_1 distribution profiles clearly demonstrated the evolution of porosity and particularly the formation of two distinct pore reservoirs assigned to small and medium capillary pores.

The use of a portable magnet shows the great potential of ^{1}H NMR for studying both at the laboratory and in field the hydration process of lime-pozzolan mortars. The ability of the method to monitor continuously the setting process and the evolution of the microstructure provides a promising tool for people involved in conservation of architectural heritage to accurately evaluate in field the durability and service life of lime-pozzolan mortars.

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II.16

Desalination of Concrete Sculptures on the Battle of the Nations

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Abstract The Monument to the Battle of the Nations (Völkerschlachtdenkmal) in Leipzig is in large parts made out of concrete. The inner dome roof is decorated with 342 cavalier sculptures of tamped concrete. The reliefs show severe damages as a result of the presence of moisture and salts. Binder elution and the corrosion of the armour owing to concrete carbonation are further damages. X-ray diffraction characterisation of efflorescences shows mainly sodium sulphate with high damaging potential. Surface deposits were analysed as calcite ($CaCO_3$). The composition of historical concrete samples, determined by chemical analysis show a binder-to-aggregate relation of 1:4 wt-%. Microscopy investigations of polished thin sections show a high pore volume. For the conservation of the precious historical tamped concrete cavalier sculptures, the soluble salts were reduced by a threefold application of a bentonite-cellulose poultice. The desalination actions were examined by chemical concrete analyses showing a clearly detectable effective desalination of near surface concrete parts.

1 Introduction

The Monument to the Battle of the Nations (Völkerschlachtdenkmal) in Leipzig is a highly renowned monument in Germany. It is dedicated to the remembrance of the Battle of the Nations which took place near Leipzig in 1813. The largest European monument was built for about 15 years and was completed in 1913 for the 100th anniversary of the battle. Extensive parts of the monument are made of concrete. The concrete was firstly casted and later tamped in layers [1]. The facade is made of the Beucha Pyroxene-Granite-Porphyry once referred to the German term “Mikrogranit” near Leipzig. The inner dome roof is decorated

with 342 cavalier sculptures made of tamped concrete. The cavalier sculptures are arranged in 11 arrays on top of each other. They symbolise the homecoming of the victorious warriors. The cavalier sculptures are supported by iron reinforced gypsum moulds mounted with the dome. The monument's place was once Napoleon's command post during the battle. The gravel sand came initially from the foundation pit and than from a gravel pit 2 kilometres away. A total of 120,000 cubic metres of concrete and 12,500 cubic metres of natural stone were used. Up to 20,000 tonnes of cement and 190,000 t gravel sand were applied for the tamped concrete. The cement was made in the "Sächsisch-Böhmischen Portlandzement-fabrik" in Dresden. The mixing ratio for the tamped concrete was 1:9 of spatial equivalents [1]. The cavalier sculptures relief shows severe damages due to moisture and salts [2]. Salts have been soluted by soaking water via constructional joints and cracks. This led to a re-deposition weakening the outer structure and enhancing surface material losses. Binder elution and the partial corrosion of the armour due to concrete carbonation are further damages.

Currently the whole building is being restored. The construction work is supposed to be finished by the 200th anniversary of the Battle of the Nations in 2013. Desalination by poultice application is often used for stone and masonry materials [3, 4, 5]. For the conservation of the precious historical tamped concrete cavalier sculptures, the soluble salts were reduced by a threefold bentonite - cellulose poultice application [6]. The desalination actions were monitored by chemical analyses of the concrete before and after every salt extraction. The ongoing procedures and results of salt extraction treatments are covered by reports [7, 8]. Surface deposits and efflorescences were analysed. The composition and structure of historical concrete samples were determined.

2 Experimental

The composition of historical concrete samples was determined by chemical analysis and X-ray diffraction (Siemens D5000). For structural investigations polished thin-sections were prepared and analysed by microscopy [9] with an Olympus BH-2 microscope. Surface deposits and efflorescences were analysed by X-ray diffraction and chemical analysis. The desalination actions were also controlled by chemical analyses of the concrete before and after every salt extraction.

2.1 Chemical salt analysis

Drill samples (powder) were taken by a spiral driller (diameter = 12 millimetres) from depths of 0.0-1.0, 1.0-2.5 and 2.5-5.0 centimetres. Eluates were prepared from the drilled powder samples for qualitative and quantitative salt analyses. Out of the eluates soluble components, electrical conductivity (WTW

Cond 315i/Set) and pH- values (Behrotest pH81) were determined. The qualitative and quantitative ion-determinations of K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and NO_3^- were made photometrically (HACH DR/2000). Sodium (Na^+) was determined by the HACH Sension 2-methode.

2.2 Chemical concrete analysis

The concrete samples were taken from a separated foot of the cavalier sculpture 12 in row 4. Fig. 1 shows the tamped concrete foot. Investigations with phenolphthalein show a complete carbonated concrete-texture.
To describe the binder-aggregate-ratio concrete analyses were performed by acid dissolution and binder separation from aggregates [10]**.** The chemical composition of the acid-soluble binder was determined for soluble silica. Wet chemical analyses were performed on the acid filtrate for the characterisation of soluble Me_2O_3, CaO, MgO and SO_3-ions. The carbonate amount was determined volumemetrically.

Fig. 1 Separated foot of the cavalier sculpture 12 in row 4 (VD_M_4_12)

3 Results

3.1 Results of salt analysis

The X-ray characterisation of efflorescences shows mainly sodium sulphate Thenardite (Na_2SO_4). Preliminary investigations of the cavalier relief concrete-texture served as a standard for any salt reduction (desalination) efforts. After the

application of the first, second and partly the third salt depletion (desalination) cycle, drilled powder samples were investigated. Table 1 compares the results of these salt analyses which were taken out of the concrete-texture from sample point A from depths of 0.0-1.0, 1.0-2.5 and 2.5-5.0 centimetres.

Table 1 Results of the chemical salt analyses in wt-%

Sample depth	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	SO_4^{2-}	Cl^{-}	NO_3^{-}
Value before desalination							
0.0-1.0 cm	0.259	0.019	0.241	0.316	1.805	<0.01	0.061
1.0-2.5 cm	0.155	0.006	0.101	0.083	0.604	<0.01	0.038
2.5-5.0 cm	0.214	<0.005	0.052	0.027	0.498	<0.01	<0.01
Cycle 1							
0.0-1.0 cm	0.403	0.036	0.084	0.052	1.008	<0.01	0.031
1.0-2.5 cm	0.122	0.011	0.051	0.040	0.350	<0.01	0.034
2.5-5.0 cm	0.090	0.010	0.046	0.014	0.239	<0.01	<0.01
Cycle 2							
0.0-1.0 cm	0.157	0.030	0.066	0.086	0.292	<0.01	0.023
1.0-2.5 cm	0.128	0.027	0.046	0.046	0.400	<0.01	0.021
2.5-5.0 cm	<0.01	0.025	0.031	0.029	0.140	<0.01	<0.01

The success of the salt depletion is evident by the reduction of damaging salts and cations. An enrichment of damaging salts is observed in the poultice material. The results display a higher depletion of easy soluble salts than the other not readily soluble phases.

Generally the ion concentration is decreasing with an increasing depth. The sulphate pollution of surface realms correlates with higher sodium and potassium values, thus indicating the damaging salts sodium- and potassium sulphate.

It is supposed that the sulphate paths relate mainly to calcium sulphates which are used to control the cure of the concrete and sulphate has been percolated with water due to air pollution.

The alkalines may have derived from the cement. The high calcium values relate mainly to binder solutions. A direct comparison of drill flour samples of both preliminary and follow-up investigations of the appropriate juxtaposed drill profiles is problematic due to a varying ion-distribution of the damaging salts within the tamped concrete. Clear depletions show up within surface realms in a depth of 0.0- 1.0 centimetre. In depths of 1.0-2.5 and 2.5-5.0 centimetres only minor contents of building damaging salts could be verified. This is especially characteristic for the sulphate contents. Five sample points which were eye falling for efflorescences were quintessentially, analytically accompanied by desalination provisions. At three points (A, B and C) after the second poultice application a clear desalination of the concrete-texture has been accomplished. At sample point

D desalinations could only be reached after three poultice applications, despite a significant lower salt concentration. At sample point E no depletion of damaging salts within the texture has been registered. An increase of all relevant values is to be observed after the third cycle.

The reason of the enrichment of these appropriate ions within the sampled texture is probably due to the previous application of wax augens which lead together with surface moisture both to an ion-mobilisation and enrichment at the surface.

3.2 Results of concrete analysis

Table 2 shows the results of the chemical mortar analysis and Table 3 shows the calculation of the binder composition.

Table 2 Results of the chemical mortar analysis in wt-%

Sample	HCl-unsoluble	HCl- soluble SiO_2	Me_2O_3	CaO	MgO	CO_2	SO_3
VD_M_4_12	80.54	1.83	1.27	7.00	0.43	4.51	0.43

Table 3 Calculation of the binder composition in wt-%

Sample	HCl- soluble SiO_2	Me_2O_3	CaO	MgO	CO_2	SO_3
VD_M_4_12	9.40	6.53	35.97	2.21	23.18	2.21

The high contents of HCl-soluble SiO_2 metal-ions show a high hydraulic composition of the binder- cement. (The content of soluble silica relates to hydrated calcium silicates in the binder and thus the hydraulicity of the binder.) Minor MgO-contents but a significant composition of sulphate-compounds was detected. One can suppose that the sulphate-composition was primary contained in the binder. This is proven by the salt analyses showing a greater sulphate-composition with increasing depth. The composition of historical concrete shows a binder-to-aggregate relation of 1:4 wt-%. The particle size distribution of quartz sand additives were determined by sieve analysis. The results are summarised in table 4. Accordingly to the results show a gravel sand of a grain size between 0.0-8.0 mm. Several bigger aggregates with diameters of ca. 30-40 mm were found which were not detected by the sieve analysis.

Table 4 Grain Size Analysis, grading curve in wt-%, aperture in mm

Sample	0.125	0.25	0.5	1.0	2.0	4.0	8.0
VD_M_4_12	1.46	8.77	42.76	68.55	83.54	95.35	100

The X-ray diffraction analysis of a separated binder from the aggregates shows a phase composition of calcite, quartz and significant amorphous composition.

3.3 Concrete microscopy

The microscopy investigations of polished sections show a binder – aggregate-matrix of mainly white quartz and light brown binder. The pore structure is shown in blue. Fig. 2 shows ca. 30 to 35% pore (volume), 15% binder and 50% aggregates. The grain shape is rounded to rounded at the edges (Fig. 2). Fig. 3 shows the presence of un-hydrated clinker relicts in the concrete matrix. The mortar is uniform and shows a clear binder-aggregate-contact.

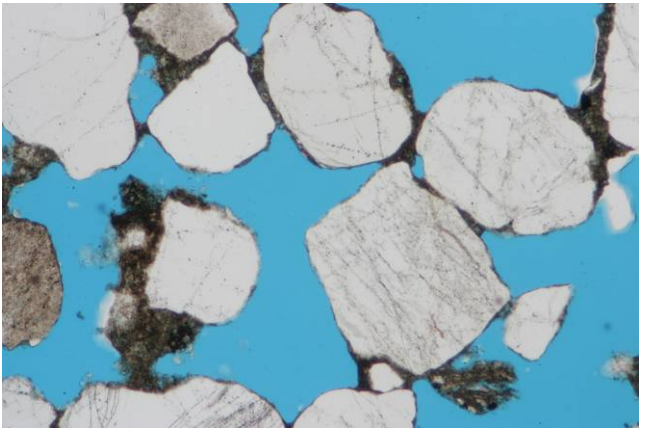

Fig. 2 Microscopic image of tamped concrete shows a high pore volume, transmitted light, field of view 1.9 x 1.29 mm

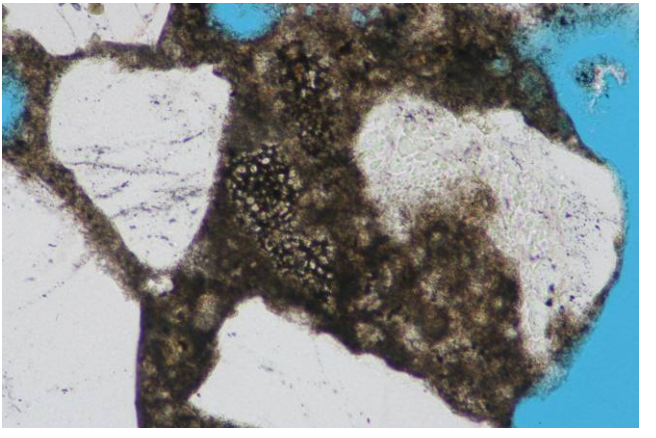

Fig. 3 Un-hydrated cement clinker grains. Microscopic image, transmitted light, field of view 0.078 x 0.052 mm

4 Conclusion

Yearlong water exposures lead to binder dissolutions, causing a high pore volume. The once applied layered tamping of the concrete caused a high pore volume and cavities. The stability of the concrete-texture is guaranteed by binder bridges between the aggregates and a stable framework has been evolved. The high pore volume offers appropriate paths for salt migrations from greater depth but also an available crystallisation pore volume.

The current results show a significant desalination success within the tamped concrete-texture of the cavalier sculptures, proving both the restoring procedures and applicability of the poultice material. The results of the drilled powder samples prove the insights made on wall surfaces. There the verified compounds are contained within the concrete-texture thus being transported in solutions and accumulated on the surface. The gathered experiences for desalinations of concrete-textures contribute basic results for further surface treatments.

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Theme III

Conservation and restoration issues

case studies, values, authenticity and compatibility of mortars, restoration and conservation techniques

III.01

Rui Barbosa Museum's Architectural Surfaces in Rio de Janeiro: Reflections and Planning Issues

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Abstract The challenges for the conservation of historic surfaces at the Casa de Rui Barbosa Museum, a building from the 19th century that has been greatly re-plastered with cement in the nineteen-seventies, is presented in this paper. Furthermore, within the Brazilian conservation field, problematic issues concerning the conservation of architectural surfaces are discussed as well as the development of a strategic plan, involving research, experimentation, training and education. In its pre-investigation approach, this paper presents the goals of the plan, emphasizing the importance of bridging the gap between theoretical, technical and practical attitudes towards the traditions within heritage conservation of establishing a compromise to maintain authenticity and integrity without accelerating decay; of developing compatible materials and techniques, developing the skills of builders and craftspeople and of developing building conservation techniques to remove damaged, deteriorated, contaminated and incompatible areas of plaster, among other specific issues in the framework of sustainable heritage preservation.

1 Introduction

The Casa de Rui Barbosa Museum in Rio de Janeiro is a national monument built in 1849. Rui Barbosa was a prominent lawyer, writer and statesman, active at the end of the 19th century and the beginning of the 20th century. In 1930, Rui Barbosa´s house became the first historic house museum in Brazil, with a varied collection including a precious library with books on law, humanities and culture.

Amongst the activities taking place at the Museum, preventive conservation strategies are being developed for better conservation of the building and its collections: including the installation of an alternative climate control system in

the library to provide a suitable preservation environment for the collection and comfort for visitors.

Since its architectural conception almost two centuries ago, the building has been changed by historical use, alteration, deterioration, evolution and intervention, mainly in the 1970's. During this period, the building underwent interventions which significantly altered the external surface characteristics and properties due to introduction of extended areas of cement. Research is being developed to clarify the extent of the changes that have resulted from these alterations; such changes include variations in the paint colours and surface details, all of which are apparent when compared to former images of the building.

Conservation work, involving the use of lime in one of the building's facades, confirmed the need, in Brazil, for an increase in the quality of the practical execution, contracts and management of such sites to guarantee that conservation is based on correct principles and guidelines (as discussed by Kanan [1]). This paper presents a reflection upon the issues of the conservation of the historic surfaces of the Casa de Rui Barbosa Museum and the planning steps towards the research of, and the development of, a strategic plan for research, experimentation, training and education within the field of Brazilian conservation.

Fig. 1 Casa de Rui Barbosa Museum in Rio de Janeiro.

2 Reflections on conservation and restoration: issues of historic surfaces

The conceptual framework for the conservation and restoration of the surfaces of Casa de Rui Barbosa Museum is based on the perspective of current general principles that sustain the conservation and restoration of the building's heritage, by maintaining its authenticity and integrity with a focus on the technical and aesthetic requirements and properties of the building and its surfaces. [2]

Although it is not clear for many professionals, managers and owners of cultural heritage; mortars and plasters play an important role in not only conservation but also in the determination of the significance of the cultural built heritage. Currently, a lot of attention is being dedicated to such studies. The importance of the proper conservation and restoration of architectural surfaces relies mostly in the following:

- they give a historic cultural appearance and identity to a building.
- they present an aesthetic function and reflect the colour, texture, finish and style of a period.
- they provide evidence of techniques, materials, cultural practices, etc.
- they protect the building envelope against physical and environmental forces.

The understandings of these plural aspects make the conservation of these surfaces a real and practical restoration issue, which can not be considered only as ordinary maintenance. In this sense, conservation must be conducted using the established principles of the field because such action involves both the form and fabric of a building which therefore requires historical research, formal analyses and technical knowledge. Furthermore, these works can't be developed as an external layer treatment, in a formal sense, but should consider the architectural object as a whole, with its functional, aesthetic and structural complexity.

Relying on today's conservation principles, the action taken on architectural historical surfaces can have two main approaches, the first, as suggested by Carbonara [3]: is when minimal intervention is possible to consolidate the plaster and stabilize the painting, keeping the sense of passed time. The second is related to a situation where it is impossible to avoid surface renovation. In this case the solution must be seen as an addition, based on critical judgment and technical analyses, developed to preserve the aesthetic and historical values of a building. Such a solution must not be a retrospective falsification, and must bear in mind technical compatibility and the ability for its removal in the future.

3 Architectural surface research at Casa de Rui Barbosa

Since its architectural conception almost two centuries ago, the building has changed mainly due to intervention actions in the nineteen-seventies. In order to

investigate the problems and to establish principles and procedures for the house's surface conservation, architectural surface research was implemented in two stages: one theoretical and the other more practical. The following steps illustrate what has been done so far:

3.1 Theoretical/ technical approach:

- An architectural and historical survey to consolidate the understanding of the place in relation to its original concept and the changes that have occurred throughout the previous two centuries.
- An architectural analysis and critical assessment of the significance of the heritage.
- Conservation assessment and mapping of the deterioration problems.

Fig. 2 The deterioration of cement plaster at Casa de Rui Barbosa Museum

Fig. 3 The deterioration of cement plaster at Rui Barbosa's House

3.2 Practical approach – the evaluation process

In 2008 the facades of a part of the built complex (a small pavilion and a former stable) were conserved using lime plaster to replace cements which had caused an accelerated rate of deterioration. The results exemplify the problematic issues of surface conservation.

Soon after the end of the works the surfaces presented spots in the paintings and renders became detached; large areas were also affected by salt efflorescence. The first analyses were restricted to a visual evaluation of the surfaces and to the procedures used in the repair, the results of which showed the need for a more detailed specification and stronger field control. The problems were related to high humidity, the use of cement in the repairs and the alteration of the traditional characteristics of the building. Further analysis and a deep understanding of the process as a whole are required to better understand the decay mechanisms, as until now only a visual observation of the repairs has been completed. The solutions for the problems should be based on an understanding of the materiality of the walls and plasters, the causes of the deterioration process, and the compatibility of the intervention materials.

3.2.1 Thoughts for a conservation project

The architectural surfaces of Casa Rui Barbosa present both general and specific difficulties for their conservation and restoration. In the specific case where the house has an architectural value, a museum function, and the actual surfaces are not from the time of its construction but from later intervention (i.e. from the seventies), the conservation and restoration decisions made are very complex [4, 5]. The project should be based on a complete study to understand the whole process and the restoration principles; critical assessment is required to validate the intervention in terms of these conservation principles and to ensure that any intervention is not solely focused on minimizing the deterioration problems and attending purely to functional needs.

Fig. 4 Stable façade restored with lime plaster two years after the intervention.

3.3 Questions related to authenticity, integrity, deterioration, materials and skills

In order to help format a research project for the conservation works of the architectural surfaces of Casa Rui, some questions need to be discussed in regards to:

Authenticity and integrity

- What are the historic and architectural values of Casa Rui and its architectural surfaces?
- Are the plasters changing the historic architectural significance and integrity of the house? Is there a need for another intervention to minimize visual problems?
- Does the building have any evidence from the former plasters that could give a key to the restoration?

Deterioration

- Are the plasters incompatible and causing damage? What kind of damage? Are they too impermeable, too strong?
- What is the extent of the damage?
- Will removal of the plaster damage the building? Will it be necessary to develop special techniques?
- Does the damaged render need to be replaced? Totally or partially? Using what type of technology? Will traditional technology be wise and sufficient in the future [6]?

Materials and Skills

- Is it possible to develop high quality compatible materials without experimentation?
- Are qualified builders and craftspeople easily available today and in the future for the conservation and maintenance of the structure? Is there a need to train and increase the skills level before the development of the works?

3.4 Proposal: plan for a research project

Considering the above situation the authors understand that a research project to provide sufficient and consistent information in answer to the questions, relating to the conservation of the architectural surfaces of the house and to the improvement of the levels of the work, should be developed before the final project [7]. The research project should include the following phases:

- Survey and typological analysis phase: Historic documentation, research, building inspections to identify values, materials construction techniques and construction phases, etc; typological analysis to evaluate the specific characteristics of the architectural surfaces of the house.
- Diagnostic phase: to identify and evaluate the state of conservation and problems of deterioration, incompatibility etc. using scientific methods.
- Experimental and laboratory analytical phase: to carry out material analysis (including the documentation and the compositional and physical characterization of the original materials and substrates) in order to determine the basis and the range of acceptable properties of any proposed new render; to search sources of materials and suppliers; to review the literature to asses current approaches to specification and the properties of available materials; and to develop formulations to be tested. After detailed analysis of original materials using lab methods, experimental formulations will be developed and tested in a field assessment prepared for the house.
- Training/ education phase: to train a team of craftspeople and develop workshops to provide qualifications and increase the skills level of the professionals involved.
- Critical assessment and guideline phase: to review results and develop technical parameters and procedures for the conservation project and works.

4 Final considerations

During historical times the Casa Rui Barbosa was used and the architecture of the building was kept and maintained as a residence. When the house was changed to a museum, other alterations occurred, changing the architectural characteristics

of the house and the maintenance routines. Today as a result of all these changes the architectural analysis and the state of conservation of the house are more complex. The house needs to be investigated and critically assessed to form a foundation for future conservation and maintenance.

It is expected that the reflections and proposals of this paper will contribute to an increase in the conservation works at Casa Rui Barbosa as well as at other sites throughout Brazil that present similar challenges.

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III.02

Practical Case Study: Mortar Conservation for the Connaught Building, Ottawa, Ontario, Canada

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Abstract This paper refers to a case study, the Connaught Building, a heritage classified building constructed between 1913 and 1916 in Ottawa, Canada. The following issues will be discussed; the philosophical approach for conservation of masonry in Canada based on the Federal Heritage Buildings Review Office of Canada (FHBRO) Code of Practice by Public Works and Government Services Canada (PWGSC), the condition of the Connaught Building masonry prior to the conservation project completed between 1996 and 2000, the conservation philosophy followed during conservation, issues encountered during design and construction, the importance of the production of accurate record documents and maintenance manuals, the program of monitoring of stone parapets for thermal movement performed by Heritage Conservation Directorate (HCD) of PWGSC, current findings of masonry condition in 2008/2009, and maintenance work currently being executed on the building. The study will conclude with lessons learned and on-going work being carried out in Canada to further improve the work of heritage masonry conservation.

1 Introduction

The Connaught Building (see Fig. 1) is a "Classified" federal heritage building, constructed between 1913 and 1916 to the designs of Chief Architect David Ewart. Located in a prominent location in downtown Ottawa, and built to house the new Ottawa Customs Examining warehouse and offices for the Department of Customs and Internal Revenue, the building continues to be occupied by Revenue Canada. Under the leadership of Sir Wilfred Laurier, the government of the day began numerous projects to begin the transformation of Ottawa from a city

dominated by the lumber industry into "The Washington of the North". The heritage character of this property is defined by the exterior elevations which were designed in the modified Tudor Gothic style. The symmetry of the massing reflects an underlying Beaux Arts layout. Various elements of its architectural design contribute to define the heritage value such as; articulated stonework, buttresses, corbelling, niches, carved embellishments and elaborate window and door surrounds. The wall finish is primarily of sandstone with granite plinth detailing.

Fig. 1 Front façade of the Connaught Building

The building is a seven storey steel structure with a mechanical penthouse above. The steel is encased in concrete with concrete floor and roof slabs. The exterior walls consist of stone cladding, with multiple wythes of brick backup, and terra cotta with plaster on the interior. The stone cladding is of varying thickness keyed into brick backup in various locations. Below the third floor level, the stone exterior is Ashlar Granite, while above this level consists of Nepean and Wallace Sandstones. The scotch work is Nepean Sandstone. The quoins, window surrounds, ledge stones, buttress capstones, and all stone above the roof ledge, such as parapet and turrets, are Ashlar Wallace Sandstone.

There are no control joints on the building. Therefore, at each change of direction on the exterior masonry, there is an opportunity for movement to occur in the building without damaging the masonry. The large windows and doors in the elevation provide natural breaks for masonry walls, and these points are also a way for the building to move. The layout and the perimeter parapet walls present challenges in conserving and maintaining the historical masonry façade. These challenges, lessons learned, and on-going work will be discussed further throughout the paper.

2 The philosophy for conservation of masonry in Canada in the 1900's

The original mortars used to construct the Connaught Building were lime based mortars, with lime as the principal binder. However, in the 1920's the cement industry was developed. Due to this, the regular practice of repointing evolved to raking out the outer layers of the existing mortar for 12 to 25mm and replacing it with cementitious mortar. The cement base mortars were seen to be stronger and more durable, and at that time there was no experience with the consequences of that decision. Results in the short and long term were shrinkage, debonding, damage to adjacent stone, and build up of salts in stone adjacent to repointed joints. No attempt was made to fill voids deeper in walls, or remove and replace deteriorated or debonded mortar deeper within the joints, mainly because maintenance was done when a failure was evident. This practice appears to have been common around the world.

There was no site quality control on repointing work. Correctly designed details were not always implemented in the construction processes. Lack of curing was common, which lead to premature shrinkage and failure to bond. Proper maintenance was often lacking, leaving joints open, which is detrimental in the Canadian climate. Some additional poor conservation practices include: stone damage during removals, use of incompatible materials such as caulking to seal joints, application of mortar over stone face, and insufficient removal of existing mortar. In conclusion, in the early 1900's the change of mortar formula was not assessed properly, and this issue occasioned a negative impact on historical masonry.

3 The philosophy for conservation of historical masonry by PWGSC

All classified buildings must follow the code of practice provided by FHBRO that states less intervention leads to increased value of heritage character. Therefore, the minimum intervention is the preferable option for any action on a classified building. In many cases, however, when maintenance has not been done, the degree of intervention required to improve the condition of the building may be higher.

Fig. 2 demonstrates the relationship between intervention and conservation of heritage character.

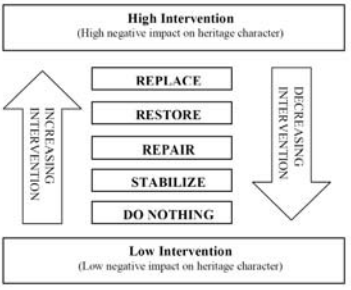

Fig. 2 FHBRO Code of Practice – Level of Intervention

The Standards & Guidelines for the Conservation of Historic Places in Canada is published by the Government of Canada "to provide sound, practical guidance to achieve good conservation practice; to develop a pan-Canada set of Standards and Guidelines; to assist people who intend to apply for government financial incentive for conservation"[1]. This guideline also promotes minimal intervention for conservation of any heritage building.

4 Mortar research in Canada in 1990's

During the early 1990's a series of buildings in the National Capital region were assessed by PWGSC, especially those located in the Parliamentary Precinct. Following this review, it was felt necessary to develop a mortar research program. This was initiated in September 1994, with a primary objective was to identify durable repointing mortars which would be practical in their application and compatible with the specific traditional stone masonry. This research program was the most comprehensive on a Canadian level. Physical and mechanical properties, as well as frost resistance, were combined under the same program. [2] The main idea was to simulate the Ottawa climate by replicating the rainfall history from the particular façade of the wall, and recreating 25+ cycles of freeze thaw. This research was a collaboration among PWGSC, the Institute for Research in Construction (IRC) and Suter Consultants Inc. (SCI). The research program focused primarily on Nepean and Ohio sandstones.

In conclusion, two mortar mixes were found adequate for Canadian climate: Cement:Lime:Sand = 1:2.5:8 and Cement:Lime:Sand = 1:1:6 with air entrainment agent (AEA). AEA was a great advance in frost resistance, however it was difficult to control on site. Therefore, PWGSC, with NRC, started a group of interested professional manufacturers and practitioners to meet and discuss issues related to heritage masonry in Canada. From this exchange of ideas, the manufacturers of lime created type "SA" hydrated lime that solved the problem of adding air entrainment by drops on a construction site.

Since 1995, PWGSC and their partners have undertaken a major program to study several elements that impact historical masonry. [3] The close collaboration between conservation professionals, the Heritage Masons at PWGSC, and the NRC and their mortar researchers, was the ideal way of working. Issues which arose on-site were immediately addressed with a study in the laboratory; the results were then directly applied, and monitored over time. One of the main gains of this association was the introduction of the Vicat-cone test on construction sites as a way to test the workability of the mortar immediately after preparation. This test is related to the compressive strength test, therefore the immediate result on site can predict the compressive results of the mortar.

5 Condition of the masonry prior to 1996 Conservation Project (The Connaught Building)

Observed conditions included all of the poor practices noted in Part 3, as well as inadequate repairs on stones, use of non compatible materials, and cementitious patches on stone spalls. These issues all contributed to damaging the exterior masonry of the building, in addition to damage caused by the severity of the Canadian climate. There is an 80°C variation in temperature throughout the year which causes severe thermal movement of stones. When the mortar in stone joints is debonded, either due to thermal movement or lack of curing, water will permeate the joints. With just one change of season, the effects of freeze/thaw will cause the saturated joints to open wider. Additionally, heavy usage of salt during winter in Canada causes severe damage to mortar and stones. This damage not only occurs at grade level where the salt touches, but also occurs on higher levels of buildings as a result of evaporation of salt water.

The lack of control joints on the building results in excessive opening of vertical joints next to quoins and around window jambs. Infrared Thermography on the Connaught Building showed extensive air leakage around windows, carrying moisture through walls. There were also major problems with air leakage on high turrets due to stack effect. Lastly, changing mechanical conditions inside the building over 100 years has caused greater negative pressure which drew more moisture into masonry.

6 Conservation philosophy carried out on the Connaught Building between 1996 and 2000

Starting in 1996, a conservation program of the entire building façade was initialized by PWGSC, based on their philosophy for conservation of historical masonry by PWGSC.

Unlike previous common practices, the importance of full depth repointing was highly recognized. Full depth repointing was performed to eliminate deep voids in the mortar joints, with the goal of minimizing moisture in the wall and the resulting damage due to freeze-thaw. Solid full depth mortar joints improve both seismic and thermal performance of a masonry wall as mortar acts as liaison between masonry units. This also prevents masonry units from rotating due to uneven filling of joints.

Cement lime mortar 1:3:9 was selected based on PWGSC testing in 1990's. It balances the need of using a weak lime mortar as in the original construction, with the greater durability provided by the cement to resist the severity of the climate. The lime provides the necessary flexibility and bond strength, while the cement provides the durability. Hydrated lime Type SA was used to provide air entrainment, an important factor for Canadian climate conditions. An angular aggregate was sourced to provide better strength and performance of mortar when using hydraulic limes. Curing of mortar was an area of contention until the NRC/PWGSC research demonstrated that the Canadian climate requires at least three (3) days of wet curing to keep moisture in the lime based mortars and allow carbonation to occur.

Proper architectural details such as flashing are necessary to protect upward facing ledge joints, which require high maintenance in our severe climate due to exposure, and to prevent the surface deterioration of sandstone in exposed locations, such as ledges and parapet capstones, due to constant wetting and drying.

One of the main factors contributing to the success of the masonry conservation was the site quality control of the work. One of the main issues was the need to carry out site review at each stage of repointing, as joints are raked out, backpointed and finishpointed, to ensure proper execution of work. Completion of mortar testing through all stages of work is also important to maintaining quality control.

7 Accurate record documents/maintenance manuals

The need to produce record documents and maintenance manuals is critical for the long term maintenance of any facility, and especially for heritage structures. These documents reflect any changes to the original design and record all interventions which have been carried out. More specifically, they provide information on the materials used in the construction/intervention. These materials can then be monitored for future performance and compatibility. This information is then available and provides clear direction for future maintenance/intervention.

The implementation of Building Information Modelling technology (BIM) will provide a facility management tool to make existing design information more

readily available, to better monitor how materials perform, and to improve management of building maintenance.

8 Subsequent monitoring

Further monitoring by John G. Cooke & Associates Ltd. in 2001-2002 and yearly from 2007 to the present, has revealed that the intervention work carried out from 1996 to 2000 is performing well, with the exception of failed mortar joints on all parapets and turrets above roof level, around large window openings, and on prominent water shed details. The reason for these failures is consistent with the research discussed below.

9 Monitoring of stone parapets for thermal movement

Research was done on the parapet to determine the amount of thermal movement experienced by the wall. Findings from the monitoring readings to date indicate that movements exhibit cyclical trends with respect to both seasonal and daily temperatures.

The following conclusions from the monitoring program were made:

- Both southwest turret and parapet movements are in direct correlation with exterior temperature variations.
- Movements between the turrets and the parapet wall occur independent of each other and at different rates, contributing to cracking and stone displacement.
- Turrets show general overall movement in the east-west direction. During the summer months the turrets move inward, while the parapet wall shows a slight increase in length. The movement of the turrets corresponds to the movement of the thickness of the turret wall between interior brick and the exterior stone. Exterior cracks between the turret and the parapet wall become narrower during the summer months while turret interior cracks become larger during the summer months.

Masonry joints which are repeatedly debonding can have a flexible joint filler introduced to allow movement. One of the areas with the most extreme thermal movement noted is on the Southwest turret. This turret is unheated, therefore heating throughout the winter is recommended.

10 Maintenance work currently being executed

Maintenance work is currently under way on the areas of joint failure noted above. Based on the observed performance of our previous interventions, we are

following the same procedures and using the same materials with our ongoing maintenance work. The record/maintenance documents are being updated to reflect these new interventions.

11 Conclusion, lessons learned

In conclusion we consider the following points to be of main importance:

- Understand the Heritage Values of a building and choose the appropriate intervention;
- Understand how the building works as a whole and in particular zones;
- Develop an approach that follows accepted conservation practices;
- Carry out strict site quality control (evaluation of the masons before starting the project, Vicat cone test, curing techniques);
- Look for more support if there are gaps of knowledge in existing research;
- Define practical and easy ways of implementing the tasks on site;
- Monitor results and revise approaches if negative results are obtained;
- Develop a maintenance manual;
- Re-visit the building at least once a year in spring to monitor conditions.

12 References

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III.03

Mud Mortars in Masonry Construction, Malton, North Yorkshire

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Abstract This paper deals with the historic use of earth mortars in masonry construction and the appropriate conservation and repair of buildings in which these were common. It examines their extensive use in Malton, North Yorkshire, where earth mortars were the material of choice for stonemasons and plasterers until the middle of the 18th century; as commonly in high status as lower status buildings. It demonstrates that earth mortars in masonry construction were very much more common and are much more widespread in the UK (and doubtless elsewhere) than has been generally understood or acknowledged and that this raises serious issues for the investigation and compatible, authentic conservation and repair of these buildings. The primary case study is York House in Malton, a late C15 H-plan house of high status with subsequent significant alteration as a gentry house in both 1620 and 1694. This is illustrated by our own practice during the conservation of this exceptionally significant building and by data produced from ongoing laboratory analysis of early mortars from within York House and beyond.

1 Introduction

The use of mud mortars in the Middle-East, central Asia, and the south-western USA is well-documented. Traditions of solid wall earth building – in cob or rammed earth – also exist across Europe and the UK [1.] In many parts of the world – such as the Yemen and Bhutan - there remains a live tradition of mud masonry. Elsewhere these traditions have been either lost to the methods or materials of modern building technology or are under threat of dilution and diminution. In the process, eminently sustainable and locally specific vernacular

buildings of the past and of the future are being compromised and lost to polluting, damaging and generic materials and working practices.

Little documented is the extensive historical use of mud mortars in masonry structures in the UK. Where mud mortar is noted in this context, it tends to be ascribed to a mysterious leeching away of previously present lime binder, to the poverty of the builders or the scarcity of readily available limestone with which to make lime [1]. The craft tradition of routinely using mud as a mortar when building with stone was long ago displaced in Britain and can be only interpreted and re-discovered today. Earthen building practices are identified in historic vernacular building across the UK [2], yet the one region apparently lacking in a coherent earthen building tradition has been Yorkshire.

Malton began its life as a significant Roman garrison town. It became an important Norman market centre, its economy dominated by the local Gilbertine Priory, which seems to have generated considerable wealth, much of which was invested in construction in the town. The geology is predominantlyoolitic limestone and calcareous sandstone in equal measure. The Romans quarried the limestone, and most of the older buildings in the town—many of them dating, at least in part, to the 12th/13th Century, are built with the same Malton oolite limestone. The churches, all of them Norman/Early English, utilize a finer grain limestone, amenable to carving, quarried some 3 miles from the town at Hildenley. From the later medieval period onwards, the calcareous sandstone was used as much as the limestone by masons locally, along with the Hildenley limestone. There were lime-kilns just without the boundaries of the medieval borough, as well as ready river transport along the Derwent. Hildenley limestone was burned for mortar also and probably delivered a naturally hydraulic lime.

Our own burning of local limestones, producing authentic limes for use upon York House (Figs. 3 and 7), confirms this. Both Hildenley and local oolitic limestones generate feebly hydraulic limes of appropriate impurity.

Fig. 1 Malton in 1728. Almost all of the buildings shown will have been built using earth mortars.. Note thatched roofs, brick and tile works to left of picture. Vanbrugh and Hawksmoor's Castle Howard in distance. (original painting, owned by Fitzwilliam Estate, Malton)

Historically in Malton, and for all this abundance of eminently suitable limestone, until at least the mid 18thC, local masons were using mud mortars for bedding and plastering. Even early brickwork is laid in mud mortar. Mud bedding and jointing mortar is encountered on the outside faces of buildings across town and in surrounding rural areas, where lime mortar pointing has fallen or eroded away. Mud plasters are found within houses otherwise constructed using lime mortar. Furthermore, after the early C18, plastering displays a transitional style: lime begins to be added into quite 'earthy' aggregate; lime base coats are very rich in oxhair (some even having rye grass or straw additions) and are not keyed before the application of subsequent coats, as earth base coats were not locally before them. Finish coats are typically thicker than may be considered the norm for three-coat lime plastering, and contain ox-hair. At the same time, re-facings of some higher status buildings utilized lime mortars from the later C16 onwards, even when the wall they were refacing remained bedded in mud. All stone buildings that survive from this period, in town and country, were higher status buildings when constructed. They were the houses, shops and farms of the bourgeoisie or yeomanry.Some, such as Ralph Eure's Prodigy House, of which only the gatehouse (Fig. 2) and former stables remain, were of exceptional grandeur

Fig. 2 Subsequently extended 1604 gatehouse of Eure mansion, Malton, constructed using calcareous sandstone, earth mortars and plasters

2 Case study

York House (see Figs. 3 and 7) is a high status gentry house set on a wide burgage plot just within the line of the former town wall. Probably built by the Gilbertine Priory, it later fell to the Eure family and was then the Malton residence of Sir William Strickland, who owned much of the town at the turn of the 17th and 18th centuries, among other East and North Yorkshire estates. The current appearance of the house is mostly a result of improvements made by Strickland

after 1684. Its mud mortared walls clearly demonstrate that earth was a material of high and every status at this and earlier times – it was not a mortar of the poor.

Fig. 3 S elevation, York House, Malton. Central range and windows introduced around 1690, using earth and 5% quicklime mortars and hay-rich earth plasters with limestone dust, quicklime and oxhair finish coats over.

Internally, buildings locally were then plastered with earth plaster, usually in a single coat up to 40 mm thick; a thinner, but typically 4-6mm thick, haired lime finish coat applied over, and limewashed. Earth plaster was always left 'off the float', with a smooth finish, rich in fines, even when it was intended as a scratch coat. Whilst a harder, lime rich surface is undesirable in a lime mortar, too much lime migrating, or having migrated to the outer face of the mortar, this is not such an issue with earth mortar, which does not 'set' as such, but dries, hardening as it does so. This said, the surface was commonly finished by 'opening up' the float for a final pass, leaving characteristic drag lines impressed by any hay or grit taken up by this motion.. The only key that earth mortars seem to have offered were small shrinkage cracks and 'drag marks'. Although not evidenced on all historic earth mortars locally, initial shrinkage cracking of plaster (of both earth and lime) seems to have been common and of little concern to the masons, so long as this represented a release of surface tension only, and did not announce detachment of the plaster from the substrate.

Reused earth plasters in York House shrank but remained well adhered to the stone wall behind. Our limestone- and lime-rich finish coats have crazed very slightly, much as did the original material they have sought to imitate. Neve [2], recording Sussex practice in 1726 records finish coats for lome plaster of 6 bushells of lime to 1 of hair, illustrating today the geographical spread of earth mortar use in England.

Fig. 4 York House interior, mud-mortared limestone to original wall and late 17thC blocking of original doorway.

Fig. 5 York House interior, earth plaster, surface as produced by opening up of float before limestone dust and lime-rich finish coat applied over

Although many of the historic earth plasters do not contain organic matter, as many again do. This is always hay/rye grass and never straw. Trials with local subsoils have demonstrated that an earth that shrinks quite dramatically without the addition of hay, shrinks not at all when hay is added. Added hay was typically around 100mm long. Earth mortars and plasters in York House laid up around 1690 are the first to show any deliberate lime content. This is indicated by small inclusions of air-slaked lime, consistent with the addition of small quantities of quick-lime to the otherwise earth mortar. This may be around 5%, a commonly used volume in some modern earth plasters.

The later medieval version of the Customs and Privileges of the Burgesses of New Malton, quoted here from a hand-written copy of 1729 held by the Fitzwilliam Estate, explicitly asserts that:"*Fyrst, it was graunted to the forsayd Burgeses, a Wast, of ather syde of the Town of New Malton; that the Burgeses and thare successors, shall in the sayd Wastys, gett Stone, and fro thens, stone and Erd*

take and cary, to the Edyficacyon and Beyldyng, within the sayd Town; whensoever thay wyll, and als ofte as thay wyll, withowt Impedyment of any man,"…this being the first of many liberties the burgesses "*and thayr Anteassors liberally hafe usyd before tyme; the qwhyche tyme is withowten Mans Membrance or mynde"*.

At least 8 different 'recipes' of earth mortar have been visually identified within York House, and whilst earth mortars throughout town are generally similar, they vary significantly from one building to another, suggestive of there being no consistent 'recipe'. Most buildings in town that have earth mortar also have undercrofts or cellars and the floors of these are usually of or upon the bedrock. It would seem likely, therefore, that much of the mortar used within each building was generated either from pits around the town or else during the excavation of the overburden on site. Within these undercrofts, the mortar of the walls is earth; that of the segmental vaults above, lime mortar the aggregate of which is limestone, with no added siliceous material.

Fig. 6 Cross vault with earth mortared walls and lime mortared vault; 12thC ribbed vault with lime mortared ribs and earth mortared fill illustrating informed and deliberate mortar selections by stonemasons

The material would seem to be immediately sourced subsoil, therefore, occasionally improved by the addition of grass, straw and sometimes ox-hair as well, and sometimes containing twigs, pottery and bone. It is clearly a pragmatic but well-informed use over a long period of time. Investigation of sub-soils in the immediate vicinity of isolated rural houses locally with earth mortar within has shown obvious correlation between the character of both mortars and sub-soil, even when the sub-soil and plasters have been remarkably sandy and of apparently poor cohesion. Subsequent investigation seems to confirm this analysis.

It is clear from the particle distributions in the 15 samples studied (see Fig. 10), that there is considerable variation in aggregate size groupings and in geological make-up. In all 15 samples the largest proportion of aggregates falls within the 63 to 150 micron group. Therefore fine aggregate predominates in all samples and proportionally decreases toward the larger end.

There are, however, two main categories which likely reflect mortars and plasters (correlation still to be confirmed). The two groups comprise 1) Samples with higher proportions of coarse aggregate of predominantly of limestone 2) Samples which tend toward the fine end of the spectrum, mostly of silicate or degraded lime fine sands. In both groups samples appear to reflect natural soils rather than intentionally modified building soils. We consider, therefore, that the two groups reflect two different broad sources. It seems likely that building earths were sourced from river sediments and from boulder clay over Jurassic geology upland from the river. The samples are heavy in clays and silts. All 15 contain between 50 and 60 percent clays and silts, clay representing typically 20 percent. Notably, modern specifications for earthen building materials usually prescribe lower proportions of clay and silt content. The successful performance and longevity of these historic samples likely results, therefore, from the stable properties of the local clays and from the inherent flexibility of the material itself.

Our own intuitively designed earth plaster as used in York House comprised 4 parts clay-rich soil to 7 parts 'M' grade sharp sand. It has performed well and gained toughness comparable to a high calcium lime plaster.

All new plastering in York House has been executed in a clayey sub-soil, sourced from just beyond the boundaries of the modern town, to which was added well-graded sharp sand until the mortar became workable and subsequent shrinkage manageable. Hay has been added during mixing and the mortar performed best when mixed to almost its liquid limit before application with steel floats. A lime finish coat is made with graded Portland stone dust and either putty or quicklime. (In the first case, the proportion of stone dust to lime was 2:1) Significant quantities of goat hair were added.

The interior and exterior walls of York House have been limewashed once more, in colours known to have been used on the building in the past, primarily to defend the exterior from the effects of vehicle exhaust emissions.

Traditional methods locally have proved remarkably durable and long-lived and the materials have proved themselves eminently fit for purpose. They have delivered maximum breathability and vapour permeability, as well as ample flexibility to the structure. Compression has been maximised during the course of construction, stone-to-stone contact being not uncommon in places in the rubble-stone sections of the walls. For stone bedding, the mortars were clearly laid in a very sloppy and wet state – dismantling of walls shows the mortar beds to reflect every indentation of the stone. The joints were then 'dubbed out' with the same earth mortar in preparation for plastering – although the face was never made as fair as would have been necessary to receive lime plaster.

Historic lime pointing to the north wall of York House – the face of which seems to be a refacing from the later C16, bound with lime mortar, whilst the main body of the wall is bedded in mud – was relatively unusual for containing ox-hair – was this a considered response by the masons to the presence of mud in the wall? There is mounting evidence to suggest that the exterior walls of some, at least, of the stone buildings in Malton, including the high status York House, were

treated in a similar way to the interiors, with a hair-rich lime finish coat over an earth base-coat. As typically in Malton, York house was faced on the outside with squared limestone ashlar (some of this likely recycled from Roman buildings locally) with rubblestone interior wyths. Stone walls constructed with mud mortar (typically 25" in section once plastered) display little or no deflection or separation cracking and mud-bound brickwork remains as sound as the day it was built. Except where the breathability of the walls has been compromised by the application of opc mortars inside or out, the walls are universally 'dry', they are never damp.

3 Conclusions

The presence of mud mortars would seem to raise serious issues regarding the compatibility of repair mortars, where even routinely used lime mortars – especially NHL mortars - might be considered to be too hard and inflexible. It is now the policy in Malton in recognition of the cultural value of surviving earth mortars, as well as of our current inability to answer questions about original finishes, not to hack earth mortars on the face of walls back in order to repoint with lime. Instead, the buildings are limewashed only. Where the buildings will not be limewashed but the pointing is deficient, repointing is executed in soft lime mortars mixed hot using quicklime with goat hair included.

Earth plastering is specified in all situations where it exists or may be demonstrated to have done so, upon earth mortared walls. As in the past, the earth itself will be sourced locally and used with a minimum of necessary improvement. Associated lime finish coats are similarly informed by historic practice and composition as well as upon specific analysis of examples found locally within each building. This steps back beyond more refined 19thC craft practice recorded in a number of contemporary manuals.. We have yet to venture down the road of exterior renders of earth, though external rendering is one of our chosen strategies when dealing with severely eroded and probably originally rendered facades within the town.

The presence of mud mortars would seem to raise serious issues regarding the compatibility of repair mortars, where even routinely used lime mortars – especially NHL mortars - might be considered to be too hard and inflexible. It is now the policy in Malton in recognition of the cultural value of surviving earth mortars, as well as of our current inability to answer questions about original finishes, not to hack earth mortars on the face of walls back in order to repoint with lime. Instead, the buildings are limewashed only. Where the buildings will not be limewashed but the pointing is deficient, repointing is executed in soft lime mortars mixed hot using high calcium quicklime with goat hair included.

From the evident quality of their workmanship, masons in Malton, at least, were highly skilled from the early medieval period onwards, with a deep

understanding of their materials and of the principles of compatibility. Throughout the medieval period and at least until the beginning of the 18th century, these masons *chose* to use mud mortar in the majority of their work and the architectural documents of this choice remain not only for our everyday use throughout Malton and beyond, but also as platforms for our imagination and enquiry, and models for not only our current conservation practice but for sustainable, locally specific and culturally meaningful architecture of the future.

Fig. 7 North elevation, York House, copperas pigmented limewash

Fig. 8 Old Malton Priory 12thC ashlar bedded in limestone dust/lime mortar; wall core in earth mortar

Fig. 9 Mud-mortared limestone exterior, Malton.
To be limewashed rather than repointed with lime to avoid loss of earth mortar

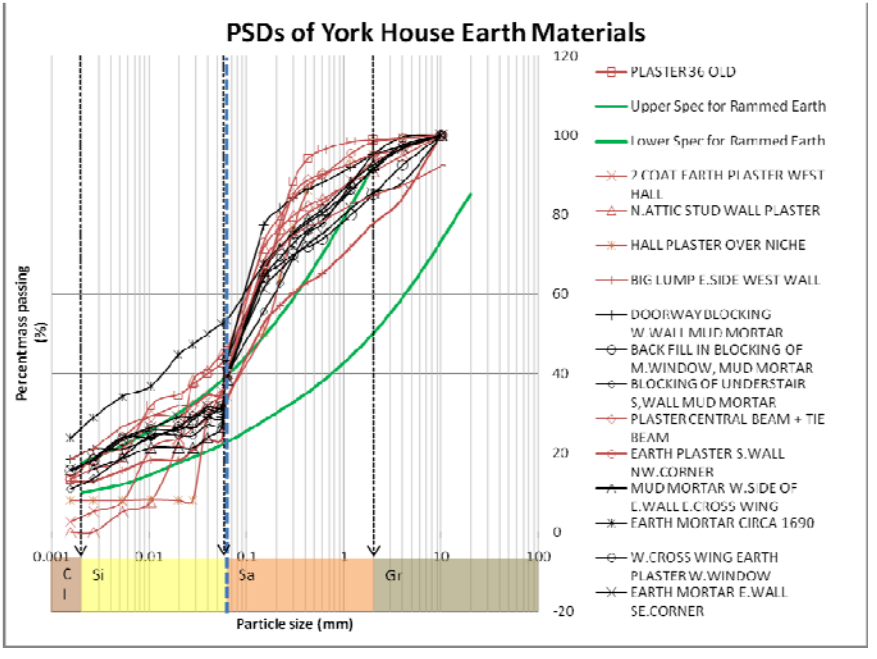

Fig. 10 Particle size distribution, sample mortars from York House and Malton. (Allen R, graph of earth mortar analysis for this paper 2010)

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III.04

Conservation of the Plaster at the *Lavriotike* Ore Washeries

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Abstract Mineral ore exploitation of the *Lavreotike* in southeast Attica reached its apogee in the 5th-4th centuries B.C. with silver revenues from the site contributing to the glory of the Athenians. The most impressive testimonials to centuries of mining activity are the vestiges of hundreds of washeries, where a novel way of ore purification was introduced: the metal rich concentrate was gravitationally separated from waste through washing. A smooth waterproof plaster covers these ingenuous recycling structures, which were vital in the semi-arid environment where water was so scarce it had to be conserved and reused as efficiently as possible. Conservation work at the archaeological site of Ag.Triada focused on the repair of the lead-rich hydraulic plaster of four rectangular washeries. Exposure to the elements (frost, rain) led to the disaggregation and subsequent loss of both the plaster and tailings (*plynites*). Thorough analysis of authentic plaster (mineralogical/petrographic, chemical analysis, porosity, strength and granulometry) led to the design of compatible repair mortars, used to stabilize the weathered plaster.

1 Introduction

The *Lavreotike,* which spans the southeast tip of Attica, is rich in minerals and ores, the most important of which are galenite and cerussite which were exploited to produce silver and lead. Copper ore was repeatedly mined at the site from the prehistoric period, through the proto-Byzantine period, until the turn of the last century; the mining of silver is inextricably related to the glory of classical Athens, the revenues of which financed many projects, including the construction of the Acropolis monuments and the city's naval fleet. The indicative yield of lead was approximately 17.5% and of silver 350 gr/ton [1].

The geological stratigraphy of the area is fairly uniform. Layers of white marble overlay layers of schist in three formations of variable thickness and direction. The mineral bearing contacts existed in pockets at the interface of

marble and schist. The third/lower contact, which was tapped into by the Athenians, lay at a depth of approximately 100 m [2].

The Ag.Triada site which lies in the upper reaches of the Legrena valley, 150-165m above sea level, features a system of washeries, cisterns and workshops. The site lies approximately 2 km from the bays of Sounion and Perdika and the modern day city of Lavrion. The climate is temperate with limited rainfall (200-500mm/yr). The median temperature is 10°C in winter and 28°C in summer. Winds are mostly of N-NE direction.

A typical rectangular washery is comprised of a wide, shallow stand tank separated from a working floor by thin stone slabs with funnel-shaped holes at half their height. The working floor, which is approximately the same width as the stand tank, is either level or gently sloping downwards. It is separated from the drying floor by one of four channels which outline the drying floor. The gently sloping channels connect two deep sedimentation basins at the far corners of the drying floor and lead back to a re-bailing basin often adjacent to a platform.

Initially the ore was manually sorted and the fragments rich in lead were sent to the furnace, those with less than 20% were sent to the washery. The washing activity (purification/separation) consists of a series of events. The ore was ground and separated gravitationally through the use of running water in the stand tank. Running water swept away all grains which did not contain argentiferous (silver bearing) lead. When the water in the tank became murky, the holes were unplugged so that it could flow into the first channel and then counter-clockwise through the channels and basins into the final rebailing basin, cleaning itself in the process [3, 4].

2 The materials

The washeries were partly hewn from the rock and partly constructed from local marble, schist and limestone in the trapezoidal rubble masonry system, where two of the four planes of the blocks are parallel, and voids were filled with stone chips. The technological innovation lay in the manufacture of an impervious, dense and durable plaster which allowed for the efficient collection and recycling of water. It has been estimated that for the concentration of each ton of ore, 10 tons of water were required [5]. The lead-rich lime plaster has been the subject of numerous studies [6, 7]; the $CaO\text{-}PbO\text{-}SiO_2$ system is basic to all syntheses involved in plaster production because of the close association of marble, quartz and lead compounds [8]. It was applied in a single coat approximately 2cm thick and was seen to contain a coarse aggregate with a medium grain size of $\varnothing$9-10mm. Preserved to this day in great expanses, the plaster is dense and smooth with a good adherence to the masonry construction. Transitions between the vertical and horizontal planes were made with uniform rounded edges.

A waterproof dark surface layer is found on plasters lining both washeries and cisterns. It is thought to have been produced as follows: a mixture of litharge, the by-product of cupellation, and *ekvolades* (discarded ores which are poor in lead, copper or zinc oxide) was melted in a furnace to form a glassy substance which was ground to a fine powder. It was added to slaked lime and applied to the plaster surface in layers which were approximately 100-200μm thick; the colour is attributed to the presence of zinc and manganese oxides [9].

Tailings/*plynites* - the sedimentation products gathered in the washeries - have been preserved on the horizontal surfaces of the working and drying floors, in layers/piles approximately 1.5-3cm thick. They are macroscopically identified by their reddish brown colour and their grainy texture. The discarded material, solidified on the floors, is embedded in a matrix of clay minerals, calcite and iron oxides [10]. Tailings often separate from the plaster surface due to differences in thermal expansion and weathering patterns.

3 Condition

The abandonment of mining activity around the 1st c. B.C., despite sporadic reuse and a brief come back in the 19th century, has led to the deterioration of the physical remains. Structurally speaking, the four washeries in Ag.Triada remain in good condition barring the occasional displacement or disappearance of ashlar blocks often from the edges of the floors. The cause of such a loss is due to both human (negligence, vandalism) and natural factors (vegetation).

Exposure to the elements over the millennia has compromised the integrity of the extraordinary plaster; once the material has been undermined, the rate of weathering is by no means linear. Disruption of the matrix (cracking) is most often observed at the edges of the floors and erosion proceeds inwards so that the loss of the plaster is most pronounced on horizontal surfaces (Fig.1). The evolution of weathering is clearly seen in the different stages ranging from the loss of the outer smooth surface of the plaster and exposure of the aggregate, to complete disaggregation of the mortar which remains on the floors as gravel. As a result, the plaster is better preserved on the more protected, internal vertical surfaces of the channels and basins. Cracking, delamination and internal voids are attributed to the combined effect of water ingress and mechanical stress induced by roots.

Frost damage seems to be the primary weathering mechanism resulting from exposure to the elements, along with temperature and humidity fluctuations. Soil entrapment, on horizontal surfaces but also in discontinuities of construction within the masonry, provides a constant source of water that is subjected to freeze-thaw cycles. In addition, the expansion and contraction of the soil's clay inclusions further disrupts the plaster matrix.

The conservation proposal focused on the selection of compatible mortar and grout mixes for the consolidation of the plaster and tailings. In order to curtail loss

it was deemed necessary to: point the edges of the well–preserved surfaces, infill small lacunae with mortar, grout internal voids and re-attach delaminations by correcting deformation and apply a consolidant/water repellent to eroded areas.

Fig. 1 Plaster at the edges of the floors is most prone to deterioration caused by water ingress.

4 Experimental program

The experimental program was devised to complement previous findings on authentic plasters and tailings in order to design compatible repair mortars in terms of composition, appearance and characteristics related to durability. Analysis of authentic plasters included mineralogical/petrographic analysis (XRD and thin section observation under a polarizing microscope) simple mortar analysis [11], chemical analysis, porosity measurements with a Mercury porosimeter and analysis of compressive strength [12], grain size distribution [13] and water absorption at saturation [14].

Authentic plasters are lime-based and contain coarse to medium-sized aggregates (0.6-2.5mm) produced with a binder to aggregate ratio of 1:1 to 1:2. The lime was probably created locally [8] with the aggregate being obtained from the area, as is indicated by the presence of cerussite and fluorite identified in the mineralogical analysis, underlining the innovative and efficient organization of the mining activity. It was observed through microscopy and simple mortar analysis,

that the tailings were used as an aggregate in the plasters of most washeries. Interestingly, the plaster of washery N°4 which predates the three others portrays different characteristics, indicating a constantly evolving mortar technology. All washeries feature plaster with low total porosity values (7-16%), tensile strength in the range of 0.2-1MPa, low water absorption at saturation values (10-12%), high hydraulicity indices, and a significant presence of lead (4-5%) and other heavy metals (Pb, Ag, Cd, Zn, Mn) located 5-15mm from the outer surface [15]. Plaster from washery N°4 features an aggregate which consists of rounded grains gathered from the nearby streambed and a small quantity of brick powder. It has a higher total porosity (22%) and water absorption value at saturation (16%) but has a lower incidence of Pb (0.2%). The tailings feature a higher apparent specific weight, low porosity value (10%) and a very low water absorption value (3.9%).

Based on these findings, two mortar mixes (LA2 with a median grain size of ø 1mm and LA5 with a median grain size of ø 0.5mm) were designed. The coarse grained mortar was designed for deep infills or edging of plaster layers >2cm in thickness. A natural hydraulic lime with pozzolanic additives (NHL-Z 3.5) by Lafarge was used as the binder which was mixed with a variety of aggregates (siliceous sand, brick powder), chosen for their colour, composition and grain size, to a binder aggregate ratio of 1:3. The grain size distribution of aggregates was thoroughly examined as good packing makes for dense, durable mortars. Optimum water quantity was selected on the basis of workability. Consolidated samples with OH100 treated with water repellent BS290 by Wacker Chemie were also evaluated.

Table 1 Repair mortar and grout formulations

Sample	Binder and Aggregate	B/A ratio	Water/Binder ratio
LA2	River sand 0-4mm	1:3 by weight	0.70
mortar	Brick powder 0-2mm		
	Siliceous sand 1-7mm		
	Hydraulic lime NHL-Z 3.5		
LA5	River sand 0-4mm	1:3 by weight	0.62
mortar	Brick powder 0-1mm		
	Siliceous sand 0,1-1mm		
	Hydraulic lime NHL-Z 3.5		
DA2	Pozzolan	8:2 by weight	0.80
grout	Hydraulic lime NHL-Z 3.5		

The testing program for the repair mortars included measurements of specific apparent weight, porosity, water absorption by saturation, water absorption rate and coefficient [16], permeability measurements [17], compressive and tensile strength [18] and durability testing with sodium sulphate immersion cycles [19].

Porosity measurements at 28 days were 16% and 17% for the coarse and fine-grained mix respectively with comparable water absorption at saturation values as those of authentic plasters (10.5% and 12.4%). Both mortars once subjected to sodium sulphate tests proved durable; at 45 cycles they had retained their shape and roughly maintained their original weight. Consolidation decreased water absorption while retaining permeability.

In addition, a hydraulic lime grout containing hydraulic lime NHL-Z 3.5, a pozzolan and a plasticizer, was tested. At 90 days, compressive strength reached 8.4MPa and tensile strength reached 2.6MPa. Segregation was <2%.

Table 2 Properties of authentic plasters, tailings and repair mortars

Sample	P (%)	Rm (μm)	CC ($g/cm^2s^{1/2}$)	AS Wt (%)	WVTR (g/ cm^2d^{-1})	ASW (g/cm^2)	CS (MPa)	TS (MPa)
LA3k	7.4	0.09	-	7.6	-	2.1	-	1
LA3k1	-	-	-	10.5	-	2.1	-	-
LA4k	22.3	0.1	-	16.2	-	1.9	-	-
LA7k	13.6	0.1	-	10.5	-	2.1	-	0.6
LA2k	15.3	0.1	-	12.6	-	2.1	-	0.2
LA6k	16.2	0.2	-	9.6	-	2.4	-	0.5
LA3p *	10.1	1	-	3.9	-	2.6	-	-
LA2	16	0.1	0.003	10.5	0.008	2	14.8	2.6
LA2-s **	-	-	0	0.5	0.007	2	-	-
LA5	17.7	0.1	0.008	12.5	0.01	2	8.4	1.7
LA5-s**	-	-	0	0.8	0.007	2	-	-

*tailings **repair mortars treated with a consolidant and water repellent

P: porosity, Rm: average pore radius, CC: water capillarity coefficient, AS: water absorption by saturation, WVTR: Water vapour transmission rate, ASW: apparent specific weight, CS: compressive strength, TS: tensile strength

5 Conservation Interventions

The scope of the conservation proposal addressed primarily the stabilization of plaster in the washeries. Cleaning with both dry and wet methods was undertaken in order to remove all loose debris and deposits from the surfaces. Pumps were used to empty stagnating water from channels and basins.

Grouting of internal voids and reattachment of delaminations also required diligent cleaning. A gauze facing was applied to the cleaned plaster surface with a 5-8% solution of Paraloid B72 in acetone in order to avoid cracking and/or bulging. Soil accumulation and debris were removed by aspiration and brushing followed by water spray. Flexible tubes of ø 2-4mm and needles were inserted into cracks or into the sides at different depths and were attached in place with the

pointing mortar (Fig. 2). Grouting was performed manually using plastic syringes which proceeded from the bottom upwards; it was monitored through the tubes, some of which acted as exit holes. A metal strut with revolving head was used over separation layers (rubber, foam and polyester film) in order to apply pressure to the injected area. The grout was mixed in a 5Lt ultrasonic mixer to increase injectability and stability. The tubes were removed 3-4 days after grouting, and the entry/exit holes were filled with mortar.

Edging and filling of small lacunae with mortar often necessitated the detachment and re-setting of a section's peripheral fragments with little or no adherence to the substrate, due mostly to the accumulation of soil and micro-organisms/roots. In cases where the plaster edges were frayed and some soil and/or roots remained at the interface of the masonry substrate and plaster, stone chips were used as galleting in order to provide a solid backing for the edging mortar. Lacunae exceeding 3-4cm in depth were filled with layers of mortar and stone chips. Mortars were kept moist in order to ensure adequate curing.

Fig. 2. Washery working floor with remnants of plaster and tailings during grouting

The pilot conservation program of four washeries in the site of Ag.Triada was part of an extensive project to develop the area into an archaeological site by the archaeologist E. Kakkavogiannis, who has devoted much of his life to the Lavreotiki, and his team under the direction of the Ministry of Culture. Plaster

conservation will ensure the longevity of the washeries as evidence of ancient mining technology.

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III.05

Rosendale Natural Cement: Reintroduction of an Authentic North American Historic Binder

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Abstract Natural cement was the predominant hydraulic binder used in engineering and architectural construction in the United States in the 19th Century. Produced from argillaceous limestone, typically high in magnesium content, calcined at temperatures below the sintering point, American natural cements were used in the construction of tens of thousands of structures of various types. The town of Rosendale, New York was the most prolific centre for production of natural cements, and its name became synonymous with American natural cements in general. Rosendale cement production was restarted in 2004, to provide authentic in-kind material for use in restoration of historic structures. ASTM Standard C10, Specification for Natural Cement, was reinstated in 2006, and aimed to maintain authenticity of the traditional material. From 2004 to 2009, Rosendale cement was used successfully in more than 100 historic restoration projects in the United States and Canada. Two case studies are used to illustrate the challenges of the material selection process and the ultimate performance of Rosendale natural cement in major historic restorations: The repointing of the south range of the American Museum of Natural History in New York City and the partial reconstruction and repointing of Fort Jefferson, Dry Tortugas National Park in Florida. Testing, analysis and mix designs are reviewed.

1 Historical Uses

The historical production and uses of natural cement in the United States are well-documented. In 1899 alone, 76 natural cement manufacturers in 16 American states engaged thousands of workers in the production of some 3 billion pounds (1.36 million metric tons) of natural cement [1]. In 1898, Uriah Cummings wrote that natural cement was used in "fully 95% of the great engineering and architectural works of this country" and listed several hundred prominent examples of same, along with the sources of the natural cement used in their

construction [2]. Modern petrographic analyses performed to date have invariably confirmed Cummings' representations. Although natural cement production waned in the early 20th Century, overshadowed by the explosive growth of the portland cement industry, two manufacturers remained in operation until the early 1970's. The use of natural cement in Canada is not well-documented, but at least two production sites were known to have been operating during the same period [2].

2 The American Natural Cement Revival

A portion of the American restoration industry has embraced the concept of in-kind repair and replacement for historic mortars, and a variety of traditional limes and imported hydraulic limes have been marketed for such purposes. Hydraulic lime was never intentionally manufactured in significant quantities in the United States, however, as it was deemed less valuable than natural cement [2, 3, 4]. In the absence of a commercial source for American natural cement, however, utilization this of historic hydraulic binder was not an option. To overcome this limitation, mining of natural cement rock was restarted in Rosendale, New York, and small scale production of natural cement for use in historic restoration work was begun in Plainville, Connecticut in 2004. From 2004 to 2009, more than one hundred historic restoration projects in the United States were completed utilizing authentic Rosendale natural cement. The challenges associated with the reintroduction of this historic technology were considerable, and may be best illustrated by two significant projects: Repointing of the south range of the American Museum of Natural History in New York City, and repointing and partial rebuilding of Fort Jefferson, on Garden Key in the Gulf of Mexico.

Fig. 1 1994 aerial photograph of Fort Jefferson, Garden Key, Florida. Demonstration phase installation of natural cement-lime mortar was in progress at that time.

3 Challenges to Natural Cement Acceptance

Despite its 180 year history of positive performance, natural cement was not immediately embraced for use as a restoration material for either project. Obstacles included inaccurate analyses of original materials at Fort Jefferson, and procedural problems in preconstruction testing of mortars for the American Museum of Natural History.

3.1 Fort Jefferson

The mortar used at Fort Jefferson was historically documented to have been composed of a mixture of natural cement from Rosendale, New York and calcareous beach sand, ground in a roller pan mortar mill [2, 3].

In June, 2004, water vapour transmission testing was performed, comparing 150-year-old Fort Jefferson mortars with two proposed natural cement mortars for the then-pending restoration project [5]. The proposed restoration mortars both utilized natural cement and differed only in their aggregate: binder ratios. The aggregate utilized was calcareous beach sand from Garden Key, as was used in the original construction. The laboratory report concluded that both of the proposed mortars were higher in permeability than the 150-year old mortar, noting that with increasing age the proposed mortars may also become less permeable. Results are summarized in Table 1. It was further concluded that all three mortars were compatible with the harder, pre-civil war Maine brick, but only mortar #2 would be expected to be compatible with the softer, Civil War-era Pensacola, Florida brick. The lower permeability of the original mortar notwithstanding, consequential distress to the Pensacola brick was not evident.

Table 1 Water Vapor Transmission test results at 28 days for original and proposed mortars at Fort Jefferson, ASTM E96. Results are averages of 3 cubes each.

Specimen	Water Vapor Transmission, grams/hr m^2	Water Vapor Transmission, grains/hr m^2	Permeance, perms	Permeability, perm-in.	Aggregate - Binder Ratio by volume
Proposed #1	10.9	15.6	21.8	12.2	2:1
Proposed #2	13.5	19.3	27.1	13.5	2.5:1
Original*	8.8	12.5	17.5	11.1	1-1.5:1 [7]

*Mortar samples removed intact from 1850's brick

Mortar analyses of various samples of Fort Jefferson mortar were performed using XRD as the primary means of binder identification. This method has been criticized as unsuitable for primary identification of historic binders, however, because although it is an excellent method for determining mineral phases, it cannot image the binder residuals that are the key to identification [6]. The

laboratory hence erroneously concluded that the binder was a form of lime with clinkered impurities. The project conservator subsequently designed a mortar mix based on high calcium lime putty and beach sand, mixed and ground in a roller pan mill. Natural cement was added as a minor constituent only. Phase 1 construction proceeded with this mixture in 2005. The high lime mortar proved a poor visual match to original materials (Fig. 2) and it performed poorly in the salt-contaminated masonry structure. It was soon damaged by severe exposures that included direct hits by two hurricanes in 2006.

Fig. 2 High lime content, Phase 1 mortars (embrasure openings, at right) were a poor visual match to original materials, which contained no lime. Demonstration phase mortars (left), containing more natural cement, performed and matched better.

Early in Phase 2, new mortar analyses were performed. Utilizing ASTM C1324 petrographic procedures, ASTM C457 Procedure B Modified Point Count method, and ASTM C114 Chemical Analysis, the geologist/petrographer concluded that mortars and coral concrete at Fort Jefferson contained no lime, the binder being composed entirely of natural cement [7]. After protracted conflict, the restoration mortar binder was changed to natural cement. Repairs now blend seamlessly with original materials (Fig. 3).

The restoration of Fort Jefferson remains ongoing as of this writing, and to date, more than 35 tons of natural cement have been installed at the site in various locations.

Fig. 3 Phase 2 work fully implemented use of natural cement, providing a "remarkable improvement in the overall aesthetics and virtual seamlessness of the new work abutting to existing work" [8].

3.2 The American Museum of Natural History

The historic south range of the American Museum of Natural History was constructed from 1888 to1899 using red granite from northern New York State and Rosendale natural cement mortar. Petrographic analyses of multiple samples of the building's red mortar confirmed the presence of natural cement, and despite some problem areas, the overall condition of the mortar was determined by the project architects to be remarkably good. The museum was committed to the highest standards of authenticity in the restoration work. Original wood windows were retained and restored, rather than replaced. The original granite quarry was reopened to obtain matching replacement stone. The use of historically accurate natural cement mortar for repointing was also favoured, but it was not a foregone conclusion.

Concerns over the use of natural cement centred around workability, shrinkage and bond strength to the building's dense granite building stone. Laboratory testing was undertaken in 2005 by the project consultants and problems developed early on. In attempting to utilize testing protocols more suitable to other masonry materials, the laboratory prehydrated the specimen natural cement mortars for 30 minutes before readjusting with water to standard flow and casting 50 mm cubes. The time of initial setting for the natural cement being evaluated was somewhat less than 30 minutes, however, much shorter than is typical of portland cement-lime mortars. Attempts to adjust mortar consistency with additional water after 30

minutes therefore resulted in disruption, producing erroneous reports of low strength, high shrinkage and negligible bond strength. As a consequence, the project's specifications went forward calling for use of portland cement-lime mortar, but the consultants left the door open to reconsideration of natural cement, pending development of further data and supporting information.

In 2006, a number of efforts were undertaken, all of which contributed to the reversal of the decision to use portland cement-lime mortars for the project. ASTM C10, *Standard Specification for Natural Cement* was reinstated. Among the requirements of the standard was a minimum time of initial setting of 30 minutes. Natural cement processing had already been altered in anticipation of this requirement, earlier the same year. A year-long study of natural cement curing rates and performance was also initiated at that time, and new bond strength and shrinkage testing were undertaken.

Fig. 4 In 2007, the first phase of masonry repointing was begun at the American Museum of Natural History in New York. The decision to use natural cement mortar was not reached until shortly before work commenced.

In early 2007 the laboratory studies were completed. Results showed that the proposed natural cement mortar developed approximately twice the bond strength to granite of a 1:1:6 portland cement-lime-sand mortar after 28 days. Shrinkages were found to be equivalent for both types of mortar, at approximately 0.05%. Strength development for Rosendale natural cement was found to be most dynamic in the period from 30 to 90 days after casting (Fig. 5), in contrast to

portland cement, which typically develops the majority of its strength in the first 7 days.

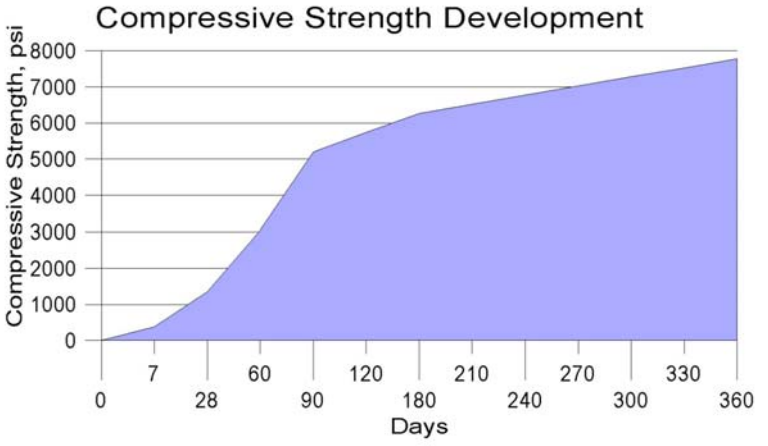

Fig. 5 Rosendale natural cement's strength development is most dynamic between 28 and 90 days' cure [9]

The final testing was a workability evaluation, performed on site in the Spring of 2007 (Fig. 6). Candidate mortars in several colours, including both portland-lime and natural cement formulations, were installed on the building in a mock-up area. The masons installing the various mortars agreed that they found the natural cement mortar to be more workable. The Museum accepted the subsequent recommendations from the project consultants and reaffirmed its commitment to preserving the building's integrity by using historically accurate materials. Some 20 tons of natural cement mortar were installed over the course of the next 2 years.

Fig. 6 Masons preferred the workability of natural cement mortars to portland-lime, when both types were installed in mock-up areas.

4 Conclusions

Natural cement has been able to overcome significant technical scepticism and perceptual concerns to re-emerge as a mainstream 21st Century restoration material in the United States. As performance data for natural cement based on modern testing protocols continues to be developed, its capacity to provide permeable, compatible, low shrinkage structural restoration mortars is confirmed. As the experience of restoration tradespersons has expanded, utilizing natural cement in a wide variety of situations and recipes, their confidence in its workability and reliability has grown accordingly.

The demonstrated successes at Fort Jefferson and at the American Museum of Natural History serve as examples of the potential to maintain historic integrity and authenticity, while restoring and preserving America's great engineering and architectural works of the 19th and early 20th Centuries. With competent analysis of original materials and knowledgeable mix design of natural cement-based restoration mortars, the caretakers of natural cement buildings and structures are able to preserve the standing examples of a major historic building technology unique to its time period.

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III.06

Traditional Portuguese Techniques for Application and Maintenance of Historic Renders

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Abstract The Portuguese architectonic heritage is mostly composed of old buildings needing intervention, especially on exterior renders, plasters and finishes. Preventive and conservative interventions are preferred in order to avoid the extraction of historical elements that are representative of the artistic and the inventive character of past generations. Subsequently it is necessary to use efficient, compatible and viable repair methodologies which are adapted to the situation. In order to adapt such methodologies to the historic renders and masonries and to improve the compatibility of conservation actions and to increase the link between modern conservation work and traditional techniques and communities, it is fundamental to gather and analyze traditional techniques, tools and materials for render application, decoration and protection. A review of traditional application and maintenance techniques, materials and tools that have been used to produce, protect and decorate historic renders are presented and their importance and viability are discussed, in order to contribute to the development of a methodology for conservative intervention on historic renders.

1 Introduction

The urban image of many Portuguese historical localities is changing quickly, due primarily to uncontrolled renovation practices and to a lack of heritage culture concerning the old urban districts. There is currently a degree of ignorance towards the cultural and technical value of old exterior renders, plasters and

finishes which creates difficulties within the subsequent decision making process and the adoption of adequate conservation and restoration techniques.

Many elements of the Old Portuguese architectonic heritage are in a state of decay due to natural ageing and a lack of maintenance. The old building façades are mostly based on mortar renders, plaster work and paintings [1] and represent a great diversity of styles. Renders and wall surface finishes have the double function of protecting in-wall materials (often poor materials) and improving their appearance; often being used to simulate richer materials like stone. The aesthetic appearance and the capacity to protect the wall from external actions such as rain, wind, chemical or biological agents, are therefore very important. Renders and finishes also serve the purpose of allowing the exchange of moisture between the building and the environment to occur.

To meet requirements and to avoid the loss of important historic representations of past generations, preventive and conservative interventions must be programmed. Therefore it is necessary to use efficient, compatible and viable repair methodologies that are adapted to each situation.

Scientific knowledge about materials and skilled restorers are important contributors in the conservation of monuments and classified buildings. However, concerning the vernacular heritage, it is necessary to study in-situ the techniques used in each region and to involve the inhabitants in the conservation practice through the re-appropriation of traditional techniques preserved by the people.

The study of the techniques used to produce the renders and finishes of old buildings requires further development and a more methodological systematization for the techniques, materials and tools used in order to complement existing work in this field [1-3].

To allow the adaption of repair methodologies, to improve the compatibility of conservation actions and to increase the link between conservationists and communities in Portugal, the traditional techniques, tools and materials for render application, decoration and protection should be systematically gathered and analyzed.

2 Materials

Over time a close relationship has been established between landscape and construction; thus the materials used contribute to the definition of the urban landscape and establish a link between territories and buildings. The knowledge of the renders' constituents is a step towards the construction of a dynamic between heritage conservation and restoration.

The following information, regarding the materials traditionally used in Portuguese renderings and façade finishes, has been sourced from oral history.

- **Earth** – A variety of earth was used in mortar, often mixed with a small amount of air-lime (Fig. 1, 2). If the earth was very rich in clay, some sand was

added. Earth mortars were less expensive than lime mortars, being collected rather than purchased, but they were also less durable. Ochre and other coloured earth was frequently used as a natural pigment. The search for and choice of the coloured earth and clay required experience.

- **Air-lime** - Lime was traditionally the preferential binder for mortars, plasters and paints. Issues like water and biological protection inherent to the use of lime were underlined [1-5]. The preparation techniques of air-lime (stone extraction, burning and hydration) were commonly known by lime producers [6-9], builders, plasterers and the population in general. This was often due to the constant re-application of limewash that was usually an important social activity of many communities, as regular maintenance of the dwellings.
- **Sand, water, additives, and admixtures** - Sands used in mortars were carefully chosen by plasterers and master builders whose knowledge was the accumulation of many generations of craftsmen. Coarse sands were used in the internal layers and finer sands were used within the finishing layers; such sands were often sourced from local creek beds [2]. Pozzolanic additives were sometimes used to increase the hydraulicity and durability of the mortar as well as to provide colour [2]. Other products could be added in order to improve a mortar's behavior; for example stone dust was used to increase the compactness of external mortar layers and vegetable fibers or animal hair were used to increase the resistance to cracking.
- **Pigments** – Earth, such as ochre with goethite, was used as a natural inorganic pigment providing hues of yellow, green and red. Such inhomogeneous material was collected by women, who worked in the fields, from oxidised environments near marshlands or water sources. Prior to use the earth was disaggregated, any herbs were eliminated and particles were wetted to dissociate grains before being dried, milled and sieved. The domestic tradition and knowledge of natural pigment extraction is now almost lost in Portugal [10,11].

3 Tools

Many of the tools used were made by the artisans themselves, to suit their individual needs and their specialized work. They were passed from father to son, or master to apprentice and were customised for each type of task, each being designated by a popular or regional name. They differed from modern tools by being crafted from natural, more flexible basic materials, and by being more diverse in shape and nature; of the trowel there were many different types in use including the brick layers trowel, gauging trowel, bucket trowel, dashing trowel, pointing trowel, float trowel, laying-on trowel and finishing trowel or smoother; some of which were specific to a particular area of work. Other tools in use

included a scraper, spatula, putty knife, hawk, plaster scarifier, rake, comb scratcher and a variety of paint brushes (Fig. 3) [2, 7, 8, 12].

Fig. 1. Different types and colours of aggregates.

Fig. 2. A lime-earth mortar mix.

Fig. 3. Finishing application tools.

4 Historic rendering and finishing techniques

The selection and preparation of the constituents and the execution and application of mortars and paints was first carried out by trial and error with the acquired knowledge being transmitted through generations of craftsmen. As a result they possessed a profound knowledge and understanding of the available resources and the processes involved in the production and application of the material.

4.1 Mortars

Calcitic lime and dolomitic lime were used extensively in Portuguese mortars. Dolomitic lime was less pure, cheaper and darker (due to the presence of iron in the chemical composition) than calcitic lime. It was mainly used in masonry mortar, but occasionally for renders which in general were composed of calcitic lime; finishing plaster and lime paints were also calcitic in nature [4, 5, 13-16]. When money was a problem, lime was not purchased and mortars and paints were made with clay (or lime-earth mixtures). However, earth mortars and earth paints were recognized by the artisans as poorer, less durable solutions than those based in lime [2, 17].

The proportions between the mortar constituents were empirical but carefully adjusted by the master builder in accordance with the weather and application conditions.

The render was applied in multiple layers, with a pause between each layer to allow it to set. The first layer contained coarse aggregates, sometimes with broken brick or stone for initial wall surface regularization; the following layers were thinner, with selected finer aggregates and a lower percentage of clay [8]; the last layer was usually very thin, prepared with lime putty and low percentage of a very fine sand or stone dust.

4.2 Finishing techniques

The old buildings of Portugal used relief renders, plasters and decorative paintings to decorate their dwelling façades. In times when resources were scarce, such architectonic coatings would be made of basic materials resembling more expensive materials. Such coatings would also be used to transform and up-grade pre-existing buildings.

The architectonic decorations were often associated with particular areas of a building, such as the top of an exterior wall, the eaves, talons, gargoyles, spans, window and door frames. A bricklayer would smooth and prepare the surface before the master plasterer would lay and shape the mortar or plaster and apply a finish. Common finishing techniques are as follows:

- **Barramento or finish stucco coats** - The finish stucco consists of multiple thin layers of lime putty with additions of brick or stone dust, which could be coloured by adding a pigment to the outermost layer. The stucco was applied with a wood trowel allowing the absorption of excess water, or more commonly with a flexible metallic trowel [1, 3].
- **Sgraffito and graffito** - The sgraffito technique was produced by revealing the interior surface layer of an application, in accordance with a specific pattern or design, by extracting parts of the exterior layer of the render [17, 18]. The drawings were marked on the surface with wood or paper card moulds which belonged to the artistic repertoire of the master plasterer. The motif relief was generally marked with pigments and a pounce bag. The under layer was pigmented or differentiated with the presence of selected aggregates and turned visible when the upper layer was eliminated inside the marked motifs, with specific tools [1, 3, 18]. Such decorative mural techniques were usually executed within specific zones of a dwelling, for example the top of exterior walls and window and door frames (Fig. 4). The sgraffited motifs generally express nature, geometry or personal emblems and the complexity of the drawing, execution, application of plaster work and applied pigments in the under layer, all serve as a testimony to the skill of the master plasterer.
- **Relief mortar works** - Relief mortar works were executed over a freshly rendered surface or were fixed onto a façade. These carefully prepared mortars usually consisted of lime and a specially selected aggregate. Wooden moulds were used and part of the exterior layer was extracted to define the re-entrant relief. When salient reliefs were produced, decorative motifs could be moulded and fixed over the façade. This last type of application is similar to the sgraffito technique (Fig. 5) but the relief motifs used are much thicker.
- **Simulations of stone and other decorative paintings** - Fake coatings were used to simulate the application of more expensive materials or homogeneous stone – like marble, breccia or even brick (Figs. 6, 7) [1, 17]. They could be executed over a surface of less noble stone, masonry, render or finish stucco coat. Other techniques such as graffito or sgraffito were also used to simulate

stone masonry (Fig. 7) [1, 17]. The use of a variety of drawings, paintings, and perspectives allowed diverse visualizations to be produced. The complexity of the design, execution and surface polish often served to define the master plasterer and his family. Often masters, like artistic painters, would leave a signature mark (sometimes their name) in a hidden place on the painted surface [2].

Fig. 4 Sgraffito decoration

Fig. 5 Relief mortar works

Fig. 6 Simulation of brick masonry

- **Rough cast finish to simulate stone (marmorite**) - In Portugal the rough cast finish of a façade to simulate stone was created by washing a freshly mortared surface (which was applied over a regularization render (Fig. 8)) to reveal selected aggregates [19]. It was mainly used between 1950- 1970 and was popular during the Estado Novo administration. It was a resistant and durable finish, which could endure many years without maintenance. The traditional mortar for rough cast finishing was a very rich mortar based on air-lime or, in later periods, on hydraulic lime or cement; stone dust and aggregates of different colours and dimensions (pebbles of different stones or sometimes glass) were also included. The mortar could be pigmented or naturally coloured by the aggregates.

4.3 Limewash and other paintings

Limewash, white or coloured, is commonly used in the South of Portugal (Fig. 9); it has been popular since the 18th century due its affordability and easy application as well as its antiseptic and antibacterial properties [1]. The limewash was applied either over a render or directly onto the masonry.

The lime paints used for limewashes could be coloured by inorganic pigments to assure compatibility with the lime. With careful maintenance traditional lime paints can be preserved for years [2]. A centuries old tradition in the regions of Southern Portugal, is the annual restoration of the limewash. Commonly performed in May (due to the mild temperature and lack of rain), the limewash would be over-painted with a mixture of slaked lime diluted with water. More than a conservative intervention, it was also a social practice, followed by generation after generation, with specific materials (lime wash, eventually natural pigments and/or animal fat products), particular tools (traditional brushes) and technologies

(number of coats, direction of the brush). These practices were upheld mainly by the women who would traditionally keep a portion of aged lime putty in a container to apply whenever small maintenance interventions were needed [1, 2, 10].

Fig. 7. Simulation of stone masonry.

Fig. 8. Rough cast finishing to simulate stone.

Fig. 9. A Limewash surface finish.

5 Gathering traditional techniques as a tool for conservation

As referred by Menezes and Tavares [20, 21], one of the key difficulties in the preservation of historical renders and finishes is the loss of technical information regarding traditional techniques, materials and tools. The knowledge of those techniques permits a better choice of conservation technology and works to promote the re-appropriation of those techniques by the population.

The gathering and registration of relevant information is crucial within conservation practice. Such knowledge is often in the hands of elderly artisans; thus, the systematic gathering of this knowledge can also contribute to the social inclusion of these artisans within a community. In parallel, this information gathering can be framed by a work plan within a specific formation, where the artisans can be involved as transmitting agents of a specific know-how. This can be very attractive to younger professionals, contributing to the improvement of their skills and integration. On the other hand, information gathering can be linked to a systematic registration of the involved instruments which can be combined with the techniques, methodologies, materials and extraction locations [20, 21].

6 Final considerations

The diversity of construction materials and techniques is an issue of their cultural richness, contributing to the drawing of the characteristics of urban landscapes. However, the lack of sensitivity for heritage preservation, in particular in this case for historical renders and finishes, is a fragility of the policies of safeguarding urban and architectonic heritage. Additionally, there is a difficulty in the efficient reproduction of knowledge about the use of traditional materials and

techniques. The importance of the recuperation of technical memory should be stressed, namely in an artisan environment where information is scarce, considering the ageing of old masters and the disappearance of experience socially transmitted, together with uncontrolled renovation actions carried out on historical monuments and urban centres during the last few decades. The lack of education and training structures in this area sensed in Portugal is an equally important issue. That is why the establishment and diffusion of correct and viable conservation methodologies are so important.

Each region of the country followed different ways of constructing, specific details and particular ways of covering the walls. This is particularly true in what concerns vernacular heritage, where the communities were predominantly self sufficient and did not resort to external masters. Maintenance and conservative interventions should not tend to standardize this rich, diversified reality.

In order to adapt repair methodologies to the historic renders and masonries, to improve the compatibility of conservation actions, and to increase the link of conservation work with the traditional techniques and with communities, it is fundamental to collect and analyze traditional techniques, tools and materials for render application, decoration and protection [9].

With an interdisciplinary team, Project LIMECONTECH (Conservation and durability of historical renders, compatible techniques and materials) co-financed by the Foundation for Science and Technology of Portugal (PTDC/ECM/100234/2008) aims to contribute to the gathering, registration and preservation of Portuguese traditional techniques of exterior rendering and plastering, based on site surveys of privileged information in contexts of patrimonial richness of renders and finishes, and laboratory and *in situ* tests used to characterize materials and experiment with techniques.

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III.07

Drayton Hall: a Case Study, Mortar Analysis and Replication

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Abstract Drayton Hall, located on the banks of the Ashley River just outside of Charleston, South Carolina, is one of the finest examples of Georgian Palladian architecture in North America. Originally constructed 1738 - 1742, the three-story Flemish bond masonry structure has managed to survive the American Revolution, the American Civil War, its ensuing economic depression, and a severe earthquake in 1886 remarkably intact. Evidence of such perseverance is visible, however, as the building's exterior exhibits at least seven distinct mortar campaigns over its lifespan. Since 1974, Drayton Hall has been owned and protected by the National Trust for Historic Preservation. This NGO has struggled to preserve and maintain the house within the restrictions of a limited budget. A recent collaboration between Drayton Hall and students and faculty of the Advanced Conservation Lab course; a part of the Clemson University/College of Charleston's Graduate Program for Historic Preservation provided the opportunity to analyze the mortar from the second campaign (ca. 1810) and formulate an easily reproducible replacement mortar.

1 Introduction

While traditional mortar analysis using dilute hydrochloric acid has been an established method to determine the composite makeup of mortars, stuccos and renders, and is commonly taught in historic preservation graduate programs in the US and Europe, it is not however the best method to analyze mixtures made with calcium carbonate aggregates such as shell, coral, limestone or marble. The need for adaptation of this method became evident when 1738 era Drayton Hall; an American National Trust for Historic Preservation site asked graduate students from the Clemson University/College of Charleston Historic Preservation program to investigate the masonry walls of the house. Specifically, they wanted to develop

an easily reproducible tuck pointing mortar using readily available materials for an upcoming repair project. The group was able to develop a more sensitive acid digestion process for the Drayton Hall mortar, which helped preserve the aggregate and identify the original formula. Using this information they could then adjust it for use with readily available materials, not sacrificing, strength, porosity or visual appearance.

2 House History

Fig. 7 Exterior view of Drayton Hall

Drayton Hall is considered one of the finest surviving examples of Georgian Palladian architecture in North America. It has exceptionally complex and rich handcrafted detail for a building completed in the first half of the 18th century in the southern colonies. As one of the most prominent and important citizens of Colonial South Carolina, John Drayton's house was built intentionally to reflect his wealth and status. Commissioned between 1738 and 1742, the two-story Flemish bond brick dwelling, raised over an English basement, would have been more at home in the English country side than the low country of South Carolina. It is significant that Drayton Hall remained in the Drayton family for over 240 years. This remarkable record of continuous ownership allowed the house to remain virtually unaltered in subsequent years, as it exists today without the invasive additions of plumbing, electrical and mechanical systems. Thus, the integrity of the original building fabric is relatively sound. Notably, Drayton Hall is also the only plantation house along the Ashley River to have not only survived numerous storms, hurricanes and one 7.2 magnitude earthquake, but also both the American Revolution and the Civil War [1].

While the house managed to survive the Civil War, the ensuing economic depression afterwards created an impoverished class in the once wealthy plantation aristocracy. The Drayton's in some ways were no different than their neighbors; who not only lost their fortunes but had also lost their grand plantation

mansions. Although the Drayton's managed to retain ownership of Drayton Hall, it still fell into decline. During the late 1870's Charles Henry Drayton was able to restore some of the family's wealth when deposits of phosphate were found on the property and subsequently mined. A powerful earthquake rocked the house in 1886 and using profits from the phosphate operation, Drayton had the means to renovate Drayton Hall and repair damages to the building. Charles greatly respected the integrity of the house and made sound repairs and slight alterations which were considered fashionable in the era.

The early part of the 20th century marked a 70 year period of limited occupancy at Drayton Hall. Although Drayton Hall remained in the family, the house was mainly used for annual family gatherings or as a country retreat for a few weeks each year [2]. By the early 1970's the building was entirely vacant and consequently deteriorating [1]. The large house was an iconic representation of the families past importance, but at the same time a burden to repair and maintain. In the 1970's the family began to explore options for the long term preservation of the buildings and its site. With the help of the Historic Charleston Foundation, the Drayton's generously agreed to let the National Trust for Historic Preservation, an American NGO, take on the role of owner and caretaker for the property. They were acutely aware of the vast needs of the property, but also had a selfless and scholarly sense of how important the site was to the low country of South Carolina and the nation.

When the National Trust (from this point forward referred to as the Trust) assumed ownership of the property in 1974, they were able to begin to survey and study the buildings and grounds. A Historic Structures Report was commissioned resulting in a set of recommendations which lead to the necessary stabilizing repair work. Care was taken to not over-restore or alter the buildings fabric or design. It was the intent of the project team and the Trust to maintain the site and dwelling as it was when the Drayton family transferred it to them. This property would be interpreted as an empty building with no furniture, fixtures or added decorative elements on the walls, floors or ceilings. Drayton Hall pays tribute to the workmanship and craft of the building. It is therefore extremely important to maintain the building through sound craftsmanship, quality materials, compatible techniques and formulas in the trowel trades as well as the latest preservation and conservation science methodology. Overall, the site offers visitors a unique glimpse into South Carolina history, while today simultaneously portraying contemporary issues facing historic sites and their scenic settings.

3 Project background

The impetus for this project came during a grant proposal meeting concerning long term maintenance of Drayton Hall, present were then director of preservation Matt Webster and Richard Marks, a local restoration contractor and adjunct

professor in the Clemson/College of Charleston graduate program in Historic Preservation. It was apparent to Webster and Marks that the track record for maintenance and repairs at Drayton Hall was largely uncertain. Although the property had remained in the hands of the Trust for the past 30 years, changes over the years in staff, hired outside consultants and advisors had lead to repairs and interventions that were well intentioned but not always successful and rarely well documented. It was clear that an academic approach to several key maintenance problems might shed the best light on the issue.

One factor that had bothered Matt Webster since his arrival at Drayton Hall was the lack of documentation of the exterior pointing mortar. There were obviously several early campaigns of mortar that predated the Trust's ownership. Also of concern were several campaigns of tuck pointing by the Trust that were not holding up well and exact data on the mix and application was scant. He hoped that the students could provide initial documentary research into past repair work, a time line for the mortar campaigns and conduct an exterior building condition survey. Webster hoped for an easily reproducible formula that any hired mason could replicate on site over time.

A conditions assessment was the first task. The brickwork was surveyed on all four sides of the building's exterior and some open areas in the house interior. A photographic record was taken and notations were made on HABS drawings provided by the Trust. The brick sizes, bonding patterns, mortar joint size and tooling was also noted. Care was taken to develop a clear evolution of the walling from original bedding and pointing to subsequent re-pointing, repairs and alterations. Samples were taken from every type of mortar identified on the building. Patterns emerged in the mortar mixtures that seemed to coincide with known periods of work by the family or later campaigns by the Trust.

The initial student findings were interesting; seven different mortar campaigns were documented. Documentary research from the historic structures report, finished in 1988, found that Drayton Hall had both a brick kiln, for the production of brick and an egg shaped reverbarotory furnace on site for lime production [2]. The earliest pointing joint from the time of construction was tooled or scribed. The second campaign, during the time period of Charles Drayton, c. 1810 is characterized by a struck joint. It was this time period of significance which was chosen by the director of preservation for analysis and replication.

Fig. 2 Tooled/scribed pointing circa 1740(left) Struck pointing circa 1810 (right) (Drawings R.Marks)

The students spent weeks on site conducting the exterior building survey, identifying the areas of intact second generation mortar joints and removing mortar from all pointing campaigns for analysis. The second part of the project would be to head back to the conservation lab to examine the mortar samples and determine the correct lime/aggregate formula ratios through gravimetric analysis, acid digestion and compression cube tests keeping the ultimate goal in mind of creating as accurate as possible match to the second mortar campaign but using modern materials and creating an easily duplicated formula.

4 Laboratory Analysis

In order to reproduce Drayton Hall's, c. 1810 second campaign mortar, analysis of pointing and bedding mortar samples was performed using a combination of several different methods. The various methodologies employed for this project included a magnified visual analysis, acid digestion, particle separation through sieves, and compression cube testing of the new replica samples.

Each sample was first inspected visually to look for similarities or anomalies, and then photographed on site before being removed. Care was taken to only remove loose or damaged samples. After samples were taken on site, they were catalogued into the time line matrix to help place them in context. Next, a basic visual analysis was performed in the lab for each mortar sample under magnification with an American Optical Micro Star stereo zoom microscope using a 40x lens. Representative parts of each sample were postured in resin cubes, then cut and polished flat to reveal the mortar in cross section. Observations were recorded in regard to aggregate particles, binder and the visual ratio of the composition, enabling a better understanding of the mortar composition before a more destructive analysis was performed. Most samples were observed to have pieces of quartz, sharp angular red aggregate and long angular gray and white aggregate. The binder matrix was predominately a whitish yellow substance which profusely coated the gray/white aggregate. This aggregate was potentially identified as oyster or clam shells which would have been manually crushed to become aggregate for the tuck mortar. Samples from beading mortar did not have

the shell, only quartz and sand particles were visible. It would be desirable to reproduce a mortar with this shell aggregate in order to achieve the appropriate color, texture, and strength of the replica pointing mortar.

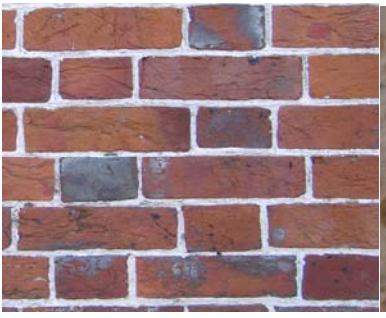

Fig. 3 Mortar joint in situ

Fig. 4 Mortar in cross section

After completion of this visual analysis and a few tests using 31.45% hydrochloric acid, it was observed that most of the sample was digested, leaving little or no aggregate. It was felt at this point that the shell was present in large enough quantities to be essential to the final replication mortar. It was determined that standard acid digestion procedures would have to be altered to best uncover the original mortar mixture. Attempts were made with some samples to gently crush the mortar and clean the aggregate of its lime binder. This proved difficult without some re-agent to dissolve the lime. Finally, an attempt was made to stir the sample in a beaker which held a mild vinegar solution (5% acidity). The entire procedure was monitored under magnification to determine the level of attack by the vinegar on the aggregate. When the aggregate was suitably clean, the vinegar was filtered and the aggregate rinsed with water. The shell aggregate could then be weighed free of most of its lime binder.

After recording the initial visual analysis, students sought to find the appropriate mortar aggregate ratio of the existing Drayton Hall mortar samples. This ratio compares the volume of aggregate (sand/shell/brick dust, etc.) to that of the cementitious materials (lime and/or cement). The students used the following procedure to determine the proportions of the three principle components of Drayton Hall's historic mortar [1. The binder (essentially calcium carbonate, or $CaCO_3$), which is soluble in acid. 2. The fines (finely textured impurities such as clays or brick dust) 3. The aggregate (sand/quartz/shell)].

The Drayton Hall mortar samples were ground by hand using a mortar and pestle. While grinding of the samples did not specifically yield the original particle sizes, it was useful in determining the percentage of each constituent part through visual inspection and weighing each sieve. The resulting particles were then separated through a series of sieves (Sieve models used were USA Standard Test Sieve ASTM E-11 specification made by Gibson, Co. Inc. The following sizes were used: #10 (2mm), #20 (850 μm), #40 (425 μm), #60 (250 μm), #100

(150 μm), and #200 (75 μm)) and brick dust, sand/quartz and shell were visible. After each sieve was visually inspected, weighed and recorded, a light wash of mild acetic acid (5%) was used to dissolve the lime binder coating around each particle. Each washed aggregate sample was then allowed to dry and an approximate constituent percentage was visually determined. The remaining aggregate samples were also weighed again. The sieve analysis concluded that the approximate aggregate percentages of the c. 1810 second campaign mortar are 80% sand/quartz, 10% brick dust and 10% shell.

Bedding mortar samples were also analyzed. Early visual inspection found aggregate consisting of only sand and quartz so a more traditional method of mortar analysis was chosen for these mortar samples. After acid digestion, and gravimetric analysis, a comparison between the sample constituent sand and present-day river sand found near Drayton Hall yielded identical consistency, color, and texture.

Based on the observed sample particle sizes, colors, and approximate aggregate ratios, a test formula for the new replica mortar was determined. The initial test mortar mix consisted of a 3:1 ratio of aggregate to binder, and the aggregate ratio consisted of 4:1 marble dust to crushed oyster shell, with a minute amount of brick dust added for color and texture (historically added to pointing mortar and speculated by many to also act as a pozzolan). Marble dust was used as the main aggregate component; a source of calcium carbonate, readily available and at a low cost (per Drayton Hall's needs), allowed the formula to require only a small portion of crushed shell for visual texture. Three types of readily available binder; lime putty, hydraulic lime, and a 2:1 lime cement mixture were then created for use with the sample aggregate.

Each test mortar sample was hand-mixed in the laboratory, and samples were placed into 2" cubes for additional compression cube testing. The compression test provides information needed to evaluate mortar performance based on tensile strength, soundness, expansion and setting time. The compression tests themselves were actually performed outside the Clemson laboratory, however, by a private mortar consultant. Sample mortar joints were also created to mimic the style of joint that would be used for the pointing work at Drayton Hall. Each of the sample joints was misted before curing to allow the aggregate texture to stand out. The test cubes and joints cured inside the laboratory and were re-examined after seven days.

5 Results

After the initial sample curing, the first sample mortar was determined to be too light in color to use as an adequate replica pointing mortar; too much marble dust was used in the initial aggregate ratio, resulting in the lighter hue. The second

aggregate ratio was adjusted accordingly to 6:2:1 marble dust to shell to sand. After this second sample cured, the desired color and texture was achieved.

6 Conclusion

Drayton Hall was pointed later that summer by professional restoration masons. The lime was slaked off site and then mixed as it was needed at Drayton Hall using the historic method of beating the lime and aggregate in a tub. The struck joint was also replicated. Since the pointing campaign has concluded, further research using primary documents has been conducted into the information which was actually recorded by Drayton Hall's second owner, Charles Drayton. His diary's which cover the periods from 1784-1820 provides a time line of brick and mortar production at the site. In the early days it is noted that both brick and "barrels of lime" are being brought to Drayton Hall for use [3]. On November 5, 1791, Charles states that:

> "John Phaley, bricklayer finished my reverbarotory kiln furnace for burning shells to lime. It is shaped as an egg & is 9 ½ feet deep: diameter at the floor, 1 ½ d greatest, 6 ft D at the upper orifice, 4 ft. The furnace took him and my brick-layer Carolina, 10 days to lay the bricks including Carolina one day to deepen the hole into the earth. Two other fellows were at the same time employed in carrying water, tempering and carrying mortar and handling bricks [3]."

Charles then goes on to further describe the furnaces operation:

> "…In order to form the furnace truly, a gauge frame, like to the dotted lines Fig. 1, is by a pivot at the bottom and another on top, made to turn round at the will of the work-man: and close to this gauge he lays the bricks. By confining and reverberating the heat and flame, it does not require ½ the fewel (fuel), as when shells are burnt in the open air. It will perfect the burning in 4 or 6 hours. It will contain 60 bushels of shells and 20 of wood. One bushel of burned shells will yield nearly or fully 2 bushels of slacked lime [3]."

Of great interest was the discovery of not just the written description of this furnace and its construction but also sketches in Charles Drayton's own hand.

This new insight into the actual production of lime on the plantation grounds for use in mortar for repair and new construction at Drayton Hall is a wonderful confirmation of the student findings where oyster shell was found to be such an important mortar ingredient both for strength and visual appearance. The real world concerns of cost, availability of materials and consistent replication posed interesting preservation issues for the students when developing the modern mortar formula. A collaborative project such as this one between graduate students who need real world opportunities and a non-profit site struggling to stay ahead of ongoing maintenance was a win-win situation for both.

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III.08

Santa Ana Church – Lagos - Portugal, Tender for Renovation and Restoration

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Abstract At any stage of the work progress we could not disregard the photographic records, not only as registration subject, but also as great analysis method. Following the previous study, and the methodical and rigorous examination, we designed a small historical-art study, with aim to obtain the possible acquaintance of the property. So, our involvement in this work would respect the mix of specificity and identity of artwork and the artistic, historical, scientific, spiritual and religious values. In essence, the art whole works has been examined within the purpose of their identity of construction in the original sense. Consequently, the role of technical conservation and restoration is the cultural objects preservation, for the benefit of present and future people generations.

III.09

Comparison between Traditional, Lime Based, and Industrial, Dry Mortars

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Abstract This contribution faces the problem of choosing, preparing and applying render mortars to be used in restoration and repair of historic buildings. The results obtained in this work clearly show that some industrial "dry mortar" products, even if they are not based on slaked lime binders, can be compatible with traditional, lime based ones, with regard to mechanical and physical properties and, therefore, should have a comparable behaviour.

1 Introduction

Lime based mortars have successfully been used in historic constructions in many different functions: as bedding mortar of masonry, for internal and external coating, as component of ancient structural concrete or of watertight linings in cisterns and aqueducts, as substrate material for pavements, etc. Malinowsky 1982 [1]. Vitruvius in his "The Ten Books on Architecture" recommends the use of particular mixes with addition of sieved crushed brick in damp situations, or the addition of pozzolan for the constructions under water level, Vitruvius 1960 [2]. The fall of the Roman Empire was followed by a long period of decline in which important technological knowledge and experience went lost. Only with the translation and new lecture of Vitruvius' work, the lime mortars technology was rediscovered and newly applied. At the beginning of the 19th century new binders, hydraulic lime but specially Portland cement, were discovered and, since considered to be better, stronger and more durable, gradually replaced lime. The use of hydraulic binders in conservation practice has been connected to a large number of failures, Newsom et al. [3], Holmström 1995 [4]. This fact, along with the general acceptance of the principles of compatibility and "like for like" philosophy in the conservation practice, have produced a regain of interest for the lime technology and the gradual reintroduction of the lime based mortars in the field of historic building conservation, [4], Gibbons 2003 [5], IFS-Bericht 2004 [6], Peroni et al. 1981 [7], Elert et al. 2002 [8]. Despite the fact that a basic

understanding of the lime technology has newly been developed, the reintroduction of lime based mortars has been, and still is, accompanied by disappointing failures. This contribution faces the problem of choosing, preparing and applying external coatings to be used in the restoration and repair of historic buildings. The results reported here correspond to an on-going research project conducted in collaboration with the Cultural Heritage authorities, Jornet and Romer 2008 [9], Jornet et al. [10]. The final goal is to reach a better knowledge about composition and behaviour of some industrial, dry mortar products, available in the Swiss or in the Italian market (five products) and to gather useful information regarding site practices for the traditional, lime based mortars (four mixes), in order to be able to make the right choice in every situation.

2 Materials and experimental

2.1 Materials

Two traditional mixes T1 and T3 were prepared using a commercially available dry hydrate lime (powder) produced in Switzerland, corresponding to the class, CL 90, according to the norm EN 459-1, 2002 [11]. The mix T2 was prepared using a about 2 years old lime putty obtained by slaking at the laboratory the same quick lime used to produce the hydrate lime powder employed in mixes T1 and T3, and the mix T4 was prepared using a commercially available lime putty. Also a commercially available, well graded sand having a maximum grain size of 4 mm and composed by metamorphic quartz, both as individual crystals and as poly-crystalline aggregates, micaschists, feldspars, micas and amphibolites, was used in all the traditional mixes (Fig. 1a). In the mix T3, brick dust obtained from an illitic clay fired at about 800°C was added.

Five different industrial dry mortar products, produced for the conservation and restoration field to be used as external coatings, were selected (P1 to P5). According to the technical data available, the product P1 is composed by "special hydraulic binders" with pozzolanic reactivity, natural sands with a maximum ∅ of 2.4 mm, special chemical admixtures and synthetic fibres. The product P2 is cement free, and composed by natural hydraulic lime NHL 3.5, hydrated lime, siliceous sand with a maximum ∅ of 4 mm, and is free of synthetic additions. The product P3 is composed by a natural hydraulic lime NHL 3.5, natural pozzolan, siliceous fine sand, washed sand from a pit and dolomitic limestone with a maximum ∅ of 2.5 mm. The product P4 is composed by natural hydraulic lime NHL 5 and calcareous sand with a maximum ∅ of 3 mm. Finally, the product P5 is composed by natural hydraulic lime NHL 3.5, calcareous sand and marble powder with maximum ∅ of 1.5 mm. The grain size distribution curves of these five products were determined and the results are shown in Figure 1b.

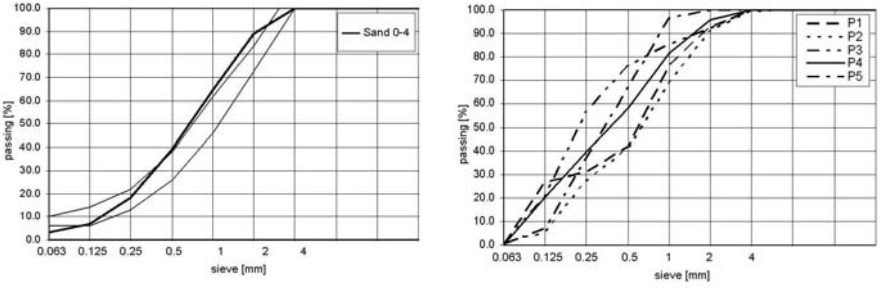

Fig. 1 a) grading curve of the sand used in the traditional, lime based, mixes, b) grading curves of the dry ready mixed industrial products

2.2 Mixes

The mixes T1 and T2 are considered basic mortars and were prepared using respectively, hydrate lime powder or lime putty as binder and a binder/aggregate proportion of 1:2 by volume. The first one was prepared using a paddle mixer, matured for 2 weeks and then thoroughly knocked up before it was applied. The second one, mixed with a hand held mortar whisk, was matured for one week. The third mix (T3) was prepared adding half a volume of brick dust, related to the binder, to the basic mix T1. The fourth mix (T4) was prepared by an experienced restorer using a hand held mortar whisk and a binder/aggregate proportion of 1:3 by volume. This mix was also matured for 2 weeks and knocked up thoroughly before it was applied. Water was added to all the mixes in order to reach a suitable workability corresponding to a plastic consistency.

The mixes corresponding to the industrial products were prepared using a hand held mortar whisk, adding the amount of water indicated by the producer and, in general, following the indications given by the producers.

Table 1 contains the available data regarding the composition of the different mixes used.

Table 1 Composition of the different traditional mixes (indicated by volume), dosages as dry mass of the dry mortar products, and water content in % of all the mixes except T4

Mixes Composition	T1	T2	T3	T4	P1	P2	P3	P4	P5
Sand 0-4 [mm]	2	2	2	3					
Binder	1	1	1	1	25 kg	40 kg	25 kg	25 kg	30 kg
Addition	---	---	0.5	---					
Water [%]	24	19	17	---	15.2	20.0	20.4	22.0	20.0
Water/Binder	2.3	1.6	1.7	---	---	---	---	---	---

At the laboratory the mixes were prepared following the procedures indicated in the Norm UNI EN 1015/2:2000 [12].

2.3 Fresh mortar

Consistency, UNI EN 1015-3, 2000 [13], porosity, UNI EN 1015-7, 2000 [14], and bulk density, UNI EN 1015-6, 2000 [15], were measured on fresh mortar. The results obtained have been summarized in Table 2.

Table 2 Fresh mortar properties of all the mixes

Mixes Properties	T1	T2	T3	T4	P1	P2	P3	P4	P5
Ø Spread [mm]	147	172	173	162	168	198	150	178	170
Porosity [vol.%]	2.5	2.9	1.5	3.8	16	15	30	10.5	26
Unit weight [kg/m^3]	1865	1922	1994	1933	1880	1847	1485	1955	1610

All the mixes show spread values within the range of the plastic consistency (140-200 mm). Larger variations can be observed by the mixes corresponding to the industrial products. Significant differences can be observed looking at the porosity as well. While the traditional, lime based, mixes show values comprised between 1.5 and 3.8 volume %, the values measured by the industrial ones go from 10.5 to 30 volume %. Roughly, the higher porosity values are related to the lower unit weight ones although the different amounts of water used modify the theoretical relationship.

2.4 Test specimens and curing

From each mix following testing specimens were prepared: 9 standard prisms 40x40x160 [mm], 3 discs with a ∅ of 100 mm and other 3 with a ∅ of 50 mm, both 20 mm thick. Compaction was achieved using a vibrating table. All the testing specimens were stored for 90 days in the laboratory at 20±2°C and 65±5%RH. In addition, every mix was applied with a thickness of about 20 mm to a substrate of brick which was stored in a rain protected area out side.

An external masonry brick wall, 12 m long, 2 m high and about 0.43 m large, with a little roof, was constructed on top of one the buildings of the campus (Fig. 2). The 9 mixes were applied by casting with the trowel, covering a surface of 2 m^2 facing south and the same surface facing north. After dampening down the wall, a thin first coat of about 5 mm, and two other coats of about 6-8 mm each were applied either after one or two weeks or after the "right" maturing time. The surface was finished by floating on and pressing back the coating, using a wood

float, when the mortar starts to stiffen up. Half of the surface was finished as mentioned before and, on the other half, a final, thin (1-2 mm), finishing coat composed by half volume of lime putty and half volume of marble dust was applied with a steel float and finished up with a sponge float. Only in the case of mix T1, a third area of 2x0.5 m^2, on both sides of the wall, was finished applying three layers of lime wash. A protective enclosure with roof covering and frames covered with fine debris netting and hessian sheeting (dampened when required by the environmental conditions) was provided before the coating application began in September, and was maintained during winter time till the end of March.


Fig. 2 External masonry brick wall showing the protective covering (left side) and the different coatings (right side)

2.5 Testing programme

Compressive and flexural strength were determined respectively on 28, 56 and 90 days old prisms of 40x40x160 [mm] UNI EN 1015-11, 2001 [16]. The carbonation depth was determined spraying a freshly broken surface with phenolphthalein. From the 90 days old prisms, about 10 mm thick slices were cut and used for the preparation of thin sections on which, observations using optical and fluorescence microscopy were performed. After 90 days of curing, the water absorption coefficient was determined on 50 mm ∅ discs, DIN 52617, 1993 [17], while the porosity parameters were determined on small prisms of 40x40x50 [mm] prepared from the standard prisms, SIA 262/1, Annexe A, 2003 [18]. The 100 mm ∅ discs were used for the determination of the water vapour transmission properties UNI EN 12572, 2006 [19].

The specimens prepared casting a 20 mm thick layer of render on a substrate of brick will be used to perform accelerated artificial weathering. The renders applied on the external wall will be monitored by visual inspection and by means of non destructive tests. The results obtained should allow the evaluation of the mixes used, in terms of performance and of compatibility.

3 Results

3.1 Mechanical properties

The compressive and flexural strength values obtained have been summarized in Table 3. In this Table it can be observed that, if we consider 2.5 N/mm^2 as upper limit, according to the norm UNI EN 998-1, 2004 [20], the traditional, lime based, mixes (T1 to T4) and the mixes P2 and P4 belong to the same group (class CSI), while mixes P1, and P3 belong to the class CSIV and mix P5 belongs to class CSIII. The comparison between the mix prepared using lime powder (T1) and those prepared using lime putty (T2 and T4) shows clearly higher values by the latter ones. Mix T3, with brick dust addition, shows values similar to those of the mixes prepared with lime putty. The industrial dry mortar mixes show quite variable values going from 1.5 to 9.5 N/mm^2 at 90 days.

Table 3 Compressive (f_{cp}) and flexural strength (f_{fl}) on standard prisms at 28, 56 and 90 days

Mixes Properties	T1	T2	T3	T4	P1	P2	P3	P4	P5
f_{cp28} [N/mm^2]	0.5	0.8	1.1	0.9	9.5	0.8	4.6	1.9	3.7
f_{flp28} [N/mm^2]	0.2	0.6	0.4	0.6	1.9	1.0	1.8	1.0	1.8
f_{cp56} [N/mm^2]	0.6	1.0	1.2	1.0	9.7	0.8	7.3	2.2	4.0
f_{flp56} [N/mm^2]	0.3	0.6	0.6	0.6	1.9	0.5	3.0	1.2	1.7
f_{cp90} [N/mm^2]	0.6	1.4	1.2	1.2	9.5	1.5	8.1	2.5	4.5
f_{flp90} [N/mm^2]	0.3	0.8	0.4	0.7	1.8	0.7	3.2	1.2	1.7

3.2 Physical properties

Porosity parameters, water absorption coefficient and water vapour transmission values have been summarized in Table 4.

If we consider the air void porosity, which corresponds to the volume of not saturable pores, (LP) and we compare it with the porosity values measured on fresh mortar, it can be observed that the traditional mixes show clearly higher values, while by the mixes corresponding to the industrial, dry mortar products the opposite is true. This is probably due to the development of shrinkage cracks by the former mixes and to the loss of some air by the latter ones. If we consider the capillary porosity values, pores saturable by capillarity (U_E), the larger variations can be observed by the traditional mixes which have also mostly higher values. The total porosity values (n), sum of air void and capillary porosity, vary not that

much among the different mixes except by the mixes with very high amounts of air voids (P3 and P5).

Regarding the water absorption it can be said that rather than the coefficient measured at 24 hours, w_{24}, (very much dependent on the thickness of the testing specimens), the one measured at shorter times (mostly already at 10 minutes) gives a much reliable information related to the speed at which water is absorbed by capillarity.

Table 4 Porosity parameters (initial humidity= U_B, capillary porosity= U_E, air avoid porosity= LP, apparent density= ρ_{110}, density at 110 °C= ρ_{R110}; water absorption coefficient (w_{24}), and water absorption coefficient after n minutes (w_{10} – value), $^{(1)}w_{30}$, $^{(2)}w_{360}$, $^{(3)}w_{60}$; water vapour resistance factor= (μ), water vapour diffusion-equivalent air layer thickness= S_d

Mixes Properties	T1	T2	T3	T4	P1	P2	P3	P4	P5
ρ_{110} [kg/m^3]	1688	1691	1743	1716	1787	1687	1532	1736	1483
ρ_{R110} [kg/m^3]	2694	2680	2695	2717	2677	2719	2680	2705	2699
U_B [vol.%]	0.5	0.7	0.5	0.6	1.1	0.6	0.8	0.7	1.0
U_E [vol.%]	29.2	27.6	32.1	24.2	22.0	24.7	20.3	25.7	25.9
n [vol.%]	37.2	36.9	35.3	36.9	33.3	38.0	42.84	35.8	45.0
LP [vol.%]	7.9	9.3	3.2	12.6	11.3	13.3	22.57	10.1	19.1
w_{24} [kg/m$^2\sqrt{h}$]	1.2	1.2	1.4	1.1	0.9	1.2	0.6	1.1	0.9
w_{10} [kg/m$^2\sqrt{h}$]	14.3	12.7	16.5	13.4	$5.6^{(1)}$	13.9	$0.9^{(2)}$	12.3	$4.2^{(3)}$
μ [-]	13	15	15	12	26	13	20	15	13
S_d [m]	0.35	0.31	0.34	0.28	0.57	0.31	0.47	0.34	0.28

Considering the values at these shorter times (w_{10}) it can be said that, as it happened with compressive strength, the traditional, lime based, mixes along with mixes P2 and P4, form a group characterized by high absorption values, varying from 12.3 to 16.5 kg/m$^2\sqrt{h}$. Mixes P1 and P5 show values around 5 kg/m$^2\sqrt{h}$, while mix P3 shows the lowest value with 0.9 kg/m$^2\sqrt{h}$. The traditional mixes along with mixes P2, P4 and P5, show water vapour transmission values comprised between 13 to 15, which are rather higher than expected as far as the traditional mixes are concerned. Mixes P1 and P3 show a higher water vapour diffusion resistance with clearly higher values.

3.3 Microstructure

The observation of the thin sections of the traditional, lime based, mortars shows that they are characterized by a mostly angular and sub-angular siliceous sand, with 4 mm maximum grain size, quite uniformly distributed in a homogeneous lime matrix with microcrystalline texture. Shrinkage cracks and irregularly shaped air-voids are also frequent. Lime lumps are clearly visible in the mixes prepared with lime putty as well (Fig. 3a and 3b).

The presence of hydraulic lime characterizes the industrial mortars which are composed by a mainly siliceous sand (P1, P2 and P3) or by a mainly calcareous one (P4 and P5) in a homogeneous microcrystalline matrix. The maximum grain size in most mixes is smaller than that of the traditional ones. Synthetic fibres are visible in the mix P1. Another characteristic feature of the microstructure is the presence of rounded air-voids indicating the use of an air entraining agent in the composition of the mixes (Fig. 4a and 4b).

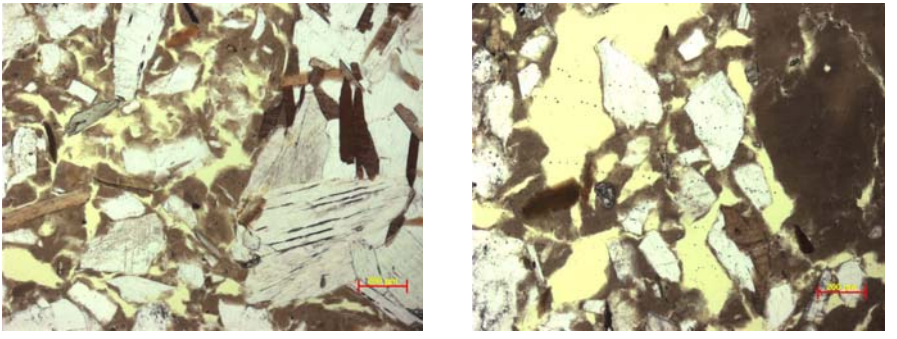

Fig. 3 Photomicrograph of mix T1 showing shrinkage cracks (left side) and of mix T2 showing irregularly shaped air voids with lime lumps (right side)

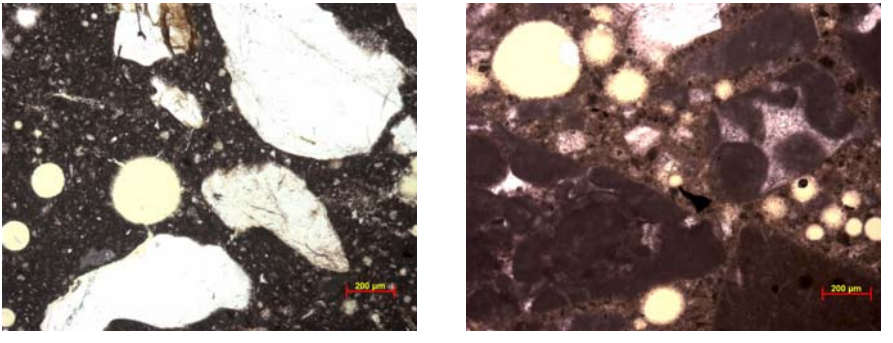

Fig. 4 Photomicrograph of mix P1showing a dense matrix with some air voids (left side) and of mix P4 showing several rounded air voids and calcareous sand grains (right side)

4 Discussion

The results obtained related to the traditional, lime based, mortars can be summarized as follows: lime based mortars are mainly characterized by low compressive and flexural strength values, by high capillary porosity and water absorption, and by a low resistance to water vapour transmission. The mixes prepared with lime putty (T2 and T4) clearly show higher strength and lower capillary porosity values if compared to the mix prepared with lime powder (T1). The addition of brick dust can significantly increase the strength of the mixes. In addition, the main features related to the microstructure of the matrix, showing a microcrystalline lime texture, are the frequent presence of lime lumps in the mixes made using lime putty and the presence of shrinkage cracks in the mix prepared using lime powder. It is generally accepted that lime mortars are rather weak and vulnerable mainly to frost action and salt crystallisation, in particular at a young age. However, due to their characteristics, they are able to accommodate minor structural and seasonal movements and they allow a quick re-evaporation of moisture absorbed by a porous masonry, Newsom et al, 2001 [3].

On the other side, the industrial, dry mortar, products included in this work show basically higher compressive and flexural strength values, lower capillary porosity and water absorption and a higher resistance to water vapour transmission. Two of them (mixes P2 and P4) show clearly lower strength values than the other three, corresponding to class CSI. In this regard, they are very similar to the traditional lime based mortars. The microstructures of the dry mortar products are mainly characterized by an important air-void content and by the presence of hydraulic lime as binder. The mix-design used is based on a concept which aims at the development of higher mechanical strength employing a hydraulic binder, and at the introduction of air voids as space available to counteract frost action and salt crystallisation. Due to their specific properties and to the frequent use of upper coatings with low water vapour transmission capacities they tend to trap moisture inside the masonry, which finally leads to the failure of the external coating and to damage the whole structure.

Where conservation work involves the repair or replacement of an external lime coating, a detailed investigation in order to establish the nature and the condition of existing coatings and their masonry should be performed. It is assumed, that the compatibility principle and the “like for like” philosophy should be established and applied. However, the principle of compatibility can be apprehended from different points of view as discussed by Hughes and Válek 2003 [24]. From a practical point of view, Groot et al. 2000 [25] distinguish to approaches to specify new mortars, a “traditional” one, based on the use of traditional materials, and a “modern” one, based on reaching compatible requirements, using if necessary modern materials. Which approach should be followed?

The results obtained in this work clearly show that industrial dry mortar products, even if they are not based on slaked lime as binder, can be compatible with traditional ones with regard to mechanical and physical properties and, therefore, it can be assumed that they should have a similar behaviour. The selection of the right product for external coating in historic buildings has to be performed with the awareness that, in addition to the knowledge required to produce a lime based mortar of good quality, skilled craftsmanship and good site practices are fundamental to the success of the conservation project. If these requirements, for one reason or another could not be met, industrial, performance compatible products, could be an acceptable alternative.

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III.11

Types of Mortars in Wall Paintings by the "Older Villach's Workshop" and their Followers (15th Century)

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Abstract An interdisciplinary research on mortars used as the support for wall paintings by the so called "Older Villach's workshop" and its founder Friedrich of Villach (15th century) has been carried out as a collaboration between Slovenia and Spain. The most important mural cycles of this workshop and some other independent, but related painters were selected in Mariapfarr, Millstatt, St. Gandolf an der Glan, Deutschgriffen, St. Lorenzen bei Sillebrücken, Unterferlach and Feistritz an der Drau, and were compared to the major works made by Friedrich's son Johannes of Ljubljana (Janez Ljubljanski) and those by anonymous Masters in Selo near Žirovnica, Veliki otok near Postojna, Srednja vas near Šenčur and in Žirovnica. The aims of this research were to get more information about the composition of mortars and find any technical similarities between all these stylistically related works. Small samples were analyzed by OM, SEM-EDX and XRD. The results showed that Friedrich's mortars were made by clean sand and lower quantity of lime, while the followers used lime and sand or lime and crushed marble or limerock with small quantity of sand. Variations were observed in the quantity of binder and cleanliness of aggregates, the form and colour of sand grains, as well as in the roughness of the surface.

1 "Older Villach's Workshop" and its followers

The present work is the result of an interdisciplinary research project carried out on a group of wall paintings in Carinthia (Austria) produced by the so called "Older Villach's workshop" and its followers, and not previously studied in either Austria or Slovenia. This workshop was found by Friedrich of Villach (Friderik von Villach, Friderik Beljaški) and was based in the town of Villach in the

southern part of modern day Austria, in Carinthia. This region was in late Middle Ages an important trade way between Italy (especially Venice) and northern Europe (Salzburg, Vienna, Nüremburg). The town of Villach became a busy trade centre and a crossing point for different stylistic influences, which culminated in a rich artistic production at that time. The mentioned workshop produced both wall and panel paintings, although few of either now survive. Four of the workshop's most important mural paintings, in the parish churches of Mariapfarr (1420–25), Millstatt (signed and dated in 1428), St. Gandolf an der Glan (1435–40) and Deutschgriffen (chore after 1452, nave around 1455), were chosen for this project. Three other closely related works were also included in the study. The one in the parish church of St. Lorenzen bei Sillebrücken (1435–40), was painted by Friedrich's son Johannes of Ljubljana (Johannes da Laybaco, Janez Ljubljanski) who latter moved to what is now Slovenia, where he produced other major works. The other two, in the parish churches of Unterferlach (1420–25) and Feistritz an der Drau (around 1440), are works of two different anonymous painters, representing two independent workshops, but are stylistically close to Friedrich [1, 5, 9].

The results for these works have been compared with those of a stylistically related group of paintings in modern Slovenia, attributed to Johannes of Ljubljana and several other anonymous Masters. As said above, Johannes carried out a high number of wall paintings in Slovenia, which are mostly all signed and dated. The most important can be found in parish churches of Visoko near Kurešček (1443), of Muljava (1456) and of Kamni vrh near Ambrus (1459). Two anonymous artists directly related to the "Older Villach's Workshop", have left high quality paintings in Selo near Žirovnica (around 1430) and in Veliki Otok near Postojna (around 1430-40), while two other painters whose *opus* show connection with Villach worked in Srednja Vas near Šenčur (1440-45) and in Žirovnica (1450-55). Their technical and painting skills are worse, with local tendency, however their general lines still show towards Fridrik's tradition [7, 8, 10, 17, 18, 19].

2 Objectives of the research and the analytical procedure

The main aim of this study was to examine the materials and painting techniques used in the production of these paintings, with particular concentration on the composition of the mortars. Additional information was obtained regarding the quantity and cleanliness of lime and sand used, the nature of the sand grains, the mixtures of binding media and aggregates, polishing of the surface, the number of mortar layers, the use of *giornattae* and possible applications of lime-wash [3, 12, 15].

All paintings were first studied *in situ* before the removal of small samples from carefully selected areas. Depending on size and purpose, these samples were prepared either as powders or mounted cross-sections. Analysis was carried out

using optical microscope (OM) with a digital camera, scanning electron microscope with energy dispersive X-ray spectroscopy (SEM–EDS) and X-ray diffraction (XRD). For a few samples Raman spectroscopy was also employed.

The international project on selected mural cycles was prepared with the interdisciplinary collaboration of art historians, restorers, chemist, physicists and geologists. There was no previous research of this group of paintings carried out neither in Austria nor in Slovenia. Reports on restoration and conservation interventions in the state archives (Bundesdenkmalamt in Vienna, Landeskonservatorat in Klagenfurt) are very seldom and contain no information on materials and techniques originally applied. The research on Slovene wall paintings was carried out recently [13].

3 Results and discussion

3.1 Composition of mortars

The *in situ* examination gave the first information about the composition of mortars, their thickness, hardness, colour and size of sand grains, as well as smoothness of the surface. Further information was obtained by samples prepared as cross-sections or as a fine powder. The conclusions made on the bases of the obtained results, are as follows.

The mortars of paintings attributed to "Older Villach's workshop" in Mariapfarr, Millstatt, St. Gandolf and Deutschgriffen are all made of lime and sand. The characteristic feature is the relative low quantity of lime, while there is more sand. The sand grains vary in form, colour and size from one location to another (Figs. 1, 2, 3a, 3b). In most cases, the sand is clean and therefore it was thoroughly washed, which can be confirmed also by cross-sections and by XRD analyses (low presence of clay and feldspars).

Fig. 1 OM micrograph. Cross-section of a mortar sample. *Mariapfarr*. Lime and sand. (x50).

Fig. 2 OM micrograph. Cross-section of a mortar sample. *St. Gandolf*. Lime and sand. (x100).

Only in St. Gandolf and in the chore of Deutschgriffen the mortar has yellowish colour and contains a higher presence of impurities (mainly silicates as anorthite, chlinochlore andmuscovite). The XRD analyses showed a slight difference between the mortar in the Deutschgriffen's nave and in the one in the chore, having the second one more impurities, but also more lime, which could also be observed already on some cross-sections (Figs. 3a, 3b). Generally, the surface of all mortars in this group is well polished, smooth and prepared for the painting layers, but the mortars are not very consistent because of the lack of sufficient binding media, i. e. lime.

Fig. 3 a) OM micrograph. Cross-section of a mortar sample. Nave. *Deutschgriffen*. Lime and sand. (x100).

Fig. 3 b) OM micrograph. Cross-section of a mortar sample. Chore. *Deutschgriffen*. Lime and sand. (x100).

The mortars of wall paintings in Unterferlach, Feistritz an der Drau and St. Lorenzen show different composition. The *intonaco* used in Feistritz an der Drau is made as a mixture of lime and sand (Fig. 4), and therefore close to Friedrich's works. Binding media and aggregates are thoroughly mixed together and the surface is well polished. According to the XRD analysis there are almost no

impurities in the mortar, but it contains more lime than Friedrich's mortars. That is why it is more solid and of better quality.

Fig 4 OM micrograph. Cross-section of a mortar sample. *Feistritz an der Drau*. Lime and sand. (x100).

On the other hand, the mortars found in Unterferlach and in St. Lorenzen are whiter. The quantity of lime is higher, while there is less aggregate. This is why they are solid and consistent and, therefore, of higher quality than the ones made by Friedrich's workshop. In Unterferlach crushed marble or limerock was used as a main aggregate, while only a low quantity of sand was added (Fig. 5). XRD analyses show the presence of dolomite, calcite and quartz, while there is practically no presence of clay, feldspars or other impurities. Such mortar is white and offers a perfect support for *a fresco* painting, known from the Italian Trecento [2, 3, 11, 12, 15]. However, the binding media and aggregates are not thoroughly mixed together, and also the surface is not well polished, as it is normally found on Friedrich's wall paintings.

Fig. 5 OM micrograph. Cross-section of a mortar sample. *Unterferlach*. Lime, crushed marble or limerock and small quantity of sand. (x100).

Similar to the mortar in Unterferlach is the one in St. Lorenzen, made by Johannes of Ljubljana. According to cross-sections (Fig. 6) and XRD analysis, it is also made by lime, crushed marble or limerock and small quantity of sand, the same composition which can be found in his latter works in Slovenia. The mortar is white and clean, while the surface thoroughly polished for the painting layers. Since his mortars are different as Friedrich's, Johannes must have got some painting experience also in another workshop and not only with his father.

3.2 Mortar layers and Giornattae

The mortar was applied on walls in relatively thin layer, about 3-5 mm. In most cases it was not possible to find out whether there was more than one layer used for the mural paintings, because the *intonaco* layer is generally well preserved. Only in St. Lorenzen and in Deutschgriffen two layers can be distinguished already by the naked eye, however the lower one is, in both cases, most probably of older date. In Deutschgriffen it is even painted with a layer of white colour which shows that it must have been put on walls before wall paintings were ordered. The painters used the already existent rough mortar as *arriccio,* as the base for a fresh layer of *intonaco*.

In most cases it was possible to distinguish borders and sizes of daily mortar portions, "*giornattae*", and their sequence. In all Carinthian paintings that were subject of this study, the *giornattae* could be big as a single scene or as a single figure. They were usually applied in downward strokes from left to right, which shows the direction of workshop's work. Only in Mariapfarr it could be observed that the painter started on the right and went towards left.

3.3 Lime wash

Lime-wash can be observed very rarely, applied only locally under some carnations or other elements. However, due to relatively small quantity of lime as the binding media in the mortars of "Older Villach's workshop" and therefore their fragility and tendency to pulverize, a wider use of lime wash over the painting surface was expected. With certainty it could have been confirmed only on the cross-section taken from the dragon on St. George's scene in Mariapfarr. Besides, in Millstatt, on the lowest stripe of the wall painting, wide brushstrokes of white colour can be distinguished by the naked eye under the painting layer. In St. Gandolf the lime-wash was probably applied under some carnations of secondary figures. It seems that the *giornattae* were small enough to finish the work in one day without having to freshen up the mortar with another layer of lime.

Fig. 6 OM micrograph. Cross-section of a mortar sample. *St. Lorenzen in Sillebrücken*. Lime, crushed marble or limerock and small quantity of sand. (x100).

In Unterferlach and in St. Lorenzen lime-wash was found only locally, mostly under carnations. Johannes applied it also under some draperies, always in a thin

layer (Fig. 6). On the other hand and despite a good and solid mortar, the wall paintings in Feistriz an der Drau are made almost entirely on a thick layer of lime-wash. It can be observed *in situ* especially with the use of a light source in different angles, but it was also confirmed on cross-sections (Fig. 4). In many areas it is falling from the walls, destroying as well the paint layers. That is why this mural cycle is in the worst conservation condition among all selected in this research. The lime technique was, therefore, an important technical feature in Feistritz, which confirms that it could not have been carried out by the "Older Villach's workshop".

3.4 Comparison with the mortars of the selected Slovene mural cycles

Technically the best mediaeval wall paintings in today's Slovenia are those, stylistically related to the "Older Villach's workshop" [13]. Among those, the most important are the ones made by Friedrich's son Johannes, who continued using the same composition of mortars as in his Carinthian works: a mixture of lime with crushed limerock or marble and a small quantity of sand. He also continued applying very thin layer of lime-wash under some carnations or draperies. Another two painters, Master of Selo above Žirovnica and Master of Veliki Otok near Postojna (according to two locations where they carried out their best wall paintings), stylistically directly connected to Friedrich's workshop, also used the same high quality mortar as Johannes, but without the sand. Therefore, in the material and technical aspect, differ from the Friedrich's supports. The lime-wash was found only in Veliki Otok under some carnations, while the *giornattae* are small.

Indirectly connected to Villach's workshop are Master of Srednja vas near Šenčur and his disciple Master of Žirovnica. Their style is still close to Friedrich, but it became more lineal and merged with the local tradition. But their mortars are similar to Friedrich's, as they are made by lime and sand. The sand is clean, but the relative quantity of the binding media (lime) is lower, so the mortars tend to pulverize. The *giornattae* were large and applied on wall in relatively thin layers (ca. 3 mm), however, no lime-wash was found in any of these two locations.

4 Conclusions

An international interdisciplinary research was dedicated to the mortars as a support of wall paintings made in the 15th Century by the "Older Villach's Workshop" and its followers (Mariapfarr, Millstatt, St. Gandolf, Deutschgriffen, St. Lorenzen, Unterferlach and Feistritz an der Drau). The main objective was to get more information on the composition and the materials applied. All cycles

were first precisely studied *in situ* and second, mortar samples were analysed by different laboratory techniques, OM, SEM-EDS and XRD.

In the wall paintings directly attributed to Friedrich of Villach's workshop, mortars are made of relatively lower quantity of lime and more sand, that is why they are not very consistent. The surface is thoroughly polished, while lime-wash was used very seldom. In latter works, the mortars contain more impurities and are of yellowish colour. In Feistritz the mortar is also made of lime and sand, but there is more binding media, so the mortar is solid. However, a thick layer of lime-wash can be found under most secondary figures. On the other hand, the mortars in Unterferlach and in the works of Johannes of Ljubljana (also in Slovenia) are made of lime, crushed marble or lime-rock and small quantity of sand. The lime-wash was found only under some carnations. The results were compared to selected mural cycles on the territory of what is today Slovenia, which are stylistically related to it. The Master of Selo above Žirovnica and The Master of Veliki otok near Postojna used almost the same mortar composition as Johannes, while the Master of Srednja vas near Šenčur and the Master of Žirovnica are closer to the local tradition with lime-sand mortars, which contain less lime and tend to pulverize. Lime-wash was found under some carnations only in Veliki otok.

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III.12

The Restoration of the Cathedral at Kirkjubøúr in the Faroe Islands

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Abstract For centuries the ruins of the Cathedral at Kirkjubøur in the Faroe Islands was exposed to the very humid and saline north Atlantic environment. Traditional maintenance of the mortar joints was needed to ensure mechanical stability of the structure. The original lime mortar, locally referred to as 'skílp', was quite hard and had excellent adhesion to the basalt blocks. The lime for the mortar was possibly made of seashells, and the aggregate was a mixture of black, volcanic sand and shell fragments. Hydraulic components were identified in samples taken from the areas with high structural load. Different mixtures of lime mortars were tested in the laboratory and on site to determine the resistance against weathering. This work is not yet terminated, but it appears that only a hydraulic lime will be durable in this environment.

1 History

The cathedral in Kirkjubøur is located on the south side of the island Streymoy, 10 km from the main town Tórshavn. The construction began in the beginning of the 12th century, but it is not known when the building was completed [1]. Today only the walls are left, but structural details and stone fragments found around the monument indicate that the church may have had vaults. By the end of the 20th century the ruin was in a poor condition, so a temporary shelter was erected to protect against further environmental degradation. The shelter was designed also to stabilise the walls, in case the inside of the wall structure was already severely damaged by frost. A study of the microclimate concluded that episodes of frost were rare, but there was a risk of accelerated salt decay on the sheltered surfaces [2]. The monument would be best preserved by maintaining the joints of the walls with an appropriate restoration mortar.

2 Construction

The walls of the monument are approximately 9 m high and 1.6 m wide at ground level. The arches for the windows and porches are constructed of regular blocks with even joints. In contrast, the walls in between consist of basalt boulders in various sizes and shapes, collected from the hillside next to the site (Fig. 1). The cavities between the boulders are filled with smaller pieces of rock and mortar. Two core drillings in the south wall confirmed that the inside has solid mortar infill too. The mortar inside the wall is rather hard and adheres well to the basalt. It is a substantial part of the construction and serves a structural purpose. Once hardened the mortar infill transfer the vertical load from one block to the next, so the stress is evenly distributed over the cross section. But even more important is the ability to transfer the horizontal load from the vaults, which were supported by the walls 5 m above ground.

Fig. 1 The ruin of the cathedral in Kirkjubøur is located at the foot of the hill facing south to the Atlantic Ocean. The temporary shelter protects against the very humid and saline environment.

3 Original mortar

The islands do not have any geological limestone deposits, so seashells are the only natural source of lime to use for mortar. The shells mainly occur as fragments mixed with particles of eroded basalt, as it is washed up on the beach. It is reasonable to assume that lime was a limited resource, which was difficult to procure in sufficient quantities for such a project. As a rough estimation a total of 50 m^3 of lime was needed to construct the walls in their present appearance. It must have been a huge effort to collect enough shells or to separate shell fragments from the gravel. But the main problem was probably to prepare the lime. The forest, which may have covered the islands in prehistoric times, was

already exterminated prior to the medieval period, so it was difficult to provide fuel for firing the lime.

Fig. 2 The walls of the cathedral are made of irregular basalt boulders. The cavities in between are filled with smaller pieces of rock held in place by the mortar. Test area for restoration on the north side of the north wall

A total of ten mortar samples were taken from different positions at the monument for analysis [3]. The sampling may not be entirely representative, because there was not access behind the shelter. Samples were taken from the drilled cores of the south wall, from the mortar joints in the arches and the wall, and from fragments of plaster found a few places in protected areas. Thin sections were prepared from each sample to study the microstructure of the mortar and determine the composition. Chemical analysis was made on the lime fraction to calculate the hydraulic index of the lime. The results of 5 samples are displayed in Table 1.

All samples have rather similar volumetric composition and structure (Fig. 3). The pores are mainly round and separate, sometimes connected by fissures, in average 15% by volume. In some samples the pore volume is partly filled with crystals of precipitated lime, an evidence of the extreme humid environment. The silicate aggregate makes up 27% of the total volume. It is a mixture of white, rectangular quarz grains and black, round grains of basalt. The aggregate is similar to the natural sand deposits at the beach nearby the monument.

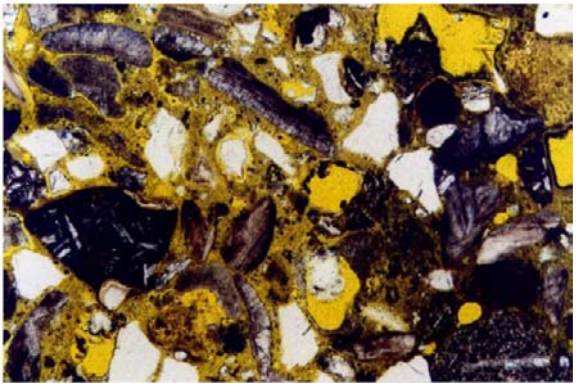

Fig. 3 Thin section of the original mortar in sample 12. The black grains are basalt, the white grains are quarz, the light brown matrix is lime and the grey particles are shell fragments. Yellow areas are pores. The total area is approximately 7 mm^2 . Photo by Thorborg von Konow.

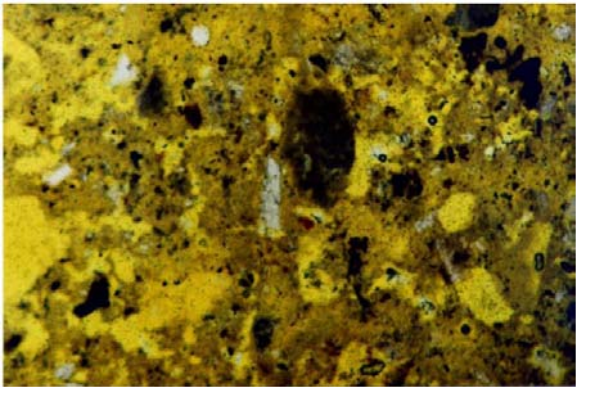

Fig. 4 Thin section of the original mortar. Detail of the lime matrix. The dark brown areas are possibly hydraulic minerals. The total area is approximately 1.2 mm^2
Photo by Thorborg von Konow.

The average lime content is 41%, and there is an additional 18% fraction of unfired seashell and lime inclusions. The presence of shell fragments indicates that the shells were also used for the lime binder. The dark brown areas within the lime matrix might be unfired fragments of the shells, or a hydraulic silicate component (Fig. 4). Such minerals do not come from the shells themselves, but may derive from silicate particles mixed with the shells, or deliberately added prior to firing. The hydraulic minerals would evolve during the firing process as in a natural hydraulic lime. The silicate particles may also have been mixed into the lime before slaking or even after slaking to act as a pozzolan.

Table 1 Composition of mortar samples in % volume, and hydraulic index calculated from the chemical composition.

Sample no	4	7	8	10	12
Location	plaster	joint	window	infill	core
Pores	13	15	19	16	12
Silicate aggregate	18	27	33	20	29
Lime aggregate	29	18	9	26	21
Lime binder	39	41	39	38	38
Hydraulic index	0.14	0.11	0.23	0.27	0.75

The hydraulic nature of the lime is confirmed by the chemical analysis. The sample taken from the drilled core of the wall has moderate hydraulic index at 0.75. Two samples taken from a window niche have hydraulic indices at 0.23 and 0.27. Two samples taken from pointing mortar and plaster at the surface have hydraulic index below 0.15, which is considered to be pure lime. The difference in hydraulic content relates to the position of the mortar. The moderate hydraulic lime is needed to resist the compressive stress inside the wall. Furthermore, the diffusion of carbon dioxide deep into the structure is very slow, so it may take years for a pure lime to harden by carbonation. A hydraulic lime will harden much faster and allow the construction work to continue. Similar to this, the mortar joints in the window arches are exposed to compressive stress, and need therefore to gain strength by hydraulic minerals. A pure lime mortar was used at the surface, because the mortar needs little compressive strength for structural reasons.

4 Restoration mortar

The local tradition of firing and slaking lime from sea shells have not survived to modern times, so it is not straight forward to develop a restoration mortar based on local resources. Some initial observations and investigations indicate the performance of imported materials. When the relief on the east wall was put back in place, a lime mortar was used for the joints. After some time the lime started to leach out after rainfall, and after a few years there was a thick crust of lime deposit below the relief (Fig. 5). It is not acceptable to have such an effect all over the wall surface. The areas under restoration must be protected against driving rain until the lime has carbonated, but this may take years if the repairs extend deep below the surface.

In the summer 2007 three test areas were established on the north side of the north wall (Fig. 2). Each area is approximately 2.0 x 2.0 m, located 1 m above ground level. The facade is little exposed to wind and sun, so this part of the monument is protected against the natural drying and wetting cycles. Two types of premixed lime mortar were used for the joints, one with lime putty matured for

3 years and one with lime and aggregate slaked together. A premixed hydraulic lime mortar NHL3.5 was also tested. During the first winter lime was leaching from the joints made with the two pure lime mortars, whereas the hydraulic lime mortar remained unaltered. After two years the leaching of lime has stopped, possibly due to full carbonisation.

Fig. 5 The lime deposit below the relief on the east wall has leached from the lime mortar used for the joints.

The results of the first test encouraged the use of a hydraulic lime for the restoration mortar. Four different types were tested in the laboratory [4]. Type A is a NHL3.5 also used for the site test. Type B is a NHL5-Z, mixed from a natural hydraulic lime and a natural volcanic puzzolan. Type C is a mixture of lime putty and white Portland cement in 2:1 by volume. Type D is a 10:1 mixture of lime putty and an artificial puzzolan produced from kaolin clay. All binders were mixed 1:3 by volume with sand aggregate, grain size 0.1- 1.4 mm. Test specimens by the size 40 x 40 x 160 mm were manufactured in steel forms and stored at 85% RH.

Some results are displayed in Table 2. The compression strength was measured after two and four weeks and after one year. Type C reached a maximum at 7 MPa already after four weeks, whereas it took 6 months for type A and B to reach maximum at 8-9 MPa. The fast hydration is a characteristic of C_3S, which is the dominant mineral in Portland cement. The slow hydration is typical for natural hydraulic lime, which mainly contain the mineral C_2S due to the lower firing temperature. It is often claimed that the late hardening makes the mortar more flexible, but the modulus of elasticity for the natural hydraulic lime and the Portland cement mixture are equal. The compression strength of type D was below 1.0 MPa, which is similar to a pure lime mortar, so the amount of puzzolan was probably too little to have any effect.

Table 2 Compression strength, modulus of elasticity and capillary water uptake for mortars under test.

Mortar type	Time	Unit	A	B	C	D
Lime type			NHL3,5	NHL5-Z	Lime/cem	Lime/puzz
Compression strength	14 d	[Mpa]	2.0	2.0	5.3	0.7
Compression strength	28 d	[Mpa]	2.4	2.5	6.8	0.7
Compression strength	153 d	[Mpa]	8.3	8.7	6.2	0.4
Elastic modulus	28 d	[Gpa]	13	14	11	2
Capillary uptake	28 d	[$Kg/m^2s^{½}$]	0.10	0.23	0.18	0.51

The mortars had different capillary water uptake. Type D took up water 5 times faster than type C, whereas type A and B were twice as fast as type D. When exposed to natural conditions of drying ad wetting, type D would probably take up more rain water than the other types. However, it is not clear if this is good or bad for the durability of the mortar. Specimens were mounted at the south wall 6 m above ground to test the performance in the local environment. The position was not sheltered in any way, and the specimens did not enjoy the thermal stability of the solid wall. After one year the type D mortar had suffered severe degradation and would probably fall apart during another season. The hydraulic mortars were not much affected, so it seems to be the right choice for a restoration mortar.

5 Conclusions

The conservation of the monument involves restoration of the mortar joints to ensure structural stability of the walls. The original mortar is probably mixed of lime from seashells and local sand from the beach nearby. Some samples contain hydraulic components, which may originate from volcanic particles mixed with the lime. The hydraulic effect is needed to ensure sufficient mechanical strength of the mortar in the areas with high compression stress. It is difficult to use a pure lime mortar for the restoration, because the lime tends to leach out before it is entirely carbonised. A natural hydraulic lime will probably resist the natural environment better. Further work is needed to develop a restoration mortar based on local resources.

6 Acknowlegdments

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Archaeological Department, Andras Mortensen, Director of the National Museum of the Faroes, Susanna Joensson, Conservator and Kim Clementsen.

7 List of suppliers

- Lime putty and premixed lime mortars: Skandinavisk Jurakalk A/S. www.kalk.dk.
- Natural hydraulic lime NHL3.5 for type A mortar: Nordisk NHL Aps. www.nordisknhl.dk.
- Natural hydraulic lime NHL5-Z for type B mortar: Skandinavisk Jurakalk A/S. www.kalk.dk.
- White Portland cement for type C mortar: Aalborg Portland A/S, www.aalborgportland.dk
- Pozzolan Metastar 501 for type D mortar: Imerys Performance Minerals. www.imerys-permins.com.

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III.13

Restoration and Conservation of the Renderings of Santíssimo Sacramento de Alcântara Church, Lisbon, Portugal

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Abstract This article presents the restoration process performed within the Church of *Santíssimo Sacramento* (Blessed Sacrament) in Lisbon, namely covering the repair of damaged renderings on the walls inside the church. In this article, the various types of renderings found in the church are identified, the nature of the principal anomalies explained and the mortars and materials used are described as well as the restoration techniques applied to enable and ensure their proper conservation. The work presented is a part of the project for the restoration of the Convent of Santíssimo Sacramento – Restauro dos revestimentos da Igreja, Sacristia e Cripta, that in situ, Conservação de Bens Culturais, has developed for the MNE - Ministério dos Negócios Estrangeiros (Ministry of Foreign Affairs), and for the IGESPAR – Instituto de Gestão do Património Arquitectónico e Arqueológico (Institute for the Management of the Architectural and Archaeological Patrimony).

1 Introduction

Ancient renderings that cover the surface of historic buildings are fundamental elements of the character and beauty of edified constructions; for beyond their protective function, they also serve a relevant decorative role. They are both a statement of past traditions and a testimony of form and style.

In recognition of their technical, historic and aesthetic importance, these layers must be preserved for future appreciation. Their maintenance requires the

application of traditional construction methods as well as the usage of compatible restoration materials and techniques.

2 Historic and Artistic Contextualization

The Convent of Santíssimo Sacramento was built in the 17th century under the reign of Filipe II of Portugal, III of Spain (1578-1621). This was one of the most famous and important of the Dominican convents in Portugal during this century [1].

Fig. 1 External view of the Convent.

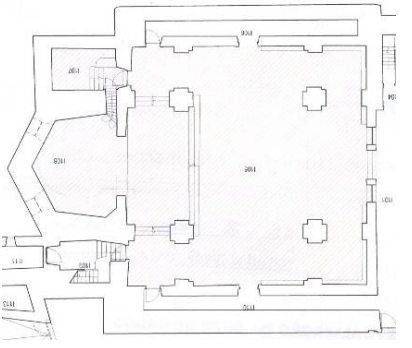


Fig. 2 Plan of the Church.

The Convent is located in Alcântara, Lisbon. It belonged to the Dominican order, who were particularly devoted to the cult of the Blessed Sacrament (Fig.1).

Having been founded on the 20th of October 1605, the Convent became occupied by nuns in 1616; in 1620 the church was demolished, perhaps for its lack of size and magnitude, prior to being rebuilt in 1635 under the third and last reign of a Spanish King; Filipe III of Portugal (IV of Spain). It must be pointed out that the construction of convents characterised the Filipino period in Portugal; a period during which the power of the church was dominant [1].

The church of Santíssimo Sacramento exhibits a unique architectural style (due to its resemblance in plan to a Greek cross), when compared to other convents on the Iberian Peninsula. It is attributed to a Master Frei João de Vasconcellos, the architect of another Dominican Church in Lisbon (São Domingos de Benfica); it is not known for sure who the real author of the architectural plans was, however the church of Santíssimo Sacramento does share similar traits to the *Convento das Bernardas Recolectas de Alcalá de Henares* in Spain [1], highlighting the possibility that a Spanish architect may have had an influence in the project.

The church, featuring a single nave and three altars facing east, was constructed using vaulted supports following a floor plan in the shape of a Greek cross contained within a square, which was lit by six lateral windows (Fig. 2).

The chapel, situated in the eastern arm of the Greek cross, was build upon a polygonal crypt or sacristy. This chapel housed an altar of gilded carved wood where the Blessed Sacrament's tabernacle and monstrance was placed for reverence.

The church underwent several transformations. Initially the church reflected the influence of Juan de Herrera and his work in El Escorial which marked the trends of a new taste of austerity and pragmatism in Mannerist architecture during the Spanish reign of Portugal, in what we have coined as *the first program* (17th century); this included features such as simple, classic and pragmatic embellishments; the use of monumental structure; suppression of the choir; approximation of the high altar; and a unique nave. In this church, faux stone techniques still feature in vertical projections, namely lime mortar renderings with false joints imitating grey and off-white granite stone, a feature very common in Madrid; granite being the main stone used in El Escorial.

During the reign of D. João V (1689-1750), constructor of the famous Basilica of Mafra, this church underwent a massive re-decoration campaign, which we coined as *the second program* (18th century) (Fig. 3). Here, decorative renderings made with Stucco and plaster-work, still present in the domes and vaults, simulate various types of ornamental Portuguese stones, thus embellishing the architecture with great beauty, colour and scenic impact, much in the styling of the French influence of Louis XIV (Fig.4, 5, 6).

Fig. 3 View of the ornamental stonework within the Dome of the Basilica of Mafra

Fig. 4 View of the polychrome stucco within the Dome of the Church of Sacramento.

Fig. 5 View of the vertical projections in stone within the Church of São Vicente de Fora.

Fig. 6 View of the vertical projections in ornamental plaster within the Church of Santíssimo Sacramento.

3 Interior renders or stuccoes

During the initial survey eleven different types of mortars were identified, corresponding to the various super-impositions of finishing layers applied during the different interventions the church was submitted to. Stone was never an option in Sacramento, even though the Lisbon area is rich in this material, with a wide range of colours available.

Fig. 7 Mapping of the polychrome studies conducted on various vertical projections and the main dome.

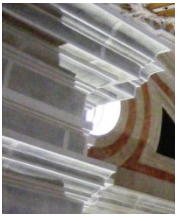
Fig. 8 Mapping of the polychromatic gamut on the lateral dome vaults.

Faux finishes are decorative renderings are based on the imitation of 'noble' materials such as certain rare and costly types of stone, using the application of paint and/or mortar to achieve the desired effect. These stuccoes offer a great architectural and compositional freedom to the builder, enhancing both the beauty and scenic impact of the site.

In Table 1 the present decorative renders within the church are described. Ongoing studies are pointing towards an important conclusion: in the seventeenth

century stuccoes were executed using mainly lime mortars, whereas in the eighteenth century gypsum was used as an additive with a lime to gypsum ratio of 4:1. However in the nineteenth century restoration campaigns, the differential between gypsum and lime had evolved to a 1:1 ratio.

Table 1 Overview of stuccoes of Sacramento

Plaster	Identification	Localization
Plaster 1 17th century	***Ashlar-work imitating stone with faux joints*** Faux ashlars by means of a corrugated surface and marking of the joint with exposed mortar. Large dimension aggregates of basaltic origin; Lime and charcoal powder paint over the corrugated area (ash colour); Lime barring over the faux joint. (2)	 Decoration of the Arches and Pilasters of de Church's nave.
Plaster 2 18th century	***Ashlar-work imitating stone with decorative fresco painting.*** Faux stone using volumetric lime render and a facing in equal parts of lime and plaster with faux marble imitation.	 Ground-level walls.
Plaster 3 18th century	***Decorative stucco -*** Sculptured elements hand-carved in lime stucco and plaster facing at 4:1; paint and gold finishing. (2)	 Decoration of the medallions and pendants.

4 State of conservation

The interior renders and stuccoes were in a very bad condition; their state of conservation being poor, with the supporting structure beneath plainly visible in many areas; urgent restoration measures needed to be undertaken.

The principal cause of deterioration was an excessive accumulation of water coming from various sources and in various forms, most notably as rain-water infiltration, excessive humidity and condensation (Fig. 8).

The building's abandonment for many years, and its usage as a warehouse and storage for military equipment largely contributed to its degradation, allowing for the accumulation of debris as well as rat and pigeon guano.

Beyond these, a number of other problems were identified, the greatest among them being the presence of oxidized metallic elements used in the fixation and support of the decorative elements in plaster; deterioration of these had resulted in fissures and fractures in, and the breakdown and detachment of the plasters. The presence of early restoration mortar containing Portland cement, was equally detected in various regions of the church, as were multiple paint-over's covering most of the decorative renderings, thus hiding the beauty and form of the original decorative work and contributing to their aesthetic degradation and deterioration. In this way, the principal anomalies observed in the renderings were: saline efflorescence, loss of cohesion, loss of adherence, detachment, open gaps, generalized dirtiness, painting over and previous interventions (Fig. 9, 10, 12).

Fig. 9 Degradation observed on the decorative layers.

Fig. 10 Detachment of the mortars, showing the brick structure.

Fig. 11 Juxtaposition of finishing, mural painting and whitewash over the original render.

Fig.12 Oxidation of the metallic structural elements

Fig. 13 Presence of salt and concretions

5 Restoration tasks

Definition of the interventions necessary to the restoration and conservation of the decorative stuccoes, strictly followed the basic principles of conservation and restoration according to international literature on the matter [3, 4]. The purpose of the restoration was to re-establish the physical and aesthetic equilibrium of the renders, allowing for the future conservation of all the existing decorative elements, in keeping with its historic value and its technical, chromatic and stylistic expression.

Equally important was the choice of materials used, and the care taken to ensure their compatibility with the original renders. To acquire the knowledge of the actual constitution of the renderings on site, as well as the chemical cause for the anomalies, we asked the LNEC (Laboratório Nacional de Engenharia Civil) to perform tests on site and in the laboratory to determine the compositional materials, cause of alteration, and the techniques of execution of the renderings, so

that we may know and chose the best methodology with which to perform the task at hand [5, 6].

All the restoration was undertaken by professionals specialized in the various areas of conservation and restoration (mural painting, decorative painting, sculpture, wood-work, stained glass and stone-work), and the technical orientation taken on by IGESPAR. Table 2 describes the different stages of restoration.

Table 2 Description of the treatments.

Previous treatments.			
Graphic and Photographic logging.	Stratigraphic analysis to locate the different layers of renderings.	Testing on site, sample extraction, lab tests (performed by LNEC)	Replacement mortar fabrication, for lab testing (with LNEC support)

Restoration	
Type of Intervention – Used materials and techniques	**Photographs**
Surface cleaning – dry cleaning with latex rubbers and soft brushes; wet cleaning with gel – carboxilmetilcelulose and sodium bicarbonate.	
Consolidating over loss of adherence - Grouting with industrial lime mixture (PLM - I®).	
Treatments of oxidized elements – Elements destined to be restored rather than replaced were treated with a rust converter; elements that could not perform their function were removed due to excessive deterioration, and those that retained a function were replaced by fibreglass.	
Fixation of the pictorial layer – located with an acrylic copolymer - Acril 33® and Klucel G according to needs.	

Removal of the juxtaposition of inadequate layers of whitewash and mortar – through mechanical means (chisels and mallets, scalpels, fibreglass pens and precision equipment in the areas with the most adherence, such as micro drills and vibrating pens).	
Filling the gaps and restitution of the decorative elements with a new mortar composed of slaked lime, silica sand (washed and graded), with similar colour and texture to the original, according to previous tests.	
Reconstruction and restitution of missing decorative gypsum plaster elements within the chapel.	
Pictorial reintegration – by an 'illusionist' approach or special techniques such as rigattino using inorganic pigments with limewash.	

Fig. 14 Before restoration

Fig. 15 After restoration

Fig. 16 Stuccoes before restoration.

Fig. 17 Stuccoes after restoration.

6 Final considerations

Igreja do Santíssimo Sacramento is an excellent example of the diverse stylistic and decorative solutions used in Portuguese architecture over the course of time. The church shows a multiplicity of different technical possibilities for decorative renderings, namely faux stone renderings.

During the restoration process of the church's renders, various distinct aesthetic solutions were discovered hidden beneath many coatings of gypsum layers and limewash. This kind of faux stone-work undoubtedly marks, with eloquence, a spatial, formal, technical and aesthetic transformation of the monument.

These renderings are architectural and artistic documentations that span various eras constituting a historic record of both the aesthetic values and technical solutions, due to the diversity of materials and techniques found in the restoration process. Their conservation will create a new critical language in the art history of monuments.

It should be mentioned that the accomplishment of this successful enterprise was only possible due to the multi-disciplinary collaboration of all the parties involved, without whom, none of it would be possible. The scientific knowledge gained through laboratory and on-site analysis of the mortars, and the studies and tests performed to find appropriate replacement mortars led to a proper definition of the conservation and restoration techniques appropriate to this site.

7 Acknowledgements

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III.14

Oscarshall (Oslo, Norway) - Case Study of the Restoration of a Natural Cement Rendered Facade from 1849

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Abstract Oscarshall was built between 1847 and 1853. It was the first Norwegian building to utilise Portland cement as a rendering material. The building had problems from its inception. Over the next 150 years it was continually repaired and redesigned to try to overcome its failings: internally it was damp and mouldy, externally it was cracked and leaking. The structure was thoroughly investigated using historical documents, scientific material analysis and a complete building analysis. Importantly the re-emergence of the knowledge of natural cements across Europe could be utilised to finally address the problematic render. The exterior was restored over three years allowing the understanding of the practical working methods and realistic solutions to the problems of restoring an old Portland cement facade.

1 The project at Oscarshall

1.1 The legal framework

Oscarshall is listed with Norwegian Cultural Heritage. Today it is the property of the Norwegian State and is placed at the disposal of the King. The administration is shared by the Royal Court and Statsbygg (Norwegian Construction and Property Management). The current restoration (2005-2009) included all aspects of the building, interior and exterior, as well as the grounds.

This paper refers only to the exterior work on the facade (2006-2009) of the main building.

1.2 The building of Oscarshall

Oscarshall, completed in 1852, was commissioned as a summer palace by King Oscar I and Queen Joséphine. It was designed by the Danish architect J. H. Nebelong (1817-71), who on a previous visit to Germany, became exposed to the new Romantic style as well as to new materials and technologies [1]. These were represented at Oscarshall in both the design and the materials. Traditionally built of brick and lime mortar, the render was specified to be Portland cement (PC) [2]. Nebelong must have believed that the cement's low hygroscopicity could prevent water coming in; a belief that very quickly proved incorrect.

Further more there are indications in the archives and on the walls that PC was not proving an easy material to work with [3, 4]. Imperfectly smoothed render can be seen as well as ongoing repairs performed whilst the building was still under construction (the PC binder matches but the colour varies). This situation was not helped when the Royal Bursar managed to take control of the project [5]. He ordered the use of a cheaper and lower quality PC and forced the work to continue into winter to reduce the cost [6]. Consequently deep cracks appeared in the render as a result of poor application, low quality materials and failure due to the harsh weather and exposed position of Oscarshall.

Fig. 1 Several different old cements with variable colours

After only one winter the first set of problems appeared [5], whilst there is no record of what or where the problems were, it resulted in the ordering of more PC, sand, bricks and decorative casts. Tellingly though, there were wooden roofs placed over all the terraces and balconies each winter [7].

1.2.1 Continuous problems

From here on there were continual problems with Oscarshall. In 1863, after only 10 years, it was considered too damp and unhealthy to live in. In 1873,

fungus, ascribed to a lack of ventilation, was discovered in the floors. The Royal Chamberlain, Holst, was annually awarded large amounts of money for Oscarshall from the Royal Exchequer, until his death in 1894. By 1908 the building was closed as render and masonry started to fall from the tower [5].

1.2.2 Previous repair

Repairs were carried out regularly over its 150 year history. These repairs included; filling cracks in the cement render (using whichever mortar was popular at the time) to try and stop the ingress of water, removal of fungus and infected wood, installing ventilation into the interior (there was none in the original design), replacement of failed render areas with lime/cement mortars and the permanent closure and roofing over the roof terraces. A central heating system was installed and used during 1910 - 1940.

There are limited records of what or where repairs were made and when but we know work was done in 1927-1928, 1952 and again in 1990-1992 [5]. At some point, rather than removing spalled bricks, the damage was hacked back, nails were driven in and 10-12 cm of mortar was laid on top. Other repairs were done without even removing the paint. A major repair in 1990 included chemical cleaning, stucco and render replacement and the impregnation of walls with a silicone resin before being painted with modern acryl dispersion paint (Drywall from Scanwall). It was believed that the humidity resulted from the cracks in the render, and as a solution the render was impregnated and all cracks were filled with a modern hydrophobic paint and filler.

In conclusion it seems that the majority of problems result from:

- the original design and usage of roof terraces and balconies without adequate drainage
- the lack of internal atmospheric control
- the poor quality brick and PC usage
- sporadic use and repair of the building

Fig. 2 The lime/cement repair seen on the left side and the original grey cement seen on the right.

1.2.3 Discussions

The cause of deterioration and how it could be solved has been much discussed. It has been questioned whether the PC render and the cement casts were the original or not [5]. It was feared that overall, PC is not compatible with the extreme Norwegian climate and the building's design (especially the roof terraces). It was therefore suggested that it would be safer to replace everything with a hydraulic lime prior to being protected with a layer of pure silicate paint. There was also some discussion as to where the damp came from; was it from rising damp originating from the ground, leaks or condensation?

1.3 The most recent restoration project

As a part of the current restoration, in 2006, a geo-membrane was installed all around the buildings to eliminate any penetration of groundwater. The pre-examinations included logging of the humidity in the walls, inspecting areas of fungus and recording the position and condition of iron beams and metal reinforcement. Finally 23 samples of render were taken to determine its actual composition.

1.3.1 The material analysis

The manufactured bricks (which were possibly local in origin) were laid in a traditional lime mortar with a good bond forming between the bricks and the old cement render. The thin section analysis proved that the original render from 1849 is PC but that there were also a few casts of Roman cement (RC) with a fine coat of PC. RC is a type of hydraulic lime burnt at a lower temperature than PC prior to being slaked [8]. Natural cement (NC) is a word used for early PC. The RC was, in the thin section-analysis was characterised by the lack of well crystallized phases of the cement clinker minerals (seen in PC) and its brownish colour, which originated from clay and iron compounds found within the impure limestone used for the lime burning. The cement clinker mineral, alite (C_3S), was absent because of the relatively low burning temperature used. Instead lumps and particles of slaked lime and unburned limestone were frequent.

The original casts were basically pure cement without any added aggregates, unlike the repairs [9]. The cement had all the characteristics of the primitive early cements; large, inhomogeneous cement grains with a grain size up to 1 mm, large well crystallized phases of belite (C_2S) and alite (C_3S), a relative low content of ferrite (C_4AF) and a high free lime content, seen as spherical hollows in cement grains. The large cement grains did not need as much sand so the mortar was relatively binder rich and had a very low capillary porosity originating from the very low water/cement ratio of the mortar used. The high cement content was responsible for the very high strength of the PC mortar. The colour varied from grey/brown to warmer grey/yellow and grey/pink.

There were 5-13 layers of paint. First lime paint, then oil paint and finally the three coats of modern acrylic paint with filler. Thankfully the silicone impregnation had not penetrated into the dense cement and could be removed with mechanical air-abrasive cleaning.

1.3.2 The cleaning

The cleaning was done with a combination of chemicals and air-abrasion systems. Torbo air-abrasion with quartz for the flat walls and JOS air-abrasion with calcite for the more delicate stucco work. The stucco work was first cleaned with chemicals to remove the organic paints and the JOS system used to remove the original lime paint.

1.3.3 The mapping and Physical Investigation

As soon as the walls were cleaned the mapping of materials and damage could start. The repair materials range from: hard, dark and grey to soft, light and white, often done without clearing off the old paint or addressing any underlying problems. The cleaned facade was mapped out by visual inspection, scientific analysis of removed sections and physical investigation using a hammer to sound walls and open up specific spots. This process also allowed for better forecasting of the extent of repair.

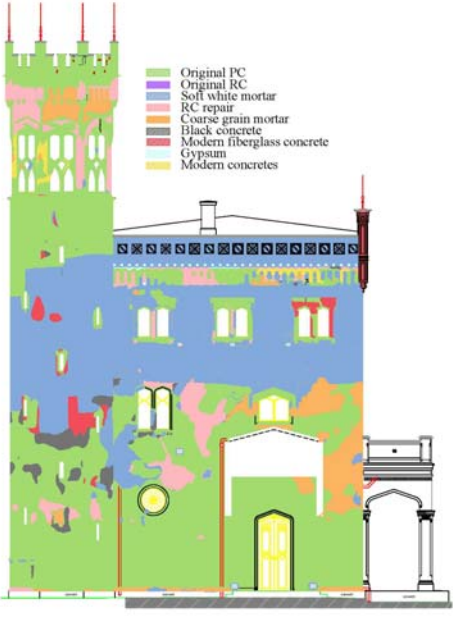

Fig. 3 All render above the 2nd floor and parts of the tower was probably exchanged in 1909-1913. Large parts of the corbel table had recently been exchanged with copies made of gypsum. The mapping is based on a visual investigation without analyses of the different repair mortars.

1.3.4 The extent of damage

Generally the PC and the RC has patterns of characteristic thin cracks which are traditionally thought not to be deep enough to allow in water [10]. Patterns of old cracks that had probably been repaired during the building process with old cements of slightly different colour, were also seen. In the very exposed area of the tower, systems of cracks probably due to movement, can be seen. Traditional weak spots such as the top of the arches and over openings also show cracks which are normally attributed to building movement and/or thermal movement; these are naturally worse on the most exposed walls.

All the fials (small towers) stand above the roofline and so are very exposed and badly damaged. The balconies have been repeatedly damaged by water penetration, as had the roof terraces prior to their covering. The corbel table on the main building had to have large parts completely replaced. This is logical as this corresponds with the floor level of the earlier open terrace. The same pattern can be seen at the top of the tower. This damage carries through into the interior of the building with obvious results.

There is little sign of salt damage to the brick core but massive areas of spalling behind and below damaged or cracked render do occur.

Fig. 4 The damage on the bricks underneath the open walkway in the tower

1.3.5 The methods used on flat walls

There was strong resistance to the idea of covering the walls completely with concrete because of the risk of the same problems reoccurring. Whilst some of these problems are hoped to be minimized through the use of internal climate control, the resistance to complete cover has resulted in the use of Natural Hydraulic Lime (NHL) where the render was replaced. In total the facade is about

1700 m^2. All bad render was removed: totalling about 50% of the wall area. The original flat areas considered sound were kept; the cleared off areas were backed with NHL 5 and finished with NHL 3.5. 5 tonnes of splatter coat and 25 tonnes of backing coat (equal to about 725 m^2) have been used in addition to the10 tonnes of mortar used to replace over 5500 bricks.

1.3.6 The methods used for the decorations

The decorative areas, being much smaller, meant there was less resistance to using NC in the backing, run moldings and the casts. Here practical tests were carried out on two different mortars; one RC from Krakow in Poland and one PC, Prompt Natural Cement (PNC) from Vicat in Grenoble, France [11]. There was no advantage found between the two except that Vicat were able to provide more guidance, a documentable history of use and all European certifications.

The original casts were removed if considered dangerous. If the casts were sitting well but heavily damaged, any old repairs were cut away and refilled in-situ. Run moldings were treated in a similar way with non-adhesive areas cut back to brick (and beyond) and re-run from brick. Any badly damaged but sound areas were again cleared of old repairs (many with layer after layer of repair) and retouched using PNC. These in-situ repairs were done on occasion onto old, very hard repair cements. This was felt to be acceptable as the PNC would adhere as easily to the newer repair as the original PC.

The aggregates used for the run moldings were 0-0.5 mm and the mix used was 1:1. The finish at the run-mouldings was pure PNC without any aggregates. Depending on the temperature, citric acid was used as a retarder. PNC requires specific handling [12], and is easy to test prior to mixing to minimize failure; it is hygroscopic so it is essential to keep the cement in sealed plastic containers on the scaffold and the short initial curing demands a controlled regime when running long sequences. The layers were thrown on wet on wet and required constant watering. The surface will discolour from the iron content during the curing, however this can be corrected by using a surface coat of paint. The PNC was used both for the splatter coat, the backing, and the finish.

1.4 Problems during the work

The main challenge came later in the project once the winter set in. In the autumn the current and recent work started to show unusual amounts of early cracking which needed investigation. Concerns regarding the range of temperatures across the area were already being raised. It was a south facing wall yet winter was drawing on and nighttime temperatures were dropping dangerously. Work was temporarily stopped as the temperature reached freezing and a delay occurred prior to the installation of a heating system: such a system is a Norwegian phenomenon which involves the complete covering of the scaffolding and the introduction of hot air blowers to increase the general

temperature to over 5°C. The heating system proved more a hindrance than a benefit as although the temperature remained relatively constant, the humidity varied dramatically, causing serious concerns about the curing of the work; when the heating failed for any reason, the prevailing temperature dropped to -20°C causing the freezing of the young render. This continued to be a problem for the remainder of the project.

Another problem was ghosting, caused by the difference in hygroscopicity between the mortars. This was and still is, highly visible after rain. Solution of this problem could either come from within the application of the fine coat or the paint systems over it.

Fig. 5 The challenge is to hide the "ghosts". Here trying out different finishes.

1.5 The final result

Fig. 6 Detail of the finished result

Overall Natural Cement was successfully introduced into a high profile restoration project in Norway. It has been proved to the Norwegian state bodies that NC is a viable product. The issues that still need to be addressed are; the problem of adhesion of a new fine coat over an old cement render, and how to mask the transfer from the old to the new mortars, often seen through the limewash with changing humidity ("ghosting").

It is too early to give a final conclusion but the repair has survived the first very cold winter without visible damage. It is hoped that having also eliminated other likely sources of humidity in the construction, that Oscarshall will remain stable.

Notably work is currently being undertaken in Bergen on another building by the same architect using similar original materials, however this building shows far less damage; this is probably due to the buildings continuous usage over its whole life and a less demanding building style that does not use roof terraces or balconies.

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III.15

Causes of Decay of the Aveleiras House Decorative Plasters (in Torre de Moncorvo)

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Abstract This paper presents historical and characterization studies undertaken to: a) clarify technical interpretation of lime-stucco and plasterwork by historic architectural treatises, and b) better understand the intentions of the early designers and plasterers: the used proportions and sizing of materials, the coverage achieved using different plasters, the nature and composition of the materials, and the causes and forms of decay of stuccos and plasters. Historical studies are important for determining the most effective courses of actions with regard to the preservation of cultural heritage, as respectful as possible to the original nature and materials of the historical buildings. The present paper includes the history of the stuccos and plasters as well as the characteristics of the materials used in plastering and the tools to model in relief. In addition, were carried out an "in situ" inspection and laboratorial analysis, as TGA, XRD, EDS and SEM on decorative and plain plasters from Aveleiras House. As a consequence of this study it was possible to quantify the percentage of binder in the mortars and to identify the causes of decorative plasters decay, suggesting their bio deterioration.

1 Introduction to stuccos and plasters of 16th - 19th centuries

Venetian buildings often have walls covered with beautiful stuccos applied above their white surfaces. During the 16th century, with the coming of the Renaissance and Baroque styles, the *barrel vault* or the *groin vault*, saw a resurgence in popularity. These were decorated with double or triple blades of ceramics and thin pieces of stone that were covered in a plaster consisting of lime and fine sand, over which was applied a final finishing coat. As described by Philipert de l'Orme, in his treatise of 1561, a further method of decorating vaults

was to use plastered lathwork (Fig. 1a). The lathwork was fixed in a wooden structure composed from a double stave of wood tied with wooden pins to form the skeleton of a vault formed from the intersection of ogival (gothic) arches [1].

Fig. 1 a) Wooden vault structure of support of a plastered ceiling (De l'Orme, 1561); b) Ceiling of Chapel Sacristy, 16th c., Aveleiras House, Torre de Moncorvo (2008); c), e), f): Plasters of Pombal Palace, Oeiras, 18th c. d) Running mould for the execution of interior cornice (SEGURADO, J, 1949).

Stuccos, until the 19th century, were applied over the rough-cast of masonry or over rendering coats applied to the lathwork of partition walls or ceilings. The renders were of a mortar composed of lime and gypsum. When gypsum was not available, marble powder, chalk, or white of Spain (calcite), was used. Such renderings provided a smooth surface to walls, ceilings and columns, and could also be used for elements with a variation in thickness such as cornices, mouldings and other decorative elements.

Antique *lime plasterwork* consisted of three layers. The *"rendering coat"* (the first layer) was made from lime/gypsum and sand (1:2) or lime/gypsum and a pozzolana and was coarse and rugous, with a varying thickness of 7-10mm; the finish of this layer could either be a simple plaster or an ironed plaster. This layer of plaster was applied with gauging trowels of different dimensions, busks, drags and steel small tools, according to the delicacy of work. The rendering coat was used for coring out the cornices or mouldings or was applied to the interior substratum of smooth plaster walls and ceilings. The next layer, the *"floating coat"* was a mixture richer in gypsum or lime, with fewer, finer aggregates in a ratio of 1:3; for use in mouldings and decorative elements, straw, rope, hair or horse-hair was added to increase the bond strength between layers. The floating coat was applied in a thin layer, between 1-2mm. If the plaster surface to which the rendering coat and the floating coat were applied was an exterior surface, then both these layers must be made entirely of a hydraulic lime mortar. The last layer,

applied in a thickness of 1-3mm, was the "*setting or finishing coat*". This comprised either of lime/gypsum in a paste, lime/gypsum in a paste with coloured powdered marble, or simply a gypsum paste. The plaster obtained as lime in paste or milk of lime, could be ironed or polished. A mixture of lime and sifted marble powder in equal parts, made a solid, durable and shining plaster. When no marble was available chalk or gypsum were used.

The decoration in bas-relief and in framing (interlaced, leaves, laurel wreath), was realized with little salience. The outlines were drawn to a natural scale and were pricked and outlined in coal dust, a strong plaster was then used to fill in the shape of the decoration and fixed bossed nails were used as additional supports to the plaster. The decoration, which was applied to a pre-plastered surface, was shaped and wetted intermittently to prevent it drying out quickly [2].

The *gypsum plasterwork* was created equally in three layers with a gypsum base. The third and final layer was a stucco made from a pure white superior gypsum which was passed through a sieve of fine silk prior to mixing. The plaster was kneaded in water where it was dissolved with Flandres glue. For a white plaster, colourless fish glue could be used; where coloured plasters were to be used, varied glues, of animal or vegetable nature could be used. The glue increased the adherence of the plasters to their support, and reduced the set of the plasters making them easier to work. To colour plasters, coloured pigments were diluted with glue in water.

To create a marble imitation (Italian "scagliola") the pigments to produce the base colour were added to the last layer (Fig. 1e). To create the marble veins the colours were diluted with glue in water and were placed in moulding cakes of different colours to produce coloured pastes that were then cut into strips and introduced into thin furrows in the fresh plaster. The ironed polish seen on some plasters was produced either with plaster and glue, wax and soup or paste of lime and wax, all with different textures. As soon as the plaster was dry, the polishing with a pumice-stone and water or with jasper or crushed chalk, or by rubbing with a felt lightly covered with wax, was performed. The brown or black plastered surfaces could be decorated with mouldings representing flowers, fruits, arabesques and human figures [3].

The *ceilings of plastered tight lathwork* were formed from laths constructed in a trapezoidal section which was nailed transversally to the inferior surface of the support beams. The laths were fixed by the narrower bases and their greater bases were spaced 1cm apart. The inferior face of the laths must be perfectly horizontal in plan to allow them to be wedged tightly together in case they were dropped. The *rendering coat* consisted of a mortar of lime, sand, and sifted gypsum (between 1:1 and 1:2) in a layer 0.04m thick, placed 0.01m under the inferior face of the laths. The *floating coat* (0.02m thick) or "the browning plaster" – of gypsum/lime and dark gypsum (gypsum, air lime in paste and fine sand with the ratio 1:2:1, or 1:1:4), or lime and marble powder– was applied with the laying trowel or with the hawk upon the dry filling layer. The surface was left rugous in order to facilitate the adherence of the next layer. The mortar of the *setting coat*

(0.01m in thickness) consisted of gypsum or lime plaster (gypsum, lime mortar and thin sand with a ratio of 1:3) or lime paste and marble powder to which a setting retarder could be added. The surface was caressed with felt-floats and was rubbed lightly with a damp linen cloth [4] (Fig. 1d).

2 Study Case – plastered ceilings of Aveleiras House

2.1 Diagnosis of identified anomalies

Fig. 2 a) Decorative plasters, in the "Adam Style", of English influence; b) cracking and unfastening of parts of the plaster; c) repair suggestion of plastered ceiling (CAVALHEIRO Photos; 2007)

The anomalies presented in this chapter were identified in a case study of the early 19th century decorative ceilings of the main floor of Guerra's House (of Aveleiras), in Torre de Moncorvo [5] (Fig. 2).

The building is in a poor state of conservation, with collapsed roof sections creating subsequent degradation to the interior subjacent zones. The ceilings and lath work present damages including: cracking, standing up and putrefaction of plaster; dirt stains, biological colonization and mould; fissures and disintegration of the mortars; and the absence of support laths for the plaster. The ceilings of plaster, which consist of wooden laths nailed to the structure of the roof, were affected by deformation of the supports owing to the progressive camber of beams caused by water retention.

This structural phenomenon created deformation of the ceilings which in turn produced cracking, loss of adherence of plaster and loosening of the plaster. The occurrence of water infiltration from the roof or floor, produced the putrefaction of the laths, the oxidation of the nails of fixings and volumetric expansion which led to the further decline of the plaster ceilings. The difference in behaviour between the masonry walls and ceilings, resulted in the appearance of cracks in the connexions between those constructive elements, namely in the coves. The poor execution of the different plaster layers, due to inadequate soaking during

application, led to the presence of quick lime; this combined with a deficient mix design has resulted in weakened areas and the loss of adherence between the different layers of plaster and the appearance of fissures.

3.2 Laboratorial analysis of the plaster from Aveleiras House

a b c d

Fig. 3 Samples of plastered ceilings from Aveleiras's House: a) Sample colonized with algae of green colouration; b) Sample from a ceiling; c) Decorative motive; d) Sample of a cornice cove.

Samples of plasters and mortars from different parts of Aveleiras House were submitted for the following analyses: *thermo gravimetric analysis* (TGA, by *TA Instruments/SDT2960*), to quantify the binder percentage in the mortars; *x-ray diffraction* (XRD, by *PAN'alytical, X'Pert Pro*), to study the mineral components of external surfaces and cross sections of the mortars and to identify altered minerals and soluble salts; *energy dispersive spectroscopy* (EDS) in conjunction with images of the sections obtained by *scanning electron microscopy* (SEM, by *Philips-FEI/Quanta400* with EDS), to characterise the crystalline structure of the materials, detect modified minerals and salts, detect biological agents like algae and lichens, to determine the proportions of different components, and to detect fine fractures in the stratum.

The results obtained through *mineralogical analysis* of one sample of plaster using *XRD*, indicated that the mineralogical components prevalent in sample are calcium sulphate ($CaSO_4.2H_2O$) (69%) and calcite ($CaCO_3$) (31%). The samples were also subjected to *TGA* to quantify the binder percentage in the plasters (Table 1 and Fig. 4). *EDS* analysis of samples A, B (Fig. 5) and D, indicated the presence of quartz (SiO_2) and traces of dolomite ($CaMg(CO_3)_2$), in samples A and D. The binders of these plasters are gypsum and lime and the aggregates are essentially of a calcareous and siliceous nature. The plasters have a low content of soluble salts, (less then 1%). Sample A, colonized with algae, showed a superior percentage of K, Na, and S ions, and oxides of Na_2O, MgO, Al_2O_3, SiO_2, SO_3, K_2O, Fe_2O.

The micro-analysis obtained by *SEM* on a cross section of a sample of plaster without biological colonization (Fig. 6 -Micro-analysis 1) indicates that the initial layer of plaster closer to the support had coarser aggregates and less binding material than the finishing layer of plaster. The micro structural analysis of the exposed surface of the plaster sample, (see Fig. 6 - micro-analysis 2 and 3) revealed prismatic and acicular crystals of calcium sulphate, and scaly and rugous

particles of small calcium carbonate crystals, which present exfoliation planes of triturated calcareous stone but do not present any specific morphology of micronized calcium carbonate.

Table 1 TGA analysis of the samples, in wt% of quicklime or gypsum

Samples	A	B	C	DI	DT
Quicklime (CaO)	14.06	8.50	18.65	5.52	7.64
Gypsum ($CaSO_4$,1/2 H_2O)	49.72	78.35	49.38	23.25	36.36

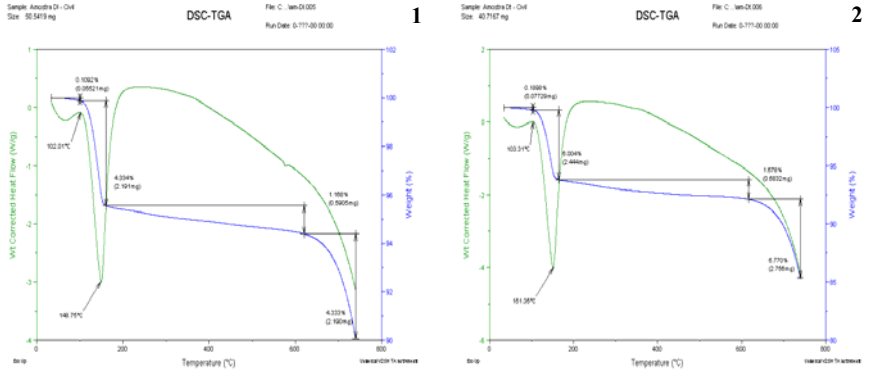


Fig. 4 Thermo-gravimetric Graphs of sample D: 1) DT, surface of plaster; 2) DI – internal layer of plaster from near the support.

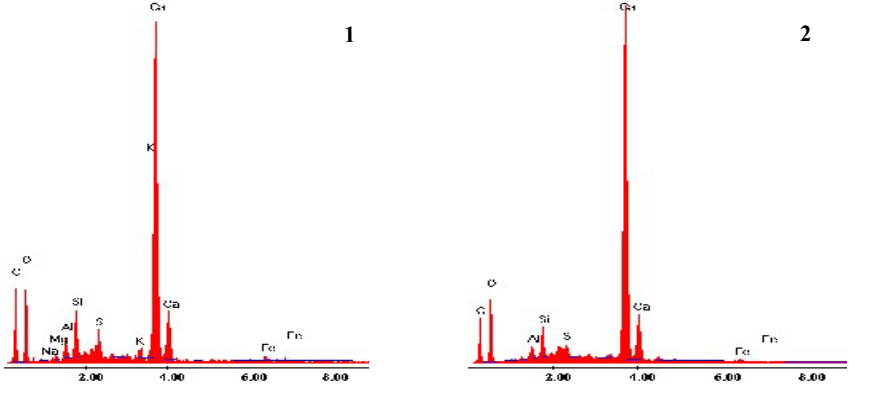
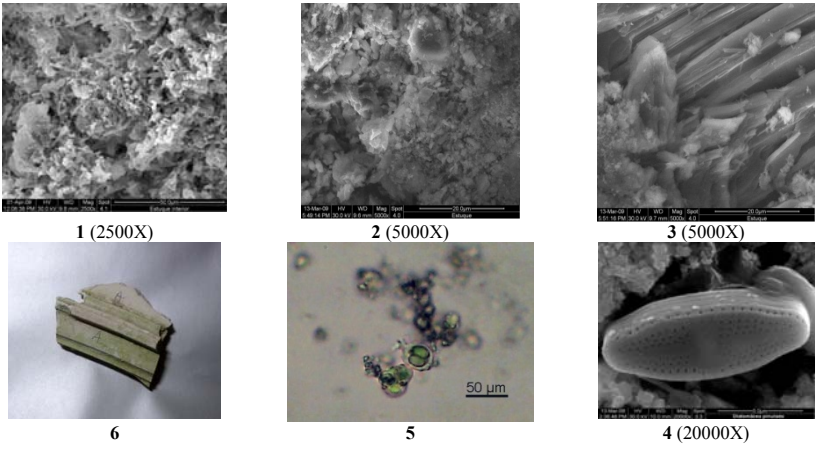


Fig. 5 Spectra of chemical analysis of the plasters of Aveleiras's House; 1) Sample A, external surface of the plaster (with algae); 2) Sample B, external surface of the plaster (without algae).

The microscopic image of samples of plaster with algal colonisation showed biological colonisation was more prevalent in the more humid areas of the ceilings. The microscopic image in Fig. 6 corresponds to the visualisation of a

sample of plaster which contains green algae. The images obtained by *SEM* on samples of plaster with algal colonization, (Fig. 4), indicate the presence of algal Diatoms of two orders, centric (or *Centrales*) and pinnate (or *Pennales*). They are, therefore, unicellular organisms which have one carapace or siliceous wall denominated frustule, localized externally to the plasmatic membrane. These structures, left by the algae, are seen on the surface of sample A.



1 (2500X) **2** (5000X) **3** (5000X)

6 **5** **4** (20000X)

Fig. 6 *Micro-analysis*: 1) Sample B, cross section of surface of plaster. 2) & 3) Sample A, surface of plaster, deposited algae having been removed. 4) Plaster colonized by algal diatoms. *Microscopic image***:** 5) Visualization of sample showing the region which contained green algae (Chloroficeas). 6) Sample A with algae.

3 Discussion / conclusion

The 19th century decorative plastered ceilings of Aveleiras House have distinct layers of lime-based mortars, covering the *Castanea Sativa* lathwork, nailed to the supporting beams of oak, chestnut, or pine wood. Thin section analysis of those plasters showed the difference in aggregate/binder ratio and aggregate size. The innermost layers closest to the supporting lathwork, have coarser aggregates and a higher aggregate/binder ratio, in the order of 3:1, similar to the mortar compositions of the historic architectural treatises (sand, gypsum and air lime, with 4:1:1 ratio). The outermost layers have very fine aggregates and higher proportions of binder, with 1 part of aggregate to 1, 2 or 7 parts of binder. Rondelet states that the ratio of the *setting coat* must be of 3 parts of lime mortar and sand to 1 part of gypsum; however, he believed that aggregates never exceed the binder in this layer.

The plastered ceiling, represented by sample A, contains 2.80% of Magnesia which has a destructive effect in the plasterwork; sample A could be broken into

pieces by hand easier than the other samples analysed. The higher proportions of K and Si in this plaster indicate the probable employment of silicate of potash to increase the hardness of the mortar, a common practice in the 19th century [6].

The lack of bonding between some areas of the plasters to the supporting lathwork indicates that the innermost plaster in contact with the wood laths is separated and totally disintegrated. Due to the decayed roof, the wood and the plastered ceiling have absorbed infiltrated rain water, which can only escape through evaporation and osmosis through the plaster of high permeability. The consequence of the presence of this stagnant water is the solubilisation of the plasters and their disintegration. This decay process is intensified by the development of microorganisms in the deteriorated areas. They inhabit fissures and holes in different layers of the plasterwork, leading to the decrease of its cohesion and consistence and a consequent loss of bonding. Algae have also contributed to the disintegration of the decorative plasters, as is represented by sample A. Many of the porous and damp surfaces of plasters are dominated by communities of algal *Diatoms* which produce H_2CO_3 and organic acids, which promote carbonate dissolution in the algae/plaster interface.

4 Acknowledgements

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III.16

Sgraffito in Portugal: a Contribution to its Study and Preservation

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Abstract This article intends to provide awareness to the particular value of sgraffito in architectonic surfaces and alert towards the need to safeguard its aesthetical and material authenticity. Recent research led to the discovery of an unknown and wide presence of sgraffiti in some urban and rural Portuguese ancient architecture; most of them are now at risk, since they are often forgotten or confused with other mural decorative techniques. One of the most important results of our research on sgraffito (developed under the scope of a PhD in architecture on the subject "Conservation of the architectural surfaces in Alentejo") is the fact that the majority of the listed sgraffito ornaments have been painted over so many times, that today we can hardly identify its original aspect, its formal and chromatic value or its textures. We will describe the sgraffito's concept, application techniques, the risks it faces, emphasizing the need to change intervention methodologies in order to promote its safeguard in urban areas and rural landscapes.

1 Introduction

Usually the technique of architectural ornament called sgraffito is seen as an exclusive manifestation of certain European regions, where it appears regularly. Italian renascence sgraffiti, as well as Prague, Segovia and Barcelona are well known.

In Portugal, there is also a growing recognition of the architectural heritage value of the sgraffito as decorative mural technique, mainly in the academic field and research (Figs. 1 and 2).

Although traditionally sgraffito is a very ancient technique it is not recognized and identified as a specific concept and it is commonly included in an

undistinguished group of architectural decorations, which includes stucco, decorative plasters, graffito or mural painting. Interventions practices are often carried out without having in mind the specificity of the sgraffito technique and the heritage value of this specific decoration.


Figs. 1 and 2 A black and white sgraffito in Quinta da Amoreira da Torre (Montemor-o-Novo) and Amieira do Tejo

Most of the existing sgraffito are currently spoilt or hidden by subsequent interventions. Many of them have not yet been identified or recognized as an element of identity or a heritage reference.

There are broad legal orientations for urban polices for preservation, although they are not specifically targeted to the conservation and restoration of the sgraffito.

Because we believe this situation is slowly changing, we would like to call the attention of all stakeholders (universities, municipalities, civil society, owners and building constructors) for the value and the at risk situation of this particularly inheritance, emphasizing the necessity of safeguarding its material authenticity.

2 Sgrafitto at risk

Our research on graffiti in Alentejo has highlighted that the majority of the listed and studied sgraffiti ornaments have been painted over so many times, that today we can hardly identify its original aspect, its chromatic values or its textures (Figs. 3 and 4).

Like any architectural surface using lime mortars, sgraffito has the ups and downs of this type of covering that, due to its own nature. Sgraffito functions as a protective layer and, therefore, is more prone to repairs, surface alterations and changes in its aesthetic presentation. Especially outdoors, it is difficult to find a sgraffito that has not been repainted and that still maintains its original aspect and the decoration of façades is hardly perceptible (Fig. 5).

Many of these actions of painting corrupt and alter the image of the building and the urban set and transform, for example, the city of Évora into a white and ochre city, despising all its previous polychromatic wealth.

The unfamiliarity with the original technique of sgraffito by craftsman and by the public in general has contributed to this adulteration with the consequent loss of aesthetical and historical values of the building as well as its authenticity.

Figs 3, 4 and 5 Sgraffito in Redondo, Almodôvar and Alter do Chão

We can identify the causes of the non-recognition of the value of sgraffito, into four clusters:

1. a lack of expertise in maintaining or repairing sgraffito technique;
2. confusion or a poor knowledge of other decorative techniques similar to sgraffito like graffito, stucco or decorative plasters simulating stone or brick masonry;
3. a deficient legal protection and absence of preservation policies;
4. a gap between the academic conservation praxis and the world of construction.

Therefore, we begin by describing what a sgraffito is.

3 What is a sgraffito?

Sgraffito is a technique of incised mural decoration applied to beautify walls of buildings. It can also describe an incised decorative technique on pottery. In the context of this paper the term is applied to the decorative technique used in walls [2 - 4].

Sgraffito consists of scratching a design into plaster before it sets, using a fine point metal tool, in order to reveal the colour and texture of the underlying plaster. Once the top layer, usually white with a fine texture, is scratched out, the plaster layer beneath, usually of a different colour and texture, is revealed (Fig. 6). The bottom layer uses plaster tinted in contrasting colours, made through the addition of coal or burnt straw (for gray and black colour – Fig. 7), or brick powder to

make it reddish, or even by using different types of sand to achieve a yellowish coloration.

The colour of sgraffito stands out, especially, due the effects of light-dark obtained by different textures and shadows. The result is an expressive plastic game of "*chiaroscuro*". This technique links both drawing and painting skills, and also requires a deep knowledge of plasters.


Figs 6 and 7 Doing a sgraffito in Mértola, a black and white sgraffito in Sabugueiro (Arraiolos)

In order to clarify the concept of sgraffito it is important to understand its origin.

4 The origin of sgraffito - First applications

The origin of sgraffito is diffuse and at times mingled with the origin of graffito or, according to some authors, with drawing itself. Despite often unconfirmed, there are several thesis about the origin of sgraffito.

Ramon Nonat Comas's [4] research on Barcelona's sgraffito formulates the hypothesis that sgraffito technique is as old as the genesis of all the arts. If the word engrave etymologically means marking or ornamenting surfaces with incised instruments, it is very likely that sgraffito's origin is the same of the oldest arts, as drawing, painting and modelling.

However, such hypothesis is refuted by the architect Jaume Espuga Bellafont [5] in his PhD's thesis about sgraffito and plaster. According to this author, notwithstanding the fact that the technique of sgraffito uses the basic idea of drawing, one cannot claim that wood engraving is sgraffito.

Since the sharp tool used in graffito's technique (Fig. 8), when pressed against the surface causes a furrow with a certain depth and, consequently, produces waste material that is removed, makes this technique resembled to sgraffito. If the wasted material resultant from both processes is valued as the predominant feature, both techniques turn out to be very similar, namely when its origins is in question.

On the other hand, if we stress the fact that in sgraffito the removal of the outer layer of plaster, while is still fresh, intends to reveal the coloration of the plaster underneath, as an aesthetic perception (Fig. 6), then both techniques have distinct evolutionary paths. In this sense, sgraffito can only be tracked in Roman Empire while graffito is surely pre-historic.

Nevertheless, according to Bruno Gandola [6], the two-coloured sgraffito is dated earlier, since such technique was found in pre-roman pottery. In this case the sgraffito decoration was produced by immersing of the ceramic artefact in a liquid soil with a different and contrastive colour. Afterwards, this layer was removed with a thin and sharp knife, stiletto, made of metal, wood or ivory. This incisive decoration produced "beautiful artefacts in Greek art, with fine figures obtained by a single furrow, whose lines perfectly define the folding of the costumes, embroidery, jewellery, armoured helmets and footwear" [7, p 20].

Others hypothesis are questioned about the origin of sgraffito: if sgraffito is a decorative technique that reveals great simplicity, isn't it possible that there could be more than a single origin?

Leopoldo Torres Baldás [8] relates the Moorish "*yeserias*" (gypsum plasterwork) work with the concept developed in Sassanid Persia. In both cases the works made from gypsum, when not produced by moulding, were manufactured with fresco technique. In this sense, the gypsum was cut with a bevel or chisel in order to carve a relief decoration. The similarities between this technique and sgraffito are clear although "*yesarias*" allow a more complex decoration (Figs. 9 and 10).

Fig. 8 An example of graffito technique produce by vandalism; **Figs 9 and 10** Yeserias in Alhambra, Granada, Spain.

Such resemblances allows us to question whether sgraffito origin can or cannot be traced as a technique which had its origin in the Andalusian "yeserias", made in fresh (fresco) and "in situ". Curiously, one of the oldest Hispanic-Moorish sgraffito (with double-layer) was revealed in Elvira's Medina (Granada). Underneath the wall's plaster a geometric decoration was found: composed with lines, squares and circles, in dark red-coloured plaster over a white background. Rafael Ruiz Alonso [9, 10] reinforces this hypothesis with archaeological

discoveries revealing the previous existence of a double-layer sgraffito before the great Segovian sgraffito productions.

Another hypothesis, traditionally formulated by Segovian scholars, is that sgraffito is the result of the evolution of plaster work on joints on masonry walls. This joint work (with distinct aspects whether it was salient, plain or re-entrant) is named in Castilian as "*rejuntado ou encitado*", meaning the effects of joints in non-plastered masonry - jointed or seamed (Fig. 10). Such definition is used for the portion of mortar which seals and fills spaces in brickwork or masonry joints. This mortar has functional purposes; however, it can also be ornamental, for instance, when it is modelled in high-relief.

Fig, 11 The effects of the plaster work on joints in a non-plaster masonry walls. This could evolved towards sgraffito; **Figs. 12 and 13** Sgraffito in Segovia, Spain

Another aspect that led us to the same conclusion is the fact that, in many joints, a bit of mineral slag is applied on the mortar while it is still fresh (Figs. 11 and 13). Such operation diminishes the risk of cracked mortar in these joints. Visually, there are many resemblances between this technique and those found in primitive Segovian sgraffiti, where the use of a slag can be seen today.

According to the idea that sgraffito might have its origin in the sealing of the masonry joints, we may presume that probably it could have evolved into two distinguished techniques: the single-layer (Fig. 12) and the doubled-layer sgraffito (Fig. 13).

Single-layer sgraffito technique may have its origin when mortars cover the entire masonry leaving the more salient stones unsealed. Afterwards, the render was partially scratched, leaving de mortar joints flat with relatively regular outlines.

On the other hand, the masonry's "*encintado*" (Fig. 11) might gradually become into a more salient joint and later into a doubled-layer chiselled or bevelled sgraffito (Fig. 13).

This theory is also questioned, in Portugal, by Correia de Campos [11], who, based on Torre Balbas's theories, suggests that this kind of decoration has an Arabic origin.

In spite of these evidences, it is after the 14th century that sgraffito is widespread in Italy, especially in Tuscany and it is only after the Italian Renaissance that sgraffito became acknowledged as an art. It became a real fashion in decoration facades in Rome, during the 16th century (Fig. 14).



Figs. 14, 15 and 16 Rome, Castelo de Vide and Elvas in Portugal

In Portugal sgraffito did not reach the splendour of the Italian Renaissance. Although the majority of sgraffito's works are anonymous, there are cases worthy of classification (Figs. 15 and 16).

The lack of specific measures and legal protection of this decorative technique is due to the non recognition of its heritage value and to the adulteration of the sgraffito technique.

5 Heritage value of graffito

Since sgraffito in facades is a decorative technique made with external plaster, some of its values, as the dual colour variation and the aesthetical tension given by different textures and colours, which are intrinsic to the nature of this mural covering, must be preserved.

The choice of texture, colour, existence or absence of ornaments reflects a coherent relation with the building conception. These are the most direct and recognizable expression within an architectonic and urban image. Knowing and identifying these architectonic and decorative surfaces is relevant for understanding and reading architecture and the city, both from an historical and artistic point of view, as a witness of its aesthetic and technological evolution.

Although the current conservation culture assumes as a *sine qua non* condition, the conservation of the substance as a cultural certification, interventions in sgraffito, tend to use solutions derived from industrial building techniques rather than from preservation criteria. Quite often sgraffiti are inadequately recovered because there is a strong unfamiliarity to its particular values and to its specific manufacturing techniques. These are due to the lack of professional specific training of workmen and architects, to the over-valuation of economic compared

to cultural heritage values, to the undervaluation of sgraffiti and to the insensibility of players. The application of (re)painting layers invert the syntax's (what was dark becomes whitish, what was whitish becomes a new and often stronger coloured) causing loss of the building aesthetical and historical values and, ultimately, loss of authenticity (Figs. 17 and 18).

In Portugal, the protection of Cultural Heritage is defined by Law 107/2001 of September 8, and other legal regulations. According to its particular cultural value a building can be classified into one of three categories: national monument, building of public interest and building of municipal interest.

According to this national Law any restoration, conservation, consolidation, modification, reintegration or demolition work in any classified building or in the surroundings needs: a project (made by an architect) that has to apply for a binding evaluation by the Portuguese Institute for the Architectural Heritage (IGESPAR and DRCultura).

Moreover all intervention in buildings needs to be in agreement with municipal management plans that might define specific rules for the preservation of architectonic surfaces.

We could conclude that the protection and conservation of all architectural surfaces, decorated or not, are safeguarded by law and regulation. But this it is not the case, since there are always exceptions.

For example in Évora if the building is in bad conditions of conservation with the risk of collapsing, regulations may allow demolition and rebuilding of the whole façade. Moreover, in case of intervention on the protective layer of a facade, painting is often proposed as a solution, instead of a lime wash. This solution is also applied to sgraffito and other decoration plasters (Figs. 17 and 18).

Figs.17 and 18 Évora, before and after the intervention (it was applied a painting layer that inverted the syntax's)

The Historic Centre of Évora was inscribed on the World Heritage List in 1985. In 2004, our research [3] showed that 80% of sgraffiti were painted or covered by painting. This solution, which has been applied for more than 25 years, has no theoretical support and ignores completely the authenticity value, expressed in recommendations such as the Venice Charter (1964), the European Charter of Architectural Heritage (1975), the International Charter on the Protection of

Historic Cities (1987), the International Charter on Cultural Tourism (1999), the Charter of Krakow (2000), the Recommendation on the Safeguarding of Sites (1976) and Nara Document (1994).

Recently, the situation seems to be slowly changing, though sometimes depending on city municipality individual policies. Initiatives such as the photogrammetric survey of the facades (in progress), the very recent conservation of architectural surfaces project, funded by the Tourism Fund (intending to replicated the good praxis carry out in a street named "Rua 5 de Outubro"), the replacement of all air infrastructures, like cables, pipes and fittings (fixed on the facades) for buried piping in order to preserve the urban image, and the continuation of the financing program *Lime wash facade* (Casa Caiada), are welcomed, but have not been sufficient to contribute to the preservation of sgraffito (Figs. 19 and 20).

6 How to preserve?

Heritage conservation is a cultural choice and action depending on the reflection and understanding of heritage values. Fernando Henriques, in a meeting on conservation in 1994, highlights the importance of this idea with the sentence "heritage conservation is a cultural activity with technical implications and not a technical work with cultural implications" [12, p.70].

To stress the concept that any action in heritage should be based on knowledge, it is urgently required to change this "fashion" of painting sgraffiti and to value the authenticity of the material. In sgraffito it is important to safeguard the notion of material authenticity whilst preserving the different layers. It requires respect for the historical value of the surface, its stratification, its aesthetic aspect, as well as of the technology used to produce it (Fig. 21).

Since the result of interventions on sgraffiti depends not only on academic expertise and on previous studies (conservation project) but also on the culture of policies, programs, town planners, operators and designers and should involve all the stakeholders in the community. Plans to manage and monitor existing sgraffito and other lime decorated surfaces need to be implemented; funds to safeguard would surely have impact on local economy, like cultural tourism. Professional qualification and certification should be required for any intervention on decorated surfaces.

Campaigns, workshops, awards, partnerships with schools or curriculum designers in order to change and promote preservation of sgraffito should be developed in the whole community.

Figs. 19 and 20 Sgraffito in Évora; **Fig. 21** Sgraffito in Almodôvar

To conclude we would say that the cultural value of the sgraffito, such as the dual colour variation and the aesthetical tension, given by different textures and colours which are intrinsic to the nature of this mural covering, must not be forgotten. It is also important to promote a "conservation culture" to take care of sgraffito, restoring, preserving the historical and material authenticity.

The conservation sgraffito in Alentejo is not only, obviously, a big conservation problem but also a great - scientific, technical, economic - opportunity!

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III.17

Environmental Decay of Ancient Stucco Decorations Subject to Outdoor Exposure

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Abstract Neoclassical "*stucco*" decorations were added in 1840 to the 14th century church of San Francesco in Fano (Italy) in order to decorate its interior, but, as a consequence of the roof demolition in 1930, they have been exposed to outdoor conditions for almost 80 years. In view of a possible restoration work without reconstruction of the roof, this study aims to assess the vulnerability of the stucco decorations, by characterizing the constituting materials, identifying the degradation mechanisms and evaluating the stucco's conservation state. Firstly, an analysis of microclimatic and air quality data of the surroundings of the church was performed to evaluate the environmental aggressiveness and the possible degradation causes. Then the stuccoes were characterized in order to evaluate their articulation in multiple layers, to identify their mineralogical composition and possible presence of organic additives, to determine their pore size distribution and to assess their conservation state. In spite of their gypsum nature, the relatively good conservation state of the stuccoes seems to be ascribable to the finishing layers, realized with the addition of lime (giving calcite, less soluble than gypsum) and/or worked to reduce porosity, so that stucco decorations designed for sheltered conditions proved to be partially resistant to outdoor environment.

1 Introduction

The term "stucco" indicates a wide range of materials used to create protective layers and decorative elements upon architectural surfaces, generally with the aim of imitating more valuable materials, such as marble [1, 2]. Usually at least two different layers were created [3-7]: (i) an internal, raw layer, with the function of support, made of binder (lime, magnesium-rich lime, gypsum or a mixture of the formers) and coarse aggregates (calcareous or siliceous aggregates, brick dust, etc.); (ii) an upper, accurately manufactured layer, with finishing and protective function, made of binder (the same used for the internal layer or even a different

one) and very fine aggregates (such as marble powder or spatic calcite) or, sometimes, no aggregates at all. As for the choice of the binder, magnesium-rich lime was often used to increase the mortar's plasticity and adherence [3, 5] while gypsum was added to reduce the mortar's hardening time and shrinkage and to enhance the fresh-state workability [8].

In order to improve the performance of the stuccoes and enhance their durability, many natural organic additives were added: (i) sugars, glycerin and citric acid were added to reduce gypsum solubility [3]; sugars were also added to reduce the amount of water needed for the binder hydration and to extend the hardening time [6-8]; (ii) fats and proteins (such as animal blood, egg whites and casein) were added to achieve water-repellent properties [6-8] and the latter also added to extend the mortar's hardening time and to increase its adherence to supports [8]; (iii) surfactants (such as soap) were used to introduce air and to give brightness to the final stucco [7, 8].

As the actual stucco works' durability essentially depends on their chemical-mineralogical composition and microstructural characteristics, as well as on the exposure conditions, this paper aims to assess the vulnerability of the stucco decorations in the church of San Francesco in Fano (Italy, XIV cent.), which were designed for sheltered conditions, but have been exposed to the outdoor environment for 80 years as a consequence of roof demolition.

The church of San Francesco in Fano, completed around 1323, was originally covered with trusses. In 1840 a restoration campaign was undertaken to repair the structural and aesthetic degradation effects on the church. New masonries were erected over the medieval ones, a new barrel vault was built and a completely new, neoclassical decorative apparatus was added to the interior of the church (Fig. 1, left). In 1930, as a consequence of several seismic events, the roof and the masonries erected in the 19th century over the medieval walls were demolished [9] and, since then, the church has been permanently exposed to meteorological and environmental agents (Fig. 1, right).

Fig. 1 The church before the roof demolition (left) and in 2002 (right).

2 Materials and methods

2.1 Samples

Four representative samples (Fig. 2) were withdrawn from different sides of the church and at different heights, to take into account the different exposure conditions. The description of the samples, their macroscopically observed articulation in layers and their degradation state are reported in Table 1.

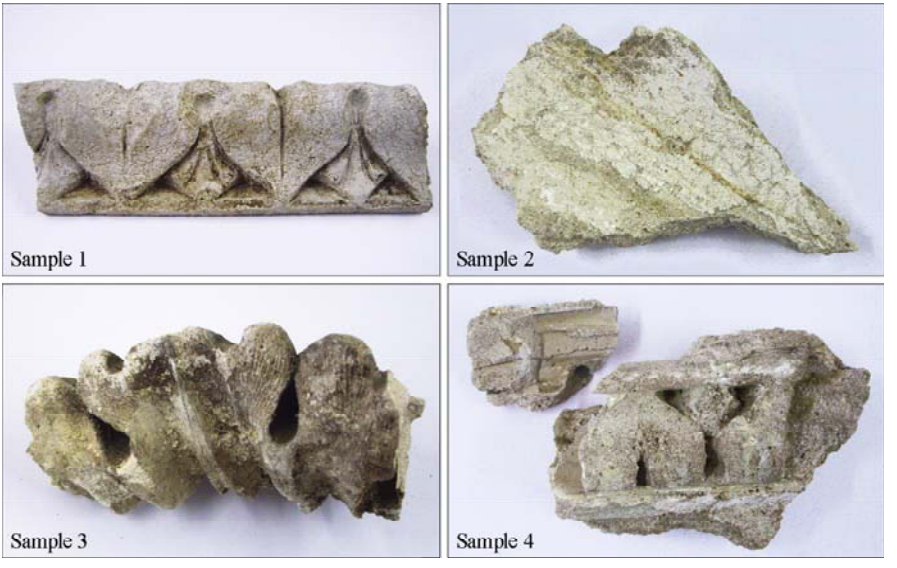

Fig. 2 Picture of the samples

Table 1 Identification and description of the samples

No.	Sampling point	Description of layers (from the external surface)
1	Decorative door frame (S-W side; height ≈2.00 m)	Crackled finishing layer (≈5 mm) with particle deposits; internal paste layer (20÷30 mm); "adhesive" layer (≈5 mm)
2	Corinthian column plaster (N-E side; height ≈1.20 m)	White paint (< 1 mm) with some deposits, spots and crusts; internal mortar layer (≈30 mm)
3	Corinthian column capital (S-W side)	Abundant dark deposits; no clear distinction between finishing and internal layers; paste inner layer
4	Decorative altar frame (N-E side; height ≈1.00 m)	White paint (< 1 mm) widely detached from the surface; no clear distinction between finishing and internal mortar layers; "adhesive" layer (≈5 mm)

2.2 Environmental analysis

As the stucco decorations have been exposed to meteorological agents and atmospheric pollutants for almost 80 years, an evaluation of the environmental aggressiveness in the surroundings of the church was performed according to previously proposed methodologies [10, 11]. Already available, urban-scale environmental data coming from survey stations near the church, collected by "A.R.P.A. Marche" (*Agenzia Regionale per la Protezione Ambientale* - Regional Agency for Environmental Protection) and "Protezione Civile Regione Marche" [Marche Regional Civil Protection]), were analyzed.

As the main causes of the degradation of mortars and plasters (e.g. dissolution, freezing-thawing cycles, etc.) originate or are enhanced by water, an estimation of the frequency of rainfall and possible relative humidity condensation on material surfaces was performed. For this purpose, the following data were considered: (i) the number of days per year when rainfall occurred in the period 1998-2007 (Tab. 2); (ii) the yearly amount of rain in the period 1998-2007 (Tab. 2); (iii) the monthly average relative humidity value in the last 30 years. In order to assess the freeze-thaw cycle risk, the number of days per year when air temperature dropped below 0°C was also considered for the period 1998-2007 (Tab. 2).

In order to evaluate the possible role of gaseous atmospheric pollutants and particulate matter in material degradation, the annual average concentration of SO_2, NO_x and PM10, recorded by a survey station about 500m from the church, were considered for the period 1998-2007 (Tab. 2).

Finally, given the proximity of the church to the sea (about 800m), in order to evaluate the possible role of marine aerosols on material degradation, the monthly main direction of the wind in Fano was considered for the last 30 years.

Table 2 Environmental data for the period 1998-2007

Year	Days with rain	Rain (mm)	Days with temp < 0°C	[SO_2] ($\mu g/m^3$)	[NO_x] ($\mu g/m^3$)	[PM10] ($\mu g/m^3$)
1998	84	825	6	6	79	68
1999	79	897	4	10	67	63
2000	69	563	13	15	41	60
2001	79	677	6	9	32	69
2002	94	726	10	7	32	53
2003	60	460	10	8	31	56
2004	97	631	6	5	-	54
2005	94	1029	3	7	-	55
2006	76	795	9	5	-	54
2007	81	585	0	7	44	48
Average	81	719	7	8	47	58

2.3 Sample characterization

In order to identify both different manufacturing techniques and different degradation states in the multiple layers identified by macroscopic observation (Tab. 1), the microstructure and composition of all the layers were characterized.

The composition of the stuccoes was determined by powder X-ray diffraction, XRD (Philips Diffractometer PW 1840, 40kV/20mA, Cu Kα radiation) and the carbonate content assessed by the Dietrich-Frühling method. As the addition of natural organic additives was a common practice to improve the properties of the stuccoes, the presence of organic compounds was investigated by TGA (TGA Q50, TA Instruments). In order to evaluate the possible degradation action due to salt crystallization inside the pores of the stuccoes, mainly as a consequence of chloride transportation from the sea by wind, the content of chlorides was assessed by sample grinding, salt extraction by distilled boiling water, filtration and titration by silver nitrate ($AgNO_3$) and potassium chromate (K_2CrO_4). Finally, the pore size distribution was determined by mercury intrusion porosimetry, MIP (Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba).

3 Results and discussion

In light of the results of the environmental data analysis, the environmental aggressiveness in the surroundings of the church can be assessed as follows: (i) given the considerable average number of rainy days per year (81) and annual total rainfall amount (719 mm on the average), and also considering the high probability of air relative humidity condensation on the stuccoes surface and inside the pores (as the monthly average relative humidity value exceeds the 80% in all the winter months), the risk of dissolution of gypsum (solubility 2.23 g/l) seems relevant; (ii) in spite of the frequent presence of water inside the stuccoes' pores, the risk related to freezing-thawing cycles seems low, as the average number of days per year with temperature lower than 0°C amounts to 7; (iii) the risk related to atmospheric pollutants seems low as well, since, in the considered period, the annual average concentrations of SO_2, NO_x and PM10 amount to 8 $\mu g/m^3$, 47 $\mu g/m^3$ and 58 $\mu g/m^3$, respectively; (iv) on the other side, the risk related to marine chlorides transportation by wind action may be not negligible, as, on the average, for seven months per year the main wind direction is East-North-East, i.e. from the sea towards the coast and the city of Fano.

As for the mineralogical composition of the samples, the results of the XRD analysis and calcimetry (Tab. 3) pointed out some important differences between the different layers constituting the stuccoes. Whereas samples 1 and 3 are mainly made of gypsum, and only traces of calcite are detectable in all the layers, samples 2 and 4 exhibit a higher amount of calcite in the upper layers. In fact, the white finishing paint of sample 2 has a calcite content of 61.7%, while in the internal

part calcite amounts to 23.6%. Similarly, the white paint on the surface of sample 4 has a calcite content of 19.0%, while in the underlying layers it amounts to 2.2-2.9%. In both samples, the gypsum-lime paint (where obviously lime turned into calcite after carbonation) was presumably aimed to enhance a better finishing effect (white colour, macro-defects absence, etc.) compared to the inner mortar layers. Such paints, thanks to their reduced solubility, gave an improved durability to the stuccoes, whose internal parts were made of gypsum, much more soluble than calcite.

Further significant differences between the layers of the samples were also found by MIP (Tab. 3), as the upper, finishing layers of all the samples showed a lower porosity and a smaller mean pore radius than the internal parts. In sample 1, the finishing layer, although having substantially the same mean pore radius, exhibits an open porosity about 8 percentage points (or 18%) lower than the internal layer. In sample 2, both the mean pore radius and the open porosity result remarkably lower in the finishing layer (the white lime-gypsum paint) than in the underlying part (Tab. 3).

Table 3 Results of XRD, calcimetry and MIP (+++ = dominantly present; ++ = present; + = traces; - = not present; $CaCO_3$% = carbonate content %; OP% = open porosity %; r_m = mean pore radius [μm]; SSA = specific surface area [m^2/g])

Sample	Layer	XRD		Calcimetry	MIP		
		gypsum	calcite	$CaCO_3$%	OP%	r_m [μm]	SSA [m^2/g]
1	Finishing	+++	+	3.3	39.0	1.6	1.18
	Internal	+++	+	3.0	47.8	1.5	3.16
	Adhesive	+++	+	2.7	43.4	0.4	4.32
2	Finishing	++	+++	61.7	36.1	0.2	9.31
	Internal	+++	++	23.6	47.1	1.5	1.19
3	Finishing	+++	-	0.9	38.1	1.9	2.51
	Internal	+++	-	1.8	43.8	2.3	2.53
4	White paint	+++	++	19.0	-	-	-
	Finishing	+++	+	2.9	40.4	1.0	0.90
	Internal	+++	+	2.2	42.7	1.3	4.39

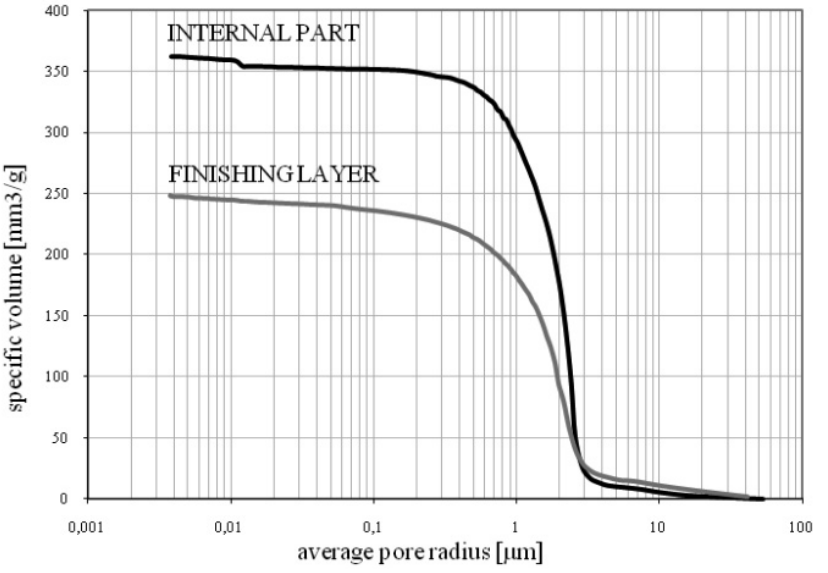

Fig. 3 MIP results on sample 3

Even if no clear distinction between layers was detectable in sample 3, both the mean pore radius and the open porosity are lower in the upper layer than in the inner part (Tab. 3 and Fig. 3). Finally, a slight difference was also found for sample 4, as the finishing layer had an open porosity of 40.4% in front of 42.7% in the internal layer, and a mean pore radius of 1.0 µm in front of 1.3 µm in the internal layer. In all the cases, particularly for the elements presumably manufactured on-site (such as samples 2 and 3, where no inner adhesive layer was present), the characteristics of the upper, finishing layers seem to be ascribable to an accurate manufacturing aimed to reduce the porosity and enhance the aesthetical outcome (colour, smoothness, etc.), as well as the durability of the final products. In the case of sample 4, presumably made with the use of moulds, the slightness of the difference between the upper and the internal layers may be explained considering that a final gypsum-lime paint was applied to the surface of the decoration, likely to improve the decoration's whiteness.

As for the possible addition of organic admixtures to modify stucco properties, the TGA analysis did not revealed any particular compounds. Only the upper layers of samples 2 and 3 showed some slight weight losses at about 200-250°C and 250-300°C respectively, but they seem ascribable to the presence of deposits of particles on the surface of both samples.

Finally, a harmful crystallization, within the stuccoes pores, of marine chlorides transported by wind action seems to be excluded. In fact, even if not negligible chloride content was found by titration in the upper layers of the samples (Cl^- up to 0.4 wt%), no significant differences were detected between the external and the

internal layers (e.g., in sample 3: 0.37% in the finishing and 0.27% in the inner part) and, hence, no efflorescence or sub-efflorescence occurrence.

4 Conclusions

In light of the results of the environmental analysis and sample characterization, the relatively good conservation state of the stucco decorations seems to be ascribable to the manufacturing techniques of the finishing layers, realized with the addition of lime (giving calcite, less soluble than gypsum) and/or hand-worked to reduce porosity, so that stucco decorations designed for sheltered conditions proved to be partially resistant to the outdoor environment.

In order to further preserve the stucco decorations from environmental aggressiveness, mainly represented by rainfall and relative humidity condensation, which may lead to gypsum and, to a smaller extent, calcite dissolution, in the hypothesis of the church's restoration without the reconstruction of the roof, the following hints should be considered: (i) protecting the stuccoes from water penetration by application of new gypsum-lime paints of the same kind as the pre-existing ones and, then, a waterproof treatment, whose efficacy should be previously tested on some available stucco samples; (ii) introducing a partially prominent protective architectural element, running all around the perimeter of the remaining masonries and whose shape and constituting materials should be purposely designed, in order to protect the underlying stucco decorations from the direct impact of raindrops and water percolation.

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III.18

The Restoration of the 12th Century Engraved Estrich Gypsum Floor from the Church in Wiślica

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Abstract The so called "floor" from Wiślica has an outstanding place among other medieval artefacts in Poland. Its latest history began at the break between 1959 – 1960 when the floor was discovered during archaeological excavations. The issues of its restoration remained complex and exceptional despite the fact that the work was preceded by all possible examinations and treatments. The greatest achievement of this project was matching the applied technology and technique of restoration with the historic fabric. The employed procedures might be suitable and applied either directly or by analogy in similar cases.

1 Introduction

One of the popular materials used throughout centuries is gypsum; its qualities and usage in art have been well recognized. However, how to cope with the gypsum floor regarding limitations related to its location *in situ*, what material should be used to stabilize crumbled elements, and what procedures and technique should be applied were all unanswered questions when the works in Wiślica began. Also, when the work was completed, one might have expected that the gathered experience that allowed him to answer all related dilemmas would help one to know what to do with similar objects, but it was not the case! Or rather, it only partially was; every artefact has its individual conditions and needs to be treated individually, which requires a modification of the methods worked out for other cases. (We could testify this notion when together with professor Zalewski we began to restore the tomb plate dated to ca 1000, which was also made of estrich gypsum, in the cathedral basilica in Gniezno. The experiences gathered in Wiślica were very useful regarding restoration techniques, but numerous new

issues occurred, including these related to the artefact's appearance and display – much different than these which we faced in the case of Wiślica [1].)

When we encounter problems related to historic fabric that we have not faced before, we search for technical solutions based on our personal experiences. When we cannot find them we shall count on the support and creativity of scientists. Also, of course, when a situation calls for immediate action, one applies some sort of effective material that will protect an artefact from damage, even if it is not optimal.

Fig. 1 Estrich gypsum floor in the crypt of first Romanesque church.

The 12th century engraved floor in the church in Wiślica survived under a four meter thick covering of soil and rubble beneath the floor of the Gothic church. The discovery came at the time of commemoration of the Polish State Millennium, which is associated with the introduction of Christianity to Poland (966). The Romanesque floor, with the representations of historic figures, had obvious indigenous features. The discovery had a great impact on scientific circles, both in the country and abroad. However – similar to the other discoveries made by the Zespół Badań nad Polskim Średniowieczem [2] (the Team of Researchers of the

Polish Middle Ages) – it could not be introduced into the commemorative events by communists for the obvious ideological reasons[1].

2 Relics and their exposition

The most precious artefact discovered in Wiślica was the floor of the Romanesque church of St. Mary, dated to ca 1175 – 1177 (according to L. Kalinowski) [3]. A vaulted crypt was once located beneath the presbytery of this first Romanesque church. It was originally supported by six columns and termed with a semicircular apse. An altar was located at its eastern end (at present it is vestigially preserved). The paving was made with an estrich gypsum floor, with an engraved central part and decorative strips running between the columns. The grooves were filled with a dark-coloured substance. The areas between the columns and the outer walls were not decorated. What we can see at present are two scenes framed with a decorative strip running between the columns; the composition entirely fills the small crypt from its eastern to western ends. The scenes depict historic figures, one of whom is presumably a founder. These depictions are supplemented with a Latin inscription that states the will of the dead, who wished to be trampled in order to reach stars (Inscription says: *HI CONCULCARI QUERUNT UT IN ASTRA LEVARI: POSSINT ET PARITER VE*)

In the scientific world, the discovery was immediately recognized, not only because of the age of the artefact but also because of its ideological complexity, history, and form; its religious and spiritual values; and finally its technique and employed materials. These factors make the floor one of the most precious Polish Romanesque pieces of artwork, along with the tomb plate and gate from Gniezno and the columns from Strzelno.

Numbers of prestigious scientists of various disciplines, including art restorers, went on a pilgrimage to Wiślica. Professor Władysław Zalewski (Academy of Fine Arts in Kraków) witnessed this discovery and was later engaged with revealing, documenting, examining, and finally restoring the floor [4]. I had honour to take part in this work as one of the co-leaders of the restorers' team.

[1] In my personal experiences of living under communist rules I simply cannot avoid mentioning the implications of Marxism ideology which had striking impact on science and social life. Marxism rebutted values of Latin civilization along with great rules of entity – the great holarchy of development (K. Wilber) along with truth, morality, religion, replacing them by simply "rationalism" – which in fact offered nothing instead. It was striking during commemorative events organized by the communist government. For instance: celebration of the Millennium of Baptism in Poland was nothing in respect to yet another anniversary of the Communist Manifesto. I am happy that this conference takes place in Prague, for I will be well understood in this country, a former part of the so called "Eastern Bloc", where, similarly as in Poland, all the values such as humanism, culture, religion, commemoration were also not respected.

Professor Andrzej Tomaszewski – at present, renowned architect and restorer – examined the stratigraphy of the place and carried out investigations of the original layout of both the Romanesque and Gothic churches. At that time he worked with the above mentioned Team of Researchers of the Polish Middle Ages at the University of Warsaw and the Technical University of Warsaw, guided by an archaeologist, associate professor Zofia Wartołowska, PhD [5].

Many decisions had to be made and many works had to be completed in order to provide public access to such an outstanding discovery. Following the concept of display, many conservators' boards had gathered, but the decision of restoration had not been made, mainly because the restoration issues had not been recognized. The other complicated concerns included unstable temperature and humidity, threat of microbiological attack, and ongoing protective and technical work in the close surroundings of the floor. For these reasons, the floor was simply unveiled, initially cleaned, and subjected to basic protective measures. However, it was not wasted time; all possible archive materials were researched, the finding's environment was under constant control, and the state of the floor was documented and studied in respect of its construction, technology, structure, and history.

At that point discussions were restricted only to the restoration guidelines of solely the floor. In these times, the concept of the overall restoration – that would in fact comprise the whole interior – was not standard, and the spectacular case of the gypsum floor was the main focus. It was seen as an entirely independent piece of artwork, which had been not related to its surroundings. In this approach was the threat that the original floor would be distorted into some spruced preparation – ready just to be presented – while its spatial context would be totally neglected. Finally, the decision was made to expose the artefacts and stratigraphic sequence *in situ*. This was a step forward, for it became obvious that the space between the floor of the Gothic church and the Romanesque estrich floor must be cleared. It was also declared that before the restoration of the floor, restoration guidelines and procedures must be established.

The beginning of the work was the turning point; soil and rubble were removed, walls of the crypt were cleaned, and the space was covered with a new vault. The technical works aimed at providing access to the church basements, including the building of a platform and barriers, were finally completed at the beginning of the 1980s - almost thirty years after this sensational discovery!

The programme of restoration, worked out in 1974 by professor Zalewski, was the basis for further decisions, examinations, and the subsequent restorative treatments [6]. The guidelines directed the stages and arrangement of the procedures. At the first stage, Zalewski suggested complex conservation and structural stabilization of the whole basement area (i.e. relics of archaeological strata, walls of the foundations of the Gothic church, and relics of both the first and second Romanesque churches). There was also some basic cleaning work to do. As the environment was stabilized, the sources of dust and dirt removed, the next stage – restoration of the floor – could begin.

3 Restoration

As the system of natural ventilation had been introduced in 1982, the environmental conditions (mainly decrease of humidity) within the crypt were improved so that we could start restoration works. They were completed in 1986 [7]; the works carried in the year 2000 were aimed at providing public access to the crypt.

We could not follow up on any former restoration procedures carried out on estrich floors dated to a similar period. There were only examples of basic conservation treatments, such as protection and relocation of broken parts, shielding a floor with glass plate, or transferring it from its original location to a store room. The only – unsuccessful – attempts that had been carried earlier on the Wiślica floor were tests of cleaning with sulphuric acid, which resulted in the deterioration of gypsum.

At the beginning of the work, the floor was extremely dirty. However it was shielded, particles of dirt, dust, and rubble gathered on the floor surface, while moisture present in some areas bonded the dirt particles with gypsum. In general, humidity in the basement, resulting from groundwater and precipitation water, was very high. This thick coat of dirt was also an effect of the conscious decision to abandon any cleaning treatments of the floor, for even the lightest touch could have resulted in mechanical damages.

4 Restoration issues

Materials that might be used in joining broken estrich floor elements had been the topic of consideration since the fabric of the floor was recognized. Estrich gypsum in the first Romanesque church was employed as mortar for plastering the inner walls of the crypt and for the whole floor (i.e. decorated and undecorated parts). The mortar, which once bonded the blocks and stones of the masonry, was subjected to mechanical damage; it was partially lost or crushed, mainly within the protruding elements. If the broken elements had not shifted their position it would have been possible to reassemble them.

Gypsum of poorer quality was used in the undecorated (not engraved) areas of the floor. These areas were cracked and crumbled, but the broken elements remained on their spots. Even small chips were not shifted as they were embedded in clay ground, in some areas in a few layers, one on top of another.

The decorated floor was made of the best quality sifted gypsum. The main damage was mechanical; the gypsum slab was crumbled with some parts broken mainly at the border areas, generally along the edges of the consecutive coats of poured fluid mass of gypsum (eastern part). Yet, another type of damage – located mainly in the eastern part of the floor – was distinguished as “clusters” of crumbled gypsum matter with clearly confined areas. This type of damage resulted

from the separation of the bottom layers of the floor, which caused a loss of stability in the upper coats and caused them to fall into pieces.

The main concern of the restoration project was related to the protection, stabilization, and rejoining of the broken parts, but not exclusively. Cleaning the gypsum surface was a separate dilemma, especially the small, crumbled chips. It was the main difficulty in the process of cleaning the area of the undecorated floor (mainly northern and southern parts). Any attempt to wash mud away from the interstices and crackles caused the small chips to shift their position. However, it was necessary to remove the soil, as it was the source of dust and further deterioration. The simplest solution – adopted in similar cases – is consolidation, but in this case, given the very unstable and humid environment (resulting also from groundwater), introduction of any new substance would not be an acceptable solution. One should keep in mind that such a substance would be irreversible and would penetrate the whole body of the floor. Yet another problem was cleaning the surface of the decorated floor (especial its eastern part) where the crumbled bits (a few millimetres in size) were grouped together in "clusters," for even touching them with a paint brush would have resulted in displacement of the minute bits.

5 Gypsum and its application

In the territory of the historic Polish Kingdom, gypsum was relatively quickly replaced by lime. Although estrich gypsum and limestone need similar calcination temperature, lime is generally easier in application; lime mortar may be easily prepared and used later, while gypsum mixed with water sets quickly and must be used soon after the mortar is prepared. The setting time of gypsum mortar is yet another issue: it differs depending on the calcination temperature, and the process is irreversible, which in some cases it is a benefit – especially in moulding. Gypsum as a material has many advantages, and for this reason, it is produced and used nowadays.

Estrich gypsum is obtained by calcinations of raw gypsum (crystal sedimentary rock) at the temperature of ca 600 – 1200°C. The material sets very slowly over a few days until the chemical process is completed. The prolonged setting time allows for shaping and manipulating the mass. Once estrich gypsum crystallizes and dries it obtains mechanical resistance. The most common forms of gypsum (hemihydrate gypsum and di-hydrate gypsum) are calcinated at lower temperatures (ca 110 – 200°C); gypsum used in building sets in about two hours, while Plaster of Paris sets in 10 minutes.

The application of estrich gypsum in the oldest architectural structures of Wiślica seems obvious, as the river Nida Valley (i.e. Wiślica region) is within the three richest in gypsum rock areas in Poland. The technology used in the floor's creation is superior; the produced material is of the highest quality, which allowed

it to be engraved. Other places where similar technology was used are quite distant and located in regions rich with gypsum deposits (e.g. in Saxony).

In Wiślica, estrich gypsum was not used only in the 12th century Romanesque church. The grave slab found at the extension of Romanesque church of St. Nicolaus (11th century) was also produced from this material. A few fragments of the estrich floor, a dozen centimetres thick, also were found during archaeological excavations on the site called "castle." In the nearby Romanesque church in Kije, other fragments of estrich floor were found; the liquid gypsum mass was poured onto stone chippings.

Other regions of Poland where gypsum stones were calcinated and employed in architecture structures are the regions of Wielkopolska, Kujawy (Romanesque church in Gniezno, grave slab ca 1000), Ostrów Lednicki ("baptism pools" and fragments of the floor in the castle chapel), and Łekno (rotunda of St. Peter discovered in 1983), the city of Kraków and its region (St. Benedict church, fragment of gypsum floor found in the square Romanesque structure located beneath the Main Court of the Wawel Castle), and Tyniec (relics of floor in the presbytery of the church).

In Europe, gypsum was used in the early Middle Ages as a mortar for plastering walls and in flooring. There are ten examples of artefacts found in the Western countries dated to the times when the Wiślica floor was executed: Quelinburg, the former collegiate church 2nd part of the 12th century; Ilsenburg, the former Benedictine church, 12-13th century; Drübeck, the former Benedictine church, end of the 12th century; Erfurt, cathedral, chapel in the northern tower, ca 1160 ; Nienburg, the former Benedictine church, crypt, after 1163; Hildsheim, cathedral eastern apse, ca 1153-1162; Helmstedt, the former Benedictine church, crypt, ca 1150; Benediktbeuern, the Benedictine church, send half of the 12th century; Basel, cathedral ca 1170. None of these have been displayed *in situ,* and none of them are as well-preserved as the one in Wiślica. The mortar of the Wiślica floor has a pink tint, especially apparent when the surface is wet, which is the effect of clay components contained in gypsum rock. When calcinated in high temperature it becomes red in colour (as in calcination of biscuit clay). In fact, depending on calcination temperature, minerals can become various colours.

There were a number of professionals involved in the part of the research carried out within the two Romanesque churches and their surroundings. Examinations were aimed at the recognition of archaeological strata, reading iconography of depiction, and the technique and technology of the floor. In-depth studies revealed complex issues [8].

The most extensive examinations of the gypsum material were made by a petrographer, Tadeusz Kawiak, PhD, from the Cracow University of Technology [reference number and list his published work at the end of the document] [9]. The samples were studied by X-ray diffraction, differential thermal and gravimetric analysis, and electron and optical microscopy; physical properties were measured by the mercury displacement method. Obtained results allowed for the identification of the mineral components of the mortar and revealed the employed

technology. The basic component of the mortar used in the floor is gypsum (91 – 96%), and the average temperature of calcinations was 500 – 1000°C.

The knowledge of the material's technology and its inner structure does not automatically provide tools and methods for conservation – these had to be created. The basic concept was to use gypsum to reassemble the broken elements, taking into account the artefact's state and environmental conditions. Therefore, the parameters of gluing and setting gypsum had to be defined with respect to the conditions on-site. The necessary tests were carried out by Kawiak, both on-site and in the laboratory; as he was a member of the team, he could recognize the specific situation of the restored artefact. The priority of conservation was to work out technological consensus of historic fabric with techniques of modern restoration.

6 The technique of bonding with estrich gypsum

Kawiak produced estrich gypsum (anhydrite $CaSO_4$) in the laboratory and continued experiments on modifying its setting time by admixtures of hemihydrate ($2CaSO_4 \cdot H_2O$) gypsum and calcium oxide. This was followed by tests of gluing with this medium, which provided data on conditions in which bonding is effective and resistant. This specially produced material was used for restoration of estrich floor, but depending on size of the broken pieces, the technique of gluing had to be modified. Large elements had to be treated differently than smaller ones and the smallest bits, yet another technique of bonding had to be used for the loosened areas of the mentioned "clusters" of tiny chips, for these had to be kept in their positions. The basic principle was to provide proper setting time by keeping the glued fragments wet with gypsum water [10].

The gluing procedure began by joining the larger pieces of mortar. They had been initially wet with gypsum water, as were the locations where they were to be affixed. Next, the joints were covered with fresh estrich gypsum mass. Once the elements had been matched, the joint was covered with a poultice of cellulose wadding, also wet with gypsum water, and wrapped with foil. On the following day the excess of putty was removed, and joints were worked out. For the following three to four days the joints had to be kept wet, thus wetting with gypsum water was necessary. Finally the protective shield was removed and the reassembled elements left to dry. The abundant saturation with gypsum water caused evaporation which lasted up to a few weeks.

As noted above, cleaning the small chips was problematic. In order to prevent their replacement or loss, the cleaning procedure was combined with the procedure of fixing these chips to their original location. One after another, the chips were cleaned and immediately set in their places.

Fig. 2 Fragment of the engraved gypsum floor.

The areas of "clusters" with tiny cracked bits – which resulted from the inner, horizontal cracks in the body of the floor – called for yet another approach. These areas consisted of tiny soiled fragments (of 1 to 3 millimetres), some of which were dislocated; they could not be moved and put back (as with the above described elements). They could not be cleaned prior to placement, as this might have washed them out and dislocated them. Thus, they had to be stabilized. To this end, the area first was saturated with methanol. This decreased the surface tension and, as it penetrated into the fabric, also introduced dirt particles, consequently increasing the spaces between them. Next, the suspension of finely ground gypsum in methanol was injected with a medical syringe; alcohol was used as a chemically neutral carrier. The composition of gypsum filler was modified according to the degree of damage of the area – whether a stronger or weaker binding medium was needed. The mortar was composed of estrich gypsum and calcium oxide. An addition of semi-hydrate gypsum shortened the setting time. As the fluent putty was introduced, the "cluster" was wet with methanol dropped from another syringe. During the process, the gypsum particles gradually set and filled empty spaces between the broken chips. As all elements were embedded, the area was left alone to allow the alcohol to evaporate. Once the evaporation had been completed, the area was saturated with gypsum water and the setting was initiated. Poultices were kept for another two or three days. Only after the setting process was complete was cleaning carried out. At this stage the crumbled bits were all secured and affixed to their original locations.

The limitation of this method is that the procedure may be carried out only on a small, restricted area. Gypsum putty must be prepared in small portions and the

composition must be properly adjusted. Finally, once the procedure has been started, it must be completed with no timing delays.

7 The stabilization of the floor

Yet another problem had resulted from the natural weathering that weakened the surface of the estrich gypsum floor. A microscopic examination carried out by Kawiak on the site identified the structural damage which had decreased the mechanical resistance of the surface when compared to the inner body of the floor. The following questions appeared: how to bring the re-stabilize the surface and what materials should be used in the conditions of unstable humidity. The issue was connected with cleaning process, as for instance, distilled water – which is considered to be neutral – was too aggressive in this case and might have caused the washing out of the deteriorated surface.

One of the methods of non-invasive surface consolidation, used in the restoration of fresco, is sprinkling the wall with lime water; and it seems to be an ideal component in terms of similar materials. Because distilled water caused destruction of the weakened surface, the tests were conducted with gypsum water (one litre of gypsum water contains two grams of gypsum), which the tests carried out by Kawiak determined was effective. So all estrich gypsum surfaces were cleaned with gypsum water only. In fact, it was used from the very beginning of the works as the only acceptable cleaning agent.

The petrographer pointed out that at a decreased temperature of 4°C, eight grams of gypsum might be dissolved in one litre of water (instead of two grams, which is the case for higher temperatures), and this specific property was adopted to stabilize the floor. As the tests of consolidation brought positive effects, the consolidation was carried out on the whole floor at the final stage of the work, with all preceding procedures carefully prepared. So first, the water was cooled down to 2°C, then the gypsum was added, and as all large particles fell to the bottom, water was filtered through blotting paper. Clear water, highly saturated with gypsum, was dispersed onto the floor, and the surface was secured with hostaphan foil. The procedure was carried out a dozen times or so, and the tests confirmed that it was effective. In order to provide optimal environmental conditions the procedure was carried out at the break between winter and spring, when the temperature in the crypt was about 4 – 6°C. Temperature was further decreased by a cooling device.

The Regional Museum in Wiślica was created as soon as archaeological, architectural, and restoration works were completed and access to the basement provided [11]. The Museum requires monitoring and general care of the floor and excavation area, as well as an interpretation of the site. The institution is not alone in the protection of the ancient artefacts, however; professors Tomaszewski and Zalewski regularly visit Wiślica and help to care for and keep historic monuments

in proper condition. During their last visit in March this year, they confirmed that both floor and its surroundings needed cleaning.

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III.19

Restoration Plaster for the Wall Paintings Presentations in three Pre-Romanesque Churches on the Adriatic coast

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Abstract Restoration of wall paintings in historical buildings along Croatian coastal area is most often motivated by serious damage of material structure caused by moisture and atmospheric salt. In this paper three historical buildings with wall paintings from Romanesque period will be presented. All of them have been built on similar location and have been exposed to similar climate conditions. As a result of material structure analyses it became obvious that they share the same kind of plaster done with certain ratio of crushed brick as aggregate and stone as building material. Fragments of wall paintings are preserved and unity of presentation has been achieved by use of restoration plaster. These paintings are located in church tower of St Mary's Benedictine monastery in Zadar, in pre-Romanesque St. Michael's Church in Ston and pre-Romanesque St. John the Baptist Church on Šipan Island near Dubrovnik.

1 Wall Paintings in St. Mary's Church Bell Tower

St. Mary's church bell tower in Zadar, situated by the sea, was built by King Koloman in 1105. Wall paintings can be found on the 1st floor of the tower where the space is square, with stone columns in four corners. There are several openings in the chapel with wall paintings. The outer surface of the tower was built by fine stone ashlers while the carvings on the inside are acclaimed. Wall paintings are partly preserved in the third plaster layer. Their very existence was discovered under several plaster layers and lime coats after severe destruction of the whole complex of the Benedictine monastery due to the heavy shelling of Zadar during the 2nd World War (1943/44). Soon after their discovery, in 1948 the wall paintings were cleaned and preserved.

1.1 Preservation and restoration interventions

More systematic preservation and restoration operations started in 1971. A survey by the Croatian Restoration Institute in 1972 explained that the main cause of the wall paintings' damage was moisture from rainfall that had been entering walls from openings on the upper floor. This created the process of soluble salt migration [1].

By construction repair of the outer tower walls and the sealing of openings on the second floor (right above the chapel) pre-conditions for further restoration actions were achieved.

Analysis of the plaster samples revealed the existence of soluble salt in harmful concentrations (according to the Austrian standard B 3355-1). Using X-Ray diffraction the mineral structure of the salts was detected: sulphates, chlorides and nitrates as well as tenardit, gypsum, haxahidrite, epsomite, halite and nesquehonite in small quantities [2].

Crypto-climate surveys were performed during the period of Autumn 2002 - Summer 2004 using an electronic *Testo data logger* and the *Testo Comfort Software Basic* program. The Autumn - Winter period showed that the average temperature was +12.02°C with a relative humidity of 70%, while in the Spring - Summer period the average temperature was + 22.56°C with a relative humidity of 68%.

An analysis of the structure of the final *intonaco* original plaster (0.2 – 0.5cm thick) after dissolving it in 10% chloride acid exhibited a dissolution of 84.6% (lime) with an undissolved portion of 15.4% (aggregate). The aggregate consisted of sand grains of varying granulation and crushed brick (4.5% of aggregate) [3].

Preserved fragments of the original plaster and wall paintings were well bound within the structure. The method of detecting loosely bonded spots by knocking and then injecting was adopted. The conservation-restoration process of removing the salts by cellulose pulps soaked in distilled water lasted until the year 2005; after that time the laboratory analysis of the pulp revealed a non-damaging concentration of soluble salt. During these conservation-restoration operations several reintegration tests of smaller *lacunae* were completed, endeavouring to maintain a close accordance with the preserved original. The analysis defined a structure of raw material for restoration plaster samples (Table 1).

Table 1 Compounds of restoration plaster samples

SAMPLES	S1	S2	S3
FILLERS	Quartz sand: crushed bricks (3:1)	Quartz sand: river sand (2:2)	Quartz sand : marble grains ¨Verona¨ : marble grains ¨Corallo¨ (2 :0.50 :0.50)
BINDER	Slack lime (1)	Slack lime (1)	Slack lime (1)

In the sample S1 crushed tiles were first desalinated by soaking in several water baths, before being dried and crushed. After the final placing of desalinization pulp and three months of drying, several moist areas were observed. Reviewing the wall surface it was noted that the moist areas were focused just on the spots treated with restoration mortars containing crushed brick. There was no sign of moisture on the pulp and walls treated with the new restoration plaster that contained marble grains. Salt efflorescence was detected visually in a niche of the north-west window. Also during the restoration activities some moist areas appeared at the rope holes in the vault. The wall condition was analyzed by thermographic scanning performed by Ser.Co.Tec., a company from Trieste; critical areas were visible on these scans.

Chemical analysis of salt in the restoration plaster with brick illustrated a detrimental concentration of sulphates and chlorides. This confirms the action of aerosols in the unstable crypto-climate conditions relative to the moisture and temperature. Crushed brick in the samples of restoration plasters absorbed both the moisture and the aerosols. Generally crushed brick was found as an aggregate in pre-Romanesque and Romanesque plasters of the Adriatic coastal area; it was used to create a specific warm tone to the plaster. Medieval craftsmen used crushed brick as a compound of plaster for the initial layer of interior walls because of its greater volume and its superior ability for spreading [4].

Crushed brick can also be found in the final *intonaco* layer that directly supports the wall painting, probably due to the fact that it retains moisture for one day (*giornate*). *Giornate* in *intonaco* is used to define a craftsmen's one-day work in fresco painting; the base should be humid enough to allow basal colours to be applied prior to painting; crushed brick prolongs the time of evaporation. It is of no doubt that crushed brick as a compound of the aggregate acts as a pozzolan in the plaster and strengthens its character [5].

It is evident that large surfaces of original plaster, referred to in this paper, have been damaged. Restoration principles of *lacunae* reintegration and the selection of restoration plaster do not support the idea of duplicating the original texture. *Lacunae* make the perception of wall painting difficult as they, following Gestalt terminology, become patterned leaving the painting in the backplane. Respecting the authenticity of the work of art, it is necessary to reduce that trend. *Lacunae* should be made integral to the backplane by reintegration and treatment and they should join together the remaining fragments of wall painting and the original plaster [6].

Reintegrated parts should in one sense differ from the original, but they should also be integrated into the work of art. *Lacunae* differ regarding their dimensions, frequency and relation to the adjacent surface. Frequently, all types are present in one damaged wall painting. The shade was an important factor in the process of reintegration of *lacunae* at St. Mary's church bell tower. Three original plaster layers were visible in presentation.

During following tests of restoration plaster, the brick compound was omitted and its aesthetic value was replaced by marble grains of a similar colour. Marble is

not unusual in plaster composites – it is often found in the final layer of *intonaco.* Its calcium carbonate structure matches the composite of the original plaster and does not have any detrimental effects. Several samples using different colour tones relating to the quantities of marble grains, river sand and crushed stone were made (tables 2 and 3). Slack lime of exacting quality produced in the traditional way in a lime kiln was used as the binder [7].

On a larger clean area in the *arriccio* level the restoration plaster was warm grey in tone with reddish marble grains which corresponded well in colour to the original *arriccio*. Using two kinds of marble grains in specific ratio's a warm tone in wall painting fragments on *intonaco* similar to the original, was made.

Table 2 Raw materials for restoration plaster RPA.

Binder	Slack lime (4)	-	-	-	-	1
Filling	Grey river sand (8)	Quartz sand (1)	Crushed stone powder (1)	Marble grains Rosso Verona, 00 rough (1)	Marble grains Rosso Corallo 0 fine, (1)	3.5

Table 3 Raw materials for restoration plaster RPI.

Binder	Slack lime (1)	-	-	1
Filling	Quarz sand (2)	Marble grains Rosso Verona (0.50)	Marble grains Rosso Corallo (0.50)	3

When treating the *lacunae* within wall painting fragments, significance was given to marble grains and their coloristic value close to the original *intonaco* because the presentation did not recreate a lost painted layer. As a result, the reintegration of architecture and original wall paintings in the chapel was achieved by using restoration plaster. In the chapel, testing of the micro climate is ongoing and control of the relative humidity and temperature has been established through rope holes.

2 Wall paintings in St. Michael's Church

Close to Dubrovnik, on the southern side of semi-island Pelješac, is the pre-Romanesque church of St. Michael, built at the *Gradac* hill peak overlooking the late Antique settlement of *Stamnes*. Next to St. Michael's Church a Dominican monastery complex was built in the 16th century for Roman Catholic Tertiary nuns. The church and the monastery dominate the hill peak overlooking Ston Field and the Ston salt pans – a major source of economy in that part of the Adriatic coast since the Middle Ages. It is a single nave church, oriented west-east and with an apse. St. Michael's Church is divided into sections by arches, lesenes and

niches with the remaining fresco paintings dating back to the 11th century [8]. This early-Romanesque cycle of frescoes is attributed to an influence of a Southern Italian Benedictine painting school [9].

On the North wall, on its first crossbeam, there is a portrait of the benefactor with a church model in his hands. In that model we can see the mentioned westwork and cupola over the central section of the church. According to that fact the church is defined as a single nave church with a cupola though the evidence for this has still to be found. [10].

2.1 Conservation-restoration interventions

The report from 1973 indicates that the church is in rather poor condition due to storm damage. The new plaster has been damaged due to the destructive effect of salt. Chemical analyses in 1987 were carried out on the soluble salts. Chlorides, sulphates and nitrates were found in 10 samples taken at different heights of the internal walls. Sulphates were found at 0.5–2.00m from the ground, chlorides at 1.5 – 2.5 m while nitrates were present in samples gathered at all heights [11]. The removal of the detrimental cement plaster was performed in 1993 [12]. The church was protected by scaffold, the roof constructed of reinforced concrete was removed and salvaging of the foundation and roof was completed using inox stretches [13].

The walls were rinsed and dried for 4 years to reduce the amount of salts. Restoration activities on the wall paintings have continued since 1995 and were concerned with the binding of the fragments of the wall paintings with aggregates. This was done by injecting PLM-A [14] with the addition of Primal AC33.

To make edgings, a specific plaster of quartz sand, crushed brick and Primal AC33 was used. Wall paintings were cleaned by pulps with an ammonium carbonate solution (10-25%) [15]. Reparation of the roof using a stone covering was completed in 1997 as was restoration of the internal walls using a restoration plaster of stone powder, crushed brick in aggregate and slack lime as binder material. The external walls were plastered with a lime sand plaster containing crushed brick to achieve the correct tone [16, 17].

After 4 years an inspection found that the restoration plaster was ruined by salt. Damage was specifically observed in the north-east and east niches in addition to the vault. A large vertical crack was found in the south-east niche, probably the result of a great earthquake (8 Mercalli grades). It was estimated that the process of salt migration had not ceased and that the restoration plaster had to be replaced; the process of removing salt continued. [18] After completing the process of cleaning the hard coating from wall paintings, which was a result of desalinization, paintings were strengthened by Primal AC33 (concentrate 2%) and also by Paraloid in toluene solution (concentrate 2.5%).

During 2002 restoration plaster was removed up to 2m from the floor level and a new plaster of hydrated lime and stone aggregate of 0.0 – 0.5 granulation (1:4) with the adequate addition of water [19], was applied.

The Croatian Conservation Institute (Department for Wall Paintings and Mosaic and the Natural Sciences Laboratory) has been active in the program of restoration of St. Michael's church since 2003. Systematic monitoring of crypto-climate changes started in 2004. An electronic device, the Testo data logger was set, reading data with the aid of the Testo Comfort Software Basic program. Samples were taken for the quantitative and qualitative determination of salts in both the original and the restoration mortar. Sampling of restoration mortar in 2003 revealed chlorides (0.23%-0.38%) and nitrates (0.293%-0.390%) in detrimental concentrations. Soluble sulfate tenardit (Na_2SO_4) was also present in a harmful concentration of 0.16% [20].

Analysis of crypto-climate measurements for the period from 2004 to 2009 demonstrated great fluctuations in the relative humidity. Changes in the temperature were expected in accordance with the changes of season. It is difficult to explain relative air humidity and relate it to the corresponding air temperatures. The greatest relative humidity, 99.9%, was noted three times – on 26 December 2004, 2 January 2006 and 6 January 2008. Measurement data and relative air humidity in the spring period indicate that the temperatures ranged from 12°C-25°C, while relative humidity was above 50%. Increased temperatures reduce the relative humidity. In the summer period, temperatures were mainly between 20°C-30°C, while relative humidity was between 40%-80%. Higher temperatures are followed by a lower relative air humidity. In autumn, air temperatures ranged from 6°C-28°C, while relative air humidity was between 30%-100%. Again, higher temperatures bring a lower relative air humidity. In winter, temperatures were between 2°C-15°C and relative humidity between 40%-100%. The relation is positive and very strong. Higher temperatures were followed by a higher relative air humidity [21]. The correlation of the air temperature and relative humidity can be explained by the specific location of the church at the peak of the hill of the Ston Bay, where humid southern winds are common.

In 2010, a measuring device was set outside the church to compare the data. Examination of the mortar composition showed that the original plaster, 0.5 to 2 cm thick, is conmposed of 75% lime binder and 25% aggregate, of which 4% are brick grains. The first layer of *intonaco* (1 cm thick, the first phase of construction) consists of 70% lime binder and 30% aggregate, which has 5% brick grains in its composition. The second layer of *intonaco* (1 cm thick), which has the painted layer directly on it, is composed of 75% lime binder and 25% aggregate with some brick fragments. Restoration mortar contains 88% lime binder and 12% aggregate.

Through the chemical analysis of mortar in April 2009 detrimental soluble salts were found in the restoration mortar on the outside wall, in the restoration mortar on the inside walls and in the original mortar. Analysis show chloride (0.77%) and nitrate salts (0.47%) in the restoration mortar from the outside the northern wall,

while the restoration mortar from inside the northern wall had chlorides (0.60%) and nitrates (0.50%), an increase when compared to the analysis from 2003. Analysis of the original mortar revealed a presence of nitrates in a high concentration of 0.47%. On a part of the southern wall, there is subflorescence in the original mortar, visible in fissures in the plaster layer and the paintings. Sampling for salt analysis in October 2009 determined the amount of detrimental soluble salts in samples of tuff materials: chlorides (0.34%) and nitrates (0.25%), while in the mortar sample it was: chlorides (0.19%) and nitrates (0.25%).

Condensed humidity from the surface of the painted layer was sampled on a piece of cotton wool. Analysis has demonstrated the presence of chlorine and bromine ions from the evaporation of sea water carried by wind [22]. Damage that has occurred to the construction material of the church confirms a constant problem in maintainence and a continuing struggle with the assaults of soluble salts on the plaster and material of the inside and outside walls. The presence of chlorides and sulfates in great quantities in restoration mortars, as well as the concentration of salt on the wall near the window openings (directly next to the source of salts) prove that the danger is mostly aerosol induced. Great variations in humidity create droplets and moisture on the internal wall surfaces.

The appearance of subflorescence on the inside walls is due to the fact that salts cannot penetrate the painted layer because it is sealed with an impermeable synthetic consolidation substance. This creates a pressure resulting in fissures and the salt is retained between plastered layers that it cannot penetrate.

Testing of water absorbency by a Karsten tube on both the original plaster without restoration intervention, and on the restoration plaster with crushed bricks identified the following results; the original plaster had absorbed 4ml of water by 8.08 minutes while the restoration plaster with crushed bricks absorbed 4ml of water in a 1.10minutes.

The restoration project of St Michael's church continues. The salted restoration mortar with crushed brick will now be removed from the external and internal wall surfaces and the process of dessalination will be conducted until the analysis of the material (stone) shows satisfactory results.

3 St. John the Baptist Church

St John's church in the southeast part of the Island of Šipan near Dubrovnik is a pre-Romanesque church from 11th century, which has become an apse of a larger church from the 15th century. By type, it is a single nave church with a cupola [23]. The church is divided by three transverse ribs. The apse is semi-circular on the inside and rectangular on the outside. There are windows on the apse, the south wall and the dome that are unprotected from atmospheric influences.

During research in the 1970s, wall paintings from the 11th century were discovered. These were of Byzantine influence and were in respect to the iconographic content of the pre-Romanesque churches.

Restoration of the church started in 1988; at this time the stone roofing was dilapidated and plaster was falling off at the front. The soil embankment on the eastern side of the apse caused constant capillary moisture. When the restoration started, draining was conducted after clearing the space around the church [24].

Reviewing the condition of the wall paintings in 2004, the Croatian Conservation Institute noted that large areas were polluted by an injection mixture, which had trickled out and created a white film. In some areas there are no preserved painting fragments, the original plaster had been completely removed during previous conservation-restoration work.

The outside walls of the pre-Romanesque church were plastered with a new restoration mortar containing a part of crushed clay brick in its composition. High moisture was noted on the front of the building, especially on the eastern side, along with the appearance of crystallized salt. Microclimate measurements were started in April 2005 and are conducted continually, with quarterly readings taken during the year. The data from the microclimate measurements in the period from 2005 to 2008 has been analyzed. There are great variations in temperature and relative humidity. Relative air humidity over 75% is pronounced in the spring and autumn months.

A qualitative and quantitative analysis of salts from 17 samples determined the presence of salts in detrimental concentration only in the samples from the external walls. A plaster sample taken from the eastern front contained chlorides (0.76%) and nitrates (0.12%) in a possibly detrimental concentration (according to Austrian guidelines ÖNORM B335-1).

Humidity measurements where plaster samples were taken from the eastern front indicate 9.96% RH, while at the northern front at the height of 20 cm from the ground 12.60% RH was measured. Analysis has shown that there is no salt in the plaster samples from the inside walls [25]. The appearance of a high basic humidity on the surface of the plaster on the fronts and also of crystallized salts indicates that the problem of basic humidity is still present. There is possibly some absorbtion of the initial salts in the mortar composition with the crushed clay brick. For the composition of the restoration mortar, marble grains were chosen instead of crushed clay brick as part of the filler. Samples were formed to determine the most acceptable tone and type of treatment for the presentation of the wall paintings.

Testing of water absorbency by a Karsten tube on the restoration plaster gave the following result; 4ml of water was absorbed by 0.30 minutes.

A year after plastering, the restoration mortar was analyzed from three different positions and it was determined that there was no evidence of soluble salts in the samples taken.

4 Conclusion

The original pre-Romanesque mortar in the presented buildings contains crushed clay brick as a part of the aggregate. Since Zadar and Dubrovnik were under strong Byzantine influence during pre-Romanesque times, it is reflected in the craftsmanship of mortar mixtures, with indications of local use. Considerable damage to the wall paintings indicates consistent problems to sustain the material structure. In several examples when it was used in restoration mortars, crushed brick proved to be a part of the aggregate that absorbs humidity from the atmosphere and the surrounding walls, especially if the process of desalinization was not conducted successfully. In such an unstable microclimate, substituting crushed clay brick with marble grains proved to be a good solution.

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III.20

Conservation of an Amun Temple in the Sudan

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Abstract Excavation of a 2000-year old Amun temple at Dangeil began in 2000 under the directorship of Drs Salah Mohamed Ahmed and Julie R. Anderson of the National Corporation for Antiquities and Museums (NCAM), Sudan and the British Museum, UK, respectively. Dangeil is located south of the 5th Nile cataract in Sudan. In 2007, it was decided to assess and explore the options available for long term site preservation. In 2008, a preliminary visit was organised to initiate a number of trials on various aspects of the architectural fabric of the site. The materials used in the temple's construction include mud brick, fired brick, lime plaster and sandstone. During the 2009 field season, the previous year's tests were evaluated and other areas of the site were selected for further trials.

1 The Dangeil Amun Temple – Goals and Objectives

Dangeil is situated in northern Sudan on the right bank of the Nile, roughly 350 km north of Khartoum. The site consists of several mounds covered with fragments of red brick, sandstone, ceramics, plaster, etc. Excavations have focused on the central part of the site where a large, well-preserved Amun temple has been discovered. Much of the ancient built environment at Dangeil has survived and as such the site represents an important and unique part of Sudan's cultural heritage. The mission's major goals are to preserve, conserve and protect the site for the future using affordable locally-sourced materials and a trained local labour force, to promote understanding of the site's cultural significance, and ultimately to make the temple accessible to visitors. To assist in achieving these goals, a capacity building programme has been initiated wherein personnel from NCAM, students from the University of Khartoum and local Dangeil personnel are trained in excavation and conservation techniques and materials.

2 Temple Description

The temple (48.5 x 33.5 m) is orientated east-west, in the desert on the edge of the cultivation, with the entrance facing the Nile. Most walls are a metre wide and preserved to a standing height between 1.5 and 3 metres. The basic unit of measurement used in construction was the Egyptian cubit (*c*. 52.3 cm) and it is evident that the structure was laid out precisely. The measurements reveal clear harmonic proportions, symmetry and regular architectural planning principles.

A mixture of materials including sandstone (quartz arenite), fired red brick and sundried mud brick were used in the temple's construction. Most walls have red brick foundations with the upper parts consisting of a mud brick core, faced on the exterior with red bricks. Column drums in the courts were created from red brick quarter circles or thirds sandwiched together with mud mortar. The floor surfaces, sanctuary columns and wall facings are of sandstone. Fine chisel marks on the external surfaces of the sandstone indicate that many blocks had been prepared for a finishing layer of painted lime plaster. The wall surfaces had been covered with a white-washed mud plaster which was painted yellow, red, robins' egg blue or some combination thereof. The pigments used have been identified by Raman spectroscopy with the red and yellow being hematite and a highly crystalline goethite respectively and the blue, a calcium copper silicate ($CaCuSi_4O_{10}$) commonly known as Egyptian blue.

The temple was destroyed by fire and Accelerator Mass Spectrometry (AMS) and C14 dating of the charred roof beams have placed construction of the most recent incarnation of the temple in the 1st century AD. This date is further confirmed by the associated ceramics and inscriptions. Following its destruction, the temple gradually decayed and collapsed.

3 Conservation of the Archaeology

3.1 Establishing Principles and Assessing Options

An initial working visit to Dangeil was conducted in November 2008 (Fig. 1).

In discussion with the site directors, the conservation principles and goals for the site were established. The decay mechanisms affecting the architectural elements of the site were identified as: the inherent fragility of the building materials; the extreme temperatures; the short seasonal period of heavy rainfall and the physical damage due to human activity.

This first visit in 2008 was intended to establish the locations and extent of the trials, the materials to be used and to discuss the aesthetic appearance of the finished work. It was agreed that: the main aim of the project was to preserve the

site's long term future; any materials used in the site's conservation or maintenance must not confuse the ancient archaeology; all materials used must be sympathetic to the original structures and be sourced locally; and that the conservation work would be continued and executed by a local work force in the future, after appropriate training. It was also important that any work could be removed easily without compromising the archaeology and essential to find a solution to prevent the continuing cycle of loss of original material due to environmental factors and human footfall impact. The materials to be conserved were the brick, stone and lime plaster elements of the temple.

Fig. 1 Aerial view of Dangeil

A capping system of a sacrificial lime mortar, combined with local building materials was proposed as protection against the various decay mechanisms. This practice has been used successfully by English Heritage on exposed architectural ruins in England and by conservators on archaeological sites in Europe; this was considered to be an appropriate system for this site. An alternative approach of soft capping using earth and shallow-rooted plants was considered, but dismissed because neither the climatic conditions nor the indigenous plants suit this method of protection.

3.2 Conservation

The initial days were devoted to sourcing suitable materials for the conservation project. Sand and bricks posed no problem. There is a plethora of sand in Sudan and an abundance of fired bricks. The lime, however, caused some issues due to the confusion in product labelling, local Arabic names and to its wide variety of local uses. It was only after several explanations and purchases, including the acquisition of casting plaster, that these issues were clarified. As the work proceeded, the working characteristics of the lime mortar mixes indicated that the lime varied in quality.

Test samples were prepared to determine the most appropriate mix of sand and lime for the mortar. Finally, a mix of 3:1 (sand:lime) was decided on. These proportions appeared to be sympathetic in colour and hardness to the historic material. A sharp sand was used in the preparation of the bedding mortars and scratch coats while a fine sand was used for the finish coats and pointing.

3.2.1 Test Areas 2008

The areas selected covered a range of the site's architectural elements; an area of the missing sandstone floor; the lime-plastered sandstone walls; the capping and rendering of the exposed fired brick walls and the plaster-rendered brick columns (Fig. 2).

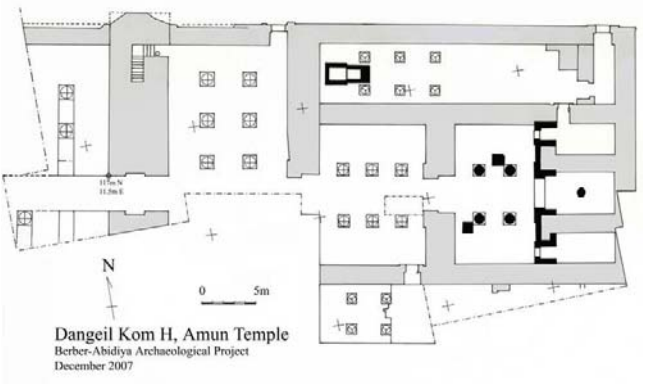

Fig. 2 Plan of the temple

With a small team of workmen to train, a missing section of sandstone floor was the first area selected. The intention was to fill the missing area with fired bricks. Sand and soil were removed and the area levelled to allow for a bedding mix and a brick depth to be laid. The area was well-damped and the bricks soaked to avoid rapid drying of the bedding mortar. It was imperative to plan the activities of the day. When possible, work was carried out in shady areas and in the coolness of the early morning. It was important to avoid working in areas directly under the midday sun and it was essential to keep the lime mortar work covered with tarpaulins. This allowed the mortar to cure slowly and in a controlled way. Retaining the moisture in the bricks and mortar assisted the pointing (Figs. 3, 4). Other trial areas followed a similar practice and approach; bedding with combinations of lime mortars; raking out and removal of excess soil; pointing. For the wall capping and brick column, a render was applied to cover the top of the new bricks (Figs. 5, 6).

Fig. 3 Laying bricks in a missing area of floor

Fig. 4 Pointing the bedded bricks

Fig. 5 Applying lime render to brick capping

Fig. 6 Finished lime render on column

3.3 Evaluation of Test Areas 2008 and Further Test Areas 2009

In November 2009, a two-week visit allowed for the evaluation of the previous year's work, to continue the trial areas and to adjust, if necessary, the methods and treatments. Regrettably, there had been some failure of the previous year's trial areas. The lime renders to the brick wall capping and the brick column had been washed away by seasonal rains (Figs. 7, 8).

The two areas of brick infill to the temple floor were successful and had withstood the rain of the previous season. Perplexed by the failure of the lime mortar, a sample from each of the various limes purchased in 2009 was retained to be analysed on return to the British Museum. It was hoped these analyses would give an indication of the lime content in the mortars being used. As in the preceding season, purchasing lime appeared to be a lottery, when one bag transpired to be a casting plaster. Three further areas were chosen to continue the work of the previous season; a larger, missing area of the temple's sandstone floor; a staircase; and another area of wall capping (Figs. 9-12).

Fig. 7 Failed render to lower area of wall

Fig. 8 Failed lime render to brick column

Fig. 9 Brick infill of sandstone floor, 2009

Fig. 10 Pointing brick infill to floor, 2009

Fig. 11 Top of staircase, 2009

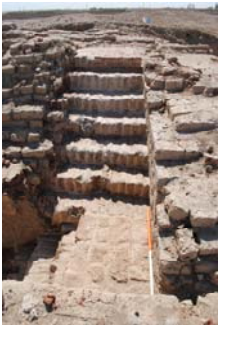

Fig. 12 Completed staircase, 2009

The same methods were used as in 2008. Whilst it was felt that the workmen required more training in building with and using lime, it was not the key reason for failure. The foremost reason was the weakness and absence of lime in the mortars as shown by the scientific analyses of the mortars (see below). The work completed in the season of 2009 will be re-evaluated in 2010.

4 Scientific Analyses

On return to the British Museum the samples of mortars prepared in Dangeil were analysed. The recipes were not specified and the samples were identified by number only. A sample of the archaeological lime plaster was also analysed. The samples were imaged using a Centaurus backscattered electron detector in an Hitachi S-3700N variable pressure scanning electron microscopy (VP-SEM: 20 kV, 30 Pa). Energy dispersive X-ray (EDX) microanalysis was conducted on all the uncoated cross-sections to analyse and map their elemental compositions. The analyses revealed that the lime content, as indicated by the calcium (Ca) peak, was negligible in the two mortar samples prepared in Sudan (samples II & IV, Figs. 13, 14).

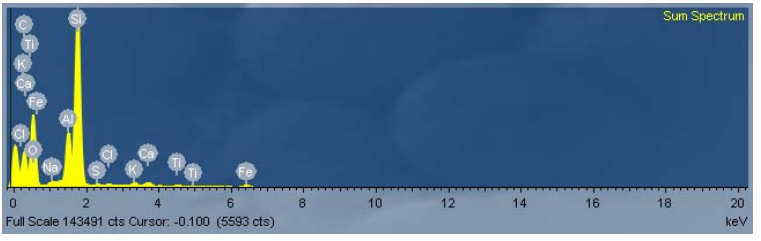

Fig. 13 Elemental composition of sample II prepared at Dangeil

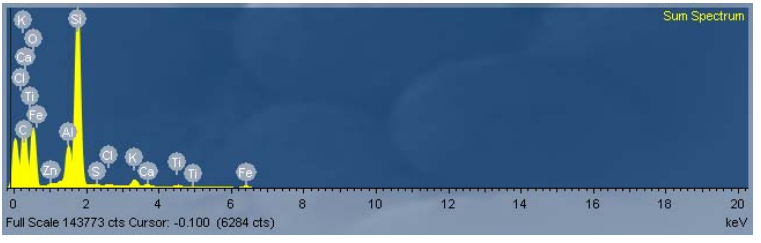

Fig 14 Elemental composition of sample IV prepared at Dangeil

In contrast, EDX analysis of sample VI indicated a level of calcium (in the form of calcium carbonate) typical of a good lime mortar (Fig. 15).

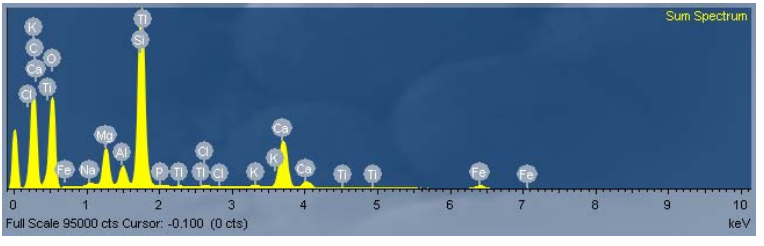

Fig. 15 Elemental composition of sample VI prepared at Dangeil

This can be compared with mortars prepared at the British Museum using the same recipes as in Sudan, but replacing the Sudanese lime with an hydraulic lime (Fig. 16, British Museum sample X) or a lime putty (Fig. 17, British Museum sample IX). These spectra show comparable levels of calcium to Sudanese mortar sample VI shown in Fig. 15.

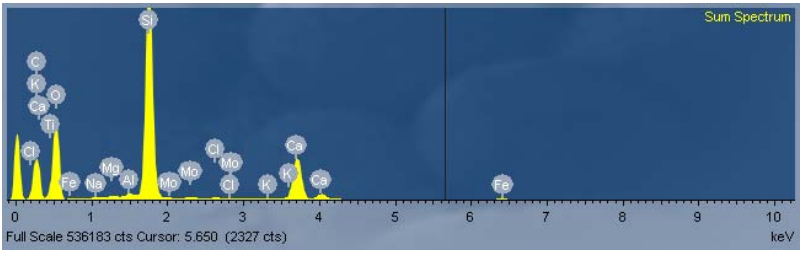

Fig. 16 Elemental composition of sample X prepared at the British Museum

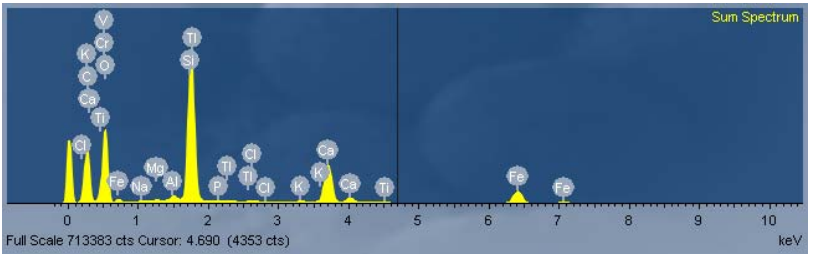

Fig 17 Elemental composition of sample IX prepared at the British Museum

5 Conclusion

The trials carried out are actual illustrations of what can be achieved with the restricted resources available at this remote site in Sudan. The following seasons will help the team understand what is practical to accomplish in this environment, and where there is failure, what adaptations are necessary. All the materials used in this project are readily reversible and will cause no future problems to the architectural elements. These trials have helped the site directors visualise the conservation possibilities and what alterations might be essential in future. Generally, the work carried out was successful; the local workmen had the manual dexterity to use the materials and were quick to learn their application. Scientific analyses have shown that the purchase of good quality lime is essential for the success of the capping. A great deal has been accomplished within the programme and with the limited choice of resources. If there has been one criticism of the project, it is that the aesthetics of the modern work might be confused with some

of the original archaeology. This is a debate for NCAM and the site directors. There are options for alterations of the methods and materials which will not compromise the conservation of the archaeology.

III.21

Grouting Mortars for Consolidation of Historical Renders Showing Loss of Adhesion

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Abstract Loss of adhesion is one of the main forms of degradation of old renders; it can cause the separation of different render layers or the separation of the render and substrate; this in turn can produce anomalies such as de-bonding, detachment, cracks and lacuna on the render. The work represented here is part of a study developed at the LNEC – National Laboratory of Civil Engineering of Portugal – to examine how consolidation using grouts for adhesion restitution can be used for the restoration of historical renders. The lime grouts used for consolidation should be mechanically, physically and chemically compatible with the original render, as this is a practically irreversible treatment. The aim of this study is to examine the characteristics of grouts, with consideration to their compatibility and efficacy. This paper details the methodology of the study and a description of the laboratory tests carried out, as well as a critical analysis of the results and a summary of the conclusions. Some proposals for future research are also presented.

1 Introduction

External renders, with their several layers, are important elements of the built structure. Their technical, aesthetic and historical content contribute to a building's identity. The preservation of traditional constructive techniques and the use of compatible repair materials (as similar as possible to the original) are significant in the maintenance of historical renders. One of the major causes of the decay of render is a loss of adhesion. This anomaly presents itself as a separation between the different layers of a mortar or between mortars and their support, producing defects such as detachments, cracks and lacunae. At present no technique exists to repair this loss of adhesion in situ, hence the current tendency

is to remove the old render and substitute it with a new one, thus resulting in a loss of traditional materials and construction technology.

To re-establish the loss of adherence, a consolidation technique with grout mortars can be used. During the last few years, grouts have become increasingly popular as a material for such repairs. To improve their suitability, their composition has undergone modification throughout time with adjustments being made to the type of binder, and to appropriate fillers and additives. Consolidation by grouting consists of the introduction of a very fluid lime paste into the void area created by the detachment of the render from the substrate.

The aim of this study is to discuss the main characteristics of grouts tested under controlled conditions in a laboratory before their application in-situ. As lime grout mortars are irreversible conservation treatments, they should be mechanically, physically and chemically compatible with the original renders [1]. Table 1 presents the basic requirements for consolidation treatment with grout mortars, as determined from previous studies.

Table 1 Basic requirements for consolidation with lime grout mortars [1-2]

Consolidation in case of loss of adhesion (grout mortars)	Capillary water absorption coefficient	Capillary water absorption coefficient 50 – 100% of substrate mortar
	Compressive strength	Lower than the substrate's (< 60%)
	Modulus of elasticity	Lower than of the substrate's (< 80%)
	Pull-off-strength	≥ 0,1 Nm²
	Shrinkage and dilation	As small as possible (< 4%)
	Consistency	Fluid enough to inject
	Set time	Not over 48 hours

2 Materials and Samples

In this study three different industrial grout mortars were tested to determine which were favourable for use in consolidation. These mortars have the following compositions:

- Mortar A – based on air lime with additives and fillers.
- Mortar B – based on hydraulic lime with additives and fillers.
- Mortar C – based on air lime with calcareous micro-sand and pozzolanic additives.

These grout mortars were prepared according to their producers' specifications and were mixed with water for approximately 5 minutes. Samples were produced in two forms for laboratory analysis:

- Those that were cast within rectangular moulds (40mm x 40mm x 160mm) (Fig. 1).
- Those constructed to simulate a loss of adherence where "detachment" between layers was artificially produced in a laboratory [3] (Fig. 2). These specimens were prepared using red perforated bricks rendered on one side with two 10mm thick layers of lime mortar (volumetric proportion lime:sand of 1:3). After the first layer had been applied, a plastic ruler was placed on top, prior to the application of the second layer; the ruler, removed after the render had dried, was used to simulate a void area between the two layers. Three months later the void area was humidified with a water and alcohol solution to facilitate grout penetration. The grout was then injected, at first with a very fluid consistency, in order to facilitate the complete filling of the hole. After the treatment the samples were placed in a conditioned room at 23º±2ºC and 50±5% relative humidity.

Fig. 1 Preparation grout mortars within metal mould.

Fig. 2 Specimens created to simulate the "detachment" between layers

3 Test methods

The following tests were selected to study the efficiency of the grout mortars:

- *Water absorption by capillarity* – to evaluate the capacity of the grout mortars to absorb water by capillarity (EN 1015 –18:2000).
- *Flexural and compressive strength* – to evaluate the mechanical resistance of the grout mortars (NP EN1015:11).
- *Dynamic modulus of elasticity* – to evaluate the deformation capacity of the grout mortars (method of resonance frequency – LNEC Report 427/05-NRI [5] and NF- B10-511) (Fig. 3)
- *Pull-off test* – to evaluate the adhesion strength between the grout mortars and the render (EN – 1015-12:2000) (Figs. 4, 5 and 6).
- *Shrinkage* – to evaluate the shrinkage of the grout mortars by comparing the variation between the initial (mould dimensions) and final (after curing) dimensions.

- *Rheology* – to evaluate the grout behaviour in fresh state through an analysis of the relationship between the product flux and deformation.

All the tests (except for rheology) were carried out after 90 days of curing.

Fig. 3 Determination of dynamic modulus of elasticity.

Fig. 4 Cut in the specimen showing cracks in grout mortar C after the pull-off test.

Fig. 5 Specimens after pull-off test, showing grout mortar B in the central section

Fig. 6 Grout mortar A in the core removed from the pull-off test.

4 Results

4.1 Evaluation of behaviour concerning water absorption

The water absorption behaviour of the moulded grout mortars was evaluated by capillarity and was plotted on a drying curve. The water absorption curve was obtained using the methodology outlined in EN 1015-18, by partial immersion of the specimens and periodical weighing. The drying process was monitored by taking the specimens out of the water and placing them in a conditioned room (23ºC and 50% HR) where they were weighed periodically. The results are presented in Fig.7 and Table 2.

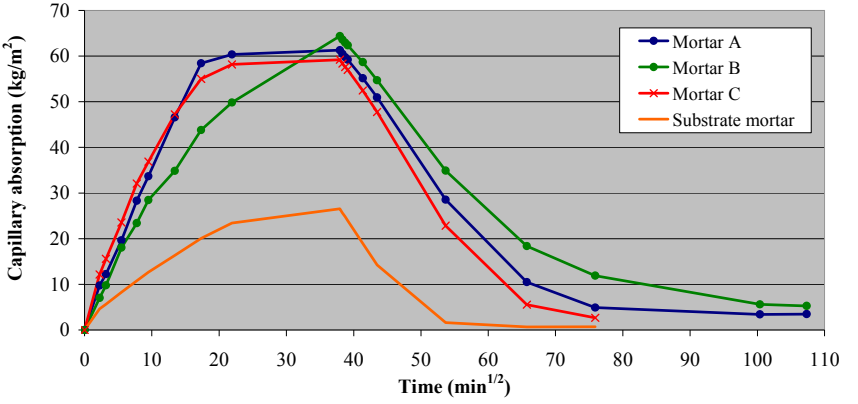

Fig. 7 Water absorption and drying of grout specimens

4.2 Mechanical resistance evaluation

To evaluate the mechanical resistance, the flexural and compressive strength was determined for the moulded samples, and the pull-off resistance was determined for the simulated samples. The pull-off test was carried out on the samples in a zone with grout (one pull-off determination) and in a zone without grout (two pull-off determinations).

The pull-off test was not possible on all samples due to the detachment of a core during cutting (before pull-off). This happened in all the samples prepared with grout mortar C and in two samples prepared with grout mortar A. The results were obtained for three samples using mortar B and one sample using mortar A and are presented in Table 2.

4.3 Evaluation of grout mortar deformation capacity

The deformation capacity was evaluated through the dynamic modulus of elasticity for the moulded grout mortars, using the frequency of resonance method. This is performed by bombarding the sample with a varied series of high frequency waves; the peak of amplitude is then used to identify the resonance frequency. The resonance frequency is similar to the natural frequency of the specimen and thus it is possible to use it to determine the dynamic modulus of elasticity. The results are presented in Table 2.

4.4 Evaluation of mortars shrinkage

The evaluation of the shrinkage of the grout mortars was determined by measuring each dimension of the moulded samples after drying, and comparing them with the dimensions taken before drying. The shrinkage was perceptible in all dimensions (length, width and thickness).

4.5 Mortar evaluation in fresh state

The rheological behaviour was studied with a specific rheometer (Viskomat PC) designed for use on mortars. The rotation speed of the vessel can be programmed and in this study, a speed profile was used in which the speed was initially set at a constant value of 160 rpm for 90 min. Each 15 minutes following this, the speed is reduced to 0 rpm and then back to 160 rpm for 155 minutes (fig.8). In these variable speed zones, flow curves of torque (T) vs. rotation speed (N) can be constructed. The relationship between torque and speed ($T = g + h\,N$) is characteristic of a Bingham fluid, where g and h are coefficients directly related to yield stress and plastic viscosity [6].

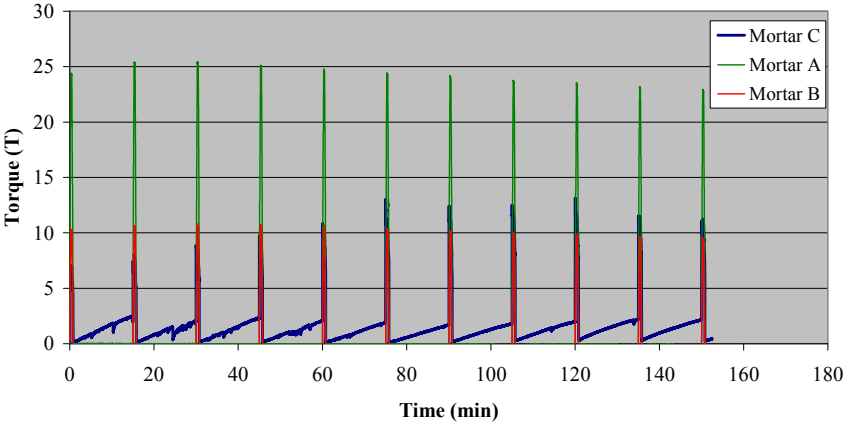

Fig. 8 Torque variation

4.6 Overall results

Table 2 Results of grout consolidation - laboratory tests

Laboratory test	Grout Mortar A	Grout Mortar B	Grout Mortar C	Render mortar
Capillary water absorption coefficient during the first 5 minutes (0 – 5 min) ($kg/m^2min^{1/2}$)	4.35	3.15	5.45	2.09
Standard deviation	0.02	0.11	0.36	0.14
Flexural strength (N/mm^2) (EN1015:11)	0.98	1.69	0.41	0.24
Standard deviation	0.07	0.14	0.10	0.04
Compressive strength (N/mm^2) EN1015:11)	1.64	3.71	0.80	0.62
Standard deviation	0.16	0.51	0.16	0.03
Dynamic elastic modulus (MPa) (NF – B10-511)	3123	4451	2025	2715
Standard deviation	162	71	60	8
Pull-off-strength (N/mm2) (EN-1015-12:2000)	Zone without grout (cohesive rupture)			
	0.03	0.05	N.D. Rupture during test	-
	Zone with grout (rupture within the grout)			
	0.04	0.06	N.D. Rupture during test	-
Shrinkage (%)	1.3	1.3	5.6	-

5 Discussion

The study of the main characteristics and the performance of grout mortars to re-establish the adherence of old renders is ongoing, however many of the initial details of this experimental research can be discussed here. The characteristics of the three grout mortars that have been studied in this paper include:

- *Injection facility*: all mortars could be easily injected, and presented a good fluidity.

- *Set time*: according to visual observation, mortars A and B began to set after 36 hours, and mortar C began to set after 48 hours; the exact determination of set time will be done later using more accurate test methods.
- *Water capillarity absorption and drying*: the capillary water absorption coefficient during the first 5 minutes was lower for mortar B compared with the other mortars. This coefficient is an absorption rate and should correspond to the slope of the linear portion of the absorption curve; thus for mortars of high capillarity, as is common with lime mortars in general, it is more accurate to determine the coefficient between 0 and 5 minutes (Fig. 7). As it can be observed in Fig. 7, throughout a 24 hours test, mortar B took more time to become saturated than the other mortars. The highest water absorption value was found in mortar C (which also had the highest drying time) and the lowest in mortar B. These grout mortars show higher water absorption coefficients when compared with the old substrates analysed in previous studies [7]; the older substrates most likely had a lower capillarity than the old grouts. However, through the analysis of Fig. 7 it can be found that grout mortars have lower total water absorption when compared with the lime render mortar (recent lime mortar).
- Mechanical behaviour: mortar B presents the highest flexural and compressive strength as well as elastic modulus; however, in general, the results are moderate. Although it could be possible to use the studied grout mortars on old and well carbonated substrates, they are too strong and stiff to be used on newer lime mortars (Table 2). Mortar C presented the lowest resistance and elastic modulus, lower than the lime render mortar; mortar B presented the highest resistance and elastic modulus (Table 2). Mortars A and C can be used to consolidate old and weak lime renders, in most situations.
- *Adherence*: the pull-off test showed that grout mortars have a similar strength to the lime mortar render (zone without grout, Fig. 2). On mortar A rupture occurred through the core (Fig.6), meaning that the grout´s tensile strength is higher than that of the render, although the test was performed on one specimen meaning that more experiments should be carried out to confirm this result. In mortar B the rupture occurred throughout the grout (Fig. 5), indicating that the grout's tensile strength was lower than the cohesive strength of the substrate´s mortar and the adhesive strength between the grout and render.
- *Void area filling*: observation of the rupture surface of the pull-off test on grout mortars A and B, showed that the hole in the specimens was uniformly filled (Figs 4 and 5). On mortar C voids and some cracks were found (Fig. 4) with a powdered appearance, possibly due to incomplete carbonation.
- *Shrinkage*: the highest shrinkage (5.6%) was found in mortar C and the lowest shrinkage, around 1%, was found in mortars A and B (Table 2).
- *Rheological behaviour*: the highest and lowest plastic viscosity were respectively found in mortars B and C. Mortar B presented a low yielding stress, which could be a positive factor for grout mortars, meaning it is adaptable to voids to be filled. The low yielding stress was prolonged

throughout the test period. This also seems to be a favourable characteristic for grout mortars: consolidation by grouting is a slow process, and this therefore means that grouts can be used for longer periods of time with a preservation of their initial properties. Through the analysis of torque values, it was verified that all the mortars were stable during the test period.

6 CONCLUSIONS

The results obtained showed that mortars A and B have in general, favourable characteristics. They fulfil the basic requirements for grout mortars, thus they can be used in the conservation of old renders for adherence restitution, as long as the renders are strong and well carbonated. Grout mortar C was found to be weaker and more deformable than the other tested grout mortars. With the low characteristics obtained, grout mortar C could be used to consolidate weak renders; however, it was observed that it didn't harden during the 90 day curing time, probably due to the difficulty of carbonation inside the voids.

The choice of grout mortar depends on the pre-existent renders' mechanical behaviour and decay (lacunae/detachment deepness, humidity rate in the wall, etc.). Hence, of the tested grout mortars, mortar B should be chosen for more resistant existing renders (compressive strength > 6.1 N/mm^2, according to the requirements defined in Table 1, which is a rather high value for old lime renders).

Concerning water absorption, all the tested grout mortars should be used only on old renders with a capillary water absorption coefficient, calculated at 5 minutes, lower than about 5 $kg/m^2.min^{1/2}$.

Of the grout mortars, only B and C present hydraulic properties. With mortar B, this is due to a hydraulic binder and the possible addition of pozzolanic additives; with mortar C, this is due solely to the pozzolanic additives. However, the powdery texture within mortar C indicates that the pozzolanic additives failed to react fully. The development of a grout with hydraulic characteristics is important; indeed it allows their hardening in spite of a low carbonation rate inside the wall where exposure to the air is minimum [8]. Mortar B presented lower water absorption, higher mechanical strength, higher shrinkage and lower deformability. However, the addition of hydraulic binders should not be excessive in order to prevent the high increase in mechanical strength which can contribute to the development of anomalies such as detachment or cracking in the old renders.

This investigation framework will eventually lead to the development of new grout mortars which can be customized for their required performance. The formulations can be improved by altering the proportion of hydraulic binder or pozzolanic additions, by choosing aggregates with better grain size distribution and altering admixtures to optimize characteristics such as: fluidity, solidification, penetration and carbonation.

The continuation of this study will allow a more in-depth understanding of the materials used, and will lead to the diffusion of such knowledge through the international and national technical community in order to contribute to the improvement of conservation interventions in historical renders through the use of traditional materials.

7 Acknowledgements

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III.22

Vitruvius and Antique Techniques of Plaster Work and Painting

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Abstract The current project *Vitruv und die Techniken des Raumdekors* is focused on the investigation of ancient plasters and painting techniques in the context of the specifications of Vitruvius' *De Architecura Libri Decem*. A multidisciplinary group of scientists composed of conservators, architectural historians, archaeologists and philologists is dedicated to the elaboration of a new German translation and critical annotation of the technical terms and descriptions of Vitruvius' work, particularly books II, VII and VIII. Instructions from the text will be compared to archaeological proof and experimental archaeology. Research on the reception of Vitruvius' descriptions in the Renaissance, both in written sources as well as in built architecture, is another aim of the project. Here again the focus is set on plasters and painting techniques.

1 The new edition and translation of Vitruvius' descriptions of art technology

1.1 Text and present translations

Marcus Vitruvius Pollio (~84–20-10 BC), the author of the *De Architectura*, was a Roman architect, art historian and engineer in military and hydraulic construction. Little is known about his life and information is mostly provided by his own remarks where he relates to his close connection to Imperator Augustus, whom he dedicated his work. Divided into ten sections or "books", *De Architectura* covers almost every aspect of architecture, from town planning, materials, decorations, temples to water supplies, etc. His work today represents

the only major antique written source on architecture and building techniques in the West.

Since its "rediscovery" in the beginnings of the 15th century, at the very latest since the first printed edition in the 2nd half of the 15th century, Vitruvius' work forms the foundation for any kind of argument with antique architecture, especially for the Roman culture. His doctrine about proportions and his descriptions of the orders of architecture, henceforth, became a central part of modern architectural theory. Renaissance architects were anxious to employ Vitruvius' descriptions in their own work, trying to get as close as possible to classical, and therefore renaissance, ideals.

The original text version is lost, but the content has been preserved through the ages by several medieval transcriptions. All of them are faulty and in addition to the difficulties in the interpretation of the Vitruvian language and the peculiarities of his descriptions, the understanding is not always absolutely certain. Its singularity does not allow comparisons to other texts with similar contents. Therefore every edition and translation cannot be more than a careful attempt to reconstruct the original text. Despite the long lasting philological tradition in interpreting Vitruvius' work there still remain many unsolved questions.

So far *De Architectura* has been translated into several languages (Italian, Spanish, English, Dutch, German, Polish and French). The latest German edition was published in 1964 [1]. A comparison of various editions points out the mismatches between them. In the context of technological content this is not amazing due to the fact that all existing versions are based only on a philological approach to the Latin and Greek manuscripts. Considering the cloudy indications of Vitruvius, augmented by the incomplete written records this is no wonder, especially as the respective references of modern technical literature provide only inconsistent information.

On the other hand, the different disciplines, which base their research on editions and translations of *De Architectura*, are confronted with a heterogeneous, and in parts simply misplaced, professional terminology. In the case of the most recent German translation from 1964 [1], the terms are partly antiquated.

1.2 Interdisciplinary co-operation between archaeologists, philologists and conservators

Besides the linguistic difficulties of translating Vitruvius' texts, the technological contents are also not sufficiently discussed in the existing translations of *De Architectura*. The different independent references, which are cited in the commentaries, can only provide limited information because the references are rarely based on systematic studies of roman wall paintings. Linking the archaeological-philological and scientific-technological disciplines involves the broad research of all the single facets and edificial details which are described by Vitruvius. The result of the investigation is set to enlighten Roman construction

and decoration techniques, diverging from the current state of research in order to provide a new reference for later studies on the topic.

The existing research and discussions in context with the brilliant smoothness of Roman wall paintings are a good example to demonstrate the difficulties presented by the interpretation of Vitruvius' descriptions. Book VII, 3 of *De Architectura* is dedicated, amongst others, to the composition of mortars, the way to apply them to walls and how they are to be treated in order to reach the special shine and firmness which at all times have invited admiration. Comparing various translations shows the wide range of possible interpretations which result from a simple translation of the latin texts.

"*Sed et liaculorum subactionibus fundata soliditate marmorisque candore firmo levigata, coloribus cum politionibus inductis nitidos experiment splendores*." [1, 3, 4]

"[…] *sondern sie werfen auch, wenn sie mit Stöcken dicht geschlagen und mit hartem Marmorstaube geschliffen, zugleich aber beym Poliren mit Farben überzogen werden, einen schimmernden Glanz von sich*." [2]

"*Wenn aber der feste Verputz infolge der Bearbeitung mit Liacula noch verdichtet und mit hartem festem Marmorweiß (Marmormehl) geschliffen ist, werden die Wände, wenn die Farben zugleich mit dem Putz aufgetragen werden, einen schimmernden Glanz zeigen*." [1]

"*Mais lorsque leur solidité, assureé en profondeur par la pression des taloches, aura de surcroît acquis par le lissage la blancheur éclatante du marbre, les murs, grâce aux coleurs étendues avec la couche de finiton, jetteront un brillant éclat.*" [3]

"*Ma una volta che la loro compattezza è stata consolidata, strofinandola con spianatoi, e levigata con il marmo lucente e duraturo, le pareti irradieranno la piú smagliante lucentezza dopo che, assieme alla rifinitura finale, vi saranno spalmati i colori.*" [4]

"*But once the durability of such revetments has been ensured by being worked over with plasterers's floats and polished with bright and stable marble-powder, they will be brillantly luminous when the colours have been applied with the final surface.*" [5]

The differences between the single translations are obvious: depending on the function of the marble in context with shiny wall surfaces, the interpretation of the sentence leads to completely diverse meanings. On one hand, marble forms the material used to polish a plastered surface and on the other, it has a metaphoric meaning describing the intended effect. From the technical point of view the cited translations involve both completely different working processes and the different associations concerning the tools used.

At the same time scientific approaches have been undertaken in order to separate the problem of translation from the built evidence. Several theories explaining the working-process can be found in related literature:

- The earliest theories focus on the technique of Roman encaustic painting (painting with pigmented, heated beeswax). During a grand dispute amongst experts in Munich about 100 years ago, there were two different beliefs: The first, represented by Berger, thought the secret of the smoothing techniques of

mortars would be the"Ganosis", i. e., the treatment of the painted walls with hot wax; this theory relates to an interpretation of a quote from Vitruvius about the treatment of cinnabar colour coats with the help of wax (book VII, 9). The second belief was represented by the "fresco theorists" Keim, Donner von Richter, Laurie, Raehlmann and Eibner. The latter led the debate in 1926: in his book"Entwicklung und Werkstoffe der Wandmalerei vom Altertum bis zur Neuzeit", he primarily described the antique wall painting technique as a fresco technique [6]. As to Eibner, there is no proof of the use of encaustic techniques in the various chemical studies of original and untreated fragments of antique wall paintings.

- The assumption that protein glues could assist in the smoothing process of wall painting surfaces is mentioned often; Klinkert [7] for example, suspects the use of animal glues for fresco wall paintings. In this context he quotes Vitruvuis' remark on the mixing of animal glue with carbon black in order to paint plastered walls (book VII, 10).
- In 1984 Mora and Philippot [8] brought a new aspect to the discussion; they presumed that the addition of clay minerals to the upper layers of mortar was done to ease the smoothing process. This theory is confirmed by the findings of yellow and red ochre with a high content of aluminates and silicates, as well as white pigments based on clay minerals like kaolin, in painting and plastering layers; also Vitruvius himself describes the use of yellow ochre to smooth the surfaces of wall paintings (book VII, 7).

All attempted explanations are associated with the opus of Vitruvius at the one hand and with several independently conducted analytical studies on the other. The described theories coexist until now, and for each, new evidence can be found in the recent past. For example the encaustic theory, which seemed to have been disproved since the final publication of Eibner in 1926, has again been picked up by Augusti during the 1960's [9], and in the last few years further articles about the application of wax to wall paintings, proved by natural scientific studies, have been published [10, 11].

The approach to the problems, which arise in context with the smoothing process of antique roman wall paintings, show the necessity of more extensive studies relative to the topic. Against this background the current research project intends to create a new German edition of *De Architectura*, focussing on wall decoration techniques, especially in respect to its technological content. For the first time an interdisciplinary interpretation will be possible by linking an archaeological-philological analysis on the one hand with scientific-technical examinations on the other, supplemented by experimental reconstructions to verify the on-site findings.

Besides better knowledge of the antique working process of wall paintings, the project will illuminate further unexplained questions. The planned chronological, geographical and sociological studies on antique architecture will also provide new insights into the significance of Vitruvius and *De Architectura* in ancient

times. Because of the lack of comparable antique sources a correlation to other literary works is not possible and today's interpretation of *De Architectura* is not easy to achieve. It becomes even more complicated due to the fact, that hardly anything can be said about the author's life. What we know is that as an architect, Vitruvius did rarely supervise building construction. Therefore, the bigger part of his opus is not based on his own experience, but on other sources: for example, his education by different masters, his own observations and the profound knowledge of various writings from primarily Greek authors.

Against this historical and sociological background it currently appears highly desirable to find out how much *De Architectura* does indeed represent antique building techniques and in which way Vitruvius' writings were adapted from the ancient world. Thus, the question as to how much of Vitruvius' descriptions are based on real ancient traditions, should be discussed in a widespread manner.

2 Project status

In addition to broad research of literature, analyses of roman buildings are the main pillars of the project. The results of the studies on buildings and mortars will then be verified within workshops where the main topics will be mortar components and the techniques of surface treatment. All samples will be available for subsequent analytical research.

In this first stage of the project, Augustan wall paintings on the Palatine will be of main interest for further examination. Parting from the fact, that Vitruvius had close relations to Imperator Augustus, the probability of finding implementations of Vitruvian techniques in these buildings can not be dismissed. Research on these archaeological sites may provide new information which can be used to solve the linguistic problems of the Latin standard text and, in addition, can provide crucial evidence for the understanding of the role *De Architectura* played in antique times.

During the project several work stays in Italy are planned – the first took place during May 2010 for one month. Besides comprehensive studies at the libraries of the Istituto Superiore per la Conservazione ed il Restauro (IsCR) and the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM), the opportunity arose, with the kind permission of the 'Soprintendenza Speciale per i Beni Archeologici di Roma', to visit buildings with Augustan wall paintings on the palatine (Casa di Augusto, Casa di Livia, Aula Isiaca) and at other archaeological sites in Rome (Villa di Livia).

In addition to the results achieved in May, ongoing research promises crucial findings. They are to be published altogether in the near future.

Within the studies, regarding the reception of Vitruvius' descriptions in the Renaissance, the focus is laid on specific buildings in Munich (St. Michael's church, the Antiquarium at the Munich residence and the arcades of the

Hofgarten) and Bavaria (Stadtresidenz Landshut, Schloß Wetzhausen). Future research will expand the topographical emphasis to Italy, where the Renaissance had its origin and from where many travelling artists communicated both stylistic and technical developments.

Fig. 1 Workshops for the experimental reconstruction of antique roman plaster-techniques at the studio for stucco-works at the Akademie der Bildenden Künste in Munich (Photo: Kilian**)**

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III.23

Mortars in the Buildings of Pre-Hispanic Peru: Structural Behaviour Studies

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Abstract The Peruvian's prehispanic constructions are constituted by buildings of religious, military and social character. The remains that have survived to the present day have different levels of deterioration caused by an action of man or environment. Their conservation is undoubtedly a necessary and also interesting task. The structural evaluation of the Monuments that constitute the archaeological patrimony of Peru should be based on a previous research of the masonry components including mortars. This demands a study that allows to classify and identify the masonry materials so that one proceeds adequately in the identification of the stress levels to which they are submitted and likewise in the design of new Compatible Repair Mortars (MRC). It is important that the new repair mortars contribute appropriately to the preservation of the structure, i.e. they are durable and also provide the required functions. The mortars used in the buildings of the civilizations that developed in the Peruvian territory, which still remains in good conditions, are in some cases more than 4000 years and were able to support hard seismic activities. One has to bearer in mind that in this geographical zone the earthquakes are very frequent and masonry has to absorb stress and displacements without coming to the collapse.

1 Introduction

According to the studies developed, the first urban settlements of America are located in the Central Coast and Northern Peru. The Peruvian coast is located in the The Pacific Ring of Fire, planet zone with more seismic activity of the world (Fig. 1-a), the land is crossed by the Andes Mountain; in the South of country occur an important volcanic activity.

The coast desert to contributed of many structures do not deteriorate completely today is possible to study the ancient cities and verify the important development in their constructions. The lack of rain due to phenomena such as *El Niño*, frequent earthquakes, avalanches, wind erosion and especially the human

factor have been the principal agents to contributed the progressive deterioration of these structures, all built with the clay mortar, a very fragile material.

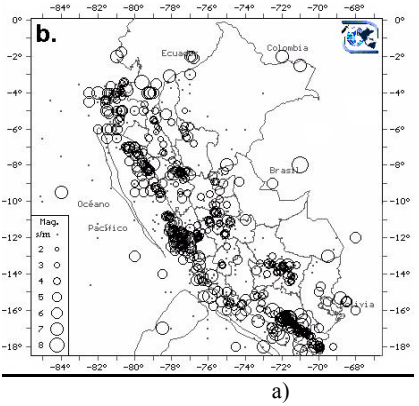
As part of the conservation work of the buildings, it is necessary, in principle, to analyze the most important structural typology and also to analyze the stress type in their parts, where the mortar clay have an important role when the material has been used in adobe or stone masonry from the first settlement of human groups, the large ceremonial centers, to the latest manifestations of Inca architecture. The mortar used was made with water, clay and sand, was built with earth, there are no known archaeological sites with features like pozzolan or binders such as cement, however due to the fragility of clay mortar were devised solutions or building systems that favour building maintenance may be trying to masonry structures that were made with clay mortar, weak in nature, were not working to capacity limit, surviving until today in good conditions at some cases.

The use of clay mortar is classified:

Decorative {Friezes
{Plaster

Structural {mortar in masonry walls Adobe
{Mortar on stone masonry walls
{Plaster plates *quincha*
{Mud wall

Fill {conglomerate of clay mixed with other elements



a)

b)

Fig. 1 a) Seismic Map of Peru (Fuente: Geophysical Institute of Peru). b) Clay figure, 2000 BC.

2 Hypothesis of development of the use of clay mortars

For have an structural analysis of constructions to the early civilizations in the coast and the highlands of Peru, we can see the technical development by clay mortars was becoming more complex as it was understood their mechanical properties to verify that weather conditions were considered, the mechanics of their physical behaviour and definitely the political and religious character. Special mention are the techniques used in the hydraulic, roads, bridges, etc., of which depended on a growing economy and infrastructure of which deserves further analysis. No doubt the ancient Peruvians found in the materials were at hand, earth, stone and water, alternative solutions for demanding construction requirements of your community, it's remarkable the ability to go was achieved taking advantage of these materials to your domain almost total in their mechanical behaviour, in some cases was combined with vegetal fibers using it a binder mortar in stone masonry walls, which gave substantial improvements in their mechanical abilities, it's known that the breaking strength of vegetable fibers is similar to ductile steel, so that we can say that these properties were exploited in these constructions [8], further research in this regard are necessary. We identified four stages, as in the technological development of the use of clay mortar in ancient Peru as a building material.

3 Stages use of clay mortar

3.1 First Stage - 2800 B.C.

It identifies a rudimentary use of clay mortar was used as filler in the platforms of the pyramids as bedding mortar on the walls of stone blocks of various sizes, with little use of the physical capabilities of the mortar, it is understood that its use was in its early days and still there was no extensive domain of this material, later shown improvements in the use of mortar for the settled of stone blocks

Uses:

- Seated stone block walls type orthostats.
- In adobe or stone masonry walls in platforms structure
- With bricks forming the filling of the platforms,
- How to fill platforms,
- In high relief and plasters, etc.

a) b) c)

Fig. 2 a) Stone wall in Chankillo [7], b) Stone wall in Caral c) Stone masonry with clay mortar and vegetal fibber in Caral.

a) b) c)

Fig. 3 a) Stone masonry, *Chavín de Huantar*, b) Fill: Conic shape adobe and mortar, *Cerro Sechín, Casma* [4], c) Wall masonry with clay mortar and vegetal fibber reinforcement, *Vichama Archaeological Site*.

At this early stage, *raised platform* is the architectural expression of more recurrent and meaning of all the Pre-Hispanic Peru. The structural system of the platform was in some cases a grillage type construction, this technique was settled the construction of walls with clay mortar, which were folded and locked together, these planes of walls that were left in a place that were filled in many types of filling: with *shicras* (vegetal fibber bags filled with stones), bricks, mortar in large quantities, and bricks in many shapes[1], this procedure allowed to gain height and volume with low weight, stability is guaranteed against earthquakes and flexibility for settlement of the soil (Fig. 4). These filling of *shicras* or mortar, are stable in themselves, that is, the force was not horizontal (the *shicras* piled on each other) in the case of dry mortar that is shaped like a large block of adobe, the push was in vertical direction of such form that the contour walls was not made a stress in their plane and supported small deformations.

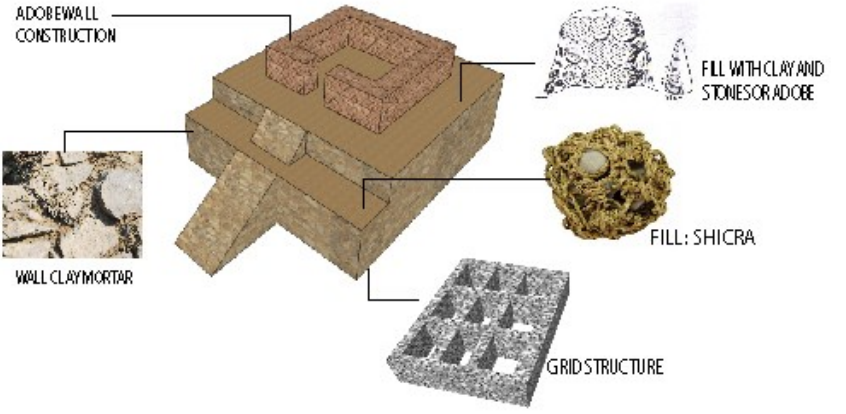


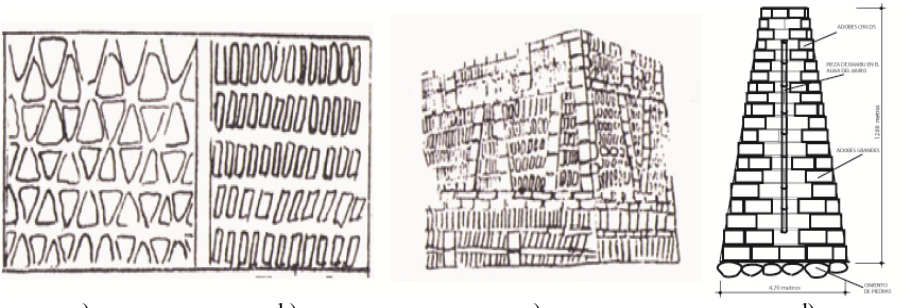
Fig. 4 Structural system of raised platform.

3.2 Second Stage – 200 B.C.

At this stage the mortar mixed with mud bricks used in several ways, tapered, and hexahedral planes, forming filled with platforms, this association adobe-mortar, followed patterns established in the blocks, forming the structures of pyramids and walls of great height (Fig. 5). They are made of plaster surfaces, handling of high relief with colour applications. In some cases, where the mortars is in perimeter walls are used as an additive of vegetal fibber reinforcement [6].The use of clay mortar at this stage was certainly more developed, the mortar was better spent on the settlements of adobe, grouped into large volumes settled in different ways but using the mortar in adept form [2], the bricks were many different shapes, (hexahedral, conical) [4], in different sizes and shapes of complex armed masonry. Although their fragility, these types of buildings could stand a long time, and its main deterioration factor is the rain and vegetation is close of the constructions.

Uses:

- Adobe wall masonry.
- Adobes shaping the pyramid platform.



a) b) c) d)

Fig. 5 a) Rigging of conic shape adobe [2], b) Rigging in book shape [2], c) Complex rigging in Pachacámac [2], d) Adobe wall with reinforcement in Chan Chan-Nord Peru [5].

3.3 Third Stage - 1000 A.C.

At this stage the mortars start to use in mass to form large masses, these casts were forming the large brick adobe or mud wall. The use of mud walls were reported in the construction of the great cities and ceremonial centers, its use was widespread in the last stage before the Spanish conquest and his technique is still in force in the Peruvian Andes. We know that building with adobe blocks involved the manufacture of molds and *brick mold* [3]. To shape in the same building site, compacted clay was carried out with blows of a wooden hammer, getting a good height walls, and straight and sufficiently earthquake resistant stability. The walls apparently had a relationship width: height to 1:3, and generally trapezoidal section which gave it good stability. You can verify that at this stage is a more technical use of clay mortar as a building material.

Fig. 6 a) Mud wall in Cajamarquilla, Lima. b) Mud wall and adobe construction, Lima.

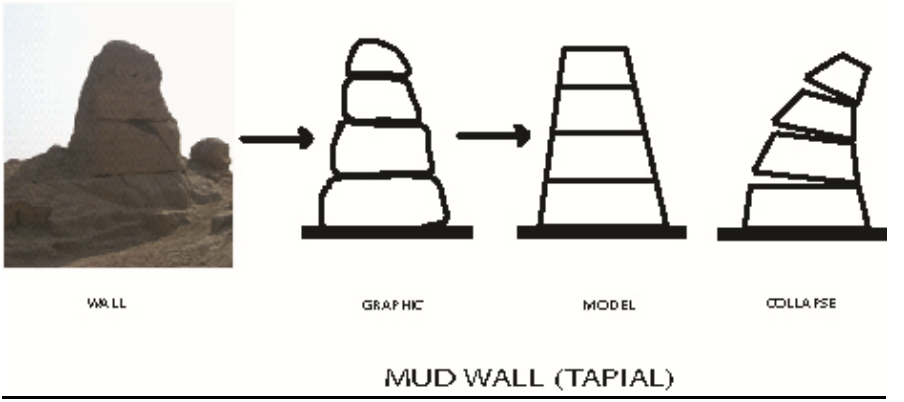


Fig. 7 Structural preliminary analysis of mud wall, Cajamarquilla, Lima

3.4 Fourth Stage - 1400 A.C.

At this stage the use of clay mortar reaches its maximum development, its manifestations are mostly associated with the use of mud wall and adobe and stone masonry. The use of clay mortar due to their fragility to face agents of deterioration such as moisture or earthquake, is used in conjunction with other construction techniques, such as quarrying, the results are the most notable achievements of the pre-Hispanic building in Peru. In the Inca period in which the masonry reaches its maximum development was dispensed with the use of mortars, this due to the fragility against the rains of the highlands. Despite these limitations are achieved remarkable structures (Fig. 8-b), with very slender walls, and even columns made of mud bricks, these examples in the Coast are impossible for your seismicity.

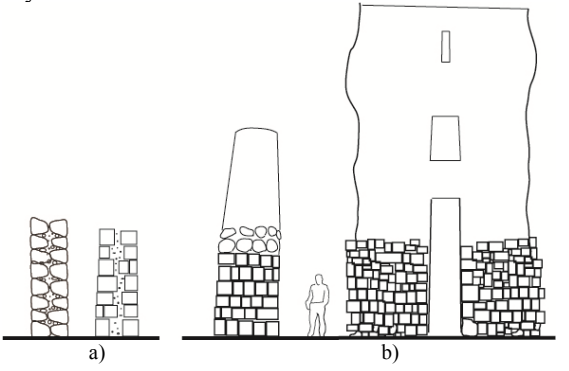


Fig. 8 a) Section of Stone wall with clay mortar fill, b) Inca's adobe wall, Templo de Wiracocha, Cusco.

4 Conclusions

As demonstrated in the paper, the mortars in the Pre-Hispanic Peru were prepared with soil and did not have a satisfactory performance itself, about your mechanical parameters however the mortars seemed to performed much better as a part of the building systems used. It is interesting to note the construction of masonry without mortar in the Inca buildings located in the mountains. The dry stone construction without mortars could be explained by the Inca's knowledge of poor durability of clay mortars. The preservation of Pre-Hispanic buildings in Peru needs the knowledge of structural and material performance. Important is also the traditional technologies of mortar production and preparation as in some cases the mortar components have been used by local societies over a thousand years.

According to this study we can identify a constant progression in the development of typologies and the use of component materials, stone, mortar and bricks. More studies are necessary to guide correctly Conservation of Archaeological Heritage of Peru.

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III.24

Strengthening of Heritage Buildings by Means of Grout Injection - Problems and Solutions

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Abstract Large part of heritage buildings in Slovenia was built with stones or mixture of stones and bricks, as up to 20th century the local stone represented the cheapest and most accessible building material. An efficient technique for improving mechanical properties of the walls of such building is grout injection. Because of lack of knowledge of the morphology and type of walls, incompatibility of existent and applied materials and errors during application, mistakes and even damages may occur. That is why methodology of work and criteria to achieve required quality should be defined. Based on the results of the extensive test campaign, chemical, physical and mechanical criteria for selecting optimal grout mixture are given and also guidelines and research needed to assess the condition and type of walls that could be strengthened by means of grout injection and to ensure the quality of executed work are presented.

1 Introduction

Many heritage buildings in Slovenia were built from stone or a mixture of stone and brick. Stone types such as limestone, sandstone and slate were used and in some cases brick inclusions were found to be included in structures. In general poor quality lime mortar was used. Thicker walls were mainly constructed in three layers (two outer layers of partly cut stones with an inner core built from leftovers and smaller stones), while thinner walls tended to have only two layers. Walls of buildings situated in urban areas are, in most cases, of a better quality when compared to those in rural areas, although shaped or roughly shaped stones are rarely found. Where they are found, they are in public and monumental buildings, usually in the corners and the intersections of walls. Because of the presence of voids and the poor quality of used mortar, the load bearing capacity of such walls,

especially towards lateral loading, is mostly not sufficient. An effective technique to strengthen and improve their mechanical properties is that of grout injection. Grout is injected into a wall under moderate pressure (2-3 bars) to achieve a better bond between stones and layers and to improve the mechanical properties of the injected wall. Frequent errors made during the execution of grout injection are a sign that technical regulations are necessary in this field of work. The main objective of this research was to contribute to the rising quality in the application of grout injection.

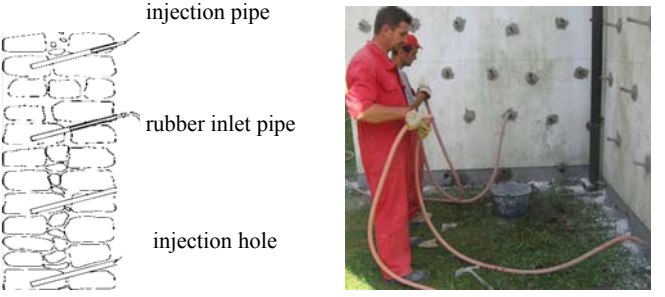

Fig. 1 The image to the left shows the setting up of the injection holes and the image to the right, the application of grout injection

2 Frequent errors by application of grout injection

Some of the most common reasons for errors that can lead to inadequate quality of grout injection or even damage of stone masonry walls can be summarized as:

- *A Lack of knowledge of the morphology of the walls*
  Lack of knowledge of the morphology can be the reason for selecting an ineffective method of strengthening. Grout injection is not effective in the case of non-injectable walls with less than 4% voids [6]. In such cases more appropriate methods of strengthening should be applied.
- *Incompatibility between existing and applied materials*
  Because of chemical and mechanical-physical incompatibility between existing and applied materials, degradation and damage of the existing materials can occur. Reasons for such degradation were described in detail by Collepardi [1].
- *A Lack of knowledge of the moisture content in walls*
  Excessive moisture content in a wall is a problem that has to be addressed before strengthening by means of grout injection. The application of the grout injection procedure without the elimination of the causes and consequences of excessive moisture content may lead to the accelerated degradation of the masonry [13].

- *Errors during application of grout injection*

During the supervision of strengthening procedures conducted as part of reconstruction works undertaken after strong earthquakes from 1998-2004 in the seismic prone area of Posočje, Slovenia; it has been found that some errors occur frequently, namely:

- Preparation of the grout with uncontrolled water/binder ratios which can lead to segregation and extensive bleeding of the grout;
- Interruptions to the working process that can cause lower workability and fluidity because of hardening of the grout;
- Inadequate preparation of the wall before injection: proper arrangement of the injection holes, angle of drilling, depth of holes and the amount of water used to wet the wall are all factors that influence the quality of grout injection;
- Inadequate pressure: a higher injection pressure enables better penetration of the grout into cracks and voids inside the wall, however at the same time it can also provoke further damage to the plaster or even the outer layers of the wall;
- Inadequate sequence of the working procedure: grout injection must always be applied gradually from the lower to the upper parts of the wall, a reverse procedure will cause the closing of voids due to the hardening of the grout which will consequently prevent the penetration of the grout to lower parts of the wall;
- Damage that occurred in buildings exposed to seismic loads after strengthening by means of grout injection has shown that the injecting of selective parts of walls or building intersections and corners, is not a good solution.

3 Laboratory tests of grout in dry, fresh and hardened state

Nine types of injection grouts containing hydraulic lime and pozzolana (LP1, LP2, LP3 and LP4), lime-cement grouts (LC1, LC2 and LC3), and cement grouts (C1 and C2), obtained in Slovenia, were subjected to laboratory tests. The laboratory tests were divided into four parts. In the first part the content of potentially harmful substances for nine different dry injection grouts were analyzed. In the second and third part, properties of fresh and hardened grouts were determined. In the fourth part, cylindrical specimens that represented the internal core of an injected wall were tested and their mechanical parameters were evaluated. For the assessment of the supplied grouts existing standards for concrete and mortar and also older standards for grouts for pre-stressing tendons EN 445-447:1996 [2-4] were used, with modifications where needed. Grouts were classified into three classes based on the chemical, physical and mechanical criteria determined through a literature survey and in collaboration with conservators and producers of grouts. Class A stands for a high quality grout, B for a medium quality grout and C for a low quality grout.

3.1 Dry grout

In the first segment the content of potentially harmful substances in dry grout, that could in conjunction with other factors cause damage to the final layers and paintings applied to a wall, was analyzed. Chloride, sulphate and alkali content were determined in accordance with SIST EN 196-2 [7]. Standard EN 447 [4] which deals with grouts for pre-stressing tendons sets the limit value of chlorides to 0.1% by mass. Sulphate can in some circumstances [1] have a negative influence because sulphate salt reactions can cause the formation of ettringite and/or thaumasite. High alkali content may be dangerous because of the efflorescence phenomena and the possibility of alkali-silica or alkali-carbonate reactions. Van Rickstal [15] recommends that for preparing grouts, cements with an alkali content lower than 0.1% by mass should be used. When using reactive aggregates to prepare concrete, the alkali content should not exceed 0.6% by mass [16]. In our research the content of harmful substances for corresponding classes were set, in the case of chloride at A ≤ 0.01%, B ≤ 0.02%, C ≤ 0.05%; in case of sulphate at A ≤ 0.1%, B ≤ 0.5%, C ≤ 3.0%; and in case of alkali at A ≤ 0.1%, B ≤ 0.5%, C ≤ 1.0%.

Content of potentially harmful substances and set limitations for each quality class are presented in Fig. 2. All grouts met the criteria set for class C, grouts LP1, LP2, LC2, LC3 and C1 met the criteria set for class B, but none of the grouts fulfilled the criteria set for class A.

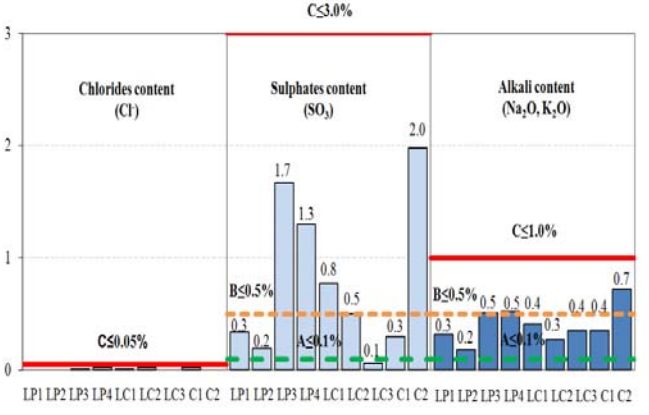

Fig. 2 Chloride, sulphate and alkali content in analyzed grouts in % by mass

3.2 Fresh grout

All grouts were prepared according to the specifications of the manufacturers. Properties which influence the workability, injectability and consequently the quality of grout injection were analyzed. Bulk density was determined in

accordance with standard SIST EN 1015-6 [8] and fluidity and bleeding according to standard EN 445 [2]. Obtained results are given in Table 1.

Table 1 Properties of fresh grout

	LP1	LP2	LP3	LP4	LC1	LC2	LC3	C1	C2
w/b ratio	0.45	0.45	0.55	0.38	0.50	0.62	0.50	0.40	0.43
bulk density (kg/m^3)	1599	1778	1563	1821	1673	1659	1712	1895	1856
fluidity (s)*	19.8/ 20.0	14.4/ 14.4	35.9/ 36.6	28.3/ 28.5	13.5/ 13.4	13.6/ 16.3	17.4/ 45.0	13.8/ 15.5	27.2/ 44.5
bleeding (%)	0.0	2.1	0.0	2.1	0.2	0.5	0.0	0.5	1.0

*measured immediately after mixing and after 30 minutes

Decisive properties, based on which grouts were classified, were w/b (water/binder) ratio, fluidity and bleeding. For w/b ratio a criteria of a maximum value of 0.60 was used by Valuzzi [14] to avoid the unfavourable effect of a high water content on the mechanical properties of a hardened grout. In our research the limit of w/b ratio was also set to 0.60 with a tolerance of 10 % for classes A, B and C. In the research performed by Valuzzi [14], time of fluidity for injection grouts was limited to 25-30 s. In our study, time of fluidity for grouts of class A was set to 25 s, with the difference between fluidity measured immediately after mixing and after 30 minutes limited to 10%. For grouts of class B and C, measured time of fluidity should not exceed 30 s with the maximum of a 15% difference between the two measurements. Bleeding of grout after 3 hours, as defined in standard EN 447 [4], should not exceed 2.0% of the initial volume of the grout; this was also set as a limit value for all classes of grout in our research (with tolerance of 10%). On the basis of the set criteria, grouts LP1, LP2 and LC1 were placed in class A, grouts LP4 and C1 in class B, and grout LC2 in class C. Grouts LP3, LC3 and C2 did not fulfil the above stated requirements.

3.3 Hardened grout

Volume change, bulk density, water absorption, flexural, compressive, and tensile splitting strength were analyzed through the test results of hardened grout. The volume change of grout was measured according to the test method described in standard EN 445 [2], bulk density according to SIST EN 1015-10 [9], flexural and compressive strength in agreement with SIST EN 1015-11 [10] and the tensile splitting test following the procedure described in SIST EN 12390-6 [12]. Obtained results are given in Table 2.

Table 2 Properties of hardened grout at age of 90 days

	LP1	LP2	LP3	LP4	LC1	LC2	LC3	C1	C2
volume change (%)	12.8	3.7	1.2	5.2	0.9	0.6	0.0	1.2	0.0
bulk density (kg/m^3)	1373	1400	1356	1620	1467	1361	1518	1815	1683
flexural strength (MPa)	1.3	2.0	0.4	0.6	6.3	2.8	3.1	4.4	4.4
compressive strength (MPa)	11.2	2.0	12.4	12.5	23.7	21.7	26.9	52.3	47.0
tensile strength (MPa)	-	0.3	0.7	0.9	0.9	1.4	1.3	1.4	1.6

Admissible volume change according to standard EN 447 [4] lays in the interval of $-1.0\% \leq \Delta V \leq 5.0\%$. In our research the volume change limits were set to $-1.0\% \leq A \leq 1.0\%$ for class A, $-0.6\% \leq B \leq 0.6\%$ for class B, and $-0.3\% \leq C \leq 0.3\%$ for class C. For the flexural and compressive strength of grouts the same criteria as proposed by Miltiadou [5] was used. For all quality classes flexural strength should be greater than $f_{fg} \geq 2.00$ MPa and compressive strength greater than $f_{cg} \geq 6.00$ MPa. For tensile splitting strength criterion of $f_{tg} \geq 0.80$ MPa was considered for all classes of grouts. Based on the set criteria, grout C2 was classified as a class A grout, grouts LC1, LC2 and C1 as class C grouts, while other grouts did not fulfil the requirements.

3.4 Evaluation of grouts

Considering that each property of dry, fresh and hardened grout had the same constraints, only grouts LC1, LC2 and C1 were able to meet the requirements and were qualified in class C as low quality grouts.

3.5 Tests on cylinders

Cylinders of 15 cm diameter and 30 cm height were prepared as a simulation of the inner core of a multiple layer stone masonry wall. Cylinders were gradually filled with limestone and sandstone, i.e. 37% wt. of fraction 45/63 mm and fraction 32/45 mm, 25% wt. of fraction 16/32mm and 1% wt. of fraction 8/16 mm. Specimens were injected with grouts LC1, LC2, C1, C2 and LP3. For each grout 6 specimens were prepared: 3 for compressive and 3 for tensile splitting tests. At the age of 90 days cylinders were subjected to compression testing according to SIST EN 12390-3 [11] and tensile splitting strength tests according to SIST EN 12390-6 [12]. The results are presented in Fig. 3.

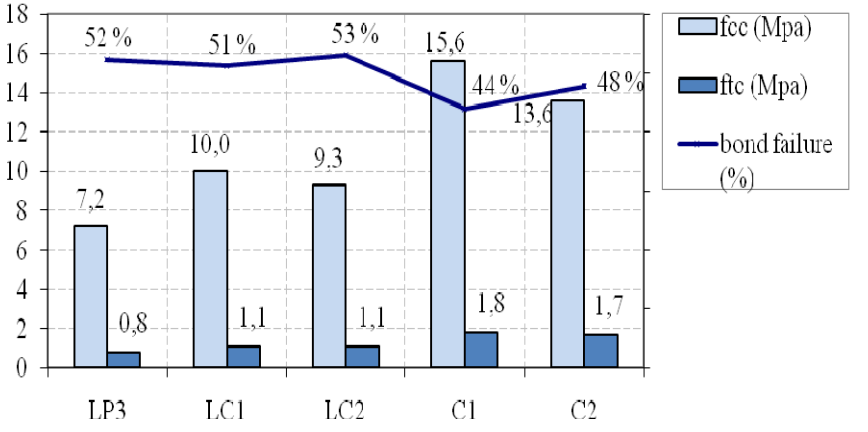

Fig. 3 The average compressive and tensile splitting strengths of cylinders

On average, the area of stone represented about 68% and the area of grout 32% of the entire cross-section. The results show that the prevailing mode of collapse was bond failure between the stone and grout regardless of the type of grout used; better bonding was achieved where cement grouts were used. Obviously, the adhesive strength achieved between the stones and grout has the most important influence on the tensile splitting strength of the cylinders.

4 Guidelines for effective grouting

- *Assessment of structure and injectability of masonry*
  Techniques such as GPR measurements and pulse sonic tests can be performed on a wide area, while surface and depth sounding or coring is preferred to be done locally in order to minimize the damage. To ensure the compatibility of existing and applied materials, chemical-mineralogical and physical-mechanical properties of the stone, brick, mortar and plaster should be known.
- *Assessment of grout properties*
  Proper criteria should be set for dry, fresh and hardened grout regarding the properties of existing materials and the morphology of the wall.
- *Limitation of the moisture content in the wall*
  Direct access by water can be limited with drainage and hydrophobic renders. Capillary action can be stopped with the execution of a hydrophobic barrier and by using hydrophobic grout in the lower parts of the wall.
- *On-site measures*
  There are some important on-site measures that have to be considered before the application of grout injection in order to ensure adequate quality:

- Injection test fields should be done on representative parts of the wall in order to obtain information about the quality of the wall and consumption of grout.
- Moistening of the walls should be performed before grout injection in order to rinse dust and dirt away and to prevent an excessive loss of water from the grout when building materials have a high porosity. Excessive moistening should be avoided if the composition and properties of existing materials is such that the presence of excessive water could induce degradation of materials.
- The properties of fresh grout (w/b ratio, fluidity, bleeding) as well as the properties of hardened grout (volume change, bulk density, flexural, compressive and tensile splitting strength) should be controlled.
- Effectiveness of grout injection should be monitored by applying appropriate techniques (consumption control, GPR measurements, pulse sonic tests)
- A correct sequence of working procedure. Injection should start at the lowest injection holes and then progress sideways and upwards with the simultaneous closing of injection tubes after the leaking of the grout.
- In the case of low quality masonry with large voids that could be interconnected, especially if such walls are high and without floors (towers, halls etc.), injection should proceed gradually in segments to prevent damage that could occur due to the combined effect of hydrostatic and injecting pressures.

5 Conclusion

The findings and aims achieved in this presented research can be summarized as:

- A list of frequent errors made by the application of grout injection;
- Criteria for grouts in a dry, fresh and hardened state;
- Tests on cylinders revealed that the prevailing mode of collapse was bond failure between stones and grout regardless the type of used grout. Better bonding was achieved where cement grouts were used;
- Guidelines for ensuring the quality of grout injection.

6 Acknowledgements

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III.25

Restoration of the Tile Cladding of a Post-War Modernist Building Complex

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Abstract The need for compatible mortars does not only apply to old historic masonry, but equally to more recent buildings. The COOVI/CERIA complex in Anderlecht (Brussels region) is a modernist ensemble, created by architect Antoine Courtens between 1950 and 1954. Nowadays the buildings suffer from severe damage of the tiles covering the facades, caused by several types of infiltrations. The choice of architectural details (protections, lack of dilatation joints…) and mortars in those days were the main cause of the degradations. A study and subsequent advices were carried out, based on the survey of the buildings, and based on a (mainly petrographic) study of the mortars. In this study we would like to show that a durable intervention is composed of both a material-approach, combined with an analysis of architectural aspects of the building, and a thorough maintenance plan. The project shows that scientific approach can lead to an ideal solution for restoration problems, but that the constraints of the actual execution of the restoration works can lead to modified solutions, which are in a way compromises, but nevertheless the best solution in the given circumstances.

1 Introduction

The building complex is a design by the Belgian architect Antoine Courtens (1899-1969). He was a student from Victor Horta, and starting from 1926 he was involved as a designer for many important art deco-buildings in Belgium. His style evolved towards modernism, from which the building complex in this study is an important example.

The name of the study object in this paper is COOVI/CERIA. These are the Dutch and French abbreviations of the full name of the complex, namely the Centre for Education and Research of the Food Industry. It consists of many buildings, grouped in a green area. The buildings are characterized by horizontal lines (Fig. 1), with one main exception, the tower.

Fig. 1 View on some buildings of the COOVI/CERIA complex

In 2004, the building complex was split in two, and each half became the property of the Flemish and Francophone community in Brussels. The French part underwent since then a thorough renovation, even though heavily disputed, including the construction of a whole new façade, with thermal insulation in between the old and the new walls. Needless to say that this changes drastically the aspect of the facades: the details in the corners are different, the windows are no longer in the plane of the façade (which is very typical for this style), etc.

For the buildings in the possession of the Flemish community, it was decided to treat the building as if they were listed as a monument (even though this is not the case) because of the high intrinsic qualities of the architecture.

2 Technical aspects of the buildings

2.1 Construction

The buildings consist of a structure in reinforced concrete, with fill-in brick masonry. The structure and masonry are not visible. At the ground level, the facades have a natural stone parament, in a very good condition. This level is very well protected, because of a very broad cornice. Starting from this level and upwards, the facades are covered with ceramic glazed tiles. These tiles are rectangular, with more or less the dimensions of bricks, giving the impression that we are not seeing a cladding, but masonry instead.

At the top of the facades, there are covering tiles (in prefabricated reinforced concrete), laid directly on the masonry. The level of the roof and gutters is lower than the top of the facades, so no roof is visible from the ground level.

There are (as far as we know) no dilatation joints, even though the facades are very large (tens of metres).

Window sills and the borders of doors and windows are constructed in prefabricated ceramic elements, separated by joints. As far as we know, no protection against water infiltration is foreseen under these window sills.

2.2 Visual survey of the facades

During construction, the building contractor was also occupied with the maintenance of the facades that were already finished. When the construction finished, hardly any work was carried out on the facades anymore. This results in the aspect of nowadays: quite large surfaces from which the tiles have disappeared (Fig. 2, bottom left). The situation looks more serious than it actually is: also tiles surrounding falling off tiles have been removed preventively.

The buildings are for many people known as having green facades. To prevent tiles falling on people's heads, the buildings are wrapped in green security nets, giving them a green appearance, seen from a distance.

Micro-crack formation between joints and tiles is very general. This is not surprising: these large surfaces suffer from high thermal dilatations, causing tensile strengths in the façade. Since no dilatation joints are foreseen, the logical consequence is that such joints are formed automatically at random, at the weakest parts, being the interface between tiles and joints.

We see also large damages in window sills, where missing joints between the ceramic tiles are very general (Fig. 2, top right).

Also the joints in between the concrete tiles on top of the facades are missing (Fig. 2, top left).

These defects are all responsible for potentially large water infiltrations in the facades.

Fig. 2 Different risks for water infiltration: missing joints between covering stones (top left), defects in window sills (top right), missing tiles (bottom left).

2.3 Sampling of the facades

On selected areas, drilling cores were taken in order to obtain a clearer view on the structure of the façade, and to perform analyses on the materials.

These cores (Fig. 3), together with a petrographic analysis on the mortars, learn the following:

- The tiles are put into place in a bedding mortar, directly on the underlying masonry. The binder of the mortar is a mixture of cement and hydrated lime. This is a very traditional and efficient mortar, that is durable (in conditions of 'normal' exposition), workable, and does not dry out easily when the weather is warm. This kind of mortar is also more flexible, which is an important property for such large facades with important thermal movements [6].
- The joints in between the tiles are executed with a pointing mortar with cement as main binder.
- The pointing mortar in the joints is usually in good condition (no damage due to frost or other alterations – except for the micro-cracks between mortar and tiles). The bedding mortar used for attaching the tiles to the masonry seems to

be frost-sensitive. This is easily seen through petrographic analysis on mortar taken from damaged areas.

- The tiles exist in two versions. One version is a tile that is coloured in the mass (Fig. 3, left). These tiles have a kind of 'hook' on their back, which serves as an anchor in the bedding mortar. On later buildings on the site, the tiles seem to be red on the inside (Fig. 3, right), with a thin coloured glaze on top of the tiles. Both type of tiles seem to have a good resistance to degradation, the tiles are in very good condition.

Fig. 3 Two drilling cores from the facades. On the left a drilling core with tiles that are coloured in the mass, on the right a core from a façade with tiles with a superficial colouring. Note the mechanical 'hooks' on the back of the tile (left photo) that ensure a good mechanical adherence. Also note structure of the façade on the left photo, with from right to left the structural masonry (a part of a brick is visible), the bedding mortar, the tile. On the right photo also the pointing mortar between the two tiles is visible.

A very important conclusion of the survey is that water infiltration, combined with frost action, is a major, probably the most important, problem for the facades. This water infiltration comes through the cracks in between tiles and pointing mortar, and through open joints in façade covering stones, and open joints in window sills. When such infiltration happens, humidity is not likely to escape easily the facades. The ceramic glazed tiles are water vapour tight, and so are the dense cement-based joints. Water infiltration, combined with almost no escape possibilities for humidity, and combined with frost action, might cause severe damage on the facades.

The restoration of the facades should therefore be aiming at the reduction, as much as possible, of the water infiltration, and to minimize the possibility of water accumulation in the facades.

3 Recommendations for the restoration

3.1 On the construction level

Because of the fact that the aspect of the facades should be conserved, one is limited in possible solution. On the construction level, there are two main improvements:

- Water infiltration on top of the façade should be stopped. In principle this should be done by the maintenance of the joints between the covering stones on top of the facades. Since such curative maintenance never can stop infiltration (one fixes defect joints who have been open for quite a while), and since one can never be sure that maintenance will be carried out in the future, a more certain measure has to be carried out: placing of a continuous membrane (metal or other) under the covering stones, with a 'nose' on both sides of the facades (to prevent from rainwater falling off running over the façade). Even when the joints between the covering stones are open, no water will infiltrate in the masonry under the stones.
- Water infiltration on the level of the window sills should be stopped as well. For the same reasons as above, it is preferable that this is done by inserting a membrane under the sills.

We strongly believe that these improvements are absolutely necessary to reduce the maintenance of the facades in the future. They are also durable interventions, meaning that, even in the worst-case scenario that no maintenance is carried out on the facades, the damage will be reduced drastically.

3.2 On the level of the façade materials

The facades have to be restored, and the question rises if exactly the same materials should be used. We are inclined to say that this is not the best option. First of all from the point of view of authenticity: exactly the same tiles cannot be found anymore (tiles with the same aspect are still available, but they do not have anymore the typical anchor at their back). It was therefore decided that we are also not obliged to make exact copies of the mortars.

From the technical point of view, an adaptation of the repair mortars was even more necessary. Because of the lack of the anchor at the back of the new tiles, the adherence of the tiles to the façade might come somewhat problematic with the original bedding mortar. Moreover, we know that water infiltrations inside the façade can be reduced seriously, but it cannot be stopped (because of the lack of dilatation joints, causing cracks between tiles and pointing mortar). And we know that the presence of the cement-bound pointing mortar was one of the causes of

water accumulation in the bedding mortar. Therefore the composition of the pointing mortar should be adapted as well.

In the end, the following solution was accepted:

- Only the damaged tiles on the facades will be restored. All tiles that are intact will stay in place. The same goes for the pointing mortar: when the pointing mortar is intact, it will not be changed. The latter would cause enormous amounts of work and a serious increase of the budget, but also the risk of damaging the tiles adjacent to the mortars was too large (especially the vertical joints, that are only a few millimetres in width) [2, 3]. The following prescriptions should also be followed when repairing damage to the façade cladding in the future.
- In the damaged zones, the bedding mortar will be removed entirely.
- On such a 'cleaned' surface, a mortar (cement-based for a good adherence, and polymer-modified for a better deformability) for smoothing the masonry will be applied [4].
- On this cement-layer, the new tiles (with a flat back!) will be glued using a mortar-glue for exterior use. This glue is not supposed to take up water when hardened, and should therefore be frost-resistant. This will enable a better adherence to the façade. And moreover, the elastic properties of the glue will give better resistance to the inavoidable thermal dilatation [6].
- The joints between the tiles should be repaired with a pointing mortar that is water vapour permeable and also less rigid than cement mortars. The choice has been made to use a mortar with hydrated lime as a binder (with a small amount of cement). The chance of creating micro-cracks between tiles and pointing mortar will therefore be reduced. And for the zones where only the pointing mortar has to be repaired, this new pointing mortar will allow a better drying out of the original bedding mortar, when it gets wet [1].

There has been a discussion with respect to the application of a cement-based mortar for smoothing the underlying masonry. It was stated that this smoothing layer should be water vapour permeable as well. This is however an irrelevant demand. Firstly because the nowadays façade cladding is not water vapour permeable at all (cement-based pointing mortar, with glazed ceramic tiles at the surface), and furthermore glueing tiles to the smoothing mortar will make it water vapour tight anyhow. So whether the smoothing layer is water vapour tight or not, this will not make any difference.

3.3 Modifications during execution

A restoration advice, based on a scientific research, is one thing, but the reality is something completely different and might change things a lot. The most important change had to be made because of an inconvenient planning. The application of the pointing mortar in newly restored zones, and the repair of the

damaged pointing mortars, had to be carried out in late autumn, winter and early spring. The risk of frost damage is therefore very high, and that risk increases spectacularly when applying a mortar based on hydrated lime [7]. A compromise had to be found, and it was therefore decided to use a mortar based on hydraulic lime. That way the joints would still be somewhat more 'flexible' than the original cement-based joints. Moreover, also the risk of micro-cracking between the joints and the tiles would still be less. This situation will however be less favourable than the original hydrated lime solution, but it is still better than the original situation with a dense and rigid cement-based pointing mortar.

A discussion on how to stop all water infiltrations in the façade followed this compromise. A solution with a water repellent agent was proposed. In this specific case not a good solution:

- From the technical point of view, one can be almost certain that a water repellent agent will not stop the water infiltrations in the façade. Even with the most favourable choice for a pointing mortar (being a mortar based on hydrated lime), the risk of micro-cracking cannot be excluded. And it is generally known that water repellent agents not always are able to stop water infiltration in cracks [5, 8].
- From the practical point of view, it is almost impossible to apply a water repellent agent on the pointing mortar, and not on the tiles. The application of such a product on the tiles should be avoided at all costs: these tiles are glazed, and the application of a product on these tiles will surely result in stains and changes in colour and gloss. In principle one should apply the product with a fine brush on the joints, which is an almost impossible task.

3.4 Consequences of the choice of the mortar

Evidently the new mortar will behave differently from the original mortar, and will have a different effect. Luckily, otherwise it would not be very useful to use another mortar recipe.

It has been suggested to test the water absorption of the new mortar, and to compare this with the old mortar. This has not been done because of the following reasons:

- We know very well that the water absorption will be different. The difference in water absorption between cement-based mortars and lime-based mortars has already been confirmed in numerous other cases.
- The measurement of water absorption of a joint on site is not evident: the width of the joints is in the order of a cm, so a Karsten pipe always has to be placed on the border between a tile and the mortar. Especially on the original cement joints it is almost impossible to find a place where there are no cracks between the tiles and the joints. A Karsten measurement will always be faulty.

The capillary water absorption of the new joints is a parameter that is not very important. It is much more important that the facade is tight, by which we want to say that no cracks will develop between mortar and tiles, and that is why another mortar composition has been chosen. Also the fact that a more 'open' mortar will enhance drying of the bedding mortar of the tiles, is in favour of the choice of a lime mortar.

We realize that any choice of mortar has advantages and disadvantages. An as-built document and a maintenance manual therefore has to be drawn up. A regular monitoring of the facade, and regular repairs, are the conditions to obtain a facade that continues to be in a good shape. This advice has been communicated towards the architect of the restoration and towards the owner of the building.

4 Conclusion

The need for a compatible repair mortar does not only apply to ancient heritage, but equally well to more recent heritage. Also there we encounter specific problems that need a suitable solution.

In the discussion what kind of mortar to use, there are always two main options: going back to the historical situation, or change the mortar recipes to avoid (or at least diminish the risk of) damage. It is our opinion that 'authenticity' is an illusion, when replacing old mortars by a new one (the new mortar is simply not the same as the old one). Regarding the fact that restoration works are partially at the cost of the community, and regarding the fact that some ancient mortars are technically not always the best choice, we think that the option for a technically compatible mortar is the better to ensure a maximum durability *for the building as a whole*. Regarding the fact that the restored situation will be quite far from the original situation (the anchor at the back of the tiles being the most important witness of this), the choice has been made to change the application method of the tiles, and to change the recipe of the pointing mortar. In this specific situation, it might sound a bit awkward that a more original 'modern' mortar has been replaced by a (at first sight) ancient mortar. But it is technically a better solution.

We have indicated that the material aspects should never be seen separately from the architecture and structure of a building. Even the best materials behave badly when they are incorporated into a poorly (from the technical point of view) designed building. Restoration problems are always to be considered in their technical context, and material research should never be seen separated from the architecture and the exposition of the building.

As a final remark in this conclusion, we would like to point out that a restoration is not finished when the scaffoldings are taken away and the bills have been paid. Especially in this case, the restoration continues afterwards. During the restoration, only the visibly damaged parts of the facades have been restored. One can be almost completely sure that there are still damaged parts (weathered

bedding mortar) that gave not yet rise to visible damage. It might well be the case that in the near future these areas will be damaged as well. The option of completely removing the original tile cladding might solve this problem, but this will be time- and money-consuming, and even more important, this way we are very far from what is be considered as a restoration. It is therefore very important that the restoration improves the building as much as possible, but leaves intact the parts that show no problems. It is therefore also important that the owner of the building afterwards regularly carries out an inspection and regular maintenance of the façade. With the improved protection against water infiltration, we estimate that the damage will be reduced in the near future, or in the best case, will not appear again.

We do not claim that the works as they are carried out are the best solution, but they are definitely one of the best solutions in the given circumstances.

5 Acknowledgements

This study and its results are a product of a fruitful collaboration between the actors involved in this project. The BBRI acted as a research institute, but the test programme and the advice are the product of the discussions between the main architect, Xaveer De Geyter, the architect responsible for the restoration works, Barbara Van Der Wee, the main building contractor, Strabag Belgium, and the suppliers of the products, Cantillana, Seiffert and Arte Constructo.

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III.26

Repair Mortars for the National Congress Building, Argentina

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Abstract The architecture of the Honourable National Congress had its origin in a project contest that took place in 1885. Argentines and foreigner architects participated in this contest. Some of them were foreigners living permanently in Argentina. The building was designed by an Italian architect Victor Meano. Meano´s project refers entirely to the architectural vision that recognizes as fundamental principles three central ideas: academicism, eclecticism and classicism. This tripartite condition confirms it as a paradigmatic architectural work of the time of its creation: the ending of the 19th Century and the first decades of the 20th Century in Argentina. This building has stone blocks walls up to a certain height, and then there is a masonry wall with an external stone coat, a granite socle in the lower section and limestone in the upper sections. This job is limited to the base sector in the Dome Building.

1 Introduction

This report represents a preliminary approximation to the restoration topics of the Honourable National Congress, a building of patrimonial value. The restoration works will have to be supported by technical assistance during the whole process. Fig. 1 shows the Main Façade of the National Congress.

Fig. 1 Main facade of the National Congress

2 Survey of existing information about the construction site

The construction company Paul Besana y Cía. began the construction works in 1898 under the direction of architect Meano. On July 1st, 1904, Víctor Meano was murdered, so the building was finished under the direction of the Belgian architect Julio Dormal, who respected the original design.

This building of the palace of the congress was declared Historical and Artistic National Monument in 1993. The building possesses a socle of 6 meters in height composed by granite from Uruguay. The rest of the components are about 75.000 limestone tooled stones from the province of Cordoba (centre of Argentina). Fig. 2 shows the facades of the National Congress without the stone cladding.

Fig. 2 Façades of the National Congress without stone cladding

3 Research topics

3.1 Climatic and exposure conditions

The climatic conditions can give an idea of the external factors that affect the building under study.

In Buenos Aires city, the average temperature is about 17.6°C and the annual rainfall is 1147.0 mm. This building is located in the center of the city where there are over 760000 cars plus another 740 000 vehicles that enter every day from the suburban areas. Also 9600 buses (belonging to 134 different lines) and 44 000 taxis are moving around. All these vehicles send pollutant gases towards the atmosphere that are in permanent contact with the surrounding exteriors of the building.

3.2 Fragments of pathologies in exterior facades

During the survey of pathologies, images of the different problems were taken. The following pictures show them (Figs. 3 to 10)

Fig. 3 Black crusts on stone

Fig. 4 Fissures in stone cladding

Fig. 5 Superficial deterioration

Fig. 6 Previous repair mortars

Fig. 7 Stains of oxide

Fig. 8 Missing elements of decoration

Fig. 9 Replaced stones

Fig. 10 Deposit of salt

3.3 Interior survey and sectors of interest

There is a large drainage on the main cornice marked in Fig. 11 that was inspected due to a high number of fissures in the stone claddings. Internally this

drainage shows equidistant points with metallic elements, which were previously partially removed. Remaining parts of these metallic elements (see Fig. 12) are affected by corrosion which causes deterioration of the stone by increasing the volume of the metals.

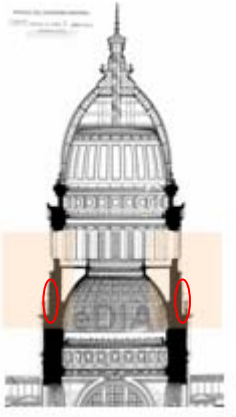

Fig. 11 Big drainage on cornice

Fig. 12 Equidistant metallic elements

3.4 Infrared thermography

We used infrared thermography to detect points of water accumulation in the base of the dome which was inaccessible.

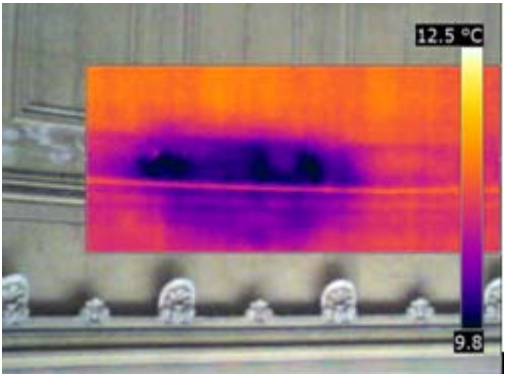

Fig. 13 Thermographic image shows the accumulated water

The thermographic image on Fig. 13 shows a small area of water accumulation. The most probable cause for it could be the obstruction of drainage in the exterior, or the incorrect slope of drainage. The definitive diagnosis needs an exterior survey to evaluate this sector.

3.5 Mapping of pathologies

An image of each façade was drawn, summarizing the pathologies found in the survey. Fig. 14 shows the west façade.

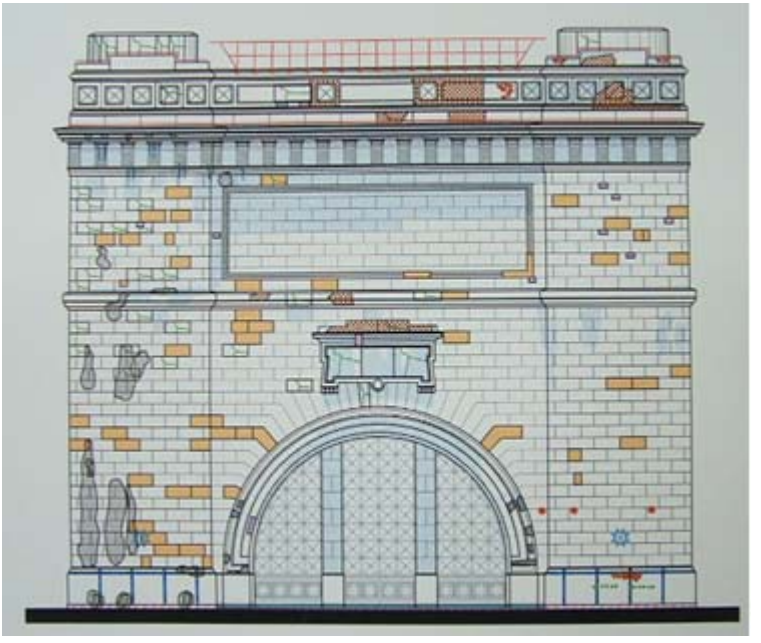

Fig. 14 West façade with graphical expression of the found pathologies.

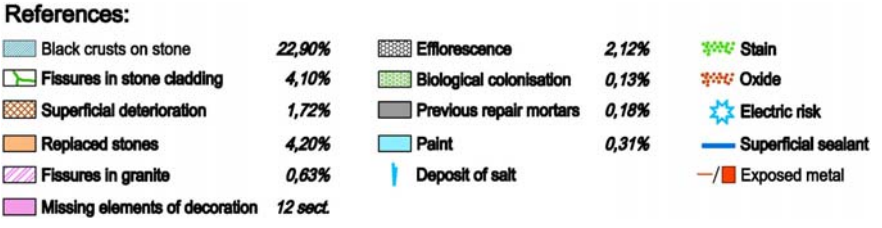

Fig. 15 The references show the partial percentage of surface affected with pathologies.

4 Characterization of stone

The building of the dome is totally stone cladded. We note a granitic socle that surrounds the whole tower and from there towards the top sectors, the rest of the coatings, ornaments, cornices and columns are made of limestone.

The characteristic damages on the limestone, which has been affected by so many years of exposure (climate and pollution), are external superficial alterations as granulation, exfoliation and detachments. Fissures along the structure of the rock that in some cases generate important detachments are also observed. Environmental dirt and dust alter the façade by showing darkness in the surfaces to the point of forming black crusts in the protected areas, where also small plants grow.

Fissures in stone cladding are of two types. Small slabs present vertical central fissures due to constructive problems (Fig. 16). On the other hand, big slabs, located in the upper rectangles and ornamentation, show fissures that follow the original rock structure (Fig. 17).

Equipments of optical microscopy, X-ray diffraction and SEM with microprobe were used for mineralogical and chemical studies.

Fig. 16 Fissures due to constructive problems.

Fig. 17 Fissures that follow the original rock Structure.

4.1 Granitic rock

It is a gray rock composed of large grains of feldspar, quartz, biotite and other accessory minerals. After cleaning the dirt, salt, remains of paintings and other materials that cover it, the rock presents good condition of conservation, without noticing important differences between the exposed surface and the interior of the material.

4.2 Calcareous rock

Due to the evident heterogeneity of the calcareous rock that constitutes the claddings and ornaments of the facades, different samples were taken for its analysis. We concluded that the variations are derived from the original quarries, since the basic characteristics of all the samples are the same.

The samples are dolomitic limestones with some evidences of metamorphism. The size of the crystals is medium, and the smaller crystals are near the zones with

fissures. The principal minerals are dolomite and calcite. In fresh material, where the layer of alteration was removed to observe the original characteristics of the rock, carbonates appear without alteration.

Also, groups of silicate minerals appear making heaps with frequent concentric structures and slight alterations. Here, the existence of serpentine, flogopita and talc was identified. In the pink zones, there are concentration of oxides and hydroxides of magnesium and iron.

5 Conclusions of the initial survey

Different meetings were conducted with the personnel of the Palace of the Congress, with its advisers in restoration and our team of work, with the objective of choosing an intervention criterion for decelerating the process of deterioration in the facades of the building. This intervention should be reversible.

It was decided to design a mortar to repair the limestone slabs. It should have specific proportions to apply on the stone in the case of fissures, fractures, and impacts in the stone cladding The stone slabs, where the deterioration or the missing elements is greater than 90%, a replacement of the whole stone block should be evaluated, depending of its position in the façade.

6 Characterization of the mortar for stone repair

Bearing in mind the original composition of the ornamental rock, research was conducted looking for different aggregates for the mortar that possess a mineralogical compatible composition. The following composition has been proposed (Table1).

Table 1

BINDERS 24% (vol.-)	AGGREGATE 76% (vol.-)
White Portland cement	Sienna Dolomite from Olavarria
Gray Portland cement	White Marmoline from Alta Gracia
Lime	Green Serpentine from San Luis
	Gray Crushed Marble (San Juan)
	Crushed Quartz from Entre Ríos

The repair mortar is being developed by a private company and the exact proportions will be defined by the compatibility with the rocks.

Other requirements were solicited to the private company:

- Reversible repair

- Chemical compatibility: chemical composition of aggregates should be similar to the original stone.
- Achieve a similar coloring by a combination of aggregates, not by pigments.
- Achieve an appearance and texture similar to the stone.
- Similar permeability to rain water both for the mortar and the stone.
- Capacity of permeability to water vapor that should allow the passage of moisture from the inside to the outside of the cladding.
- Similarity in absorption and superficial hardness between the repair mortar and stone.
- Adhesion to the substrate ≥0.15 MPa
- The tensile strength should not be higher than the cohesive force of the mortar.
- Mortar should not change its colour after 1500 hs of ultra violet ray exposure.

6.1 Initials Tests

Materials for test received in laboratory:

1) Repair Mortar (company: Tarquini), Figs. 18 and 19. Composition detailed in point 6.

Fig. 18 Specimen with substratum for adherence, resistance to the impact and permeability to rain water.

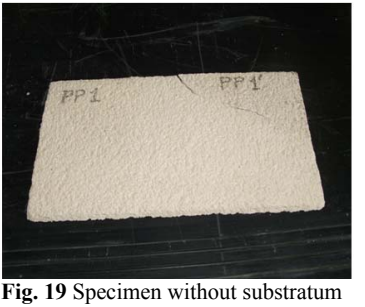

Fig. 19 Specimen without substratum for absorption test.

2) Sample of original stone (Fig. 20), extracted from the facades of the National Congress.

Fig. 20 Original stone

6.1.1 Permeability to rain water

This test was realized following the methods in the Note of Technical Information Nº 121 from the CSTB (France), also described in reference 10.

Initial measurement consists of placing the Karsten tube on the substrate for 24 hours and making readings at 1, 2, 5, 10 and 30 minutes and at 1, 2 , 4 and 24 hours. The results are expressed in millimeters of decline in the level of the water column (Initial water column: 50mm). From Table 2, we observe that permeability is very different between the mortar and the stone, since the first one is more permeable than the last one.

Table 2

SAMPLE	Decrease of the water column (mm)									
	1 min	2 min	5 min	10 min	15 min	30 min	1 h	2 h	4 h	24 h
STONE	0	0	0	0	0	0	0	0	8	32
MORTAR	7	9	13	23	32	41	42	46	50	*
MORTAR	1	2	4	5	7	15	38	41	42	*

(*)Note: Without water.

6.1.2 Absorption

This test was realized according to method ASTM C97 “Absorption and bulk specific gravity of dimension stone” (2009), while the intensive method was realized according to IRAM 1522 “Cement tile” (Argentina 1971).

The weight percentage absorption method done, consists in the determination by difference of weight of dried specimen and weight of the specimen after immersion in water for 24 hours at laboratory temperature.

Bulk specific gravity: Calculate as follows:

$$\text{Bulk specific gravity } [g/cm^3] = A/(B-C)$$

A: weight of the dried specimen in water.

B: weight of the soaked and surface-dried specimen in air.

C: weight of the soaked specimen in water.

The Intensive method (Weight percentage absorption) done, consists in the determination by difference of weight of dried specimen and weight of the specimen after immersion in water for 3 hours at 100ºC temperature.

From Table 3, we observe that the absorption is very different between the mortar and the stone, since the first one is more absorbent than the last one.

Table 3

SAMPLE	Intensive Method Absorption % (IRAM 1522)	Method ASTM C97	
		Absorption %	Bulk specific gravity g/cm³
STONE	0.25	0.37	2.04
STONE	0.90	0.89	2.01
MORTAR	10.51	9.58	2.70
MORTAR	10.89	9.55	2.56

6.1.3 Resistance to the impact

The method "Perfotest Baronnie" according to general directives UEAtc CSTB 1812 (1982) was used. It consists in performing different types of mark through the test equipment "Perfotest", which has various steel gravers, that impact on the sample producing imprints. This is just a comparative test to see the superficial resistance of the different samples. In Table 4 we observe that the stone has a greater superficial resistance than the mortar.

Hemispheric graver: it reproduces the fall of a steel ball of 500 grams falling from a height of 0.765 meters.
Cylindrical graver: with diameters between 4mm to 30mm.
Constant of the spring: 9 Joules.

Table 4

SAMPLE	**Hemispheric Graver**	**Cylindrical Graver**
STONE	Small detachments of materials	Small detachments of materials
MORTAR	Visible stamp Ø 7 / Ø 10 mm	Ø 15

6.1.4 Adherence to the substrate (Repair Mortar)

Average adherence, for direct tension obtained in 9 samples, was 1.39 MPa. We consider this result as too high with respect to what it was requested.

7 Tasks in progress

According to the laboratory test programs, compatible texture and colour of stone and mortar was achieved (Fig. 21).

Fig. 21 Repair mortar (left) versus original stone (right).

An important difference of absorption and superficial hardness between mortar/stone exists. We have suggested to the producer of the mortar to modify the capacity of the water absorption.

To achieve this characteristic, we have decided that the producer should prepare two new repair mortars:

a) Repair mortar tested with the incorporation of one additive (acrylic polymers). This additive is to be applied in water.

b) Repair mortar tested with the incorporation of silicates.

After approaching our goal, we will perform the tests "in situ" to finally define the choice of the repair mortar for the limestone slabs in the façades of the building of "The Argentine National Congress".

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Ceramic Façades in Portugal - Conservation Issues

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Abstract The use of glazed tiles on external façades became popular in Portugal in the 19th Century in a trend that was shared with Brazil. Nowadays the use of this material in external walls, providing colouring and texture, is a definite mark of Portuguese heritage. Many city centres have diverse patterns that were produced in several industrial sites, located throughout the country. The city of Ovar, with a small city centre is considered an open air Glazed Ceramic Tile Museum due to the diversity of patterns that it presents. Ceramic façades are often in a degraded state and many times, are not intervened accordingly, resulting in the total removal of ceramics and replacement by other types of external cladding. However, a few studies centred in the city of Ovar, together with the work of the city council towards the preservation of these buildings, have shed some light into the path that needs to be treaded. Ceramic tiles are usually placed with an air lime mortar and traditionally, there are no joints. Occasionally, small joints are filled with mortar with very fine stone powder. The main problems found in these façades are detachment due to the action of water or to differential behaviour of materials and loss of glaze in the tiles. Conservation actions have been performed replacing old tiles by replicas and the use of air lime mortars has been continued. However, the need to improve the process has brought about some issues: replicas and ancient tiles are very different and have a different behaviour, without joints, air lime mortars will have difficulty in hardening. Due to these issues, several tests have been performed on old façades, old tiles and old mortars and compared with areas that have been intervened and with new tiles and specifically designed mortars. This paper intends to present the specific problems related to the conservation of these façades and to create the basis for possible solutions.

1 Introduction

Glazed ceramic tile (Azulejo) façades create a lively image in many of Portugal's city centres, providing them with patterns and colour and offering a distinctive representation of the urban landscape. Given its initial Islamic influence, the use of glazed tiles has a long history in Portugal, but the practice of applying these tiles as façade protection and decoration began in the 19th Century. This was possibly due to the influence of construction practice in Brazil. There is no doubt Portuguese emigrants took the tradition of the use of ceramics to Brazil, and it is said that for climatic and cultural reasons external cladding of façades became common and was quickly adopted into current construction practice (Fig. 1).

This period coincided with the industrialization of the ceramic tile production, with a particular emphasis on the north of the country, especially in the city of Porto and its surroundings. A few factories (Massarelos, Cavalinho, Devesas, among others) began to implement industrial techniques, incrementing tile production. In addition to Porto, other production centres existed, such as Lisbon, Viana and Aveiro; different raw materials, techniques, and patterns are linked to specific production centres.

Fig. 1 Examples of houses with ceramic façades (city of Ovar)

Fig. 2 Degraded façade in Ovar

Nowadays, this heritage is notable, yet degraded (Fig. 2) and sometimes not valued. Often, ceramic tiles are missing in façades, and in certain cases, they are totally removed to be replaced by mortars or simply to leave bare stone walls. The lack of maintenance also has led to the degradation of the ceramics themselves or to a malfunction of the wall-mortar-tile system.

2 Ceramic façades – materials and techniques

Ceramic tile façades are a complex system consisting of supporting walls, mortars, and tile cladding. This complexity is enhanced by the variety of materials and techniques used in different areas of the country and in different time periods. Throughout Portugal there is a wide variation in the construction materials and techniques of external walls. While there is a predomination of limestone in the south of the country; granite is the main material used in the north, and earth construction using tapia or adobe walls is widespread.

Ceramic tile raw materials varied, as local clays were used for the manufacture; however, they were often mixed with clays from other locations in order to achieve the required plasticity [1]. Throughout the country the new factories adopted the use of the mechanic press, enabling faster production and replacing traditional moulds. Most of the production followed a quadrangular shape of 140 mm x 140 mm; however, rectangular tiles were also produced with dimensions of 160 mm x 75 mm [1].

Recent studies [1-4] focused on the north of Portugal (cities of Porto and Ovar) concluded that most of the mortars used for the application of ceramic tiles were air lime mortars with local sand. The lime/sand ratio in these mortars varied from 1:4 to 1:9 in weight, suggesting adequate proportions with an inclination towards the use of more binder. The thickness of the mortar layer is also extremely variable, and there is often a strong variation related to the roughness of the façade itself.

Joints are usually very small or inexistent, and there is lack of information on the materials used for joint mortars. They are often left unstudied due to the fact that they are very thin or eroded; however, it is quite probable that they were executed with air lime and fine sand or stone powder.

3 Degradation of ceramic façades

Due to lack of maintenance and the differential functioning of the wall-mortar-tile system, many façades are now in a degraded state. Problems of detachment, lack of ceramic elements, and loss of glaze can be considered the main forms of degradation. Inadequate conservation actions also have contributed to façade degradation.

3.1 Detachment

Many glazed tile panels suffer from detachment, as shown in Fig. 3. This may happen in the tile/mortar interface, in the mortar/wall interface, or between different mortar layers. Often this type of degradation is associated with areas exposed to water (capillarity, tubes), and its main cause is the differential behaviour of the materials that compose this system, in terms of hygric expansion. The lack of joints and the crystallization of soluble salts also contribute to this occurrence.

Fig. 3 Detachment of ceramic tiles and mortar

3.2 Lack of ceramic elements

Often a façade only lacks a few ceramic elements (Fig. 4) due to differential behaviour of wall components, as explained in the above section. However, this is a starting point for quick degradation caused by increased water uptake at these locations and the impermeability of the tile cladding.

Fig. 4 Lack of ceramic tiles

3.3 Loss of glaze

The edges of ceramic elements in façades are especially prone to loss of glaze, which is favoured by stress that is caused by differential thermal expansion and is enhanced by the lack of joints. However, this also may be the result of chemical attack, as ceramic tiles are directly exposed to the environment. Pollution, salt dissolution due to water exposure, and biological attack all cause deterioration of the glaze.

Fig. 5 Loss of glaze in a ceramic tile belonging to a façade

3.4 Inadequate conservation actions

Due to the frequent loss of ceramic elements from façades, there is a need to fill the empty spaces, and often there are no similar ceramic pieces readily available. It is quite common to find these spaces filled with cement mortars, which behave differently than the rest of the panel (Fig. 6) and contain soluble salts that may cause further damage to the façade.

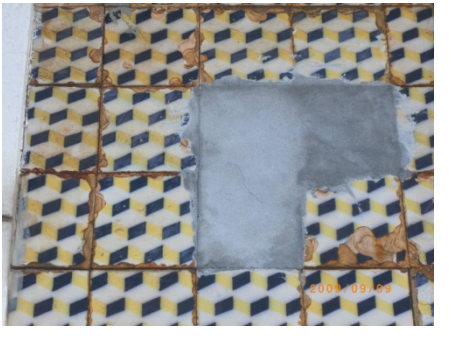

Fig. 6 Filling in of space left by tiles with a cement mortar

4 Conservation of ceramic façades

Despite the proliferation of inadequate conservation actions due to the volume, diversity, and dispersion of the heritage involved, a few institutions have become dedicated to the preservation of this particular heritage. Among them, ACRA – Atelier para a Conservação e Restauro de Azulejo (Atelier for the conservation and restoration of glazed ceramic tiles) has lead the preservation of the façades in the city of Ovar, known as the Glazed Ceramic Tile Museum because of the diversity of tile cladding patterns present in its small city centre.

In order to enable an effective conservation intervention in these façades, previous work encompassing the knowledge of raw materials, production processes, and application techniques has been initiated [1-4]. However, a deeper insight into this subject needs to be undertaken to increase the knowledge of the materials that were used (ceramic tiles and mortars), their interaction, and their degradation and to set the basis for compatible conservation actions.

Because of their specific function, mortars applied in this system have particular requirements that must be taken into account and encompassed in the general requirements for conservation mortars [5]. However, this may only occur after thorough investigation of the applied materials (Fig. 7) and the adjustment of existent testing procedures [6, 7], such as water vapour permeability test, as seen in Fig. 8.

Fig. 7 Sampling of tiles from façade – sampling areas

Research procedures will help increase the knowledge of the existent heritage and its degradation and will lead to compatible conservation actions based on laboratorial tests and *in situ* applications and tests. The development of mortars that promote adequate adhesion and may harden in a low CO_2 environment, as well as the execution of ceramic tile replicas with a similar behaviour to ancient tiles, are aims of further research.

Fig. 8 Water vapour permeability tests (LNEC)

Conservation actions also must be based on deeper knowledge of the wall-mortar-tile system, including the differential behaviour of materials and the stress induced by this factor. The adhesion between the materials used in this system and its changes with time is also crucial to understand degradation patterns and to propose adequate maintenance.

5 Conclusion

There is a vast heritage of façades decorated with glazed ceramic tiles in Portugal, mostly dating from the 19th Century and the beginning of the 20th Century. Part of this heritage is degraded, although studies have been initiated towards its conservation and there is ongoing work towards its physical preservation. However, the knowledge of the composition, degradation state, and behaviour of the materials and the wall-mortar-tile system is not sufficient; research must be undertaken in order to enable effective and compatible conservation actions.

A recently started research project – AZULEJAR – hopes to contribute to the conservation by increasing the knowledge of the applied materials and systems and studying solutions that may improve the quality and performance of conservation actions.

6 Acknowledgement

FCT- Portuguese Foundation for Science and Technology for its support through the Project PTDC/ECM/101000/2008 – AZULEJAR – Conservation of glazed ceramic tile façades.

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Investigation of 14th Century Byzantine and Serbian Fresco Painting

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Abstract Representative samples of 14th century fresco paintings (renders and colour layers) from various Serbian monuments (Byzantine influence sphere) were examined, characterized and correlated with corresponding examples from the Byzantine area. In the present work samples from eight monuments (from frescoes created by Michael and Eutychios Astrapas or by the masters highly connected to their work) were examined, in order to achieve a comparison based on characterization and . For pigment analysis Scanning Electron Microscopy (SEM) with EDX and Fibre Optic Microscopy (FOM) was used. The mortar samples were examined by Fibre Optic Microscopy (FOM), X Ray Diffraction (XRD), FT-IR Spectroscopy, Hg Porosimetry, Thermal Analysis (DT/TGA) and for their grain size distribution. All the mortars were lime mortars with aluminosilicates, calcite aggregates and organic additives like straw. The mortars from one monument displayed magnesian lime binder as well. All the identified pigments belong to the traditionally used natural pigments of the Byzantine iconography of the 14th century.

1 Introduction

The main link between Serbian and Byzantine art of the 14th century is the artistic style of the Macedonian school. The frescoes created by Michael and Eutychios Astrapas (or by the masters highly connected to their work) at the end of 13th and beginning of 14th century are the masterpieces of Byzantine wall decoration. Michael and Eutychios, from the Thessalonician family of Astrapas were the court master – painters of Serbian king Stephan Milutin, and they worked both in Greece and in Serbia. The monasteries in which the frescoes are found are situated in different geographical areas of the Balkans, with different climate and

microclimate conditions, and in monuments made of different materials. It is interesting that these masters are among the few painters of the Byzantine Era whose signatures are attested in three churches in the Former Yougoslavian Republic of Macedonia (FYROM) and two in Serbia, whereas the fresco decorations of ten more churches in Serbia, and in Greece are connected to their art. The artistic qualities of their style constitute one of the most important artistic currents of the end of the 13th and the beginning of the 14th centuries, known as the "first Paleologan renaissance", "voluminous style" or as the "Macedonian school".

2 Sampling and experimental

2.1 Sampling

Samples from eight monuments (from frescoes created by Michael and Eutychios Astrapas or by the masters highly connected to their work) were examined (ten to twenty samples from each monument), to facilitate comparison between them. In this work a representative sample from each monument is presented. The sampling has been performed with the aim of obtaining a representative picture of the mortars and to avoid further irreversible damage. All samples were taken from the lower heights up to 2m, of the fresco decorations.

Table 1 Sampling

	Monument	Sample code	Samle type
Serbian territory	St. Nikita at Čučer (FYROM)	NI – 5	Mortar/painting color
	St. George at Staro Nagoričino (FYROM)	SN – 8	Mortar/ painting colour
	Christ Savior at Žiča (Serbia)	ZI – 14	Mortar/ painting colour
	St. Prochoros at Pčinja (Serbia)	PP – 5	Mortar/ painting colour
	"King's church" at Studenica Monastery (Serbia)	ST – 5	Mortar/ painting colour
	St. Stephan at Banjska (Serbia)	BA	Mortar/ painting colour
		BA/D-4	painting colour
Byzantine territory	Virgin Perivleptos at Ohrid (FYROM)	OH – 10	Mortar/ painting colour
	Olympiotissa at Elasson (Greece)	OL – 7	Mortar/ painting colour

2.2 Experimental

The characterization of mortar properties was accomplished by the following methods and techniques: *Fibre Optic Microscopy* (i-Scope – Moritex) - for microscopic observation of matrix and aggregates, *X-ray diffraction analysis* (Siemens D5005) - mineralogical characterization of the aggregates and binder, *FT-IR spectroscopy* (Jasco FTIR-4200 type A) – to obtain qualitative information of organic/inorganic chemical compounds, *Mercury Intrusion Porosimetry* (Macropores unit 120 and Porosimeter 2000 of Fisons Instruments) – to estimate microstructural characteristics such as total porosity, total cumulative volume, bulk density, total sample porosity, average pore radius and specific surface area, *Grain Size Distribution* (set of Endecotts EFL2000 sieves was used) in order to obtain information about single components by fractionation and sieving and *Thermal Analysis* (STA, NETSCH 409 EP DTA/TG) - for qualitative-quantitative information about the nature of aggregates and binder.

Regarding the pigment observation the *Fiber Optic Microscopy* (i-Scope – Moritex) – for microscopic observation of colour layer and *Scanning Electron Microscopy* (FEI-QUANTA INSPECT) equipped with an Energy Dispersive X-ray Microanalysis system with a Super Ultra Thin Window detector for the observation of microstructure, texture of the sample sections and for elementary semi-quantitative analysis were used.

3 Results

3.1 Characterisation of 14th century fresco renders

Examination of the renders and pigments are very important in order to understand the exact step by step manner in which wall paintings were created during the Middle Ages. From the macroscopic observation of the monuments it was noticed that, in general, the interior of the monuments is considerably decayed due to salt deposition. In most of the buildings there are areas with intense salt efflorescence and color pulversation specifically in the higher and lower parts of the walls. Generally, the overall appearance of the materials and of the monuments as whole could be assigned to various decay factors, mainly to the water and salt solution movement through walls by capillarity and penetration.

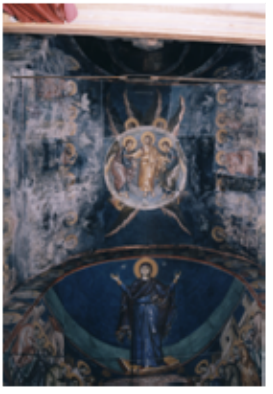

Fig. 1 Virgin Perivleptos at Ohrid

Fig. 2 Monastery Zica

Fig. 3 Monastery Olimpiotissa

Fig. 4 Monastery St. Prochoros

Fig. 5 Monastery Studenica

Fig. 6 St. George at Nagoricano

3.1.1 Fiber Optic Microscopy (FOM)

All the samples are fresco paintings composed of two layers. The mortars are whitish, fine and friable and most of them contain organic additives (fibrous plant materials - straw, Fig.7). Occasionally, where the straw isn't present anymore (due to advanced decay, decomposition or fire) there are visible imprints of where the straw used to be. All samples are very porous with numerous micro cracks (Fig.7). On some samples there is visible salt efflorescence above the color layer (Fig.8).

Fig. 7 SN-9 (x 120)

Fig. 8 ST-5 (x 120)

3.1.2 X-Ray Diffraction (XRD)

The XRD results indicate calcite as the main component of the matrix. In some cases Portlandite was detected as well. Quartz and some other accessory minerals (Muscovite, Albite) where identified too. This indicates that most probably aggregates could be composed from silicates, aluminosilicates and calcite compounds. Furthermore, in one monument (Zica momastery), in some cases magnesite [$MgCO_3$] and hydromagnesite [$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$] were detected. The development of hydromagnesite results from the hydration and carbonation of MgO in the lime paste in a moist atmosphere with the presence of CO_2. This indicates that the magnesian lime mortars were employed. The qualitative results of the XRD analysis, of some representative samples of all monuments, are presented in Table 2.

Table 2 XRD results

Monument	Sample code	Composition	
St. Nikita at Čučer	NI – 5	Calcite,	Quartz, Portlandite, Muscovite, Clinochlore, Albite
St. George at Staro Nagoričino	SN – 8	Calcite,	Quartz, Portlandite, Muscovite, Albite
Christ Savior at Žiča	ZI – 14	Calcite,	Quartz, Magnesite
St. Prochoros at Pčinja	PP – 5	Calcite,	Quartz, Muscovite
"King's church" at Studenica Monastery	ST – 5	Calcite,	Quartz, Albite, Muscovite
St. Stephan at Banjska	BA	Calcite,	Quartz
Virgin Perivleptos at Ohrid	OH – 10	Calcite,	Quartz
Olympiotissa at Elasson	OL – 7	Calcite,	Quartz

3.1.3 FT-IR Spectroscopy

The FT-IR results confirm the calcite character of binders showing a high presence of calcium carbonate at 1420cm^{-1} and 875cm^{-1} wavenumbers [1] of all the monuments. Further more, for the Žiča Monastery samples the absorption peaks at 1432cm^{-1} and 745cm^{-1} wavenumbers confirm the presence of magnesite and hydromagnesite at 3650, 3516, 3450, 1484, 1425, 1121, 877, 794, 794, 746, 595 and at 435cm^{-1} wavenumbers. The absorption peaks of quartz (1167,1081, 790, 691 and 460cm^{-1} wavenumbers) were detected in all samples and the absortion peaks of aluminosilicates (860cm^{-1} wavenumbers) were detected in samples PP – 5, ST – 5, SN – 8, NI – 5. In the samples NI, presence of $Ca(OH)_2$ (at 3640cm^{-1} wavenumbers) confirm the presence of Portlandite that is additionally verified by XRD.

The organic compounds that occur at 2980 and 2875cm^{-1} wavenumbers are present in all samples and most probably represent characteristic organic additives for Byzantine fresco mortars [2, 4].

Moreover, the presence of nitrate (at 1380cm^{-1} wavenumbers) is marked in the samples from Virgin Perivleptos at Ohrid, from Christ Savior at Žiča, and from Olympiotissa at Elasson.

Table 3 Hg Porosimetry values

Monument	Sample:	Total cumulative volume (mm^3/g)	Bulk density (g/cm^3)	Total sample porosity (%)	Average pore radius (μm)	Specific surface area (m^2/g)
Virgin Perivleptos at Ohrid	OH – 10	311.58	1.51	47.04	0.21	3.83
Christ Savior at Žiča	ZI – 14	250.64	1.60	40.10	0.16	18.17
Olympiotissa at Elasson	OL – 7	227.87	1.78	40.56	0.10	4.85
St. Prochoros at Pčinja	PP – 5	351.00	1.30	45.62	0.51	2.34
"King's church" at Studenica Monastery	ST – 5	238.12	1.64	39.05	0.46	3.32
St. George at Staro Nagoričino	SN – 8	354.77	1.45	51.44	0.13	7.14
St. Stephan at Banjska	BA	334.62	1.33	44.50	0.43	2.72
St. Nikita at Čučer	NI – 5	374.29	1.41	52.77	0.34	6.76

3.1.4 Hg Porosimetry

As far as porosimetry is concerned two groups could be discerned. The first group (OL, ST, ZI) of samples presents total cumulative volume under 300 mm^3/g, bulk density above 1.60 g/cm^3 and total sample porosity under 40%. The

second group samples (OH, PP, SN, BA, NI) present higher total cumulative volume (above 300 mm^3/g), lower bulk density (under 1.60 g/cm^3) and high total sample porosity (above 40 up to 55%). Generaly the second group of samples have a higher level of decay while the others are in a better state of preservation.

3.1.5 Grain size distribution

All the samples are fine grained (in the class of wall painting mortar layers) [9], containing additives (generally straw and pieces of wood). The grain size distribution of the aggregate ranges between 0.125 and 0.900 mm and the average size is 0.5 mm. The binding material content, ranges between 30% and 25%. The grain size distribution of the whole mortar enables the estimation of the binder/aggregate ratio from 1/2 up to 1/3 per weight of mortars.

Table 4 Thermogravimetric analyses results

Sample	<120 °C (%)	120-200 °C (%)	200-600 °C (%)			>600 °C (%)
OL-7	2.57	2.07	2.41			30.57
ZI-14	1.70	2.00	18.83			24.19
			250-280	350-420	450-550	
			3.70	4.45	10.78	
ST-5	1.17	0.66	4.20			38.63
PP-5	0.57	0.29	2.08			40.11
OH-10	1.99	1.46	5.60			35.35
NI-5	0.41	0.28	3.67			26.54
			200-400	450-550		
			1.45	2.22		
SN-8	0.90	1.12	4.95			36.85
BA	0.62	0.48	2.60			39.96

3.1.6 Thermal Analysis (DT/TGA)

Table 4 reports representative results of thermogravimetric analysis for the examined mortars. The temperature ranges correspond to the weight loss due to absorded water (<120ºC), loss of water of hydrated salts (120-200ºC), weight loss of chemically bound water (200-600ºC) when there are no other compounds identified in this temperature range and weight loss of CO_2 (>600ºC) due to the decomposition of carbonates [9].

In sample ZI-14, at the temperature range of 200-600ºC due to the presence of magnesite it was noticed that the mass loss at the range of temperature of 250-280ºC responds to the loss of chemically bound water, at 350-420ºC temperature range, weight loss due to the decomposition of $Mg(OH)_2$ whereas at 450-550ºC temperature range weight loss is due to the decomposition of $MgCO_3$.

Thermogravimetric analyses results confirm that lime mortars were employed in all monuments except the Zica monastery where magnesian lime mortars were used as well. The presence of magnesite and hydromagnesite is detected at the 200-600ºC temperature range. Further more, in some samples from St. Nikita at Čučer, Virgin Perivleptos at Ohrid and St. George at Staro Nagoričino the presence of Portlandite is identified from the higher weight loss at 200-600ºC temperature range.

3.2 Characterisation of pigments

Two wall paintings' colors (red – brown and bright red), were examined for the identification of pigments components and materials, as well as for the investigation of the pigments' preservation state.

3.2.1 Fiber Optic Microscopy (FOM)

By fiber optic microscopy it can be observed that even though, all the colour layers seemed generally in moderate preservation state, they displayed some localised flaking and detachments. Furthermore, on some samples there is visible salt efflorescence above the color layer. Moreover microscopic observation of the red-brown color indicates that the width of the red - brown color layer is 150μm whereas a thin red layer of 40μm. In addition, microscopic observation of the bright red color showed that the width of the color layer ranges between 30μm to100μm whereas a thin top reddish layer of 20μm width is presented.

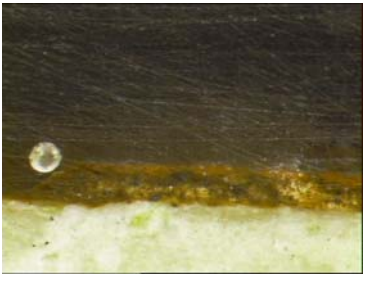

Fig. 9 FOM - Sample BA: red -brown colour

Fig. 10 FOM – Sample BA/D-4: bright red

3.2.2 Scanning Electron Microscopy (SEM) with EDX

Compositional analyses of core samples cut in cross-sections, embedded into transparent resin and carbon coated, were performed using SEM with EDX All presented values of samples' elemental composition were averages obtained from a minimum of eight measurements per sample.

Table 4 Results of the elementary SEM microanalysis

Elements	Red-brown color		
Composition	Redish area	Brownish area	bright red color
Mg	0.88	1.67	1.66
Na	-	-	-
Al	0.45	-	-
Si	1.53	4.00	2.15
P	-	0.86	-
S	6.56	6.49	4.98
Cl	-	2.00	1.59
K	-	1.02	-
Ca	15.92	22.17	25.44
Fe	1.56	62.63	-
Hg	73.08	-	64.22

The elementary SEM microanalysis showed that all samples displayed high amounts of Ca which was expected, having in mind the technology and nature of fresco painting [2].

Red-brown: The examined red area displayed high percentages of Hg, indicating the possible presence of cinnabar. However, the brownish area of the sample presented high amounts of Fe, indicating a red ferrous pigment.

Bright red: The examined red area displayed high percentages of Hg, indicating the possible presence of cinnabar, as it is also confirmed from Micro FT-Raman and XRD results.

4 Conclusions

It could be concluded that the binding material of the samples is exclusively calcite – lime mortar, except at Zica monastery (ZI), were in some cases the magnisian lime mortar was used. In some ZI samples the presence of hydro-magnicite was identified as well. Quartz and aluminosilicates show that aggregates are silicates, aluminosilicates and calcite compounds. The organic compounds are present in all samples and present characteristic organic additives of Byzantine fresco mortar.

The values of Total Sample Porosity (which in these samples vary about 45%), compared with an average value of 30-40% [3, 7], indicate a high range of material decay. The high porosity could be the result of salt crystallization inside the pores, as well as the result of additives in the mortar.

All the identified pigments belong to the traditionally used natural pigments of the Byzantine iconography of the 14th century [2].

Generally, at all investigated monuments the results show a high level of conformity between the parameters, considering pigments and mortars, with minor differences that could be explained by decay and by the use of local materials. It could be concluded that besides the technology transfer and technique of painting there is a high possibility that we have the works of the same artistic school. To verify this fact further examination with wider chronological range of monuments should be performed collecting and creating a large data base that could be used for further correlation between similar monuments, and that can give the general technical information and guidelines for future conservation interventions. Therefore, a further aim of the authors is to examine and to identify, in future works, more colour components and materials. This comparison of more materials and techniques would be particularly interesting in the cases of those monasteries where it is well established that the artists Michael Astrapas and Eutychios were employed for the iconography, thus we can search for further technical parallels between the monuments.

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III.29

Traditional Stucco Techniques in Interior Surface Coatings: Northern Portugal (19-20th Centuries)

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Abstract This paper presents the main *stucco* techniques used for decorative artwork in interior walls across the wide chronological span. This study is based on Archaeology and Art History contributions. We tried to understand some decisive artistic moments, stemming from the sixteenth century till the reconstruction of Lisbon under the Marquis of Pombal in the aftermath of the 1755 earthquake. The industrialization of the stucco art became widespread by the late nineteenth century, prompting the spread of *stucco* as a decorative solution for urban architecture, public or private. The plaster and lime-based *stucco* techniques form a complex and multifaceted corpus. In order to identify them in the context of Portuguese decorative arts applied to architecture in the nineteenth and twentieth centuries we followed an interdisciplinary approach that required laboratorial means, the review of specific terminology and the understanding of the diffusion of the Baganha and Meira workshops (the two major workshops active in Northern Portugal) and the spread of their influence in the rest of the country, especially in the South.

1 Stucco Artwork in Portugal. The Historical Context

1.1 Archaeological Materials

Stucco artwork in Portugal has traditionally been ignored by history of art, which has always considered it as a minor art, which is also the case with other decorative arts. We must turn to archaeology to understand its historical evolution, for there we find the oldest known vestiges in this country. The Roman cultural heritage is one of the most ancient and important to the Iberian Peninsula, and

lime stuccoes in its various technical expressions (moulded and surface coatings) were already present during the Roman occupation in some of the known archaeological sites: Bracara Augusta, Tongobriga, Miróbriga. The best preserved ones are the collection of moulded stucco and fragments of wall paintings on display in the Conimbriga Monographic Museum.

As introducers of the first urban culture in Portuguese territory, Romans brought their technical knowledge related to the arts of lime, which applied both to the construction or architectural decoration. Lime, more than gypsum, was the preferred material to manufacture mortars, plasters and coatings useful in multiple situations, all of them based in the multilayer technique, and whose composition varied depending on the function. Lime stuccoes were used to create sumptuous interiors decorations that combined mural painting, ornaments and figurative representations with coatings imitating rich marbles and other stones, largely due to the *marmorino* or *stucco lustro* technique. The Roman legacy of lime stuccoes remained and was reinforced with the coming of Italian artists, starting in the Renaissance period. On the other hand, its undeniable that coatings based on gypsum stuccoes like *stucco marmo and scagliola* techniques were introduced later, not before the end of the Barroque period by Italian *stucattori* in Portugal and in Spain.

After 711 the incursions of Tarik ibn Malik led to the start of the Muslim presence in the territory that became known as al-Andaluz. The Islamic legacy of stucco artwork both in Portugal and in Spain can be seen in the moulded/sculpted or carved relief plaster techniques – *yeserías,* and in the lime stuccoes for wall coating, known as *los estucos*. The fact that the Muslim occupation of Spain continued into the fifteenth century explains the existence of a greater corpus of constructed heritage and a formal distinction made between techniques, which is more in evidence than in Portugal. In Spain the term *estuco* only means coatings that can be polished to imitate marble whilst *yeserías* comprise moulded, sculpted and carved stuccoes and even structural elements applicable to architecture. The latter were introduced by the Umayyad dynasty, which was considered the symbiosis of Roman-Byzantine and Partho-Sassanid cultures [1]. The *mihrab* of the old mosque in Mértola whose origins date back to the twelfth century is the only element *in situ* to have survived the attacks of the Christian Reconquest. A systematic work carried out at Silves Archaeological Site has revealed aspects of Islamic building using rammed earth, as well as decorative architectural elements in moulded stucco belonging to the Almohad Palace of the Alcáçova (Umayyad dynasty). Nevertheless, the Muslim heritage in Portugal has not been studied to any great extent either as regards the techniques or the materials employed.

1.2 From the Renaissance to the Baroque

In the sixteenth century, whilst in Europe moulded stucco was used for interior decorations based on the exploration of the new idiom discovered by Giovanni da

Udine, in Portugal the Manueline style concentrated on decorating stone with themes from the Discoveries. The decorative programme of the Ambulatory of the Convent of Christ in Tomar is one of the best examples of Renaissance stucco decoration of Italian influence, although of unknown authorship. The presence of some Portuguese artists in Italy, in this period, is well known. Francisco de Holanda, a Portuguese painter and humanist who became Michelangelo's disciple, is the main reference for Portuguese Renaissance.

The fact that no nationwide inventory exists makes it impossible to find out about the stucco decorative programmes prior to the Baroque, reinforcing the idea that this art form had been introduced into Portugal in about 1748 with the arrival of Italian plasterers, one of them being Giovanni Grossi. The Flemish work with painted circular medallions linked by garlands and festoons, and the influence of the Antwerp engravers, and Sebastiano Serlio's drawings are highlights of fifteenth century stucco work. At the same time, it is important to underline that the various techniques of stucco artwork were exported overseas by the Portuguese and gained considerable aesthetic influence in India, where plaster and lime techniques were combined. We do not know the extent of this heritage or the composition of those stuccoes [2].

The Baroque age was the period when stuccowork, particularly moulded stucco, became more widespread. At the time this was done completely by hand *in situ* using drawings transferred onto the wall and then applying clay moulds that served to model the plaster, although some pieces were moulded off-site. The majority was plaster stucco work placed on lathwork ceilings (*tecto de fasquiado*) which replaced the overlapping board ceilings (*tecto de saia e camisa*). In 1764 in Lisbon, during the post-earthquake reconstruction, the Marquis of Pombal created the Stucco and Drawing Class to provide training for stucco workers. This city also has the artistic creations of various Italian and Portuguese stucco workers led by Grossi. In Porto two other Italians worked, Nicolau Nasoni and Luigi Chiari, the latter responsible for most of the city's neoclassical stuccoes.

It was at the end of the eighteenth century that a circumstance occurred that was to mark the following two centuries with regard to stucco artwork – the village of Afife, north of Viana do Castelo, became the cradle of Portuguese stucco workers. The skill of these men in applying plaster coatings and moulded stuccoes became famous to the point that in the few extant contemporary documents the term *afifanos* is employed to designate a professional who applies various revetment layers both inside and out, as the expression "estucador" makes a belated entry in the lexicon, as its use only became a norm in the second half of the nineteenth century.

1.3 The nineteenth and twentieth centuries

The preponderance of the Afife school marked stucco artwork during the nineteenth century and the first decades of the twentieth century [3]. From an

artistic point of view this century is distinguished for the predominance of a revivalist taste, full of eclecticism, where stucco became the material of choice for interior and exterior decorations. The technical evolution that took place in the late nineteenth century (Paris Universal Exhibitions of 1878 and 1889) was decisive for the change that occurred at the heart of this decorative art, which tended to keep pace with building needs and materials. The dissemination of Desachy's patent (1856), led to the development of plaster ceilings which tended to replace the traditional lathwork ceilings. Similarly, mouldings also changed as clay moulds were replaced by gelatine moulds. The use of wax was on a par with gelatine to make the moulds impermeable and to mould the stucco, but lost its place to silicon in the mid-twentieth century. Stucco became industrialized and moulded stucco work began to be manufactured, almost as if mass-produced, in moulds. The technical complexity of the stuccoes and their widespread use led to a career split into areas of specialisation: plasterers worked in the construction industry and stucco moulders in decorating, their training taking place as part of industrial teaching, then at its height.

Afife produced various generations of stucco workers from different families (Meiras, Baganhas, Ramos), who became famous for their work throughout Portugal. The nineteenth century migratory surge ended with a move to countries such as Brazil, Argentina, Uruguay, North America and Spain, a fact that still requires study and knowledge. The Afife stucco workers occupy a leading position in the history of interior decoration. To them we owe most of the integral decorative programmes as well as minor works in most of the buildings that today are considered as being part of our contemporary constructed heritage. The two workshops that stand out as receiving most orders were those belonging to the Meira and to the Baganha families. The Baganha workshop was founded in 1905, operated till 1974 and closed in 1975. The Meira workshop was founded in 1913 and ceased operations in 1999. Both gave rise to a remarkable museological collection that enables us to understand the relationship established between stucco as a form of decoration and the construction industry.

2 Stucco heritage. Technical typologies

2.1 Moulded stucco and surface coatings

The use of stucco as an artistic material for interior decoration, became widespread in the nineteenth century, being applied in the ornamentation of the houses of the middle classes and of the "Brazilians" [so called because they were built for Portuguese emigrants who returned from Brazil with a fortune] (1870-1890), on church and palace ceilings, palace walls and villas of eclectic style. This fact was reinforced in the first decades of the twentieth century with the surge in

building and the connection between workshop-studios and the construction industry, a fact that was visible throughout the whole country but had its high point in Porto and the North. Accordingly, the stuccoed heritage of interiors in the nineteenth century and the following decades represents the greatest repository of decorative techniques of the period. Attention is drawn to the frequent use of false marbles as well as moulded stucco and smooth polychrome stucco, which contrasted with the practice during the Baroque age, where the most common typology is moulded stucco, and imitation stone marble coatings being rarer. During the Baroque period and as far as we know to date, there are few examples of false marbles using the *stucco marmo* or *scagliola* techniques [1-6-7-11]. Apparently Portugal did not follow the tradition of other countries such as Italy or France, where the word stucco was technically synonymous with surface coatings based on plaster, animal glue and pigments [1-4], opting rather for moulded stucco. In the nineteenth century, the use of false stucco work to imitate more noble materials, either painting applied to wood to simulate a better quality of wood or coatings in stucco plaster (lime and plaster or a mixture of both) became common, particularly after 1830 [5-6], was widespread by about 1870 and continued to the 1940s and 50s.

2.2 Moulded stucco

Moulded stucco, which in Portugal was commonly called decorative, is a branch of sculpture. Moulded or relief stuccoes have always been divided into two main types: those done on site (on the actual wall) and those off site, on a bench, using moulds and shapes. The former were achieved by direct modelling of the fresh plaster. Should it be necessary to manufacture projecting elements such as capitals, cornices, coves, frames or cymas, then supports had to be mounted to underpin the structure during production. Cornices were made using metal profiles or *terrajas* [7] in hard wood covered with a fine metal (zinc or brass) sheet that reproduced the curves of the moulding. The profile was pushed along by screed, known as running mould with bed. In the construction industry in Portugal, coves and cymas acted as transition elements between ceilings and walls. The frames divided spaces on the walls which were then decorated with false marbling or painting. The latter were obtained by pouring liquid gypsum plaster into the moulds. Then a wooden "core" had to be introduced for structural reinforcement of the small pieces such as brackets, chimneys and cornices; an iron or wooden reinforcement was applied to columns and turned moulds. The most common forms for making moulds were "tacelos" (in clay and plaster) and the gelatine mould, as opposed to the lost wax casting usually employed for moulding figures [8]. There are no records of the use of shapes to make architectural moulded work in *stucco marmo* as was common in central Europe.

2.2.1 Decorative Surface Coatings: False Marble, Brescia Stone and Lioz Limestone

Of the many surface coatings that make up the interior decorating programmes of this period, those that imitated marble and other stones have the greatest patrimonial value. There are some cases of exterior marbling, but these have generally reached the present day in a bad state of repair. The predominant typologies of the north, which can probably be applied to the rest of the country, correspond to two major groups: *stucco lustro,* polished stucco and, less rarely, *stucco marmo*, both Italian in origin.

However, as the artists explored the potentials of these materials to their limits, it is important to know the composition of the stuccoes to enable correctly to identify the techniques. So, from the point of view of the materials, coatings are divided into two principal groups: lime-based (Museu Militar do Porto and Porto Cathedral Baptistery) and gypsum-based (Baganha's column, Palácio da Bolsa and Estoi Palace), each one corresponding to a certain range of techniques that can be obtained.

- Lime stuccoes – made of lime, water, minerals (pozzolanic ash, pigments, plaster) mineral fillers (aggregates) and additives; used in *marmorino, stucco lustro*, white stucco and stucco burnished with hot irons.
- Gypsum stuccoes – made of gypsum, glue, water, pigments and additives; used in *stucco marmo, scagliola* or carved stucco and also *stucco lustro*, among others.

3 Case Studies. Analytical methodology

By implementing a working methodology for the inventory based on a visual inspection of interior wall coatings in buildings of various types that took place over a period of years (2001-2007), I was able to acquire considerable knowledge of the predominant techniques, about which I wrote in my MA thesis [6]. This, however, would be incomplete if I did not resort to experimental techniques to allow me to ascertain what materials were used, the method of execution of the traditional techniques and even any possible variations. This experimental study was conducted by Teresa Domenech Carbó, senior researcher from the Instituto de Restauración del Património of the Polytechnic University of Valencia, in Spain, who applied SEM/EDX, combined with optical microscopy (LM), XRD (X-Ray Diffraction), FTIR (Fourier transform spectroscopy) and Py-GC/MS (Pyrolysis Gas Chromatography) to the selected case studies to analyse the coating samples[9].

Table 1 Analysis and Interpretation of the Selected Case Studies

Building	Sample	Composition	Technique
Porto Cathedral – Baptistery	Coating imitating pink marble on the panelling	Preparatory layer – lime stucco with added plaster, stone powder and/or kaolinite, pigmented with iron oxide. Low concentrate lipid agglutinant (wax or oil). Superficial pigmented layer with white lead and barium sulphate.	Similarities with *stucco-marmo,* without animal glue. Manufactured in layers and applied in panels.
Baganha collection	False marble coating on column	Plaster stucco with added zinc sulphate agglutinated with drying oil. Pigmented with iron oxide	Similar to *stucco marmot* without the animal glue. T. Turco [10] A plastic stucco applied with a spatula in strips.
Palácio da Bolsa – Porto	Pink marbling of first floor corridor	Plaster stucco agglutinated with animal glue, pigmented with iron oxide. Beeswax finishing.	*Stucco marmot* Manufactured in layers and applied in panels.
Museu Militar do Porto	False marble coating on hall wall and panelling – sample of pink and brown stucco.	Pink stucco – plaster, calcium carbonate, barium and strontium sulphate and clay earth pigments. Brown stucco –plaster, barium and strontium sulphate pigmented with iron oxide, litharge and red lead.	*Stucco lustro* Rough stucco application. Marbled stucco applied by painting on several layers.
eEstói Palace – Faro	Fragment of moulded stucco imitating porphyry – door	Plaster stucco agglutinated with animal glue, pigmented with iron oxide. Beeswax or drying linseed oil finishing.	*Stucco marmo*

4 Conclusions

The methodological approach adopted leads me to conclude that the techniques employed most frequently in producing wall coatings simulating natural stone

were *stucco-lustro* and *stucco-marmo*. There are no cases of the *scagliola* technique in its pure Italianate form that is, with carved plaster, being used.

Lime stucco as well as plaster stucco is present in interiors. Both materials were often combined, generally to improve the plastic properties of the putty to be worked and applied. The formal distinction between *stucco-lustro* and *stucco-marmo*, including in Portugal, was achieved by including pigments – *stucco marmo* – or applying colours independently, generally by painting – *stucco lustro* [1-11].

The traditional *stucco marmo* technique appears to have been used less frequently, although it was mastered and employed by great masters. The *stucco lustro* technique, on the other hand, was used more often, perhaps because it was simpler and continued as a mixed technique, shared between stucco workers and painters. As the variety of stone imitated depended on the region, this led to the adoption of specific pictorial solutions, and we noted a few deviations from traditional formulas.

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III.30

Overview of the 100 Mortars Project at the Archaeological Site of Herculaneum

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Abstract The Herculaneum Conservation Project is a public-private initiative to conserve and enhance the Roman city of Herculaneum, Italy. Emphasis is placed on simplifying and reducing costs of archaeological site management by reinstating site infrastructure, promoting rolling programmes of maintenance, and research and trials to improve conservation methods. After preliminary research in the site archives, the *100 Mortars Project* is now underway and aims to study the wide range of mortars present in the archaeological site – both original Roman mortars and those used in twentieth-century restoration campaigns. More than one hundred mortars have been sampled for analysis so far and it is hoped that in a few years almost a complete range of ancient and modern mortars from Herculaneum will be available. This will not only increase knowledge about the site but will also contribute to the conservation of Herculaneum and other open-air archaeological sites, thanks to the development of works strategies that consider quality, cost and time parameters when working with each type of mortar identified. This paper reviews the results obtained so far.

1 Introduction

The Herculaneum Conservation Project (HCP) is a Packard Humanities Institute project, in partnership with the Soprintendenza Speciale per i Beni Archeologici di Napoli e Pompei (SANP; the heritage authority) and the British School at Rome, which has been active in Herculaneum since 2001. The partnership was formalized by a sponsorship contract through which the private partner can undertake works in the archaeological site of Herculaneum under its own management and at its own expense with a multidisciplinary team working in very close partnership with colleagues from the public authority [1, 2].

The *100 Mortars* initiative was launched by the HCP team in order to carry out an extensive sampling campaign across the site of both original and restoration

mortars. Mortars from Herculaneum have never been systematically sampled and consequently there is little knowledge about the quality and the behaviour of the ancient mortars and those used during the nineteenth- and twentieth-century excavation and restoration campaigns. This research is providing important data on the different mortar typologies present (see below), their state of conservation and the composition of the modern restoration mortars used at Herculaneum in the nineteenth- and twentieth- century excavation/restoration onwards.

The primary focus of the initiative is on wall mortars (mortars in wall cores and joint mortars); however, research is being extended to include mortars related to decorative features (plastered surfaces and their preparatory layers, bedding mortars for mosaics and mortar pavements).

The result of this sampling campaign will be of great importance in providing additional data on the building techniques used in the Roman town, but also in understanding the effect of the AD 79 eruption on the ancient mortars and their condition after 80 years (and in some case of more than a century) of exposure to the elements as the result of archaeological excavation. As HCP is a project focused on advancing conservation methodologies and techniques, this research is also considered as the first step in a broader study which aims to understand how to manage the conservation of mortars in open-air conditions and how to conserve them where cement-based mortars were applied during modern restoration works. These results will also inform the rolling programme of maintenance that is being launched at Herculaneum, and could also be useful for other sites in the Vesuvian and Naples area.

2 Understanding mortars to consolidate Herculaneum's walls

Since 2007 the HCP team has carried out extensive mapping of Herculaneum's walls, aimed at identifying structural problems and intrinsic characteristics that could affect its survival. Since 2005 a campaign focused on structural consolidation has been one of HCP's main activities and the mapping, along with other studies on materials and construction techniques, has provided support for programming works [3, 4].

In Herculaneum the nature of the site's burial means that wall structures often survive at a significant height (32% of the walls in the archaeological site are higher than 3 m) and the buildings may have more than two floors still in place (unlike Pompeii). However, these heights are not properly supported by thick consistent walls (more than 50% of the walls are no wider than 50 cm). These structures are similar in height to those found in modern towns, but are as fragile as archaeological ruins. In addition, violent site formation processes and progressive decay have caused many walls to be in conditions at the limit of resistance to failure: bowing and leaning, erosion of lower portions, etc. are common phenomena.

The characteristics of the mortars that sealed the joints are crucial in cases of rising damp, a very common condition at Herculaneum. Erosion is also a characteristic of half-excavated structures, in areas close to the edge of site, as ground water coming from the modern town above is continual. In reality the decay by erosion in Herculaneum surprisingly affects the tuff blocks that make up the wall facing more than the mortar holding them together. This demonstrates the strong resistance of the ancient mortars used in Herculaneum (indeed, there is wide evidence for use of *pozzolana* in mortars at Herculaneum and Pompeii).

3 Ancient and modern wall mortars in Herculaneum

The composition and quality of the original construction mortars used in Herculaneum's walls do not only have archaeological value, but are also fundamental for understanding the structural capacity of the wall itself. In the case of Herculaneum, the masonry fabric has been exposed to violent natural events and slow decay processes: the archaeological site which we deal with today is the result of the AD 62 earthquake and AD 79 eruption, as well as the trauma of excavation, extensive restoration inventions (including reconstructions with a variety of modern and often incompatible materials) and gradual decay due to exposure to the elements since excavation.

Today understanding the structural capacity of an archaeological wall is of great importance in order to better carry out its restoration, and is even more so when, as in the case of Herculaneum, it is in a seismic area.

The decision to core sample the walls was made so as to gain the most information with the least invasive option possible: the core drill can extract bedding mortar from the wall facing and core filling.

3.1 Rubble core masonry walls at Herculaneum

The most widespread typology of masonry in the Roman world – and therefore at Herculaneum – are faced walls with a rubble core where the external facings functioned as formwork into which the core mixture was poured. Roman constructions vary considerably according to geographical location, construction period, wall thickness and decay suffered [5]. In Herculaneum the external facings are usually made up of geometrically arranged tuff blocks and sometimes are brick-faced walls. Instead the reconstruction of wall facings during and after excavation were carried out using an alternative arrangement of tuff blocks, which was used as a visual language for distinguishing original from restored sections.

Before the *100 Mortars* sampling campaign began, knowledge of the wall cores was limited and came from direct observation of the few unconsolidated wall crests. On the basis of this data, the core seems to be made up of large quantities of mortar containing tuff and/or brick fragments. The wall cores reconstructed

after the nineteenth- and twentieth-century excavations are instead distinguished by the use of *lapilli* as an aggregate, a clear sign that the restoration work was carried out in the modern period (as *lapilli* were a product of the AD 79 eruption).

4 Methodology

As the *100 Mortars* project is not a global sampling campaign but one for a limited number of samples, choosing areas to sample was crucial for obtaining comparable results. This is a summary of the strategy adopted:

- Building typology (public/private, bath building, house, etc.);
- Architectural typology (pilaster, colonnade, elevations, etc.);
- Construction technique (*opus reticulatum, incertum, vittatum, mixtum, craticium*) [5];
- Restoration techniques (1800s, 1927-1939, Second World War period, post-war period, after 1961).

These categories were agreed with the HCP archaeologists [6] using research that had already been acquired on the Roman period and the post-excavation restoration techniques (using the excavation diaries and photographs held in the heritage authority's archive). The main objective is to create a database of comparable information on various levels, so as to obtain results that connect the conservation risk to construction typology, construction period or restoration characteristic. In this way, using HCP's GIS database as a tool it is possible to establish works priorities using data gathered from decay mapping cross-referenced with the *100 Mortars* results.

For the internal samples a diamond-tipped core drill was used with a diameter of 2 cm, while pieces of the joint mortars were often easier to extract using a small hammer and chisel. The bored hole was also investigated using an endoscope. The location of the samples is recorded on a geo-referenced map and all the relevant data are entered into HCP's GIS database (Fig. 1) [7].

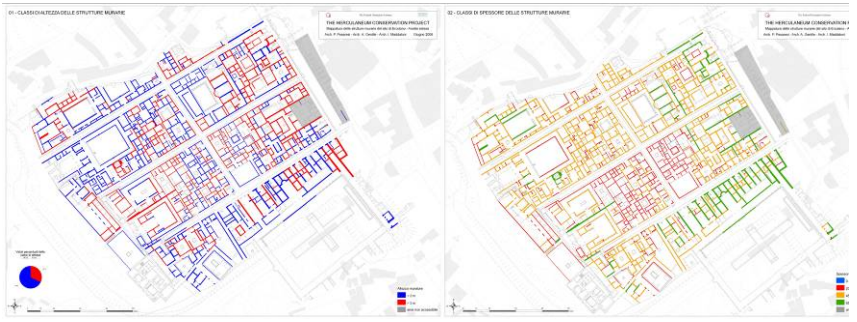

Fig. 1 Examples of HCP mapping of walls using the GIS data base (Image: Paola Pesaresi/Ascanio D'Andrea/HCP)

During the first sampling campaign on wall cores, 44 core samples were taken, of which only 4 remained intact during extraction (Fig. 2). This is already a result in itself, as it can be deduced that the decohesion of the core's component material is tied to the presence of clayey material mixed with lime. This clay component has been preliminarily identified as volcanic material (a mixture of pumice) dating to 3800 years ago (the so-called Avellino pumice) which is widely present in the geology of the Herculaneum area. The characteristic of disaggregating in water was also true for samples taken from the walls that had been entirely reconstructed during the 1800s restorations and those carried out by Amedeo Maiuri (1927-1961), probably because they used material from the eruption of AD 79 in the mix.

All samples were taken with the aim of creating thin sections to be examined under an optical microscope in order to evaluate:

- the ratio between binder and aggregate;
- the petrographic components of the aggregates;
- the presence of salts;
- the microscopic decay conditions.

Further investigation is planned in order to characterise the various types of mortar including X-Ray Diffraction (XRD) and Thermogravimetric Analyses (TGA/DTA).

Fig. 2 One of the most complete cores taken from a Herculaneum wall. A: stone; B: stone fragments mixed with mortar; C: mortar with clayish appearance; D: stone. (Image: Alessandra De Vita/HCP)

5 Sampling decorated wall plasters and restoration mortars

Outdoor and indoor decorative plasters at Herculaneum are composed of different kinds of aggregate with varied granulometry. The use of local materials such as pyroclastic sands or sand taken from the two rivers which ran alongside Herculaneum was common. In many cases a mixture of inert sands was used, though a single aggregate is found in some cases. The lower areas of outdoor plasters were usually made with the addition of ground brick dust to give the mortars hydraulic properties and longer durability.

After a careful examination of the weathered areas around site, twenty samples of decorative plasters were taken from lacunae in the painted layer. Pre-selection was also carried out using macro-photography (Figs. 3-4).

Large quantities of cement were used during the excavation and restoration campaign led by Amedeo Maiuri from 1927 to 1962 [8]. Apart from the cement used to surround fresco fragments, Maiuri used to fill in gaps with a mortar on which an outline of the decoration was sketched. Restoration mortars will also be sampled and examined. The period in which these interventions were carried out can be identified by consulting the heritage authority's archives.

6 Sampling floor mortars

Herculaneum has various types of mortar floors including *cocciopesto* (ground terracotta fragments mixed with mortar, often with tesserae or polychrome marble fragments inserted as decoration), mosaics; *opus sectile* (marble pieces bedded in mortar and arranged in geometric patterns).

Most of these floors have been restored in the past and so the selection of original mortars was determined by a team including an archaeologist and a conservator. Forty-one samples of mortars used in these types of floors have been taken from lacunae.

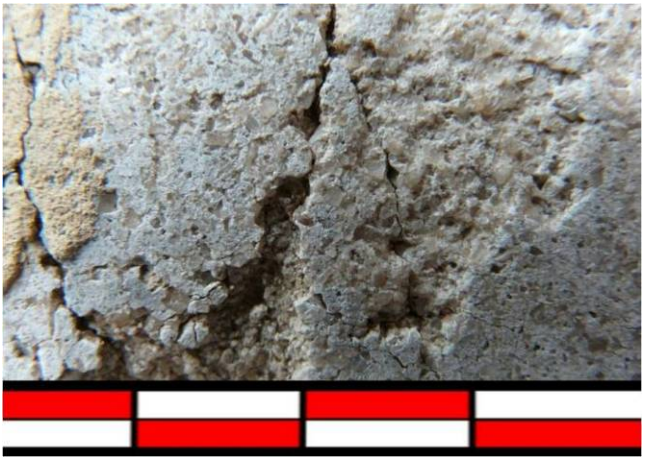

Fig. 3 Detail of plaster in the peristyle of the House of Argos where the primary aggregate can be seen. Scale marker: units of 1 cm. (Image: Alessandra De Vita/HCP)

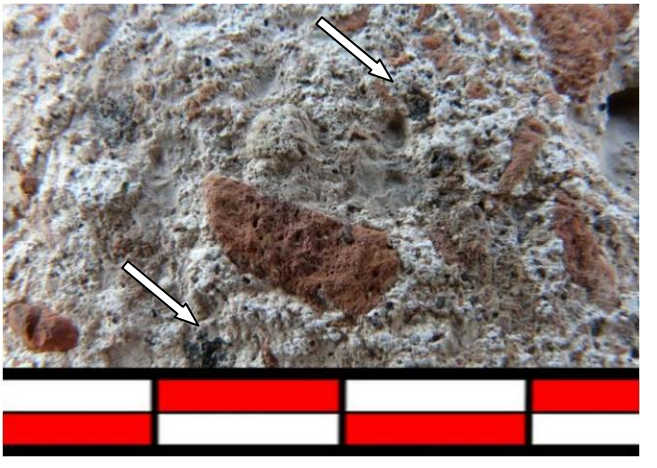

Fig. 4 Detail of plaster from the facade of the House of the Genius showing brick fragments and black volcanic sand grains (the latter are indicated with arrows). (Image: Alessandra De Vita/HCP)

7 Preliminary results

Although we are still waiting for the results of the scientific analyses on the samples taken from this first campaign at Herculaneum, it is already possible to say that the sampling methodology and *100 Mortars Project* aims are a significant step forward both for our understanding of ancient Herculaneum and for improving conservation techniques and methodologies.

After several years of activities focused on the ancient city's structures and decorative features, thanks to a continual campaign of emergency interventions and maintenance, the HCP team has entered into a new phase where it is handing over information, conservation approaches and methodologies to SANP. Through research, experimentation and pilot projects, but in particular through a long process of co-programming (where the public partner and the private partners commission consultancy and works in unison), the HCP team is attempting to launch a long-term conservation programme for the entire archaeological site sustainable with the resources of the public partner alone. Maintenance campaigns are being organised by typology, both on structures and decorative features. These are accompanied by interventions that focus on specific problems and also by more complete conservation projects. In this context, the *100 Mortars* project will constitute a particularly important contribution as an attempt to identify the best techniques for the maintenance and conservation of construction mortars and those for floors and wall plasters.

8 Acknowledgements

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Theme IV

Repair mortars for historic masonry

design and requirements for repair mortars, testing and evaluation of repair mortars, emerging materials and technologies

IV.01

Lime - Natural Pozzolan Conservation Mortars: Parameters that Affect Reactivity and Strength

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Abstract The natural pozzolans studied are commercial products and come from the volcanic islands of Milos and Kimolos as well as North Greece mainland. The materials were characterised mineralogically and chemically by XRD and SEM/EDX respectively, while their reactivity with calcium hydroxide was studied through a pozzolanic activity test. In addition, five different lime-pozzolan mixtures were prepared and studied for their compressive strength at four preset curing periods (one, three, six and twelve months). The results indicated that having the pozzolans similar chemical and mineralogical composition, the main parameter that affected their reactivity and the strength of the produced mixtures was the grain size distribution of the pozzolans within the range of 0-63μm.

1 Introduction

The properties of pozzolanic mortars and concretes have been studied extensively in the past, with the interest mainly concentrated on artificial pozzolanic additives. At the same time the role of natural pozzolans was undermined and therefore, no extended systematic studies on the role of natural pozzolans in lime mortars have been published. This is because only in the recent years traditional pozzolanic mortars started to be used in conservation, especially in renovation interventions [1-3]. As a consequence there is a considerable lack of standardization in the quality of pozzolans as raw materials, the preparation of the mixtures and the testing of the final products. This is the reason why almost all the reported results cannot be compared in a straightforward manner [1, 2].

Lately, in a growing number of papers the need for using materials similar to the original ones, avoiding modern binders and cements, is underlined [3-6]. This is mainly due to the high degree of compatibility to the archaeological and historical mortars in every aspect of materials performance. More specifically, besides the obvious chemical and mineralogical resemblance by using the same type of raw materials, lime-pozzolan mortars offer the advantage of mechanical compatibility, which contributes greatly to the life expansion of the interventions. Furthermore, the compatibility is very critical for the optimum performance of conservation mortars, considering the damages caused to cultural heritage monuments during the past decades, due to the extensive use of cement mixtures and their disadvantages in terms of incompatibility with porous stones, high salt content and very different elasticity [3, 7].

In this context the investigation of the currently available products of natural pozzolans and the properties they provide to lime mortars is significant for the conservation practise, which utilizes such materials [3,7]. The present study focuses on the physiochemical characterisation of five commercially available in the Greek market natural pozzolans and their effect on the mechanical properties of the setting products when they are used as additives in lime mortars.

2 Experimental methodology

2.1 Materials

Aiming to ensure the quality of lime, the lime putty (L) was prepared in the laboratory from chemical-grade $Ca(OH)_2$ powder and left for six months to mature, instead of using a ready made commercial product. The aggregate fraction (S) consisted of standard silicate sand (quartz) [8] and it was free from reactive components.

The pozzolans studied originated from three different geographic areas of Greece, which contain volcanic rock formations. Five pozzolans, available as market products, were collected: P1 (fine) and P2 (coarse) from Milos island, P3 (fine) and P4 (coarse) from North Greece mainland and P5 (coarse) from Kimolos island. The materials were sieved and the fraction between 0-63 μm was used in the experimental procedure (P1-f, P2-f, P3-f, P4-f and P5-f).

Chemical analysis of the raw materials was performed using the energy dispersive X-ray analyser attached to the scanning electron microscope (SEM/EDX). Moreover, the mineralogical composition of the raw materials and the setting products of the mortars produced were studied by X-ray diffraction (XRD). Finally, the loss on ignition (LOI) was determined based on the provisions of EN 196-2 standard [9].

The relevant ability of the different pozzolans to react with lime was determined through a pozzolanic activity test, in a saturated calcium hydroxide solution [10]. This test provides a comparative and indirect way to evaluate the consumption rate of lime due to the reaction with the pozzolanic material and the formation of the calcium aluminium and calcium silicate hydrates (C-A-H, C-S-H). The experimental procedure was performed at 40^{o}C, using a sample to solution ratio equal to 1/40 (w/v).

2.2 Mortar mixtures

Five different mortar mixtures were prepared, by mixing equal parts (w/w) of lime putty and pozzolans. The nomenclature for mixtures follows the one of the pozzolans, so M1 stands for the pozzolan P1-f, M2 for P2-f etc. The binder to aggregate ratio was set to 1:3, as this is indicated by relevant standards [8] and commonly appearing in historical and modern mortar applications [11]. The quantity of water used for the mixtures was determined through workability measurements [12] and was set to 0.5 water/binder ratio. The mixtures were placed in cylindrical moulds [13] and cured at 98 % RH conditions.

At preset time periods (28, 90, 180 and 365 days), five specimens from each mixture were used for determining their compressive strength [4, 13-15], using a displacement rate of 218 μm/min.

3 Results and discussion

3.1 Characterization of raw materials and reactivity test of pozzolans

Table 1 Chemical composition of raw materials expressed as wt % of their oxides

	Al_2O_3	Si_2O	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Cl	TiO_2	LOI
P1-f	12.36	71.03	2.18	1.49	0.71	2.25	2.88	nd	0.15	nd	6.95
P2-f	12.23	72.51	1.54	1.18	nd	2.51	2.95	nd	0.17	0.29	6.63
P2 bulk	12.46	71.98	1.24	1.47	nd	2.84	2.82	nd	0.16	0.27	6.76
P3-f	13.51	71.23	1.62	0.95	0.51	1.87	2.84	nd	0.18	nd	7.29
P4-f	14.41	69.21	1.38	0.95	nd	1.23	2.49	nd	0.13	1.50	8.71
P4 bulk	14.22	69.43	1.65	1.10	nd	1.21	2.47	1.22	0.16	nd	8.54
P5-f	14.84	67.78	1.84	2.16	1.51	2.18	2.14	nd	0.11	0.25	7.20
P5 bulk	14.96	69.16	2.24	1.35	2.03	1.51	2.01	nd	0.13	0.29	6.33
Sand	1.87	97.00	nd	nd	nd	nd	0.88	nd	nd	nd	0.26
Lime	0.63	1.08	nd	97.10	1.19	nd	nd	nd	nd	nd	nd

Chemical analysis showed that all pozzolans have similar composition (Table 1), typical for volcanic earth formations.

Based on the diffraction patterns (Fig. 1), the pozzolans present an amorphous character, containing small amounts of quartz and secondary mineral phases. The pozzolan from the North Greece (P3, P4) present some faint peaks attributed to chlorites, illite and kaolinite, while the pozzolan from Kimolos (P5) contains small amounts of montmorilonite. The above results are compatible with those of other researchers [16].

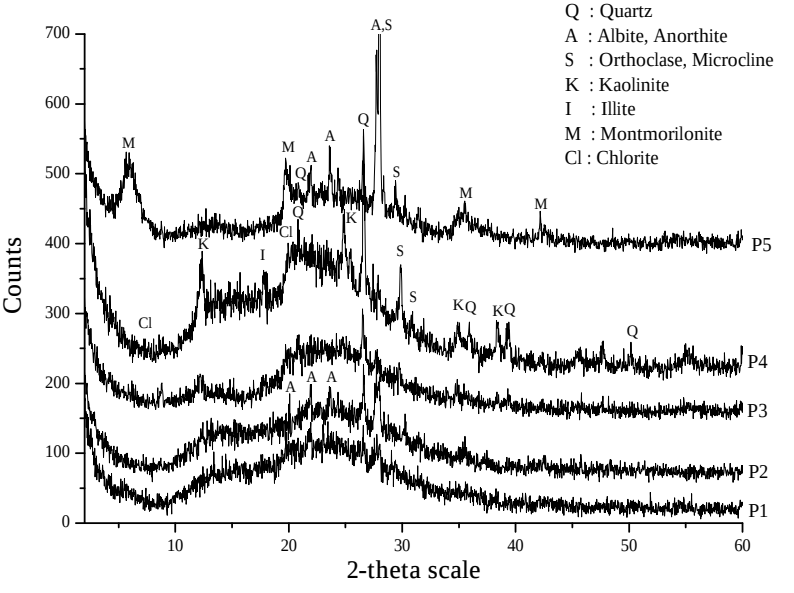

Fig. 1 Representative diffraction patterns of the fine fraction (0-63 μm) of the pozzolanic materials

The pozzolanic activity tests (Fig. 2) showed that all pozzolanic materials exhibited high reactivity, except that of P2 (from Milos), which exhibited the lowest reactivity. The one from Kimolos (P5-f) seemed to react faster during the first 24hours, but at the end it consumed relatively smaller amount of lime than the pozzolans from North Greece (P3-f and P4-f). Finally, it is noteworthy that the fragment P4-f, which was derived by sieving the initial bulk material, exhibits higher reactivity than P3-f that is originally provided in the fine fraction (0-63μm).

3.2 Setting products and compressive strength

From the diffraction patterns is derived that the majority of $Ca(OH)_2$ (portlandite) has been consumed between the third and sixth month, depending on

the relevant reactivity of each pozzolan. Mixture M2 forms an exception, since it contains the less reactive pozzolan (P2-f). Although calcite is detected in all mixtures, the main setting products are formed through the hydration process, such as calcium aluminum oxide carbonate hydrate, calcium aluminum oxide hydrate and calcium silicon hydrate (Fig. 3) [17]. The mineralogical analysis on mortars after 12 months of curing is presented in Fig. 3.

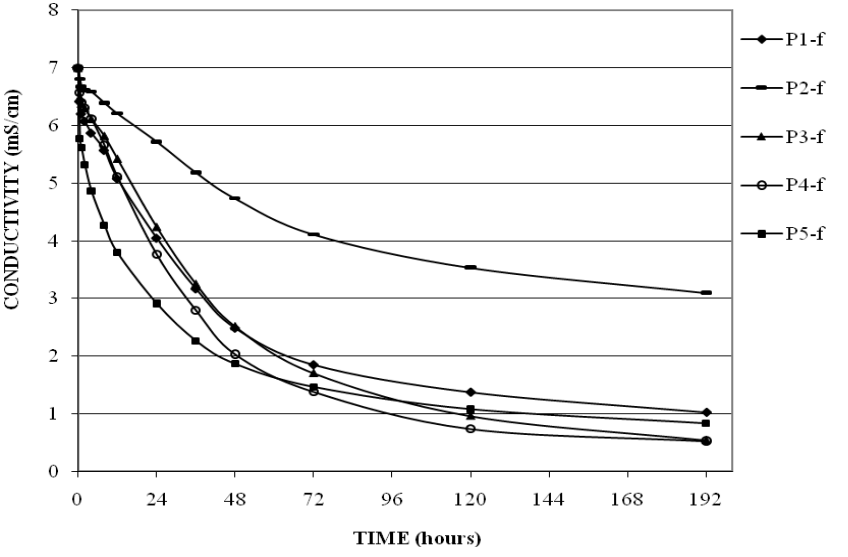

Fig. 2 Reactivity of the fine fractions of pozzolans used for the mortar syntheses

The formation of those setting products influences the mechanical properties of the mixtures, since they create a more dense and coherent microstructure. In Fig. 4, it is observed that the addition of different pozzolans greatly affects the strength of mortars during the first 28 days, while in three months the mixtures present very similar compression values. The mixtures M3 and M4 reached their maximum values in six months, by contrast to M1 and M5 that continuously increase their strength up to twelve months, presenting about 12 % higher values than M4. Mixture M2 presented the lowest strength values, corresponding to the lowest lime consumption during pozzolanic activity test. It is worth noting that neither the differentiation of the strength at the 28 days nor the final strength values correspond to the behaviour of pozzolans during pozzolanic activity test.

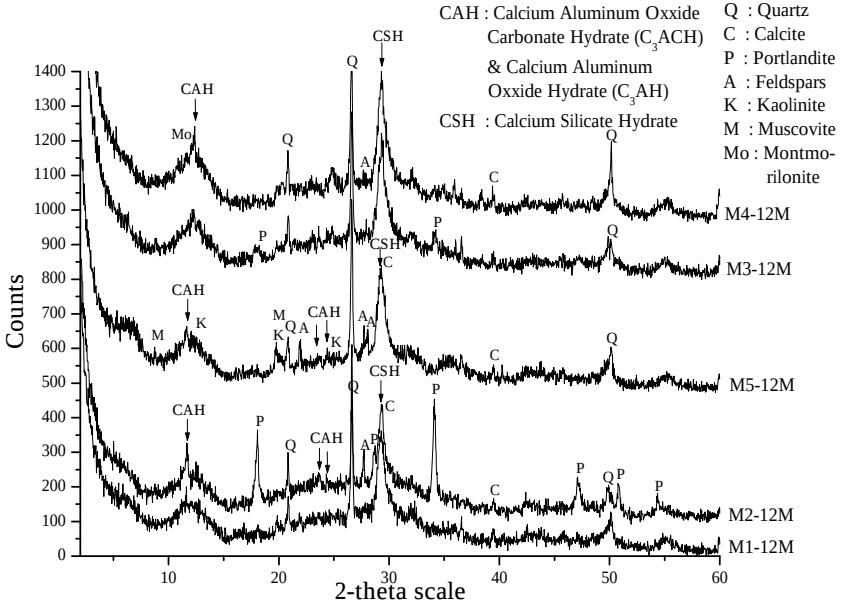

Fig. 3 Diffraction patterns of mortars cured for twelve months, presenting the main peaks of the setting products formed

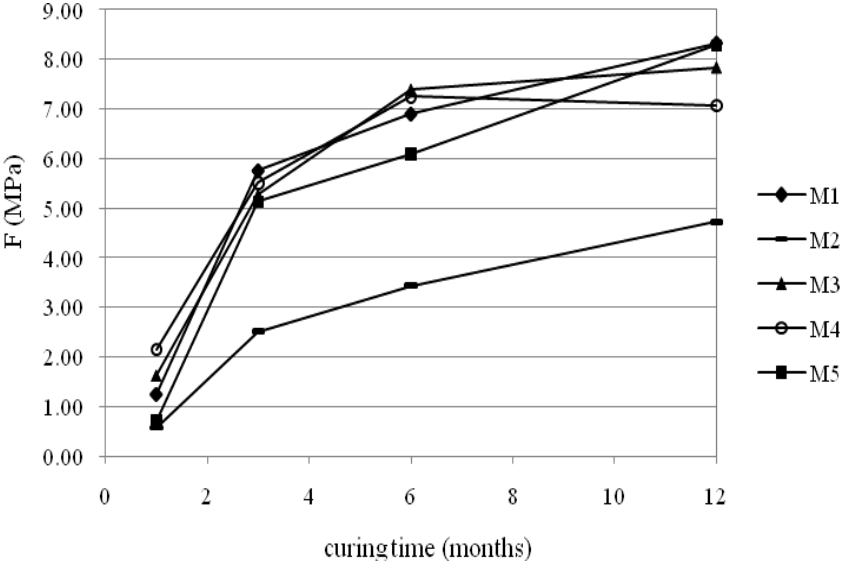

Fig. 4 Compressive strength of mortars

Considering that all pozzolans have similar mineralogy and present very similar behaviour during pozzolanic activity test it was assumed that the differences observed in mechanical properties should be attributed to the grain size distribution of different pozzolans within the range of 0-63 μm. Indeed, the examination of the pozzolans in SEM and the measurement of individual grains supported the above assumption, highlighting the differences between pozzolans P1-f and P2-f (Fig. 5). Although below 63μm, pozzolan P2-f presents a distribution with the majority of grains close to 63 μm. In contrast, pozzolan P1-f presents the majority of its grains below 20 μm.

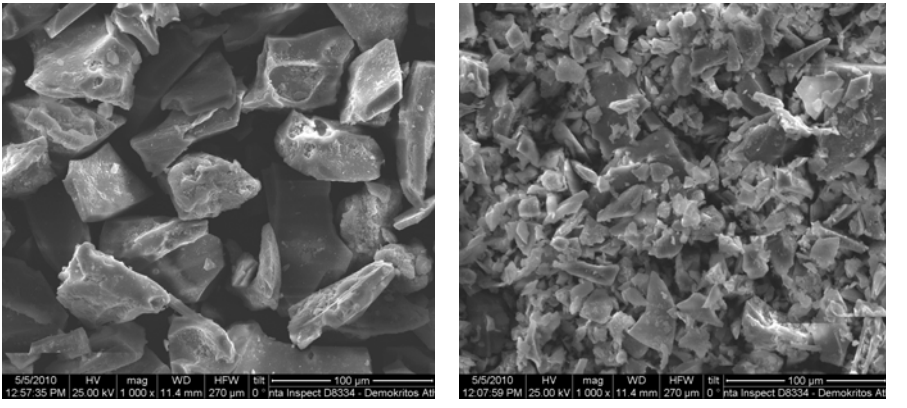

Fig. 5 SEM microphotographs of the pozzolans P1-f (right) and P2-f (left) exhibiting their different grain size (scale at 100μm)

Therefore, it seems that apart from the mineralogy of pozzolans, the development rate of strength is mainly affected by their grain size distribution within the range of 0-63 μm, giving preference to distributions of smaller grain size. In the above context, the use of the same amount of water in the mixtures studied could also affect their strength values, by slightly modifying the porosity of the mixtures.

4 Conclusions

From the interpretation of chemical and mineralogical composition of the pozolans it appears that they do not differ significantly. They are all amorphous materials of volcanic origin and contain some small amounts of clay phases. Similarly, based on the reduction of conductivity values during pozzolanicity test, it was proved that four out of the five materials presented almost similar reactivity behaviour.

In contrast, the examination of the pozzolans in SEM showed that, although all materials had grain size bellow 63 μm, they were presented different distributions

within the range of 0-63μm. This parameter can explain the observed differences in the pozzolanicity test and compressive strength values of mortar mixtures. Therefore, it was proved that apart from the curing period of mixtures, the main factor that affects their strength is the particle size of the pozzolans and especially their grain size distribution within the range of 0-63μm.

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IV.02

Effect of Pozzolanic Activity of Metakaolin on the Mechanical Properties of Air and Quicklime Mortars

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Abstract In building conservation practice, there is some difficulty in formulating compatible mortars for use in renders and joints, due to requisites of low elastic modulus, sufficient flexural and compressive strength and adequate behaviour in terms of water intake and drying. To evolve mortars with desired properties, two sets of mortars were prepared: air lime (AL) and quick lime (QL) mortars with a lime/sand volumetric ratio of 1:3. In AL and QL mortars, lime binder was replaced by 10, 20 and 30% of metakaolin (MK). Specimens were cured for 28 days and to latter 90 days. The obtained results show the increase of the mechanical properties in lime-metakaolin mortars when compared to lime mortar, as well as the improvement of flexural and compressive strength with the addition of metakaolin content. This is a result of pozzolanic activity of metakaolin. Mechanical properties of QL/QL-MK mortars are lower compared to AL/AL-MK due to their cracking susceptibility. On the basis of the experiments performed, it can be concluded that the analyzed lime mortars with 30% of metakaolin show the best mechanical properties.

1 Introduction

Lime mortars were developed and used by the Roman civilization throughout its Empire, and calcium hydroxide, or slaked lime, has been a typical binder in mortars since ancient times. Then, during the mid-18th century, hydraulic binders were discovered. The lime was gradually replaced by hydraulic lime and finally by cement in the second half of the 19th century. However, slaked lime continued to be used until the beginning of the 20th century.

The requirements of conservators who take care of historical monuments are that the materials for rehabilitation of old renders should have a composition as similar to the historical materials as possible and should provide improvement in mechanical and durability properties. The current solution of the problem of damage to the surface layers of historical buildings is based more or less on the improvement of technology and properties of the raw materials with the preservation of visual and physico-chemical compatibility to original render.

Air lime is the most adequate binder; however, it entails some problems such as slow setting, inability to harden under water, and lack of durability. The addition of pozzolan to lime mortar modifies its characteristics. Pozzolanic materials can combined with uncarbonated lime (calcium hydroxide) to form stable compounds, thus reducing the risk of early leaching or frost damage and increasing mechanical properties and the potential durability of the mortar [1]. The use of natural pozzolans is well known, mentioned by Vitruvius as a material collected from the region of Pozzuoli and included in the preparation of mortars and concretes throughout the times [2]. The utilization of calcined clay in the form of metakaolin as a pozzolanic addition for mortars has received considerable interest in recent years [3].

In Portugal, metakaolin is still used on a small scale, whereas in some other countries (e.g. the U.K. and USA) metakaolin is commercialized and is more widely used [4]. The raw material for its production is available in Portugal, especially in the north and centre of the country [5]. Metakaolin is an amorphous material with a large specific surface and high acidic oxide ($AL_2O_3 + SiO_2 > 90\%$) content, which explains why it reacts so quickly and combines with such considerable amounts of portlandite [6]. The purposes of the present study are a) to determine the influence of various percentages of metakaolin on mechanical properties and hydration products formed in air (AL) and quick (QL) lime mortars, and b) to study the influence of thermal activation of metakaolin (MK) on mechanical properties and hydration products in QL mortars and their possible utilization in restoration interventions that take place in historical buildings.

2 Materials, mortar compositions and conditioning

Mortars were formulated with powdered commercial air lime ($Ca(OH)_2$), commercial quick lime (CaO), a siliceous river sand, and commercial metakaolin (Portugal origin) containing 65% of SiO_2 and 35% of Al_2O_3. Two sets of mortars were prepared: air lime (AL) and quick lime (QL) mortars with a lime/sand volumetric ratio of 1:3. In AL and QL mortars, lime binder was replaced by 10, 20 and 30% of metakaolin (in the text marked as follows: AL10MK, AL20MK, AL30MK and QL10MK, QL20MK, QL30MK). Pastes in which air lime was replaced by 10, 20 and 30% of metakaolin were also prepared. The quantity of water added was calculated in relation to required consistency, (i.e. similar flow table values of around 130), which corresponds to appropriate workability for this type of mortar. Mortar prisms 40 mm × 40 mm × 160 mm were prepared and conditioned in a climatic chamber following standard EN1015-11 [7]. Specimens were stored in moulds for the first two days in a chamber at 20±2ºC with a relative humidity of 95±5% and for five days at the same temperature, but at a relative humidity of 65±5%. After removing the moulds, specimens were maintained at a relative humidity of 65±5% and cured for 28 days and further to 90 days.

2.1 Methods

The mineralogical composition of the specimens was determined using a Philips X'Pert diffractometer equipped with Cu Kα radiation. The morphology of the samples was studied by scanning electron microscopy (SEM-EDS) using a Carl Zeiss-EVO 40HV microscope. Before the scanning process, all samples were coated with gold to enhance the electron conductivity. Compressive and flexural strength testing was performed following standard EN1015-11 [7] on Multiplex 50-E equipment. The dynamic modulus of elasticity was determined following Report LNEC 427/05-NRI [8] based on the determination of the vibration resonance frequency.

2.2 Materials used for preparation of mortars

Mineralogical analysis of materials used for mortar preparation is reported in Fig. 1. The sand is composed mainly of quartz with minor admixture of rutile. Metakaolin pattern contains diffraction peaks of kaolinite, anatase, and quartz. Calcium oxide was found in quick lime pattern, in which portlandite diffractions appear as a result of humidity adsorption of CaO. The air lime pattern contains portlandite, and calcite appears due to carbonation of $Ca(OH)_2$.

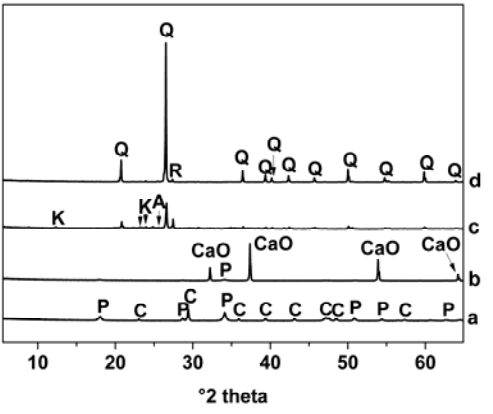

Fig. 1 X-ray diffraction patterns of random oriented materials used for mortar preparation. a) air lime sand, b) quick lime, c) metakaolin, d) sand (Q-quartz, R-rutile, K-kaolinite, A-anatase, P-portlandite, C-calcite).

3 Characterization of mortars

3.1 X-ray diffraction

Both carbonation and pozzolanic reaction rates depend on environmental conditions (temperature and relative humidity). High temperature and saturated relative humidity favour pozzolanic reaction; while relative humidity values of around 60% favour carbonation [6]. The influence of metakaolin on resulting products during 28 and 180 days of curing is reported in Figs. 2A, B. As quartz is characterized by its intensive diffraction peaks, which could cause overlapping with other minerals, X-ray diffraction patterns of air-lime pastes were used instead of mortars for characterization of the processes. The behaviour of quick-lime pastes was similar to air-lime pastes, therefore, their X-ray patterns were not included to the text. As expected, after 28 days all the patterns contain portlandite as the dominant mineral phase and calcite appears as a result of the carbonation process. With higher metakaolin content, portlandite diffraction peaks decrease. Content of calcite increases with curing time (Fig. 2B), but portlandite is still present in the patterns after 90 days of curing. It can be concluded that X-ray diffraction did not prove evidence of new mineral phases as a result of pozzolanic reaction of metakaolin with $Ca(OH)_2$. This absence can be caused by low degree of crystallinity of C_2ASH_8 and C_4AH_{13}. However, new peaks are observed in patterns of AL30MKP at 27.5 and 40.4 °2 theta, which belong to Ca_3SiO_5 and/or

Ca_2SiO_4, respectively, but intensity of that at 27.5 °2 theta can be influenced by rutile occurrence in metakaolin.

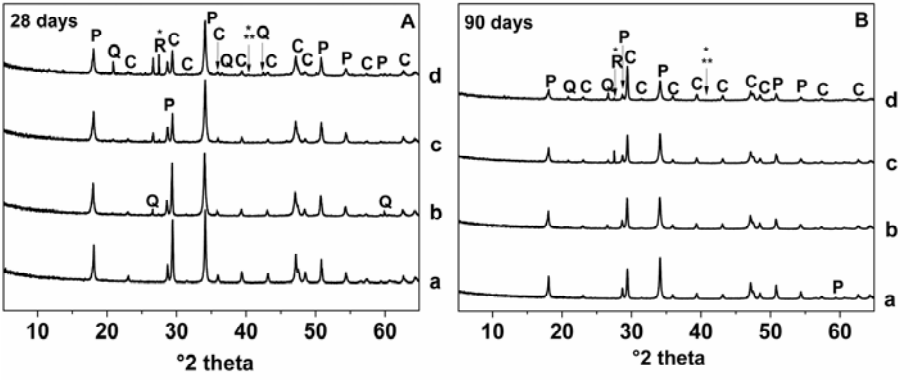

Fig. 2 X-ray diffraction patterns of pastes: a) ALP, b) AL10MKP, c) AL20MKP, d) AL30MKP; (Q-quartz, R-rutile, P-portlandite, C-calcite, *- Ca_3SiO_5, **-Ca_2SiO_4).

3.2 Scanning electron microscopy

Scanning electron microscopy observations allow a further insight into the mortars' composition and morphology. Fig. 3 illustrates the composition of AL10MK mortar. This mortar was chosen only as representative sample; similar morphology was observed in all the mortars containing metakaolin. Evidence of pozzolanic activity of metakaolin is confirmed in Figs. 3C, D, in which formation of new pozzolanic products such gehlenite (C_2ASH_8) and CSH gel are observed, following evidence given by the observation of morphology and chemical composition provided by EDS.

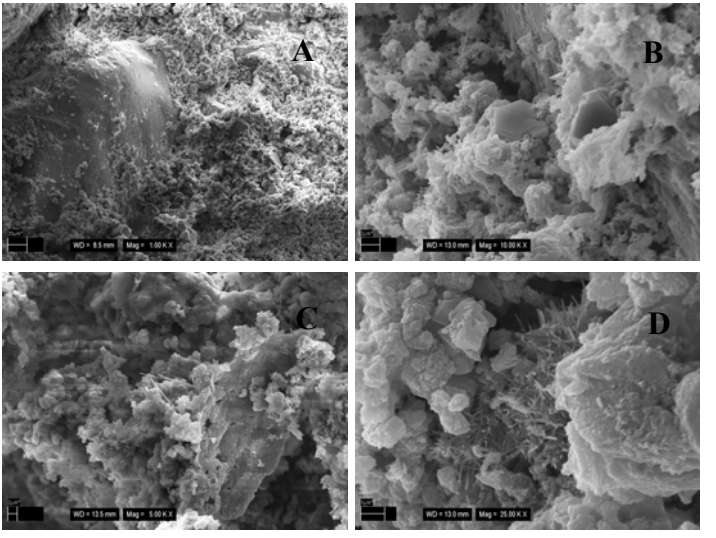

Fig. 3 SEM images of AL10MK mortar after 28 days. A) microstructure of lime matrix on sand grain, B) detail on portlandite structure, C) creation of calcium aluminium silicate crystals, D) CSH rod network throughout the area between silica aggregate and mortar matrix.

4 Mechanical properties

4.1 Flexural strength

Results of the flexural resistance test indicate the increase of the strength in lime-metakaolin mortars when compared to lime mortar (Figs. 4A, B). Compared to the air lime mortar, flexural strengths increased around 20% for air lime-metakaolin mortars after 28 days of curing. Flexural strength of quick-lime mortar is 50% lower than that of air-lime mortar. It could be a consequence of creation of CaO grains with a size 1-2 mm in the mortar matrix, the presence of which lowers compatibility of the system and influences its mechanical strength. Addition of metakaolin to QL mortar results in flexural strength values comparable to AL-MK mortars. Increasing the amount of metakaolin has no significant impact on mechanical strength after 28 days. A gradual increase of flexural strength occurs after 90 days, when 90% of portlandite is consumed by carbonation. Higher MK content causes improvement in the flexural strength of mortars.

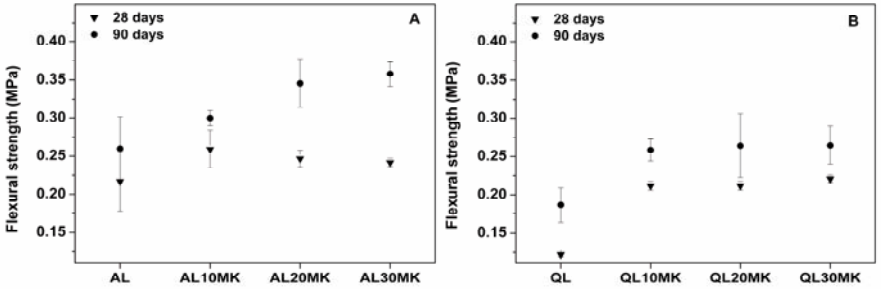

Fig. 4 Flexural strengths (MPa) of A) air lime, B) quick lime mortars.

4.2 Compressive strength

Compressive strength results show a similar trend with those of flexural strength (Figs. 5A, B). AL systems reach higher values compared to QL in both curing times. An interesting observation is related to compressive strength for AL/AL-MK mortars after 28 days, where the results are comparable with those of QL/QL-MK after 90 days. At 90 days of curing time, compressive strength achieved 43 and 63% higher values for AL and QL mortars compared to 28 days, respectively. In addition, incorporation of MK to lime systems shows significant influence on mechanical resistance of the mortars. The addition of 10, 20 and 30% of MK increases the strength by 37, 49, and 58% and 26, 29, and 37% compared to AL and QL mortars after 90 days, respectively. 30% of MK appears to be best addition to lime mortars. Lower values of QL/QL-MK mortars are due to their cracking susceptibility. In terms of both flexural and compressive strength results, lime-metakaolin mortars reveal higher mechanical strength than the lime mortars.

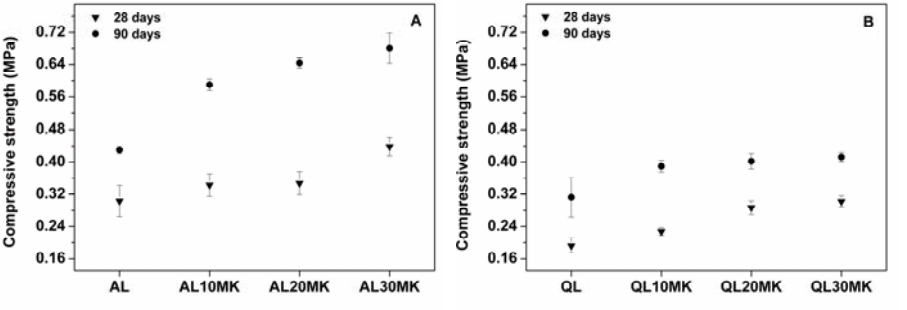

Fig. 5 Compressive strengths (MPa) of A) air lime, B) quick lime mortars.

4.3 Elasticity modulus

The elasticity modulus of all tested mortars (Fig. 6) is low, ranging from 1.5 GPa to 4 GPa. Variations from 28 days to 90 days are not significant for either AL or QL mortars. MK addition to air lime caused only negligible changes after 28 days. Such a low elasticity modulus is suitable, as renders with high moduli have low deformation capability and are therefore unadapted for use in conservation work.

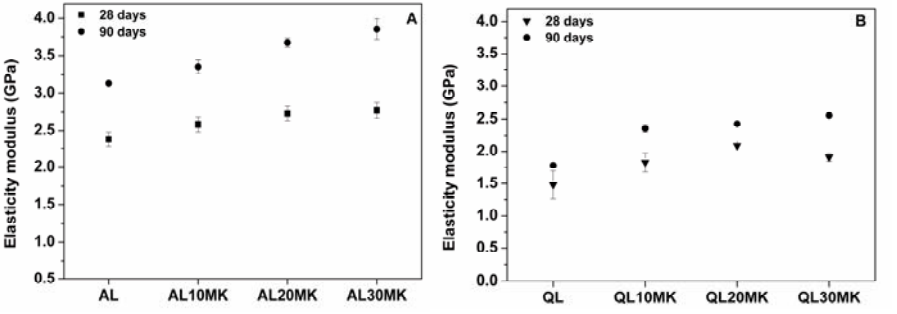

Fig. 6 Elasticity modulus (GPa) of A) air lime, B) quick lime mortars.

5 Conclusions

Pozzolanic mortars made with lime and metakaolin are promising materials for application in the conservation and restoration of cultural heritage, thanks to properties such as:

- their mechanical properties are higher than those of air/quick lime mortars. Higher metakaolin content, improved mechanical properties were observed. Addition of 30% of metakaolin to mortar systems appears to create the most favourable mortar mixture.
- elasticity modulus ranging from 1.5 GPa to 4 GPa, meaning that mortars have high deformation capability and are therefore suitable for use in conservation work.

Although the metakaolin used in this work contains impurities such as quartz, kaolinite, and anatase, it shows considerable pozzolanic activity. SEM analysis confirmed formation of typical pozzolanic products like gehlenite and CSH gel.

A similar trend of increasing mechanical properties with higher metakaolin content was verified in both air and quick lime mortar systems. However, quicklime binder appears less effective with respect to mechanical properties when compared to air lime binder. This is the result of its cracking susceptibility due to prolonged hydration reaction with a substantial volume increase.

The pozzolanic activity of metakaolin produced an improvement of mechanical properties, which makes them promising materials for the repair of ancient masonry that could be successfully used for applications in the conservation and restoration of cultural heritage. In addition, some other properties (water transport, porosity, dilation, etc.) also must be taken into account.

6 Acknowledgement

FCT- Portuguese Foundation for Science and Technology for its support through the Project PTDC/ECM/100431/2008 – METACAL – Study of lime-metakaolin mortars for building conservation.

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IV.03

Comparison of Different Methods to Determine the Packing Density of Fresh Mortars

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Abstract Packing density is considered one of the most influential factors in fresh performances of mortar and concrete. There exist standardised methods for its determination, both direct and indirect, but in most of the cases they do not give a realistic estimation of the voids content. For this reason, these methods should be substituted by the "wet packing method", more recently developed and valid for binders, aggregates and mixtures of both. In this work, the "wet packing method" has been used to assess the optimum water/binder ratio at which the packing density is achieved in mortars of different composition and binder/aggregate proportions. To support the validity of this method, the obtained values have been compared with those obtained by measuring the bulk density of the dry granular components, with and without vibration applied, and the consistence of the pastes by means of the flowability test. This work aims to diffuse an alternative, easy and more precise method which could indirectly improve the performances of both fresh and hardened mortars, designed for restoration processes in Architectural Heritage.

1 Introduction

The packing density of a mixture (φ), which represents the solid volume in a unit total volume [1], is influenced by the random arrangement of the particles and, in turn, depends on particle shape and size distribution (PSD). The dependence on particle size distribution is evident in the case of a broad PSD, in which the smaller particles fill up the voids between the coarser ones, thus increasing the value of maximum packing. The influence of particle shape is widely recognized by several studies [2-3].

In a mortar where a high density is achieved, all particles (i.e. binder plus aggregate) are densely packed, and the number of voids between them is reduced compared to less densely packed mixtures. This minimal porosity is saturated by a

minimum water dosage. The excess water, the amount of water free in the mixture, allows the mobility of particles, thus influencing the flow of the mixture. On the other hand, if the water in excess is too high, the shrinkage during drying will be too great and the strength of the hardened mortar will decrease significantly. To design good mortars and concretes, it is fundamental to determine the water/binder ratio (W/B) at which optimum workability is achieved by estimating the maximum packing density of these mixtures. Several theories and models have been created to identify the most appropriate aggregate packing for concrete [1, 4-6].

The value of packing density of individual components has been estimated in the past by measuring the bulk density of the dry materials (i.e. lime, cement, aggregates). The value of φ is determined as:

$$\varphi = \frac{\rho_b}{\rho_s} \tag{1}$$

where ρ_s and ρ_s represent the bulk and the solid densities of the granular component, respectively. The voids index (u) of the dry component is:

$$u = \frac{\pi}{\varphi} \tag{2}$$

in which π is the porosity, calculated as: 1-φ. The dry method not only depends very much on the state of compaction, but also tends to overestimate the void content and underestimate the packing density of fine particles [7].

In the case of a mixture of cementitious material and aggregate, indirect and standardized methods exist for the determination of void content in terms of the amount of water needed to form a paste with a certain consistency (i.e. flow tests, penetration depth of a plunger). These methods assume there is a minimum amount of water for the formation of a paste in which the void content is also minimized, and the water volume can be considered as the porosity of the dry packing [1]. However, some problems are correlated with the water content needed to saturate the voids and the air content of the paste, therefore, the methods mentioned above for determining packing density of finer particles are neither precise nor realistic. To counter these inconveniences, Wong and Kwan [7] proposed another method to determine the maximum packing by estimating the solid concentration of the wet mixture instead of the packing density of the dry one. The solid concentration obviously depends on the amount of water added, and, for this reason, it does not coincide with the packing density. According to these authors [7], a minimum amount of water produces a mixture with a maximum solid concentration, which corresponds to the packing density. The *wet packing method* was demonstrated to be valid not only for cementitious materials, but also for fine aggregates and mixtures of both [7-9]. According to this method, the solid concentration (φ) in a mortar is determined as:

$$\varphi = \frac{\frac{M}{V}}{\rho_w u_w + \rho_\alpha R_\alpha + \rho_\beta R_\beta + \rho_s R_s} \quad (3)$$

where M/V represents the wet bulk density of the paste; α and β are two different cementitious materials; *s* is the sand; ρ_w is the density of the water; ρ_α, ρ_β, and ρ_s are the solid densities of α, β, and *s*; u_w is the W/B ratio by volume; and R_α, R_β, and R_s are the volumetric ratios to the granular material. In mortars where only a binder is present, ρ_β and R_β values in the equation (3) are equal to zero. By applying this equation to the suspensions prepared with different dosages of water, a maximum value of Φ is obtained, corresponding to the packing density of the mixture [10].

The voids content, indicating the porosity (ε) of the wet mixture, is calculated as:

$$\varepsilon = \frac{u}{1+u} \quad (4)$$

where u is the void ratio, estimated by means of the following formula:

$$\varphi = 1 - \varepsilon = \frac{1}{1+u} \quad (5)$$

A minimum value of voids ratio is obtained by plotting u against u_w, and it corresponds to the basic water ratio [7], that is, the water content necessary to fill up the voids.

The objective of this work is to establish the optimum W/B ratio at which the packing density is achieved in mixtures of different composition and binder/aggregate ratios, in order to achieve mortars with good workability, without the use of any superplasticizers. Since other authors [8-9] have already adopted the wet packing method as a successful way to fix the packing density of granular mixtures, its validity has been proved in this work and compared with other methods, including the determination of the bulk density of the dry granular components and of the consistence of the fresh mixtures by means of the flow test.

2 Materials and methods

Components used in this study were a calcitic aggregate (CA), with a continuous grading between 0.063 and 1.5 mm in size, and a calcitic lime (CL), which is a standardized CL90-S [11].

Packing density of single components was measured by means of the dry method (Eq. 1). Pycnometer analysis was performed to measure the solid (or particle) density (ρ_s, gr/cm^3) of lime and sands. Measurements have been carried out following the ASTM, D 854-92 standard [12]; pycnometers have been calibrated and filled with white spirit. Dry bulk density (ρ_b, gr/cm^3) of components

was determined by simple pouring, with and without vibration applied. The vibration was led at an amplitude of 0.3 mm during 300 s; the value of dry bulk density obtained after vibrating was indicated as ρ_b^* (gr/cm^3).

Regarding the determination of mortars packing density, four types of mortars were obtained, differentiated according to their binder/sand ratio by volume (B/S): CC1:1, CC1:2, CC1:3, and CC1:4. Six mixtures of each mortar were prepared, maintaining the fixed B/S ratio and changing the water content. Solid concentration and the void ratio of every mixture were calculated by applying Eqs. 3, 4, and 5. Values of minimum water content (or *basic water*), corresponding to the maximum solid concentration and to the minimum void ratio, were used for the preparation of mortars whose flow was determined with the flow test [13].

3 Results and discussion

As shown in Table 1, values of packing density obtained for the dry materials change depending on their preparation procedure. When the powder is simply poured into the container without any forces applied to it, the quantity of voids (indicated in Table 1 as porosity, π) is bigger because particles cannot arrange in a more dense system. The reduction of porosity due to vibration, with the consequent increase of packing, is much bigger in the case of CA, characterized by a continuous grading in which the smaller particles can easily move and set between the coarser particles.

Table 1 Values of solid density (ρ_s, in g/cm^3), bulk density (ρ_b, in g/cm^3), packing density (φ), porosity (π) and voids ratio (u). * is referred to the values obtained when vibration was applied.

Name	ρ_s	ρ_b	ρ^*_b	φ	φ*	π	π*	u	u*
CL – lime	2.421	0.496	0.611	0.205	0.253	0.795	0.747	3.877	2.959
CA-aggregate	2.550	1.514	1.831	0.594	0.719	0.406	0.281	0.682	0.390

Another factor causes an error in the estimation of the packing density of dry fine powders. Lime is formed by micro- and nanoparticles (under 50 μm), which agglomerate due to the inter-particle forces acting on them [14]. When water is added, repulsion forces between charged portlandite crystals cause the agglomerates to disperse [15], and particles rearrange into a denser system, achieving a higher packing density in suspension. As shown in Table 2, φ_{max} of CL suspensions is about three times higher than the value of packing density found in the dry powder. In the case of the calcitic aggregate, a similar increase of packing density was registered, although the value was only 1.5 times higher than that measured for the dry aggregate. This is because in CA only 19% of the total aggregate is formed by particles smaller than 100 μm in size, which disagglomerate in water.

Of the four mortar mixtures, CC1:3 demonstrated the best packing (Table 2). The basic water content (u_{wmin}) corresponding to this packing was also optimal for the achieving good workability (flow).

Table 2 Values of water ratio (u_{wmin}) and maximum solid concentration (φ_{max}) of the suspensions of lime (CL), aggregate (CA) and the mortar mixtures, determined by means of the wet packing method. Values of water content on the total granular material (in %) and flow (in mm) were determined only in the case of the fresh mortar mixtures.

Mortar name	$u_{w\ min}$	φ_{max}	% water	Flow (mm)
CL	1.950	0.77	-	-
CA	0.838	0.98	-	-
CC1:1	0.813	0.59	32.30	172
CC1:2	0.808	0.62	31.94	>180
CC1:3	0.491	0.74	20	143
CC1:4	0.576	0.73	22.68	>180

In the other mortars, the water content (corresponding to the maximum solid concentration) used for the preparation of mixtures was too high, creating quite fluid pastes. It is interesting to note that in all the cases, the value of flow is within the range established for a plastic mortar (140-200 mm of flow) [16]. Nevertheless, according to the consistence appreciated during the manual mixing, the limit of plasticity of mortars corresponded to a maximum of 170 mm of flow. However, we must consider that the flow test is not a precise method for the determination of the optimal amount of water, especially because of the low adaptability of existent standards [13, 16] to lime mortars.

In general, it has been observed that the value of φ_{max} increases with increasing S/B ratio, except in the case of the highest proportion of sand. The basic amount of water, represented by the value u_{wmin}, does not present the same linear trend, because there is a sharp decrease in this value from the 1:2 to the 1:3 B/S ratio. This can be explained by considering the decrease in the amount of lime. In CC1:2, the packing is a bit higher than in CC1:1, but the minimum void ratio (u_{min}) is almost the same (Fig. 1), as is the basic amount of water (u_{wmin}), which is only slightly reduced. The most influential difference is the amount of lime present in the two mortars, considering that CC1:2 contains half the amount lime as CC1:1. This means that water is not entirely absorbed by the lime but is free in the mixture, producing a much more liquid mortar.

On the other hand, we obtained for CC1:4 a packing density a bit lower than that of CC1:3 with bigger water content, which produced a mixture with high flow. In this mortar, the high packing density is produced quite exclusively by the continuous grading of the aggregate, because the lime content is very low and insufficient to fill the voids while absorbing the excess water present in the mixture. The flow is, however, a bit lower with respect to that of CC1:2 because of reduced quantity of water.

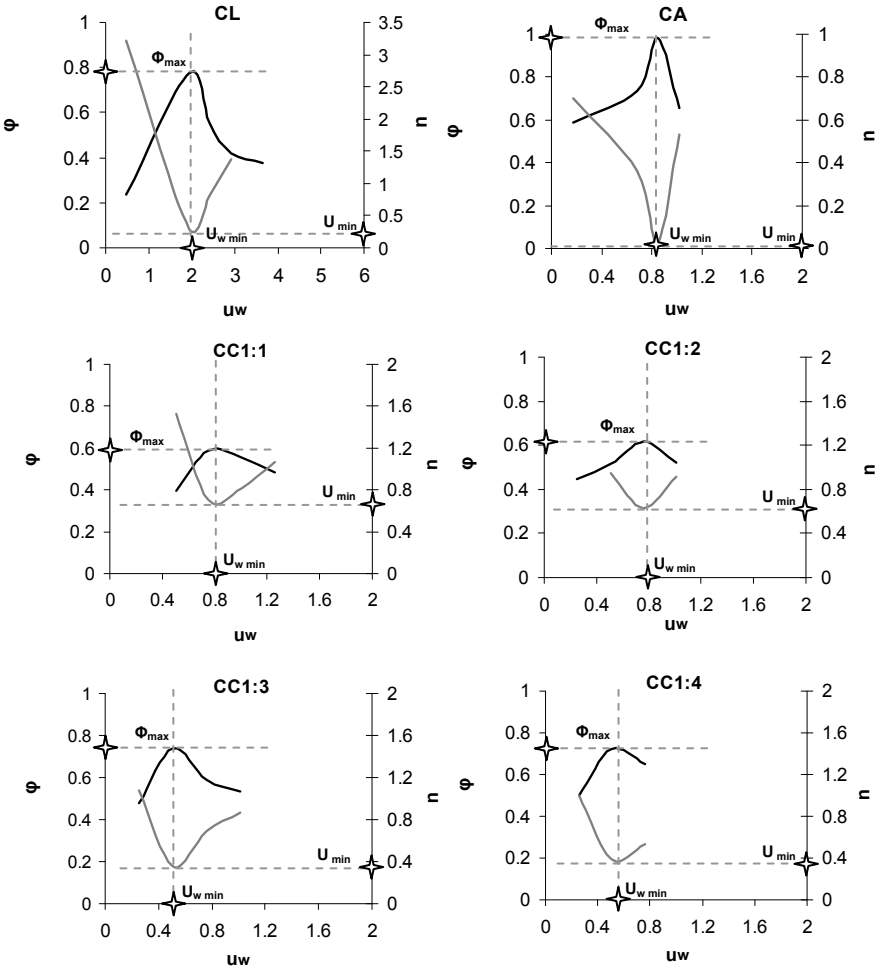

Fig. 1 Curves representing the water ratio (u_w) versus the solid concentration (φ) (black lines) and the void ratio (u) (gray lines) for the calcitic lime (CL), the calcitic aggregate (CA) and the four mortar mixtures. Maximum solid concentration (φ_{max}), basic water content (u_{wmin}) and minimum voids ratio (u_{min}) are indicated in each graphic with a ✦.

4 Conclusions

The determination of the packing density of the dry granular materials used for the production of mortars (calcitic aggregate and lime) was proven to be strongly dependent on the procedure used for the preparation, being always higher in the vibrated powders compared with the non-vibrated ones. The measurement of solid concentration in fresh pastes by means of the wet packing method has found to be more realistic with respect to the dry method, but also with respect to the flow test, which is imprecise, especially when lime mortars are studied. Among the four types of mortars, the best values of φ_{max} and u_w were found in CC1:3. The binder/sand ratio used in this mortar produces the most packed mixture, in which the quantity of voids and the amount of water necessary for their saturation are minimal. These important characteristics produce a mortar with optimal workability.

5 Acknowledgments

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IV.04

Characterization of Stone Masonry Panels Consolidated by Injection of Grouts in Buildings Damaged by the 2009 Abruzzo Earthquake

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Abstract This contribution is part of a research project aimed at developing a methodology for the emergency stabilization of historic buildings damaged by the 2009 Abruzzo earthquake through compatible injection grouts. Several portions of multi-leaf stone masonry walls from buildings in the towns of Onna, Tempera and Sant'Eusanio Forconese, all located near L'Aquila, were selected for experimental injection tests, planned and verified by means of multiscale characterization studies. The procedure and results of the preliminary studies on the historic mortars and the grouts are here reported. The materials were characterized from the petrographic, textural, mineralogical and chemical point of view through a multianalytical approach including petrographic examinations, particle size distribution studies, XRPD analyses, bulk chemical analyses by XRF and microchemical and microstructural studies by SEM-EDS. The original mortars were subdivided in different groups and a thorough knowledge of the chemical and mineralogical characteristics of the grouts was achieved, as background information for the restoration procedure according to the historic structures.

1 Introduction

The consolidation of damaged multi-leaf masonry walls constitutes one of the most challenging tasks for the structural stabilization of historic buildings, given the heterogeneous compositional nature and brittle mechanic behaviour of the structural elements. Grouting is the most common technique used for the restoration of damaged masonry walls, primarily for its property of maintaining

continuity between the constituents of the structures, while improving the deformability and mechanical properties without significant alteration to the morphology and load bearing system of the walls. Several studies regarding the use of injection grouts for the masonry restoration are reported in literature [1-4]. A few studies focus on the use of restoration products that differ from the classical cementitious and ternary grouts [5, 6], and generally they underestimate the importance of an adequate chemical-mineralogical characterization of the materials.

This contribution is part of a research project aimed at verifying the effectiveness of the emergency structural improvement of multi-leaf masonry walls damaged by the 2009 Abruzzo earthquake by means of compatible injection grouts to develop a protocol of intervention to apply in case of future earthquakes. Several portions of walls from six buildings in the towns of Onna (four buildings denominated CR, CB, VI, and BA), Tempera (TE), and Sant'Eusanio Forconese (SE), all located in the province of L'Aquila, were selected for experimental injection tests, planned and verified by means of non-destructive and destructive multiscale characterization studies. The original mortars of the six buildings were fully characterized from the petrographic, textural, mineralogical, and chemical points of view to select the most suitable restoration products. Then, six typologies of commercial injection grouts specifically designed for the restoration of historic masonry structures (denominated MI, M21, O2, O3, BC, and AI) were chosen and characterized through a multianalytical methodology similar to the one adopted for the characterization of the original materials. Moreover, the selected masonry portions were characterized by means of non-destructive sonic tests, and the shear strength and deformability of some of the masonry walls were evaluated by means of diagonal tests carried out in the non-reinforced state. The remaining masonry walls were injected with the selected grouts and then re-tested by means of sonic and diagonal compression tests in the strengthened state to assess the effectiveness of the interventions. The present contribution deals with the characterization of preliminary materials.

2 Characterization of the historic mortars

2.1 Materials and methods

A selection of mortars was sampled from the infilling leafs of the walls. A general homogeneity of mortar typology within each building was observed, hence a single mortar sample was analyzed for each structure. First, the samples were studied from a petrographic point of view, followed by analytical procedures for the study of mortar-based building materials described in UNI Norm 11176: 2006. A microscopical semi-quantitative determination of the material's total

porosity also was performed through comparison with visual estimation diagrams. Then, the binder and aggregate were separated [7], and the fraction with grain-size above 63 μm was dry-sieved according to standard UNI EN 933-1: 1999 to determine the aggregate granulometric curve. The fraction below 63 μm, comprising the binder and the finer aggregate fraction, was mineralogically characterized with X-ray powder diffraction analysis, with associated ethylene glycol treatment for an optimal characterization of the clay fraction of the materials [8]. Finally, the samples were studied by scanning electron microscopy (SEM) for microtextural and microchemical characterization. Semi-quantitative concentration of major elements was determined both on selected areas of the binder and on secondary calcite lumps (when present) using an energy-dispersive X-ray system (EDS). Data allowed the determination of the hydraulicity of the mortar, as measured by the hydraulicity index (HI) [9].

2.2 Results

Based on the petrographic and granulometric analysis the mortars were classified into three groups:

Group 1 (Samples CB, CR, VI; Fig. 1a); these mortars are discernible macroscopically by strong earthy appearance and low coherence. Microscopically, they are composed an inhomogeneous matrix, consisting of cryptocrystalline calcite permeated by an abundant fraction of clay minerals. The aggregate: binder ratio is always about 1:2, and the porosity generally constitutes 20% of the total volume. The filler shows a wide grain-size distribution, ranging from fine gravel to silt, with a bimodal distribution centred on the fine gravel and the fine sand fraction, respectively; the granulometric data determined microscopically are consistent with the results of the granulometric separation (Fig. 2). Both fractions have a predominant carbonate composition, characterised by subrounded to rounded fragments of partially dolomitized spathic and bioclastic limestones. A subordinate siliceous fraction is also present, mainly composed of subangular fragments of quartz and rare clinopyroxene, plagioclase, and K-feldspar crystals.

Group 2 (Samples SE, BA; Fig. 1b); these mortars are discernible macroscopically by a less earthy appearance and a greater coherence with respect to the mortars of Group 1. Microscopically, they are composed of a homogeneous matrix consisting of cryptocrystalline calcite with a low fraction of clay minerals. Submillimetric lumps of secondary calcite, probably due to incomplete mixture of lime with water and aggregate, were also identified. The aggregate: binder ratio is always about 2:1, and the porosity generally constitutes 10% of the total volume. The filler shows a wide grain-size distribution, ranging from fine gravel to silt, with a unimodal distribution centred on the coarse sand fraction; the granulometric data determined microscopically are consistent with the results of the granulometric separation (Fig. 2). This fraction has a predominant siliceous composition, characterised by subrounded to subangular fragments of quartz and

chert with rare clinopyroxene, plagioclase, and K-feldspar crystals and a subordinated carbonate fraction.

Group 3 (sample TE; Fig. 1c); texturally similar to Group 2 mortars, it is discernible by the presence of a local accumulation of clay minerals and the nature of the inert fraction, which is mainly composed of micritic and bioclastic limestone with a very low amount of siliceous fraction.

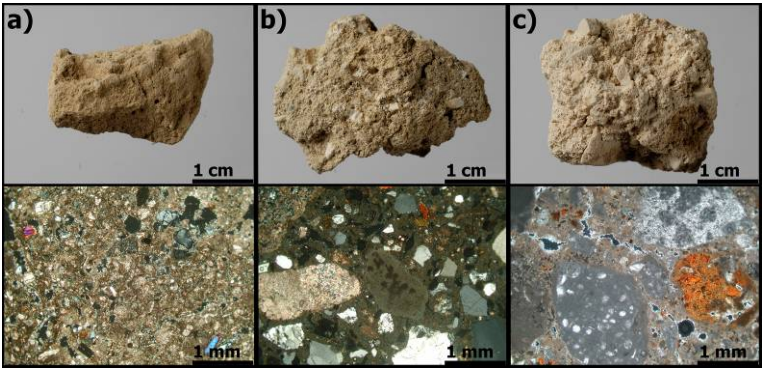

Fig. 1 Macroscopic images and polarising light micrographs (taken in cross polarized light) of the three petrogroups: a) VI sample; b) SE sample; c) TE sample

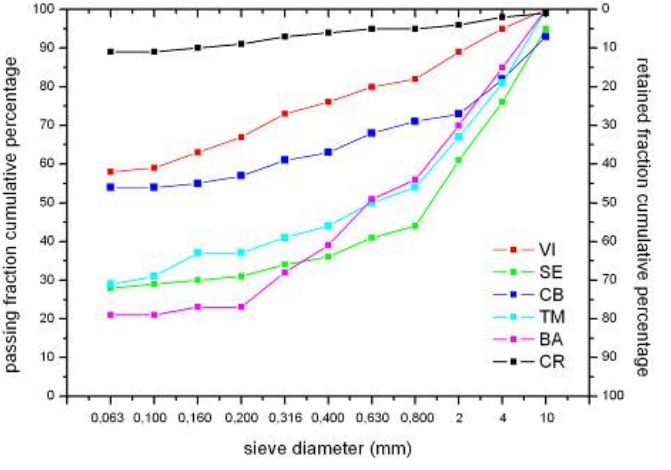

Fig. 2 Original mortars: cumulative size distribution graphs of the aggregate fraction greater than 63 μm

The XRPD analysis of the fine fraction of the mortars gave a mineralogical assemblage with a predominant carbonate fraction, mainly composed of the calcite of the binder, and a subordinate siliceous fraction containing predominant quartz and subordinate feldspar and clinopyroxene. A variable fraction of clay minerals is also present, mainly constituted by illite and subordinate chlorite. The ethylene

glycol treatment showed a consistent fraction of expansive, probably interstratified clays of the smectite group. Semi-quantitative XRPD data, obtained by means of the RIR method, are consistent with the results obtained from the petrographic study: group 1 mortars are characterized by a great amount of clay minerals in the binder fraction, as shown by the scatterplot of the calcite quantity *vs.* the amount of clay minerals (Fig. 3a), while other mortars are distinguishable for the greater purity of the binder matrix. A principal component analysis of the data also was performed (Fig. 3b). The results confirmed the subdivision into the three groups identified by means of petrographic analysis, according to differences in clay content and the mineralogical nature of the finer aggregates.

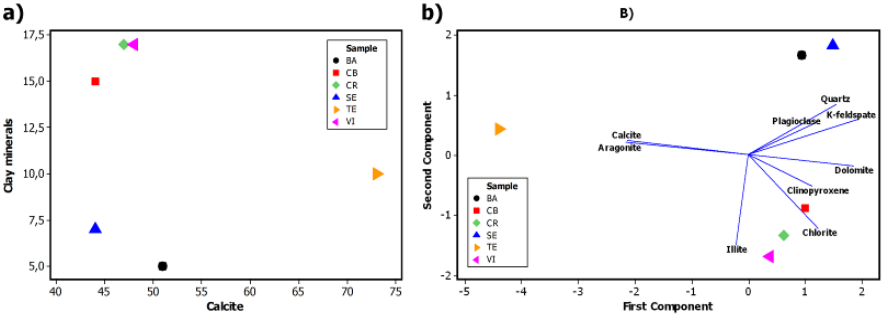

Fig. 3 XRPD semiquantitative data: a) scatter plot of the abundances (mass fraction %) of calcite vs clay minerals; b) Principal component analysis of all the crystalline phases: first two components are plotted (79% of the variance expressed)

Table 1 reports the concentrations of major elements Al, Fe, Si, Ca, and Mg obtained by microchemical analysis of different areas of the binder and that of secondary calcite lumps using SEM-EDS, in addition to the calculated HI. The low values of HI (below 0.1) determined in the majority of mortars, indicate the use of a lime-based air binder for the manufacture of the materials.

Table 1 Mean concentrations of major elements Al, Fe, Si, Ca, and Mg expressed in wt% of the oxide for the binder of the samples analyzed (standard deviation reported in brackets). The suffix –l indicates the analysis was performed on the secondary calcite lumps

Sample	Al_2O_3	Fe_2O_3	SiO_2	CaO	MgO	HI
CB	2.5 (0.80)	1.13 (0.36)	1.59 (0.91)	91.87 (2.82)	2.91 (1.16)	0.05 (0.02)
CR	3.26 (1.22)	1.16 (0.26)	2.73 (1.94)	89.58 (3.1)	3.27 (0.76)	0.07 (0.05)
CR-l	3.99 (1.20)	1.86 (0.01)	6.80 (0.62)	85.21 (2.45)	2.15 (0.80)	0.13 (0.04)
VI	3.36 (0.52)	1.03 (0.04)	3.67 (0.82)	89.09 (1.29)	2.86 (0.21)	0.09 (0.01)
BA	3.35 (1.38)	1.50 (0.17)	2.78 (2.46)	89.68 (4.20)	2.69 (0.66)	0.08 (0.04)
BA-l	3.82 (0.49)	1.34 (0.51)	2.35 (0.28)	89.79 (1.50)	2.71 (0.42)	0.08 (0.01)
SE	3.21 (1.34)	0.66 (0.37)	2.14 (1.38)	91.4 (3.82)	2.93 (1.46)	0.06 (0.02)
SE-l	2.92 (0.34)	1.45 (0.49)	2.26 (0.60)	90.47 (1.07)	2.89 (0.49)	0.07 (0.01)
TE	2.21 (1.00)	0.71 (0.29)	1.35 (0.67)	92.62 (2.25)	2.81 (1.07)	0.04 (0.02)
TE-l	3.09 (0.35)	1.14 (0.10)	3.14 (1.43)	90.39 (0.11)	2.24 (0.87)	0.08 (0.01)

3 Characterization of the restoration grouts

3.1 Materials and methods

For each grout, several test prisms were prepared according to standard UNI EN 196-1: 2005. Half of the prisms were cured *in situ*, while the remaining were cured in laboratory. After an appropriate curing period, the mineralogical assemblage of both *in situ*- and *ex situ*-cured grouts was determined through XRPD to identify possible alteration dynamics. For comparison, XRPD analysis was performed also on anhydrous grouts, coupled with bulk chemical analysis by means of X-ray fluorescence (XRF). Finally, six samples of grouts cured *in situ* were studied by SEM for microtextural and microchemical characterization.

3.2 Results

The grouts were subdivided into three groups according to differences in chemical and mineralogical characteristics:

Group A (MI, M21, AI): grouts based on lime + pozzolanic agent + carbonate microfiller. The anhydrous grouts (Fig. 5a) have a mineralogical assemblage constituted by portlandite and carbonate filler (MI-M21: calcite, AI: dolomite). Two broad bands are also present in the XRD patterns of the grouts: a stronger one peaking at about 31° 2θ and a weaker one peaking at about 48° 2θ. This pattern is typical for the blast furnace slags [10]. The nature of the hydraulic agent is confirmed by the SEM-EDS microanalysis performed on unreacted grains of

slag, consistent with literature data [11]. Considering the intensity of the diffractometric contribution of the slag, the bulk chemical composition of the grouts by XRF (Table 2), the loss on ignition (LOI) data (Table 2), and the visual estimates on quantities of the residual slag grains by SEM-EDS observations (Fig. 4a), it is possible to estimate the use of a comparable quantity of slag for the manufacturing of MI and AI and a greater amount for M21.

The XRD patterns of the hydrated grouts (Fig. 5a) are characterized by the absence of portlandite reflections, associated with the increase of the intensities of the calcite reflections. Moreover, it is possible to observe an increase of the background band at low angle, associated with a series of broad peaks between 8.5° and 12.0° 2θ, which are related to the formation of CSH and AFm cementitious phases, respectively [12]; these data confirm reaction between lime and pozzolanic agent, associated with partial air reaction of portlandite.

No significant differences have been found in the mineralogical assemblage of *in situ*- and *ex situ*-cured grouts, indicating a substantial inertia to chemical degradation phenomena of the materials in the short term. On the other hand, heterogeneity between exposed surfaces and internal portions of the prisms was observed, the latter being characterized by a greenish color. According to literature [13], this phenomenon is related to the release of S^{2-} within the amorphous structure of the slag during the reaction process with portlandite and its subsequent entrance into the crystalline structure of the AFm phases, resulting in the chromophore effect. The chromophore effect disappears on the external portion due to changes in the sulfur oxidation state.

Group B (BC): grout based on hydraulic lime + pozzolanic agent + predominantly siliceous filler. The anhydrous grout (Fig. 5b) has a mineralogical assemblage constituted by C2S (belite) and gehlenite, associated with the aggregate phases (predominantly quartz, subordinately plagioclase, K-feldspar, white mica, serpentine, cordierite, calcite, and dolomite). C2S and gehlenite are the main mineralogical constituents of hydraulic limes produced through calcination of marls at temperatures under 1250° C [12]. SEM-EDS analyses of the aggregate fraction confirmed the predominant siliceous and metamorphic nature of the filler with a subordinate carbonate fraction; the granulometric distribution is unimodal centered on the medium sands granulometric class. Furthermore, SEM observations highlighted the presence of incoherent volcanic scoria fragments (Fig. 4b) mainly constituted by a siliceous-aluminous glass whose chemical composition, determined by EDS, is compatible with the chemical profile of Campi Flegrei pozzolan [14]. This evidence confirms the addition in the mixture of a natural pozzolan as hydraulic agent.

The XRD pattern of the hydrated grout (Fig. 5b) is characterized by the absence of C2S reflections, associated with an increase in the diffractometric contribution of portlandite, CSH, and AFm phases. This evidence confirms both the hydraulic reaction of the low-temperature cementitious phases and the latency of the pozzolanic effect between portlandite and pozzolan in the short term.

A low amount of ettringite and gypsum was found in the grout sample cured *in situ*, indicating a reduced sulfate attack due to reaction between atmospheric sulfates and portlandite and hydrous aluminates in the binder matrix [15].

Group C (O2, O3): ternary grouts based on hydraulic lime + ordinary Portland cement (OPC) + carbonate microfiller. Regarding the binder fraction, the anhydrous grouts have a mineralogical assemblage composed of not only C2S and gehlenite, but also C3S (alite), C3A (aluminate), and C4AF (ferrite) (Fig. 5c), which are the principal mineralogical constituents of the OPC clinker [12]. The presence of cement in the grouts is confirmed by SEM imaging of residual clinker grains (Fig. 4c). An amount of gypsum is also present in the mixture, added to the Portland cement to prevent flash set [12]. Given the intensity of the diffractometric contributions of the clinker phases, the bulk chemical composition of the grouts (in particular Fe_2O_3 and Al_2O_3 content, Table 2), and the visual estimations of quantities of the residual clinker grains by SEM-EDS observations, it is possible to estimate a greater quantity of cement in O2 with respect to O3. The aggregate fraction is composed primarily of carbonates (mostly calcite) and subordinate silicates (mostly quartz). SEM-EDS analyses have evidenced a unimodal granulometric distribution, centered on the silts granulometric class.

The XRD patterns of the hydrated grouts (Fig. 5c) are characterized by the absence of C3S and gypsum reflections and by a reduction in the relative intensities of C2S, C3A, and C4AF reflections, associated with an increasing contribution of CSH and AFm phases, portlandite and ettringite. This evidence confirms the hydraulic reaction of the cementitious phases [12]. Moreover, the greater quantity of portlandite and ettringite in the O2 sample with respect to the O3 sample confirms the higher cement content in the former grout.

No significant differences in the mineralogical assemblage between *in situ* and *ex situ* cured grouts have been found, indicating a substantial inertia to chemical degradation phenomena of the materials in the short term.

Table 2 Bulk chemical composition (obtained by XRF analysis) and LOI of the analyzed grouts

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI
MI	19.78	0.36	7.26	0.46	0.28	4.38	65.45	0.50	0.34	0.07	1.02	23.58
M21	30.74	0.50	11.21	0.45	0.51	6.54	47.65	0.40	0.56	0.01	1.43	4.83
AI	16.79	0.61	8.65	0.48	0.06	22.83	49.25	0.08	0.30	0.02	0.93	34.19
BC	43.30	0.35	7.54	2.54	0.04	2.73	40.57	1.27	1.26	0.06	0.34	19.96
O2	24.77	0.29	5.33	3.45	0.11	2.04	60.21	0.52	1.17	0.10	2.01	13.92
O3	24.50	0.25	4.85	1.63	0.06	1.46	63.25	0.73	0.93	0.08	2.26	18.97

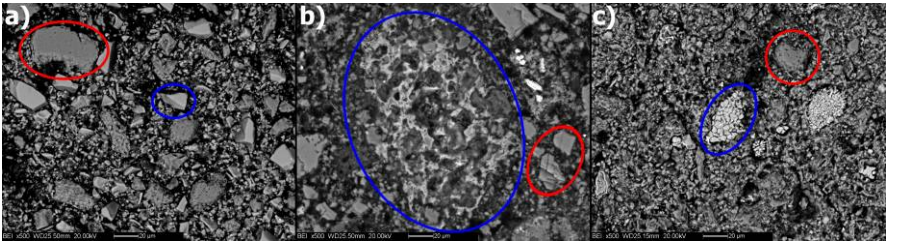

Fig. 4 SEM-BSE images representative for the three groups of grouts: a) group A (MI), unreacted blastfurnace slag fragment circled in blue, carbonate filler circled in red; b) group B (BC), pozzolan fragment circled in blue, siliceous filler circled in red; group C (O3), unhydrated clinker grain circled in blue, carbonate filler circled in red

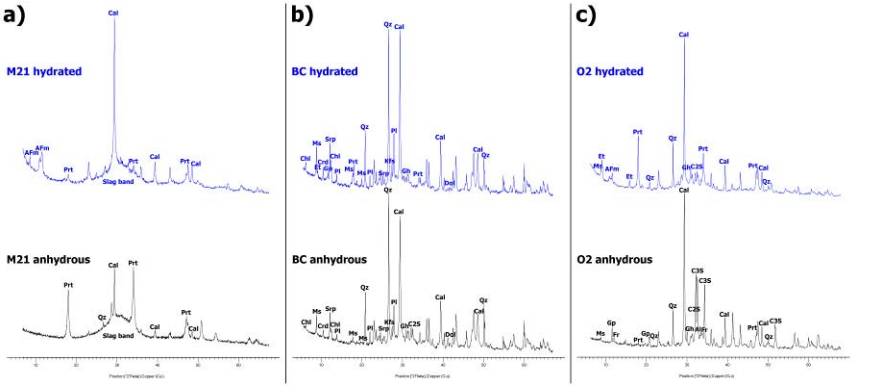

Fig. 5 XRPD patterns representative for the three groups of grouts (anhydrous grouts in black, hydrated grouts in blue). The main reflections of the recognized mineral phases are labelled as: Cal = calcite, Prt = portlandite, Qz = quartz, AFm = AFm cementitious phases, Chl = chlorite, Ms = white mica, Crd = cordierite, Pl = plagioclase, Srp = serpentine, Kfs = K-feldspar, Gh = gehlenite, Dol = dolomite, C2S = belite, Et = ettringite, C3S = alite, Al = aluminate, Fr = ferrite

4 Conclusions

The multianalytical approach led to a good characterization of both the mortars of the investigated historic structures and the selected restoration grouts.

As regards the original mortars, they are all constituted by air lime with an inert fraction compatible, from a minero-petrographic point of view, with the continental deposits of the Aterno river [16]. Moreover, they are discernible in three groups according to binder:aggregate ratio, quantity of dispersed clay fraction in the binder matrix, and compositional and granulometric characteristics of the inert fraction. In particular, the high quantity of clay minerals in group 1 mortars, associated with an enrichment in fine aggregate with respect to the mortars of the other groups, suggests a voluntary addition of soil fraction during

the manufacturing of these materials to reduce production costs, with pernicious effects on the quality of the mortars.

The restoration grouts have been divided into three groups according to minero-petrographic characteristics: group A includes grouts made with lime, blastfurnace slag, and carbonate filler; group B is constituted by a hydraulic lime-based grout with natural pozzolan as hydraulic agent and predominant siliceous filler; group C is composed of ternary grouts with predominantly carbonate filler.

Group A grouts can be considered the most compatible with the original mortars, although the evaluation of their long term resistance is necessary, given the presence in the system of reactive sulfur derived from the slag. Group B grouts can be considered particularly compatible with group 2 mortars, for similarities in the aggregate typology; however, it is necessary to take into account a possible susceptibility of this product to sulfate attack, which has been observed even in the short term. Finally, it is necessary to evaluate the long-term resistance of group 3 grouts, due to possible susceptibilities to chemical attack and incompatibilities with the original mortars related to the presence of cement in the mixtures.

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IV.05

The Influence of Water Repellent Admixture on Lime and Lime Cement Mortars Diffusion Properties

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Abstract The article deals with question of determination of water resistance vapour coefficient μ of lime mortar, lime cement mortar modified or non-modified by addition of water repellent on calcium stearate base. Three sets of mortars were tested and the influence of quantity of the water repellent on coefficient μ was observed. On the base of acquired results the expected growth of μ with added water repellent was not approved. This fact can be connected with bulk density of samples after addition of the agent.

1 Introduction

Lack of any waterproofing in historical buildings is common. Humidity is usually rising from subsoil into porous system of masonry and causes deterioration of masonry material and surface layers of the walls. Every complex renovation design from humidity point of view deals with direct intervention (i.e. radical intervention to the building structures, re-insulation, decrease of hydrostatic pressure etc.) and indirect intervention (i.e. supplement remedy), which will secure maximum lifetime condition and functionality of direct intervention. Very important requirement is the maximum acceleration of drying of the wall by way of evaporation. The technology of special porous water repellent reparation mortars to restore dry surface of wall and on the other hand to allow evaporation is one of possibilities how to solve this problem. The frequent question is how much water repellent agent in mortars influence evaporation of water from walls. Is there any risk of increasing of capillary forces in porous system of masonry and pushing water higher or a risk of raise of total humidity of masonry by application of water repellent mortars? This could be very destructive

to external masonry influenced by freeze thaw cycles. There is a vide discussion in community dealing with restoration of historical buildings about this problem.

On the base of our existing experiences with structures behaviour and surface degradation process as consequence of clime impact we generally prefer plaster to be dead layer that not influence deterioration of core material of historical masonry. The properly designed plaster can simultaneously protect masonry, allow its evaporation and to ensure dry surface of plaster. The following technical requirements on plasters applied on wet walls are desirable:

- allowing transportation of water vapour from wall to the exterior,
- prevention rain water ingress to the wall,
- creation a long-time protection of the wall against external climate,
- safeguard a sufficient adhesion to the base (without cracks and bulges),
- safeguard an acceptable visual appearance (i.e. required colour homogeneity, free from salts, rots, algae and moisture maps)

Above stated requirements (almost opposed in many cases) refer to the complexity of this issue. Attention of Klokner Institute specialists in Prague is currently paid in particular to the first two points and at the same time they search for material combinations allowing maximum increase of hydrophobicity of plasters with their diffusion property preserved.

2 Test program

Series of measuring have been carried out in 2009 and still continue as well as determination of the vapour resistance coefficient from samples of various mortar types both lime and lime-cement, which contain or not containing water repellent agent. The water vapour resistance factor, commonly called μ-factor, is a dimensionless number describing how many times better a material or product is at resisting the passage of water vapour, compared with an equivalent thickness of air. Series of samples were prepared for the purpose of testing, which had been tested even 6 months after the production, allowing samples to mature. Carbonisation progress was not determined. Target of tests is to assess impact of mortar modification by water repellent agent on mortar properties mainly on the diffusion property.

2.1 Tested materials a specimen preparation

Bellow presented results include experimental testing of diffusion properties on three types of the mortar, hereafter marked as MV1, MV2 and MVC. The silica sand fraction was 0/4. The binding agent is made of dry lime hydrate (CL90) pozzolan additive (silica fume) and standard cement CEM I 42.5. Composition of tested mortars is in the following Table 1.

Individual mortars were prepared with such a dose of the water to get soft and to allow the same level of workability of 160-180 mm of the cone spreading on the vibration stage. 12 specimens of the size 40x40x160 mm and 12 disks of the diameter 100 mm and 20 mm height were produced (according to [4] WTA guide WTA 2-9-04/D). 7 days after the production, specimens were unmoulded and stored in the lab, exposed to the air until the beginning of the diffusion and other tests about 6 months later.

Table 1 Mix proportions of tested mortars

Material	Type of mortar and dry mix proportions [kg]		
	MV1	MV2	MVC
Quartz sand 0-4mm	805	845	785
Lime hydrate - type CL90 (EN 459-1)	195	135	135
Hydraulic agent - microsilica		20	
Cement CEM I 42,5			80
Total dry mix weight [kg]	1000	1000	1000
Water repellent agent: calcium stearate (dose by % of weight of dry mix)	4 doses were used: 0% (reference), 0.5% = 5kg, 1% = 10kg, 1.5% = 15kg		
Workability (EN 1015-3)	Spreading of cone: 160-180 mm		
Dosage of water (Water added to get similar workability of mortars)	Varies from 0.18 to 0.22 l/kg of dry mix – see Table 3.		

2.2 Test specification

Determination of water resistance vapour coefficient μ was carried out by the Wet Cup method in compliance with EN 1015-19, EN ISO 12572 and WTA 2-6-99/D. The following Table 3 indicates that prescribed conditions of the test. Area of mortar varies between 6361 mm^2.

Table 2 Summary of marginal conditions of the test μ

Temperature in the chamber	Relative humidity		Distance between saturated solution and tested sample	Tested area diameter 90 mm
	Dry condition - chamber	Wet condition - cup		
	Determined value	Determined value		
°C	%	%	mm	mm^2
23 ± 0.5	0+3	85± 3	35	6361

2 specimens (disc diameter 100x20 mm) were tested for each type of mortar. Each test set consisted of the sample tightly closing the cup environment filled

with an aqueous saturated solution. The set was placed in a testing glass closed chamber with controlled relative air humidity. Temperature of the room and the chamber was controlled by the indoor laboratory air-conditioning system. Water vapour permeability in steady-state condition was determined by regular weighing of the set. Deduction of weights was executed by automatic storage of data in the PC connected to scales. Measuring in the closed chamber was done simultaneously on three sets and the chamber remained shut during the measuring (in order to avoid temporary alteration of relative humidity). Air movement above samples was provided by the little fan located inside the chamber. Measuring chamber including connection to PC is shown on the Fig. 1. Summary of executed tests and description of samples is stated in the Table 4 and reached marginal conditions are given in Table 3. The interval selected for data storage was 1 hour.

As an influence of open porosity on diffusion was anticipated the determination of open pore porosity of mortar was carried out in according to WTA guideline [4]. The Isoprophyalcohol, as a medium that is not influenced by repellent agent, was absorbed to specimens at 10 mbar absolute atmospheric pressure. 3 specimens (half of beam 40x40x160) were tested for each type of mortar.

The influence of water repellent on water open pore absorption capacity was tested as common absorption test with dipping to water. 3 specimens (half of beam 40x40x160) were tested for each type of mortar.

Fig. 1 Measuring chamber with three sets of sample, scales and connection with PC. Internal chamber parameters (temperature, relative humidity, barometric pressure) are scanned by the internal data logger connected with the PC.

Mechanical-physical properties of mortars were determined according to EN 1015-1. 3 specimens (beam 40x40x160) were tested for each type of mortar. 3 results o flexural strength and 6 results of compression strength were gained. Tests were conducted at age of 6 month after preparation.

2.3 Results and discussion

Gained properties of mortars are presented in the following Tables 3 and 4.

Table 3 Summary of mechanical and physical properties – according to EN 1015-11

Mortar type	Water dose [l/kg]	Density of fresh mortar [kg/m3]	Density of hard mortar [kg/m^3]	Flexural strength [MPa]	Compression strength [MPa]
MV1-0	0.196	2040	1790	0.1	0.7
MV1-0,5	0.203	2060	1770	0.1	0.8
MV1-1.0	0.211	2010	1700	0.0	0.4
MV1-1.5	0.215	2070	1670	0.1	0.5
MV2-0	0.192	2060	1800	0.4	1.5
MV2-0.5	0.198	2060	1810	0.4	2.2
MV2-1.0	0.209	2020	1740	0.3	2.0
MV2-1.5	0.216	1970	1720	0.1	1.0
MVC-0	0.170	2190	1910	1.5	7.4
MVC-0.5	0.185	2120	1860	1.1	6.4
MVC-1.0	0.200	2060	1770	1.2	6.5
MVC-1.5	0.207	2030	1810	1.3	5.9

Table 4 Results of the tests of porosity and μ factor

Type of mortar	Water absorption capacity by weight [%]	Isopropyl - alcohol absorption capacity by weight [%]	Open pore porosity by volume [%]	Bulk density [kg/m^3]	Vapour resistance coefficient μ [-]
Lime mortar MV1					
MV1-0	14.3	12.6	29.2	1822	9.1
MV1-STE 0.5%	1.3	12.6	28.9	1802	7.3
MV1-STE 1%	1.5	13.8	30.5	1743	7.1
MV1-STE 1.5%	1.3	11.9	26.5	1756	9.6
Lime mortar with hydraulic admixture MV2					
MV2-0	13.2	11.9	28.1	1856	8.8
MV2-STE 0.5%	2.6	11.6	27.4	1863	8.3
MV2-STE 1%	1.3	13.2	29.6	1758	7.4
MV2-STE 1.5%	2	13.7	30.5	1747	9.0

Type of mortar	Water absorption capacity by weight [%]	Isopropyl - alcohol absorption capacity by weight [%]	Open pore porosity by volume [%]	Bulk density [kg/m^3]	Vapour resistance coefficient μ [-]
Cement lime mortar MVC					
MVC-0	12.1	9.9	24.6	1937	16.9
MVC-STE 0.5%	2.2	11.3	26.7	1850	11.5
MVC-STE 1%	1.9	12.7	28.8	1770	14.3
MVC-STE 1.5%	2	13.1	29.3	1753	12.7

Based on the analysis of results following conclusions had been made:

- As was expected type of binder composition significantly influences mechanical a physical properties of mortars. The strength of pure lime mortar (MV1) is the lowest (compression strength < 1MPa) and lime+cement mortar (MVC) the highest (compression strength > 6MPa). Small amount of hydraulic admixture helps lime mortar type 2 (MV2) to be significantly stronger (compression strength > 1MPa and < 2.5MPa).
- The effect of water repellent admixture on lower absorption of water was evident for all mortar types after addition already 0.5% of water repellent agent. Water absorption decreased from 14.3% to 1.3% for MV1, i.e. nearly 10 times.
- Application of water repellent agent causes decrease of density and simultaneously decrease of strength in correlation with quantity of added agent.
- Vapour resistance coefficient μ of all tested mortars fluctuated between 7.1 to 16.9. Lime based mortars (MV1 and MV2) shoved significantly lower values of μ factor (7.1-9.6). This coefficient is almost double (11.5 -16.9) when combination lime+cement (MVC) was used as a binder. Lover coefficient means better diffuse transmission of water vapour.
- In cases of lime mortars MV1 and MV2, values μ slightly decreased after addition of water repellent agent in comparison with values of reference non-modified samples. This phenomenon is caused probably by decreased bulk density and increased of open porosity. For example after addition of 0.5% of the agent the average decrease of μ in the set MV1 was about 20% in comparison with reference non-modified mortar.
- On the other hand there was measured slight increase of μ factor (worse diffusion) in correlation with quantity of added water repellent if only modified mortar samples are compared (see Table 4.). This indicates a expected influence of water repellent agent on decreasing of water vapour permeability of mortar. Transmission of water vapour would be slightly worse for mortar with higher dosage of agent.

- Highest dosage of agent (1.5% of dry mix mass) of all tested mortar types shoved lower factor μ then reference non modified mortars.
- Obtained results do not confirm hypothesis, that application of water repellent agent into mortars causes significant worsening of mortar diffusion properties. Significantly higher influence on diffusion properties of mortars has type of binding system, i.e. amount of cement as has showed this testing program.

3 Conclusion

It is known that application of water repellent admixture into mortar mass can improve its durability and aesthetics appearance of surface if it is applied on wet masonry. As is mentioned at the introduction the frequent question during reparation of wet walls of historical buildings is, how much water repellent agent in mortars influence evaporation of water from walls? Is there any risk of increasing of capillary forces in porous system of masonry and pushing water higher or a risk of increasing of total humidity of masonry by application of water repellent mortars? This phenomenon could be very destructive to external masonry influenced by freeze thaw cycles. There is a vide discussion in community dealing with restoration of historical buildings about application of mortars modified by water repellent agents.

Series of comparative tests are still carried out at Klokner Institute laboratories to get some relevant data about influence of water repellent agents on diffusion properties of different types of mortars.

Results obtained until now do not confirm hypothesis and opinion of many people, that application of water repellent agent into mass of mortars causes significant worsening of mortar diffusion properties. In fact with lowest dose of the water repellent the coefficient μ was slightly reduced in comparison to the reference mortar without the additive. In this particular case this is most probably related to certain aeration of mortars due to used additive. Aeration led to reduction of the density thus causing higher open porosity and water vapour permeability. However with increased quantity of the additive the aeration effect is exhausted and assumed gradual but relatively slow increase of the μ is visible up to the level approaching the reference non-modified mixture. Hydrophobic additive in the mortar mixture in certain quantity therefore does not have to have an impact on water vapour resistance of the mortar but may even slightly reduce it.

Results obtained until now on the contrary prove assumed and expected significant influence of binding system (amount of cement) on increase of the vapour resistance coefficient μ.

Presented data relate to one type of water repellent agent. The influence of different kinds of additives may be very different. To get more accurate

information and wider more general view on this problem more war has to be done.

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IV.06

Energy Renovation by Lime Renders

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Abstract Lime renders can help improve the energy balance of the building itself given their position in the external layer. Indeed, historical masonries have high rates of thermal transmittance; however, their thermal inertia can contribute to their effectiveness in areas with important temperature fluctuations. Hence, it is possible to preserve this thermal inertia if the transfer rate of energy is improved from outside. There are many commercial systems (SATE or ETICS) which improve the thermal efficiency of outer walls by reducing heat conduction, but they require a considerable increase of the thickness of the wall. However, in façades where it is not possible there seems to be no available solution. This paper analyses how the energy balance in a building can be improved based on a render that works not only on reducing thermal conductivity but on optimizing heat transfer by radiation.

1 Introduction

Rehabilitation-renovation implies at least 60% of reduction of energy consumption opposite to demolition and rebuilding [7], so, their preservation and reuse is considered as an strategy not only from the heritage point of view, that is, the conservation of the cultural identity of the society [5, 6], but also from the ecological one.

On the other hand, climate change is an ascertained reality [1] consequence of emissions of greenhouse effect gases. However, according to the forecast, an increase within 25 and 90% in a period of 30 years [2] is expected, unless the use of renewable energy is promoted [4]. In the case of the building sector, taking into account only their use, without considering indirect emissions coming from their construction and demolition or final use, emissions of CO_2 reached 33% in 2004 (8.6 Gt of CO_2 in relation to 26.1 Gt of CO_2 of global energy [3]), although it is

expected to increase up to 11.1 Gt of CO_2 in 2020. Hence, the building sector represents an important area to alleviate the effects of global warming in terms of energy conservation and use of renewable energies [1]. Furthermore, it should be adapted to the irrevocable increase of temperatures [1, 9] that, in the case of Spain, means higher daily thermal fluctuations and the intensification of "extreme climatic events" in relation to the temperature [10, 11]. So the passive use of energy in buildings should be prioritized as a key strategy in energy conservation.

In Spain, constructions that were built before the first thermal standard from 1979 (NBE-CT-79) have some specific constructive constants on which this research is focused. The main characteristic feature is that they are massive dwellings built with monolithic structural walls and without a specific thermal insulation. In their façades, the energy loss and/or gain, over the whole constructive systems, was estimated within 67 and 74% [8]. However, they have a good thermal behaviour from the point of view of a high thermal inertia with a decrement factor higher than 90% and time lags of eight hours minimum. However, when their thermal transmittance is analyzed, none of the studied walls fulfilled the Building Technical Code (Código Técnico de la Edificación CTE-HE) except for the one 96 cm thick when the building is placed in the A area corresponding to the capitals of the provinces of Santa Cruz de Tenerife, Las Palmas de Gran Canaria, Melilla, Málaga, Cádiz or Almería, where 0.94 W/m^2K is required [29].

From this point of view, considering the importance of thermal inertia in buildings, ecological rehabilitation proposals are centered improving the thermal transmittance with specific systems located outside. They are available in the market since the 70's [12, 13] and collected in European standards with different names depending on the language: SATE, EIFS, ETICS or WDVS. Regarding these, there is no doubt that the increase of the thickness insulation means a considerable energy saving which can reach 70% if the intervention is made in façades and roof [14]. However, this outside insulation system poses an important drawback, because in order to improve thermal resistance ($R=e/\lambda$, where e is the thickness and λ is the thermal conductivity), the thickness plays an important role [24]. Nevertheless, there are circunstances in which the increase of outside thickness in façades is not feasible (i.e., decorative elements). If it comes to this, the only possible solution is inside insulation which implies the loss of habitable surface and the possibility of thermal storage but, what is worse, the risk of interstitial condensation. Regardless of the high number of estimated buildings affected in city centers, there is no alternative to improve the thermal behaviour of the outside of façades with limited thickness. Given this circumstance, the paper focuses on the use of radiative properties taking advantages of renders.

2 Thermal analysis

Energy transmission by radiation is based on the exchange of energy through emission and absorption of electromagnetic waves [15, 16, 17] and appears in any surface with a temperature higher than 0 K. In relation to this, renders supply not only the aesthetical aspect and the conservation and preservation of masonry, but can also be used to improve the energy balance of the building.

In order to evaluate the most appropriate strategies for the proposed aims, firstly, a simplified estimation in steady state is carried out. The results are compared and confirmed with a time-dependent state calculated by ANTESOL software developed by Dr. Manuel Martín Monroy [28].

2.1 Steady state

From this point of view, thermal equilibrium is reached when radiation, convection and conduction of energy are balanced and it succeeds when they equal zero. In fact, the effect of any of the mechanisms of transmission of energy can be evaluated using the following expression [17]:

$$(\alpha_{oc} E_G) + 5.67\varepsilon_{ols} F_T \cdot (T_e - T_{se}) - 120\varepsilon_{ols} F_{ssk} F_{Tssk} \cdot (1 - f_c) + h_{cv}(T_e - T_{se}) + \frac{(T_{si} - T_{se})}{R_T} = 0$$

Where α_{oc} is the surface absorption coefficient in short wavelength; E_G is the total solar radiation; ε_{ols} is the emissivity of the surface in long wavelength; F_T is the rate of temperature by radiation ranged between 0.8 and 0.9; T_e is the outside temperature; F_{ssk} is the factor of the angle between the surface and the vault of heaven simplified to the unit if it is considered that the surface of study is infinitely smaller when compared to the vault of heaven [17]; F_{se} is the factor of the angle between the surface and the terrestrial environment; F_{Tssk} is the rate of temperature by radiation between the surface and the vault of heaven ranged between 0.8 and 0.9; f_c is the cloud factor between 0 and 1; h_{cv} is the superficial convective coefficient equal to 19 W/(m^2.K) [17] and R_T is the total thermal resistance of the wall. In this expression, it can be observed that, apart from the conductivity, emissivity and absorptivity have a clear influence on the transmission of energy.

In the case of a wall composed of brick masonry of 2000 kg/m^3 of apparent density [18], 40 cm of thickness and 0.38 m^2.K/W of thermal resistance. We suppose that the rate of temperature by radiation is $F_T = F_{Tssk} = 0.8$, the cloud factor $f_c = 0.2$ and the inside temperature 20ºC. In summertime conditions, the external temperature is 34.70ºC and the solar radiation 363 W/m^2; meanwhile during the winter, the external temperature is -10ºC and the solar radiation 150 W/m^2. Tables 1 and 2 show results for short wavelength radiation, q_{roc}, long wavelength radiation, q_{rol}, convection, q_{conv}, and conduction q_{cond}, in W/m^2. The negative values obbey to the criteria according to which a factor is positive when it "goes

into" a considered point; whereas it is negative when it "goes out" (i.e.,when it is absorbed, reflected or emitted by the wall).

Table 1 Steady state. Summertime/Wintertime conditions, $f_c = 0.2$

-	T_{se} (ºC)	q_{roc} (W/m^2)	q_{rol} (W/m^2)	q_{conv} (W/m^2)	q_{cond} (W/m^2)
$\alpha_{oc} = 0.05$ $\varepsilon_{ol} = 0.05$	33.59 / -6.14	18.15 / 7.50	-3.59 / -5.66	21.15/ -73.40	-35.75 / 68.78
$\alpha_{oc} = 0.95$ $\varepsilon_{ol} = 0.05$	48.71 / -0.89	344.85 / 142.50	-0.66 / -4.07	-266.19/ -173.01	-75.55 / 54.99
$\alpha_{oc} = 0.95$ $\varepsilon_{ol} = 0.95$	43.69 / 0.39	344.85 / 142.50	-111.70 / 3.39	-171.11/ -197.49	-62.34 / 51.59
$\alpha_{oc} = 0.05$ $\varepsilon_{ol} = 0.95$	31.10 / -4.81	18.15 / 7.50	-57.43 / 25.82	68.46 / -98.61	-29.20 / 65.29

As observed in Table 1, the key factor, in both conditions, is the absorptivity although it prevails in summertime conditions because of preventing the caption of energy. About the emissivity, it seems to have a limited influence in the wall with a light improvement as its value increases, during the summer, because of the higher emission from the surface; meanwhile, during the winter, if the absorptivity is reduced, the lower the emissivity, the lower the losses by convection and long wavelength radiation saving up to 26 and 78%, respectively. Comparing common materials (high emissivity and high absorptivity) with a surface of the same emissivity and low absortivity, in summertime conditions, the loads from short wavelength radiation entail savings up to 95%, while conduction decreases till 53%. Whereas during the winter, if it is reduce the emissivity as well, the loads from short wavelength radiation and convection decrease by 95 and 63% respectively. Although, it should be highlighted that the improvement of the conductivity should be considered as a complementary measurement.

Table 2 Steady state. Wintertime conditions, $f_c = 0.9$, solar radiation 20 W/m^2

-	T_{se} (ºC)	q_{roc} (W/m^2)	q_{rol} (W/m^2)	q_{conv} (W/m^2)	q_{cond} (W/m^2)
$\alpha_{oc} = 0.05$ $\varepsilon_{ol} = 0.05$	-6.36	1	-0.82	-69.55	69.38
$\alpha_{oc} = 0.95$ $\varepsilon_{ol} = 0.05$	-6.36	1	-0.82	-69.55	69.38
$\alpha_{oc} = 0.95$ $\varepsilon_{ol} = 0.95$	-3.95	1	60.10	-124.12	63.02
$\alpha_{oc} = 0.05$ $\varepsilon_{ol} = 0.95$	-3.95	1	60.10	-124.12	63.02

Nevertheless, according to Luxán et al, in the centre of Madrid, solar radiation in façades during the winter is limited or even null because of the inclination of the solar beams [7]. Taking into account this circumstance and the fact that, in the winter, the amount of clear days is reduced, the calculations with a solar radiation of 20 W/m^2 and a cloud factor f_c=0.9 show that absorptivity has no influence on the results (Table 2), which are mainly regulated by loads from long wavelength radiation and convection. As it can be observed in this situation, high emissivity results in a considerable increase of energy transfer by longwave radiation, higher superficial temperatures and an increase of the convection load up to 44%. Hence, according to the steady state, in wintertime conditions, a reduction of emissivity seems to be advisable.

2.2 Time-dependent state

In order to be comparable to the steady state, the same wall is used, with south orientation and whose inside properties were roughness of 0.4, absorptivity and emissivity of 0.4 and 0.9, respectively. The climatic data is provided by the Agencia Estatal de Meteorología for the Madrid-Retiro station [19]. Furthermore, the surroundings reflectance is fixed at 0.2 (supposing that the building is located in an urban area), the solar factor is assumed to be 0.8, the external wind speed 3 m/s [20] and the inside one 0.2 m/s (an intermediate value suitable for summer and winter season [15]). To highlight that, in fact, calculation is in pseudo-transient state because inside temperature is fixed at 20ºC.

Once again, in clear days (Table 3), the average flow is lower when absorptivity is 0.05, just as temperature and decrement factor are more favorable under these conditions. So, the results match up with the statements of other researches about the effect of absortivity and reflectance [21, 22]. Regarding emissivity, during the summer, the high emissivity favours the lower average flow; meanwhile during the winter the opposite happens.

Table 3 Time-dependent state. Summertime / Wintertime conditions, clear

-	T_m (ºC)	Time lag (h)	Decrement factor (%)	Average flow (W/m^2)
α_{oc} = 0.05 ε_{ol} = 0.05	22.6 / 14.4	11.25 / 9.25	2.2 / 3.6	6.9 / -16.4
α_{oc} = 0.95 ε_{ol} = 0.05	31.8 / 29.0	10.00 / 9.75	4.7 / 5.0	34.3 / 26.2
α_{oc} = 0.95 ε_{ol} = 0.95	26.9 / 20.8	10.25 / 9.50	4.6 / 5.1	19.5 / 2.1
α_{oc} = 0.05 ε_{ol} = 0.95	21.6 / 11.8	11.00 / 11.25	3.1 / 3.9	4.1 / -23.9

In comparison with the common walls (high emissivity and absorptivity), during the summer, increasing the reflectance (or reducing the absorptivity), the average flow decreases 89% when keeping a high emissivity and 65% when it is also reduced to 0.05. Moreover, the amount of energy that goes through the wall decreases 33% and 52%, respectively, during the summer, and 24% y 29%, respectively, during the winter. In cloudy conditions, during the summer, the absorptivity prevails; meanwhile, with the absorptivity fixed to the minimum, during the winter, better results are achieved when the emissivity is reduced to 19% of the thermal flow and the decrement factor is improved up to 10%.

With regard to the effect of the surface roughness when absorptivity and emissivity are fixed at 0.05, as it can be observed in Table 4, corresponding to clear conditions, the average thermal flow is lower, 30% and 65% in the summer and winter season, respectively, when the roughness decreases. This could be because the increase of roughness decreases the reflectance and increases the wall absorption [23, 25]. Meanwhile, in cloudy conditions, the situation is similar to the previous one. The average flow decreases with the lower roughness within 36% and 21% in the summer and winter season, respectively. Hence, although roughness seems to have a clear effect in conditions of clear winter and cloudy summer, in all of them, the smooth finishing decreases the average thermal flow between the wall and the outside and improves the energy conservation of the system.

Table 4 Time-dependent state. Summertime / Wintertime conditions, clear. Roughness

-	T_m (ºC)	Time lag (h)	Decrement factor (%)	Average flow (W/m^2)
Roughness= 0.1	22.3 / 17.3	21.75 / 9.50	3.9 / 4.6	5.5 / -7.7
Roughness= 0.9	22.6 / 13.2	11.00 / 11.00	2.9 / 3.6	7.8 / -21.7

3 Conclusions

In the case of decorated façades or in those in which the available thickness is reduced, both with monolithic walls without a specific thermal insulation, in order to improve the thermal properties of the walls while preserving their thermal inertia, the improvement of the radiative properties is the best option.

In relation to this, it has been observed that the suitable strategy in summertime conditions is the reduction of absorptivity or the increase of reflectivity in short wavelength from 760 to 2500 nm although using light colours (with high reflectivity in our visual spectrum) that prevent dazzle and visual discomfort [26]. Moreover, during the winter, mainly in cloudy circumstances or with no sun, the reduction of the emissivity is advisable so as to decrease the loss of energy coming from inside, in the range from 8000 nm and forward [27]. Furthermore, the use of low values of absorptivity and emissivity reduces the thermal stress in the

materials and guarantees their durability in the long term. As a complementary strategy, the use of low conductivity materials is recommended in order to reduce the transmission of energy that would be absorbed by the surface, in the summer, or transmitted from the inside to the outside in the winter.

In any case, the goal of the finishing layer of the render would be, nowdays, to avoid the outside energy in the summer and to limit the energy coming from the inside in the winter (although, if the ongoing trend were a widespread increase of temperatures, the most suitable strategy would be a reduction of absorptivity). This way, according to the time-dependent analysis, the achievement of these properties would imply a reduction in energy consumption within 65% and 87% for a sunny summer and winter, and 59 and 13% for a cloudy summer and winter, respectively.

Finally, since the proposed renders are appointed for old masonries in which the use of compatible materials is paramount in order to guarantee their conservation and maintenance in the long term, the use of traditional binders is essential. Among them, lime is considered as the most suitable for external use. Moreover, renders based on lime have an important field of performance in bio-buildings because of their closed cycle of life and their strength, elasticity and vapour transfer properties compared to similar materials.

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IV.07

Impact of Non-Uniform Distribution of Temperature on the State of Stress of Masonry

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Abstract Deterioration of masonry is caused by inordinate loading and by climatic actions. Climatic cyclic thermal stress in structure is incurred by unequal temperature gradient across the thickness of homogenous or heterogeneous masonry. Thermal gradient also causes significant stress close to the interface between stone and mortar in the masonry made of components with different thermal expansion properties. The values of thermal stress increase with higher thermal gradient. Impact of insulation, absorption of solar radiation, air temperature around the structure, heat transfer coefficient, coefficient of heat conduction and heat capacity to the temperature gradient in the wall exposed to the exterior weather conditions were investigated by a numerical model. All of these effects or material properties affect the maximal surface temperatures in masonry during summer. Especially the orientation of surface to the cardinal points, solar absorption and velocity of the wind around structure influences significantly the maximal achieved surface temperature thus the values of stress caused by the temperature.

1 Introduction

1.1 Material compatibility

Masonry of historical structures is a heterogeneous material, created from stone blocks or bricks and mortar. The individual components should have material characteristics that ensure mutual cooperation under loading and climatic action, without defects or damage. This requirement is part of what is referred to as compatibility and is usually fulfilled by a simple requirement for identical or closely similar characteristics of the two materials that compose the masonry.

Durability of masonry is influenced mainly by resistance to load, environmental cyclic thermal stress, freezing cycles, and environmental moisture stress. The influence of the environmental cyclic thermal stress of masonry is described in detail in this paper.

Thermal stress in masonry is influenced by temperature gradient, thermal expansion, and Young modulus of the individual components. Distribution of the temperatures in masonry depends on its environment and "thermal" material characteristics. The main factors of the environment are solar radiation, air temperature around the structure, speed of wind, heat transfer coefficient on the interface between masonry and air, orientation of the surface to the cardinal points, shadowing, and impact of moisture. The "thermal" material characteristics of masonry are heat conduction, heat capacity, and coefficient of heat absorption of solar radiation. Properties mentioned above influence the thermal stress of masonry and consequently its durability. The impact of each material or environmental property will be described in detail in the rest of the paper. Moisture also influenced the temperature gradient but, in this study, is simplified, and therefore this effect is neglected.

1.2 Impact of different thermal expansion of mortar and stone

Masonry consists of mortar, stone, or bricks, which could have different material properties, i.e. Young`s modulus, coefficient of thermal expansion. Masonry is created in a specific moment when both mortar and stone or brick have similar temperature. If both of the masonry materials have different thermal expansion, the increase of temperature causes the increase of stress close to its interface. This phenomena was investigated in a previous study [1], only some conclusions of this study will be presented here.

The state of stress in masonry caused by different thermal expansion of its components is significantly influenced by the value of difference of thermal expansion coefficient between masonry components, Young modulus of its components, and thermal gradient. When both the difference of the thermal expansion coefficient between stone and mortar and the values of stress are higher, these values increase with higher Young`s modulus of stone and mortar.

The previous study [1] was based on a numerical model of a typical masonry section. The section was loaded by the temperature gradient (cooling and heating representing real climatic conditions in Prague, Czech Republic), which generated high stress in the mortar and close to the interface between stone and mortar. The detailed distribution of stress is shown in Fig. 1. One node was chosen from this figure where the relation of stress to the coefficient of thermal expansion of mortar was investigated (Fig. 2). The material characteristics of masonry units were constant in this study, but the coefficient of thermal expansion and Young`s modulus of mortar ware variable.

The maximal values of stress were achieved on the surface with the highest temperature gradient. The impact of material characteristics on the thermal gradient was not investigated in detail in the previous study, therefore it is investigated in this paper.

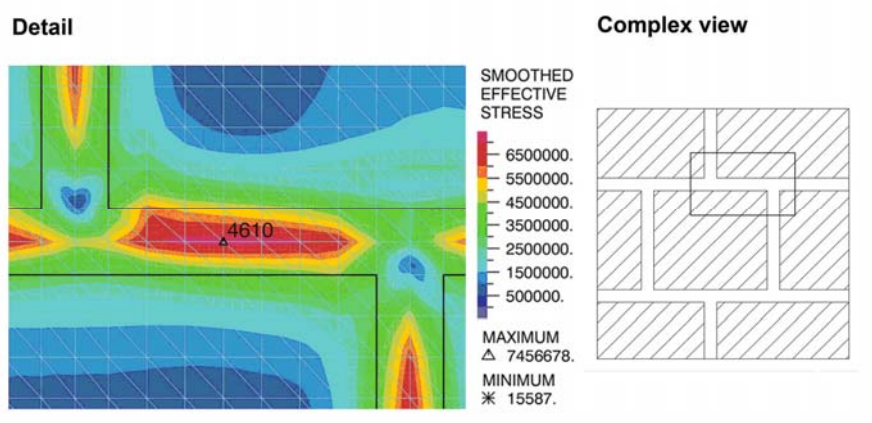

Fig. 1 Location of the node with maximum effective stress in the mortar.

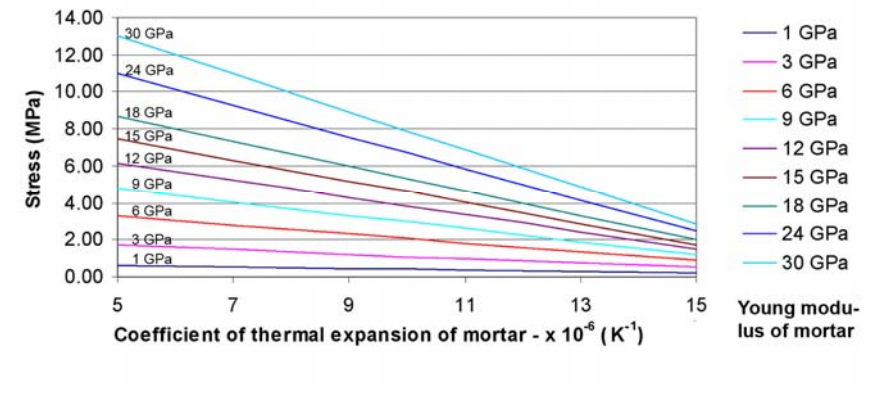

Fig. 2 History of effective stress depending on the coefficient of thermal expansion and the Young`s modulus of the mortar – this stress is caused by cooling and different thermal expansion of mortar and stone; coefficient of thermal expansion of stone (masonry block) is $18 \times 10^{-6}\,K^{-1}$, the Young`s modulus of the stone is 15 GPa.

2 Temperature analysis

The intention of this paper is investigation by numerical model which material characteristics cause high temperatures in terms of heat conduction. Also, the parameters of the environment were studied.

2.1 Description of numerical model

This study is based on one dimensional finite element model of masonry section. The numerical model represents the cross-section of the wall of 0.45 m thickness. One side of the wall was exposed to solar radiation and outdoor air, while the opposite side was exposed only to the outdoor air.

The transient heat transfer in 3-D, according to [2], is described by equation (1).

$$\lambda \nabla^2 T = \rho\, c \frac{\partial T}{\partial t} \pm G_c' \tag{1}$$

c specific heat capacity, J / (kg K)
ρ bulk density, kg / m^3
λ coefficient of heat conduction, W / (m K)
G´$_c$ source term, in this case is equal to zero, J / m^3

The 3-D problem of heat transport through the masonry was simplified into the 1-D problem [3]. The equations (1) simplify into formula (2). The heat transport through a wall is basically a 1-D problem.

$$\lambda \frac{\partial^2 T}{dx^2} = \rho\, c \frac{\partial T}{\partial t} \pm G_c' \tag{2}$$

x coordinate in direction perpendicular to wall surface, m

The equation (2) was completed with formulation of boundary conditions, which represents the effects of heat transfer from air to surface of masonry and absorbed solar radiation [4]. The full description of the formulation of boundary conditions with verification is found in a previous study [5]. The necessary climatic data for the simulations were measured at a meteorological station in Prague Karlov, Czech Republic.

2.2 Material characteristics of the masonry (stone, bricks, mortar)

The material characteristics of the masonry components in terms of heat conduction are influenced mainly by porosity, amount of water in the material, chemical composition, and colour of the surface. Coefficient of heat conduction is significantly influenced by the number of pores in the material and whether or not the pores are filled with water. The heat conduction coefficient has low values when the material has a high quantity of pores that are not filled with water. If the pores are filled with water, the coefficient of heat conduction increases. Also, compact materials without pores usually have a higher heat conduction coefficient

than materials with pores. The non-porous material usually has a higher bulk density thus also higher volume heat capacity. Specific heat capacity has similar values for all kinds of stone, bricks, and mortars. Colour of the surface affects absorption of solar radiation, and dark-coloured surfaces have higher absorption than light-coloured surfaces [6].

The material characteristics in terms of heat conduction of many types of stones are difficult to find. It is also necessary to note that one type of stone has high natural variation of material properties.

2.3 The impact of variable material characteristics and orientation of masonry to the cardinal points on the maximal surface temperature of masonry

On the façade, stones or bricks usually have significantly higher representation than the joint mortar in the masonry. Thus, the final distribution of temperatures in the common masonry is mainly influenced by the material properties of the stones or bricks [7].

The surface temperature of masonry is influenced by several factors: orientation of its surface to the cardinal points, heat absorbability of solar radiation, heat conduction of the masonry components, heat capacity of the masonry, and coefficient of heat transfer between outdoor air and masonry. The wide range of possible (realistic) values of material and environmental properties were used in simulations. The impact of the real climatic situation recorded in July 2006 in Prague, Czech Republic, was used for the simulation. This month included one of the hottest days in the known history of Czech Republic. Maximal surface temperatures of masonry were obtained with the one dimensional numerical model. The 1-D model represents the thickness of vertical wall exposed to incident solar radiation on one side and not the other. Both surfaces are exposed to the outdoor air.

2.3.1 The impact of the surface orientation to the cardinal points

The impact of the surface orientation to the cardinal points and heat absorbability of solar radiation is plotted in Fig. 3. The horizontal axis on the chart in Fig. 3 shows the azimuth of the normal of vertical surface exposed to solar radiation, and the maximal temperature achieved in July 2006 is on the vertical axis. These values were determined by numerical model. The maximal temperatures were obtained for the orientation of the surface to the west or south-west. Lower values were obtained for the orientation of the surface to the south-east or the south. The absolute values of the surface temperature significantly depend on its heat absorbability of the solar radiation.

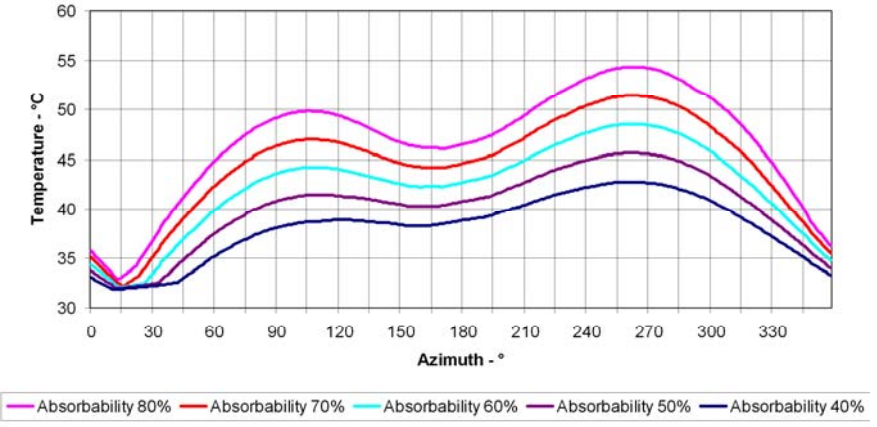

Fig. 3 Relation of maximal temperature of a vertical surface to the orientation to cardinal points. This graph was computed with coefficient of heat conduction 1.4 $W.m^{-1}.K^{-1}$, specific heat capacity 840 $J.kg^{-1}.K^{-1}$, bulk density 2400 $kg.m^{-3}$, and coefficient of heat transfer 15 $W.K^{-1}.m^{-2}$

2.3.2 The impact of heat conduction

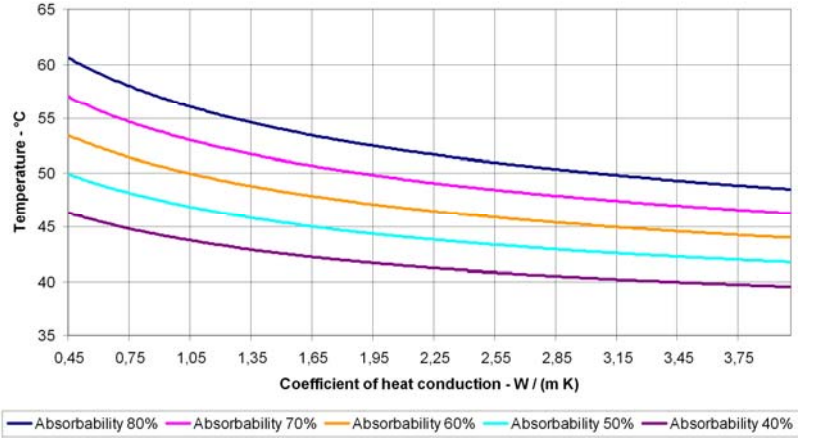

Fig. 4 Relation of maximal temperature of vertical surface to the coefficient of thermal conduction. This graph was computed with azimuth 262°, specific heat capacity 840 $J.kg^{-1}.K^{-1}$, bulk density 2400 $kg.m^{-3}$, and coefficient of heat transfer 15 $W.K^{-1}.m^{-2}$.

The impact of heat conduction on the maximal surface temperature is plotted in Fig. 4. All parameters were constant in the model except the coefficient of heat conduction. The maximal surface temperature increases as the coefficient of the heat conduction is lowered. The higher coefficient of heat conduction causes faster

transport of absorbed heat into the masonry, and thus, the gradient in masonry is more "linear" and surface temperatures are lower.

2.3.3 The impact of heat capacity

The impact of heat capacity on the maximal surface temperature was investigated by numerical model. When the heat capacity is low, the temperatures in whole masonry increase. High heat capacity reduces the temperatures in all masonry and helps to lower temperatures and, consequently, thermal stress. This reduction is lower than the reduction related to the coefficient of heat conduction (Fig. 5).

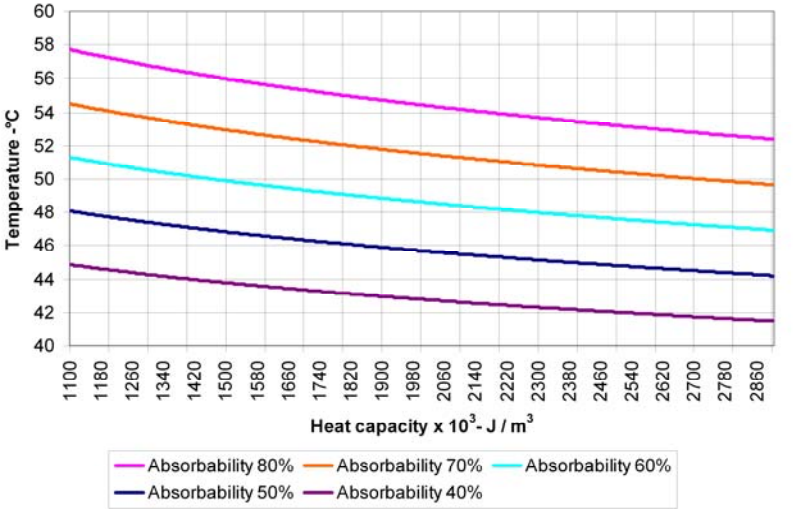

Fig. 5 Relation of maximal temperature of vertical surface to the heat capacity. This graph was computed with azimuth 262°, coefficient of heat conduction 1.4 $W.m^{-1}.K^{-1}$, and coefficient of heat transfer 15 $W.K^{-1}.m^{-2}$.

2.3.4 The impact of the heat transfer coefficient

The heat transfer coefficient depends on the velocity of the wind, size, and shape of the wall. Descriptions of the relationship of this coefficient to the velocity of the wind and other parameters exist in literature, but are significantly influenced by the specific situation. In general, when the speed of the wind is higher, the heat transfer coefficient also is higher. The value 15 $W.K^{-1}.m^{-2}$ defined by the Czech norm in summer time was used in previous chapters [8]. The range of values of coefficient of heat transfer corresponds to the possible values which could be achieved in environment. Coefficient of heat transfer is 23 $W.K^{-1}.m^{-2}$ in winter, and 6 - 10 $W.K^{-1}.m^{-2}$ at room temperature [8].

When the values of coefficient of heat transfer are low, the increase of temperatures is high (Fig. 6). The surface of the masonry structure exposed to solar radiation is cooled by the heat transfer between air and the wall surface. High velocity of wind causes high coefficient of heat transfer and, consequently, high cooling of the surface of the wall.

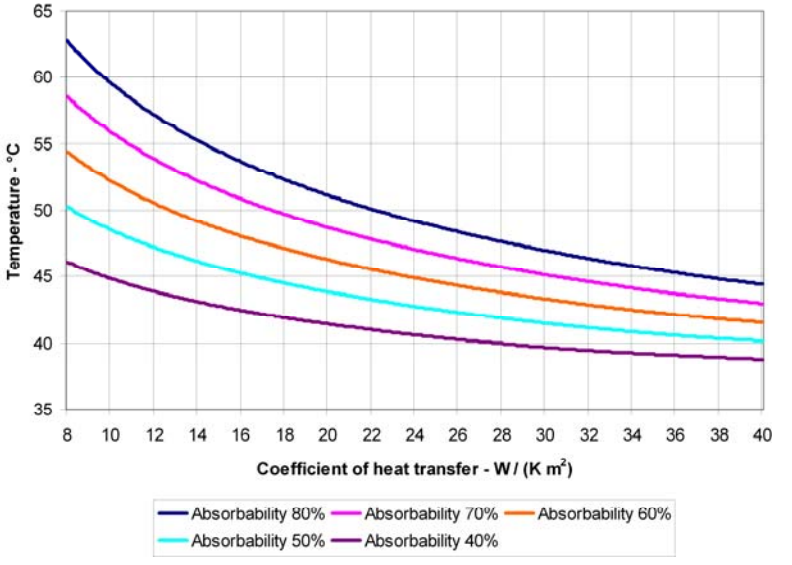

Fig. 6 Relation of maximal temperature of vertical surface to the heat transfer coefficient. This graph was computed with: coefficient of heat conduction 1.4 $W.m^{-1}.K^{-1}$, specific heat capacity 840 $J.kg^{-1}.K^{-1}$, bulk density 2400 $kg.m^{-3}$, azimuth 262°.

3 Conclusion

The parameters that influenced the value of the maximal surface temperature achieved in summer time with exposure to solar radiation could be divided into three categories according to their impact. The first category influences the maximal surface temperature significantly, the second to an intermediary degree, and the third minimally. The parameters of the first category are coefficient of heat absorption of solar radiation, orientation of surface to the cardinal points, and coefficient of heat transfer. The coefficient of heat conduction is the only parameter in the second category. Heat capacity is the parameter of the third category, which has the lowest effect on maximal surface temperature. Each parameter can be combined with any other that can cause an increase or decrease

of surface temperatures into higher or lower values than those mentioned in the paper.

Thermal stress in masonry is caused by the unequal distribution of temperatures across the thickness of masonry, which is considered as homogenous material. The highest stress is implicitly caused by the properties in the first category with a combination of the low coefficient of heat conduction.

Thermal stress in masonry, created by stone units that have different thermal expansion than mortar, is influenced by the extreme temperature in the masonry, which is usually the surface temperature. This stress can be reduced by using mortar that has maximal difference of thermal expansion coefficient between stone and mortar $2 \times 10^{-6} K^{-1}$. When the surface is exposed to high temperatures, it is necessary to design the repair mortar very carefully. Ideally, the differences of thermal expansion between stone and mortar should be zero. Stress can be reduced by cleaning the masonry surface. The absorption coefficient of a clean surface is usually lower than the absorption coefficient of a "dirty" surface. This method can be used when the original "clean" surface is light-coloured.

4 Acknowledgment

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IV.08

Repair Mortars for the Sandstones of the Cathedral of Berne

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Abstract Stone repair mortars used on the cathedral of Berne (Switzerland) have been refined from existing recipes. These hydraulic mortars without any organic additions are prepared on the building site. They are applied as two different layers, a coarser ground layer (KMtl) and a finer surface layer (DMtl) which imitates the stone material. The investigations were undertaken to understand the overall good practical experiences with these materials, and to anticipate the long term performance of this mortar system under the rough exposure conditions on the cathedral. Laboratory investigations included, petrophysical measurements and thin section analysis, of the individual materials but also on the system of DMtl-KMtl-stone. The investigations suggest that the mortars used are in many ways well adapted to the sandstones on the monument and that the diverse application methods only provoke small differences in the resulting mortars at an early stage. But only in situ observations will be able to show whether these small differences will lead to problems after long exposure to the elements.

1 Introduction

The repair mortars used for stone repair on the Bernese cathedral on two different Molasse sandstones are hydraulic mortars without any organic additions which are prepared on the building site. They are applied as two layers, a more coarse grained ground layer (KMtl) and a fine grained surface layer (DMtl), the latter imitating the stone material the mortar is used on.

These mortars have been refined from recipes of mortars that have been applied since already several decades on diverse Swiss monuments. The investigations reported here were undertaken to understand the overall good practical experiences with these mortars, and to anticipate their long term performance on the rough exposure conditions occurring on the cathedral's tower.

2 Why repair the sandstones of the cathedral with mortars

The approach to conservation and repair at the Bernese cathedral until 1998 was mainly based on stone exchange. Accordingly until then the cathedral workshop did not have much experience in stone consolidation, use of repair mortars for stone or any other remedial conservation treatment. Such works were not executed or only for very special cases sourced out to specialised enterprises. By 1998 it became clear that this kind of approach had to be changed drastically, not only it was very destructive towards the heritage materials but also it neglected to a certain extent the general maintenance of the building, was rather costly and not sustainable.

In 1998, on the common initiative of the Berner Münsterstiftung and the new architect in charge Hermann Häberli, the general approach to the maintenance of the building was changed. Nevertheless from the beginning it was clear that the cathedral workshop remained the back bone of a functioning maintenance and regular control of the building. But this workshop, not having the necessary experience in conservation works, external instructors were sought after and, for what concerns the stone conservation, found in the conservators Andreas Walser and Katrin Durheim, who kindly agreed to transfer their very long experience to the collaborators of the workshop by means of practical instructions on site. They also revealed their recipes of repair mortars they had applied since several decades on Zug sandstones on diverse Swiss monuments.

Before applying these mortars on the cathedral of Berne some of these buildings were visited to inspect the long term performance of the proposed mortars. The result of these inspections was generally satisfying and no records of failures of these mortars have been heard of so far. Nevertheless, in close cooperation with Andreas Walser and Katrin Durheim, it was decided to adapt the recipes a little, to somewhat reduce the strength of the KMtl for the use on the much weaker Bernese compared to the Zug sandstone and to adapt the appearance of the DMtl types to the sandstones at the cathedral of Berne.

3 Mortar materials and sample preparation

The apparent advantage of industrial ready-made products over on site mixed mortars seems to be their constant recipe and by that their constant quality. But usually these recipes are not revealed in detail and they are frequently improved, which means that the properties of these mortars change with time. The disadvantages of the use of mortars that are mixed on site from binders, sands and water, is that they need to be very carefully mixed, to make sure that their properties do not change from one portion to the next. But on the other hand it can be suspected that the same or very similar raw materials will still be available in decades, and hence it will also in the future be possible to produce the same

mortars. These reflections led to the decision to renounce the use of ready-made mortars on the Bernese cathedral, especially so as constancy in workmanship is guaranteed by the cathedral workshop. Nevertheless it was decided that the mortars should be tested for constancy in their petrophysical properties as well as for their theoretical suitability to be used on the Bernese and Zug sandstones of the cathedral.

All samples were prepared by the collaborators of the cathedral workshop. The mortars were applied as used on site, i.e. in layers of between about 1 and 4 cm for the KMtl (ground layer) and 0.5 to 1cm for the DMtl (finishing layer) on weathered sandstone blocks that had usually been consolidated at least four weeks beforehand with silicic acid ethyl esters. To estimate the influence of the application method, the mortars where applied on horizontal as well as vertical surfaces and some of the samples were taken from repair mortars that had been applied on site in the course of the regular restoration works. Further, to test the influence of the time interval between the application of KMtl and DMtl, series of samples with intervals of 0, 3 or 28 days were produced.

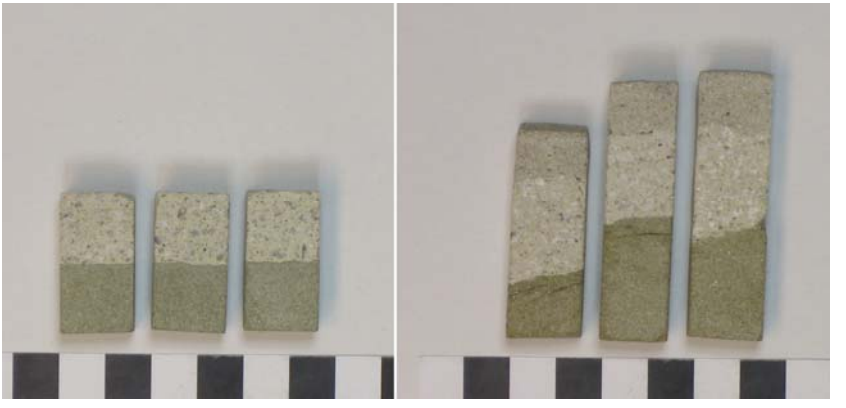

Fig. 1 Left series of two layered samples (so called bicouche = BiC) of KMtl on sandstone and right series of three layered samples (tricouche = TriC) with sandstone, KMtl and DMtl, enumeration of layers from bottom to top.

From these multilayered materials, consisting in DMtl, KMtl and sandstone, sample prisms were cut, consisting in three, two or one material layers (Fig 1). The chosen sample preparation has the advantage to well reflect the application on site and to allow extracting very similar samples on the monument but it produces samples with varying thicknesses of its layers (Fig. 1) and therefore the laboratory results are not always easy to interpret [1]. When tested in the laboratory the mortar samples were usually between one and a few month old.

The general composition of the mortar materials is given in Table 1. The binders are various mixtures of cement, hydraulic lime and air lime. The additions are a mixture of Trass powder (a German pozzolan) and diatomaceous earth. The sands are mixtures of mainly crushed limestone and quartz sand in the case of the

KMtl and diverse coloured sands in the case of the DMtl, with green sand dominating the ones for the Bernese sandstone (DMtl-BE) and rather grey sands in the case of Zug sandstone (DMtl-Zug).

Table 1 Repair mortar compositions in volume parts. KMtl = mortar for ground layer; DMtl-BE surface layer for Bernese sandstone; DMtl-Zug = surface layer for Zug sandstone. Binders: PC = Portland cement, CEM II 42.5; WC = white cement CEM I 52.5; HL = hydraulic lime NHL 5

Mortar	Sand	Additions	Binder total	Binder proportions		
				PC	WC	HL
KMtl	12	0	5	2	1	2
DMtl-Zug	16	2	5	3	1	1
DMtl-BE	5	2	2	1	0.5	0.5

4 Laboratory analysis

Mortar repairs will to a large extend be executed at the tower of the Bernese cathedral, where these materials will be exposed to quite rough weathering conditions. It nevertheless can be expected, that the weathering processes will mainly attack from the outer surfaces towards the core of the mortars and the stones. Water infiltrations from behind can largely be excluded, due to regular checks and permanent, rigorous maintenance of the building. Therefore the tests selected to examine the appropriateness of the repair mortars are such that they characterise mainly the water uptake and drying of the materials through the outer surface.

Total porosity [6] and hygric dilatation after 72 hours of water immersion [2] were tested on single materials, i.e. sandstones, KMtl and DMtl. Capillary water uptake [7] and drying rate [7] were measured on single materials as well as BiC of DMtl-sandstone, KMtl-sandstone and DMtl-KMtl and TriC DMtl-KMtl-sandstone. For the multilayer samples water uptake was measured with the water suction trough the outermost layer contained in the sample, e.g. DMtl or KMtl, and accordingly drying was tested by wrapping up the samples and leaving only the outer most surface open for evaporation.

Finally thin sections were prepared to observe the transitions between DMtl and sandstone, KMtl and sandstone and DMtl and KMtl by means of polarizing light microscopy.

No mechanical properties were tested in a first step because, wherever the repair needs to be rather big, the mortars are applied with reinforcements and plugs out of non corrosive materials as recommended elsewhere [3]. Moreover as the same repair mortars have been used for many years on diverse monuments and never have shown mechanical problems of any sort, this was considered here not to be the main issue.

5 Results

The measured laboratory values are given in tables 2 and 3 as mean values, with the standard deviation and number of measured samples in brackets.

Table 2 Values for total (Pt) and capillary (Kpt) porosity, specific (A) and linear (B) capillary water uptake, given as: value (standard deviation; number of samples). Sst-BE = Bernese sandstone; Sst-Zug = Zug sandstone; +/-w = more or less weathered and consolidated; KMtl = mortar for ground layer; DMtl-BE surface layer for Bernese sandstone; DMtl-Zug = surface layer for Zug sandstone.

Material	Pt (vol-%)	Kpt(vol-%)	A ($mg/cm^2.min^{1/2}$)	B ($cm/min^{1/2}$)
Sst-BE +/-w	17.7 (0.6; 16)	12.6 (1.2; 11)	36 (12; 12)	0.32 (0.13; 12)
Sst-Zug +/-w	11.3 (2.2; 9)	7.4 (1.2; 9)	26 (16; 9)	0.36 (0.17; 9)
KMtl	20.1 (2.5; 7)	17.2 (0.2; 4)	31 (9; 9)	0.18 (0.05; 9)
DMtl-BE	36.4 (0.3; 3)	21.3 (0.1; 3)	96 (22; 10)	0.45 (0.06; 10)
DMtl-Zug	31.7 (0.2; 3)	16.5 (0.5; 3)	48 (8; 7)	0.28 (0.07; 7)

The hygric dilatation (Table 3) of all tested materials is rather similar with the exception of the sandstone of Berne.

The total porosity of the KMtl lies between the values of the sandstones and the two kinds of DMtl (Table 2). Its capillary porosity (water uptake at the end of the capillary suction) is rather high compared with its total porosity. For all other tested materials a much bigger difference between capillary and total porosity was observed.

Table 3 Hygric dilatation (ε72h) and drying at 75% relative humidity and 20°C expressed as weight loss in % of capillary water uptake after 200 and 400 hours respectively. Values given as: value (standard deviation; number of samples). Sst-BE = Bernese sandstone; Sst-Zug = Zug sandstone; +/-w = more or less weathered and consolidated; KMtl = mortar for ground layer; DMtl-BE surface layer for Bernese sandstone; DMtl-Zug = surface layer for Zug sandstone.

Material	ε72h (mm/m)	Drying 200±10 h	Drying 400 ±15 h
Sst-BE +/-w	3.17 (0.40; 8)	82 (8; 11)	86 (5; 10)
Sst-Zug +/-w	1.40 (0.20; 6)	77 (4; 9)	82 (3; 9)
KMtl	1.00 (0.14; 6)	43 (3; 5)	50 (3; 5)
DMtl-BE	1.59 (0.08; 3)	83 (0; 3)	89 (0; 3)
DMtl-Zug	1.40 (0.03; 3)	79 (1; 3)	84 (1; 3)

The speed of capillary suction is with the exception of the surface layer for repair of Bernese sandstone (DMtl-BE) rather similar for sandstones, mortars for ground layers (KMtl) and surface layers (DMtl). When the capillarity is measured on the TriC-Samples (three layered samples) it can be seen, that the water uptake slows down at the material boundaries but it does not stop (Fig. 2).

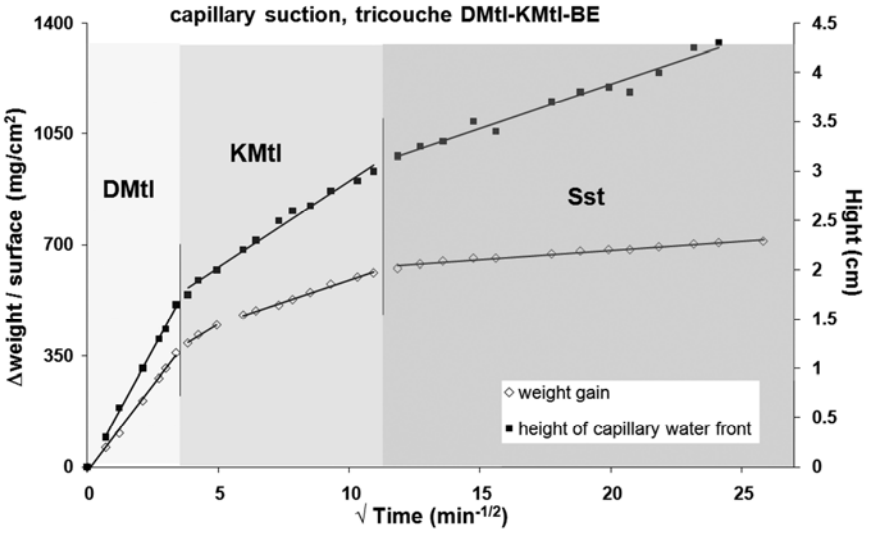

Fig. 2 Typical example of capillary suction curve, through a sample with three layers (surface layer = DMtl; ground layer = KMtl; Bernese sandstone = Sst), with linear regressions on individual parts of the curve.

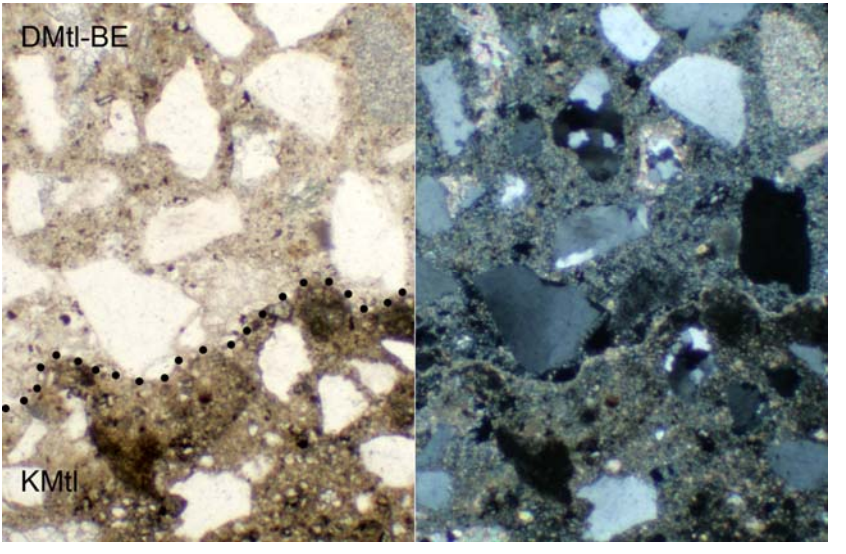

Fig. 3 Transition between DMtl-BE and the 3 days old KMtl in thin section. The boundary between the two mortars is indicated by a dotted line in the left picture. Left polarized light, right crossed polarisers, image height 1.3 mm.

In the thin section of the DMtl applied on a 3 day old KMtl a very thin but nevertheless clearly distinguishable sinter layer could be observed at the transition between KMtl and DMtl (Fig. 3). Apart from this the analytical results obtained for mortars applied horizontally or vertically, on specimen in the cathedral workshop or at the building as well as with intervals of 0, 3 or 28 days between KMtl and DMtl application were very similar.

6 Interpretation

Capillary suction experiments seem to show that no water accumulation must be expected within the boundary layers of the individual materials, but that the water transfer from one material to the other is rather good. This seems especially important if, for one reason or the other, water could penetrate from behind in spite of the measures taken to prevent this.

The big water uptake of the KMtl in comparison to its total porosity and in combination to its very slow drying, led to the conclusion that this material might be susceptible to considerable frost damage. On the other hand this material never forms the outer most layer of the building surface, because it is always covered with the DMtl. Therefore one of the practical results was that DMtl layers should always have a certain minimal thickness. Further, on the building the mortars will hardly ever and only at very rare places be exposed to as much water and over such a long period of time as in the capillary suction test. And last but not least during the regular controls no frost problems have been observed until now on any mortars applied on the cathedral itself.

7 Conclusions

The investigations suggest that the mortars used are in many ways well adapted to the sandstones on hand and that the diverse application methods only provoke small differences in the mortars at an early stage.

Regarding the KMtl it was decided to try to find a replacement material that should have a smaller capillary water uptake and a faster drying behaviour but as good working properties as the original KMtl. The work for this is still in progress, however first results using a different grain size distribution according to the suggestions by Konow [4] and rather hydraulic lime than cement, seem promising.

At the Bernese cathedral a big emphasis is put on the consistent documentation of the works and regular in situ observations of the treated surfaces are an important part of the maintenance plan that is actually in force. Only in that way we and the people in charge after us will be able to learn from experience.

8 Acknowledgments

We thank Andreas Walser and Katrin Durheim, for sharing their big knowledge and experience with us. Further we thank Fred Burri and Peter Völkle of the cathedral workshop for many discussions and careful preparation of the laboratory samples. Last but not least we would like to thank the Berner Münsterstiftung for financial support and constant encouragement.

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IV.09

Lime-Metakaolin Mortars Applied on the Soledade Palace, Recife, Brazil

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Abstract The purpose of this work was to evaluate lime mortars with pozzolanic additions of metakaolin applied as plasters on the original masonry of Soledade Palace, Recife, Brazil. The study involved the following variables: 1. Application over internal/external substrates; 2. Substrates with/without a lime-sand coat to increase the brick-mortar bond; 3. Three proportions of mortars; 4. Use of dry slaked lime or matured lime putty. The mortars were evaluated in regards to their mechanical strength and brick-mortar bond. Results indicated that these mortars are appropriate to be used in building restoration work, since they were prepared observing standards and good practices of execution and were applied in accordance with adequate techniques of restoration. Thus, these mortars will be able to assure the integrity and durability of ancient masonry.

1 Introduction

This paper presents the results of studies conducted by the Department of Civil Engineering, Federal University of Pernambuco, with the Institute of National Historical and Artistic Heritage, aiming to evaluate lime-metakaolin mortars for restoration works. Studies included plaster applied using the standard procedures of the civil works on the secular brick masonry of Soledade Palace, Recife, Pernambuco, Brazil. Built in the seventeenth century and modified over the centuries, it was adapted to become IPHAN's regional headquarters and offered by this Institution for study purposes during the restoration works and retrofitting.

2 Methodology

The performance evaluation of lime mortars involved the following steps:

- Planning - definition of traits and forms of application, calculation of the amount of materials to be used;
- Production, implementation and evaluation - substrate preparation, preparation of mortars, guidance applications, preparation of specimens and follow up for 90 days, flexural bond strength test; implementation and evaluation of mechanical strength tests and bond strength of the mortars.

2.1 Materials

The lime used here is classified as CH-I, and must have a maximum of 5% CO_2, 10% unhydrated oxides [1], and a minimum content of 88% total non-volatile oxides (CaO + MgO) [6]. This is a magnesian lime derived from the dolomitic limestone of the State of Paraiba.

Table 1 XRF of slaked lime.

Oxide	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2
%	16.1	0.98	2.07	0.0534	0.0459	0.0362	0.17	79.7	0.105
Oxide	MnO	Fe_2O_3	SrO	ZrO_2	TOTAL				
%	0.0314	0.667	0.0438	0.0168	100.0195				

Source: NegLabise - DEGEO/UFPE.

The metakaolin utilized is extracted and processed in the State; its color is white to favor the coloring of the plasters, which, after drying showed shades of gray according to the proportion of lime used. Table 3 presents data obtained from the manufacturer's technical information on pink metakaolin.

Table 2 XRF of Metakaolin.

Oxide	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2
%	0.20	41.70	51.10	0.17	0.08	--	1.54	0.13	0.61
Oxide	MnO	Fe_2O_3	SrO	ZrO_2	Rb_2O	Y_2O_3	Ga_2O_3	PbO	TOTAL
%	0.04	4.28	0.03	0.04	0.02	0.03	0.02	0.03	100.02

Source: NegLabise - DEGEO/UFPE.

Table 3 Physicochemical properties of metakaolin

Property	Values	Property	Values
Retention: ASTM# 200 sieve	1%	Loss on ignition (L.O.I)	< 2%
Blaine Fineness	1.500 m^2/kg	$SiO_2+Al_2O_3$ (average value)	91%
Specific Mass	2.560 Kg/m^3	$Fe_2O_3+TiO_2$ (average value)	4.7%
Apparent Mass	480 Kg/m^3	Pozzolanic Activity Index (Modified Chapelle-IPT)	900 mg $Ca(OH)_2/g$
Colour	Pink		

Source: Manufacturer

The washed sand was the same as that used for the coatings of the works, sieved in a 4.8 mm mesh. This was a quartz sand, maroon in colour, with mica, lacking apparent organic contamination, with a maximum diameter of 1.2 mm with 45% of particles being between 0.6- 0.3 mm.

2.2 Substrates

The tested walls were those in the lower floor of the monument, which were subject to fewer interventions and different sunlight conditions, ventilation and wetting. Six test panels were placed on three walls of the main facade (SW) and six on different internal walls, sheltered from sunlight and ventilation.

The masonry has irregular surfaces and joints (a consequence of the irregular thickness of the plastering) with thickness' ranging from 2 ± 0.5 cm to 50 ± 5cm, respectively, with a composition that uses irregular solid bricks: 20 ± 1 cm long, 10 ± 1 cm wide, and 5 ± 1 cm thick; colours vary from light yellow to dark red, spotted; some of the masonry displays breakdowns, especially where walls are damp as a result of infiltration.

2.3 Experimental Procedure

The research involved the following variables: 1. Mortars of three different mix proportions, 2. Utilization of dry slaked lime or matured lime putty; 3. Application of plasters on internal or external substrates, and 4. Application on clean substrate or on a substrate prepared with lime-sand roughcast. Three types of mix proportions (in weight) were determined: type I–1:1:4, type II-1:1.04:11.07 and type III-1:1.64:16.60 defined by previous experimental results. Water was added by a mason in the amount needed for the consistency of the plasters. The hydrated lime was mixed with water to a paste with a smooth consistency for a seven-day maturation. For the application, $1m^2$ panels were placed on the walls after removal

of the non-original plasters; they were then washed for wetting and the removal of dust. Each panel received the three mix proportions of mortar in horizontal stripes, in ascending order of the binder content. Mortar preparation adhered to the following procedure: sand, metakaolin, matured or unmatured hydrated lime were weighed; the dry materials were manually mixed on an impervious surface; water was gradually added or previously weighed matured lime putty used, and manual homogenization performed until the point of consistency indicated by the mason was reached. The mortars were applied at the same thickness of the existing plasters (2 to 4.5 cm) using the usual procedures for civil works, that is, in two layers using the masons trowel; they were then capped with aluminum slats and finished with a wooden concrete finishing trowel and a sponge.

In the experiments, the local climate was a tropical summer: intense sunlight, warm, occasional and intense short-duration showers with an average temperature of 30°C, and an average relative air humidity of 70%. Mortars were evaluated in three ways:

- *During application* using qualitative observations: homogenization, appropriate consistency for the application, instant adhesion to substrates, ease of finishing, and initial shrinkage.
- *At the DECIV/UFPE laboratory*, using tests, to determine the mass loss rate up to 90 days and mechanical strength at the age of 180 days.
- *At the monument, after 90 days*, using assays to test mortar binding with analog equipment threaded to aluminum plates bonded with epoxy adhesive to the surface of the coatings, which were previously cut with a diamond hole saw coupled to an impact drill.

3 Outcome of Analysis

3.1 During the implementation

During mortar batching, the mixture of sand and metakaolin using dry slaked lime was easier to work than the mix using matured lime, as it formed lumps of lime that were hard to mix. Matured lime mortars presented more cohesion and plasticity favourable to their application; however, mix proportions with a higher binder content of both types of lime adhered to the tools, hampering application and finishing. The rapid loss of consistency due to metakaolin reactivity forced the reduction of mortar setting times before their application and drying for levelling purposes. The evaluation of the coating shrinkage was empirical; the cracking of the coating was observed on the 90th day in terms of both number and opening of the cracks. In the beginning, all panels apparently had

an excellent interface with the existing mortar, and no significant cracking on the coating edges was found. However, all panels cracked at the interface of the different settings. Right after the application, all coatings presented capillary cracking.

3.2 At the DECIV/UFPE laboratory

The rate of mass loss indicates the water retention capacity of the mortars; the graphs in Figs. 1 and 2 relate to the rate of mass loss (dm/dt) with time (days). The rate of mass loss is achieved during a time t in days, using the coefficient:

$$dm/dt = (m_0 - m_d)/m_0$$

Where m_0 is the initial mass on the day of the removal of the specimen from the mold, and m_d the mass on any day (d). In mortars I, II and III produced with *dry slaked lime*, the rate of mass loss I is similar at the first ages, but differ from the 14th to the 28th day, during which a lower water retention is seen in mortar III, which contains less binder; in mortars I and II, the rate is similar over this period, showing the impact of lime in mortar that retains water. From the 28th day, mortars I and III present rates of mass loss similar to and higher than mortar II, which indicates an optimal content of hydrated lime for the latter binder:aggregate ratio.

Mortars with *matured hydrated lime*, behave similar those made from dry slaked lime: up to the 14th day, the rate of mass loss is similar for all three proportions, from the 14th to the 28th day, mortar I has a lower rate of mass loss, which is exceeded by the rates of mortars II and III due to a higher content of matured lime, which contributes to water retention. From the 28th day, the three mortars show no significant difference in the rate of mass loss, which indicates that the maturation of lime contributes to water retention at older ages, despite the difference in binder amount. Comparing the range of the rate of mass loss between the matured and unmatured groups of lime, both are in the range of 0.0 and 0.18. The mortars with greater water retention favour hydraulic hardening reactions with metakaolin [8].

Test results of flexural and compressive strengths are listed in Table 4. It was found that the lime maturation variable was not determinant of the outcomes, though better results were expected for the mix proportions using hydrated and matured lime since magnesium limes may contain remaining magnesium oxides, the hydration of which is more complex than calcium oxides [6, 8]. The variables that determined higher mechanical strengths were the higher binder amount and the lower water amount, as demonstrated by water/dry materials, water/binder and binder/aggregate ratios (Table 4); a significant variability in results is more perceptible in type I mortars: mortar 1nM I presented higher mechanical strengths (lower water/dry materials and water/binder ratios and higher binder/aggregate ratio) with the values obtained for compressive and flexural strengths being similar to the literature values for lime and metakaolin mortars with similar proportions and water/binder ratios [4].

3.3 In the building after 90 days

Shrinkage: The internal coatings of types I and II presented a larger number and a wider opening of cracks, when compared to those on the external coatings. These mortars also presented generalized cracking and mean openings of 6mm in the typical form of clay mineral shrinkage ("alligator leather"). Coatings of type III presented capillary cracking (<2mm) on the external panels, and a smaller number, a smaller opening and a different format (slanted) of cracks when compared to types I and II on the internal panels.

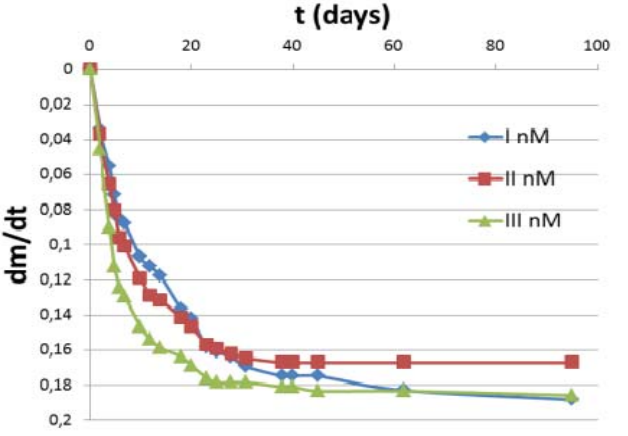

Fig. 1 Mass loss. Dry slaked lime mortars.

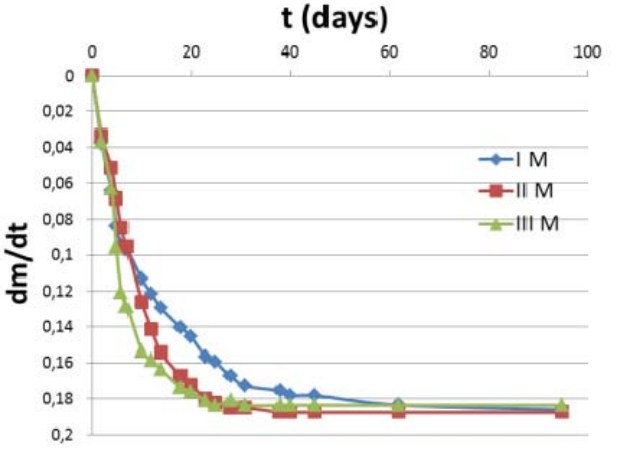

Fig. 2 Mass loss. Matured lime putty.

Table 4 Characteristics of Mortars and Mechanical Strength at 180 days

Mortar	Proportion	w/d.m.	w/b	b/ag.	f_c (MPa)	f_t (MPa)
1nM III	1 : 1,64 : 16,6	0,21	1,60	0,15	0,82	0,13
1nM II	1 : 1,04 : 11,07	0,20	1,06	0,23	0,75	0,36
1nM I	1 : 1 : 4	0,25	0,66	0,60	6,42	2,49
2M III	1 : 1,64 : 16,6	0,21	1,55	0,17	0,39	0,16
2M II	1 : 1,04 : 11,07	0,21	1,10	0,25	1,82	0,53
2M I	1 : 1 : 4	0,31	0,92	0,53	4,75	0,75
2nM III	1 : 1,64 : 16,6	0,23	1,70	0,16	0,48	0,26
2nM II	1 : 1,04 : 11,07	0,21	1,08	0,24	1,71	0,78
2nM I	1 : 1 : 4	0,28	0,85	0,50	4,75	0,75

Application stage (1-first, 2-second), type of lime (nM-dry slaked lime, M-matured lime putty) and mix proportion (I, II, III).

Table 5 Results of Flexural Bond Tests at 90 days.

Panel	f_t (MPa)	Pts.	Rupture	Panel	f_t (MPa)	Pts.	Rupture
1E-nMsC I	0.6497	13 / 0	11-A/ 2-S/A	1I-nMsC I	0.1680	3 / 0	1-A/ 2-S/A
II	0.4419	9 / 0	6-A / 3-S/A	II	0.1182	3 / 0	2-A/ 1-S/A
III	0.1850	8 / 1	7-A / 1-S/A	III	0.0935	2 / 0	2-A
2E-MC I	0.3221	3 / 0	3-A	2I-MC I	0.2390	2 / 2	2-A/ 1-S/A
II	0.0935	1 / 0	1-S/A	II	0.1668	2 / 1	1-A/ 1-S/A
III	0.0935	3 / 0	2-A / 1-S/A	III	0.0935	3 / 1	3-A
2E-MsC I	0.5349	2 / 0	2-A	2I-MsC I	0.2567	3 / 0	3-A
II	0.1669	4 / 0	3-A / 1-S/A	II	0.1400	1 / 2	1-A
III	0.1426	1 / 3	1-A	III	0.0935	1 / 2	1-A
2E-nMC I	0.6186	3 / 0	2-A / 1-S/A	2I-nMC I	0.4369	1 / 2	1-A
II	0.3151	2 / 0	1-A / 1-S/A	II	0.1584	3 / 0	1-A/ 2-S/A
III	0.2078	3 / 0	3-A	III	0.0935	1 / 2	1-A

The identification of the panels refers to the stage of application (1-first, 2-second), the location of the substrates (E-external, I-internal), lime (nM-unmatured, M-matured); substrate treatment (sC-no roughcast, C-roughcast) and mix proportion (I, II, III). The indicated tension represents the mean fracture tension. Column Pts. indicates the number of valid/lost points and column Break indicates where the flexural cut occurred: A-plaster; S/A-substrate-plastering interface; S-substrate [2].

3.4 The flexural bond tests outcomes (Table 5)

In these tests, mortars I and II (matured or unmatured) showed a high surface resistance which caused difficulties to the tubular cutting, but lower strength and internal cohesion; mortar III was the least resistant and friable both on the surface and internally. In other words, in mortars I and II, the high binder amount and the low incorporation of air in the manual mixing did not favour the carbonation of the matrix. Being hardly porous, it did not allow an appropriate degree of CO_2 diffusion inside. Surface resistance comes from the carbonation of the surface and from the binder film. External plasters showed higher bond strengths and this, along with their lower shrinkage, shows that the curing of the external panels was more efficient. As to the types of ruptures, 60 of the 77 tested points underwent cohesive mortar rupture, while the remaining points displayed adhesive ruptures at the substrate/mortar interface. As the outcomes of flexural bond strength tests show that the mortars are cohesive, it can be said that the mortar break indicates that substrate/mortar interface bond is higher than the mortar strength, which means that the adherence of these mortars to the old masonry was efficient. However, it is not possible to state that the roughcast variable had an impact on these results as there was cohesive rupture in most of the points of the roughcast panels, so it is believed that the location of the panels was a direct determinant of the brick-mortar bond regarding the roughcast variable.

4 Conclusions

From the outcome of the analysis of the three stages, it appears that as to the implementation, it is necessary to realize the peculiarities of lime-metakaolin mortars and the difference between working with them and with portland cement mortars, especially when conducting restoration works. The usual procedures for civil works should be reviewed and adapted to features such as lower plasticity [3], rapid hardening, different application and performance requirements such as adherence, waterproofing without sealing, and durability. These mortars require careful homogenization for the proper incorporation of air that, in addition to improving the involvement of the aggregate grains by the cement [3], will also provide plasticity at a lower w/b ratio. The control of the materials (type and quality of lime, grain size and sand quality), as well as the amount of water, are essential to promote the development of pozzolanic and carbonation reactions to form a cohesive and wholesome cement matrix.

As to shrinkage, the maturation variable was not decisive for cracking, presenting no significant differences as to the results. The panel location was crucial, as the external panels presented less cracking than the internal ones, that is, the setting of the latter was more efficient; this can be explained because, in general, the mortars were prepared based on a high water/binder ratios, and on the

panels exposed to the afternoon sunlight there was evaporative water loss, which did not occur inside the building. The binder content was fundamental, as mortars of types I and II cracked more frequently and presented wider cracks than type III. Other significant factors for the cracking of the panels were the width of the coating layers (~4.5cm) that should have been applied in thin layers to allow the mismatching of the cracks [3] and the use of fine and poorly graded sand, which neither promoted an efficient internal carbonation, nor the expulsion of the water unnecessary for the hardening reactions [7].The mass variation results corroborate the comments on the empirical shrinkage, as the mortar presenting the greatest mass variation also cracked more, in terms of quantity and width (I-nM).

As to bonding**,** the numerical values of the proportion I bond strength were compared with values reported in the literature, shown in the table 6 below. The results were compared to the results of mortars of the same proportion, of dry slaked lime, with similar water/binder ratios and different compositions: two mix proportions [3] consisting of lime:natural pozzolan:sand and lime:kaolin at 800°C:sand, and a mix proportion [5] consisting of lime:ground ceramic:sand. As benchmarks, the adherences obtained from the portland cement mortar used in the plasters of the work (IPHAN); another portland cement mortar [9] and, finally, old mortars [5], consisting of lime:natural clay:sand ("bastard" mortars with proportions of 1:0,3:0,1 to 1:3,4:1) were considered. The substrates were called 'M' (modern, ceramic bricks), and 'A' (ancient, solid bricks, stone-filled joints in [5]). Portland cement mix proportions used roughcast. Adherences of mortar I had results superior to the adherence values of experimental mortars found in the literature [3, 5] and above the values of compared portland cement mortars [9]; this shows good adherence to the substrate and shows the strength of the studied cement. Compared to the adherence data of the old mortars [5], the values are also superior to the values of the latter, noting that the old mortars came from the ruins of façades [5].

Table 6 Comparison - Actual flexure bond versus the literature

Data	Proportion	Comp.	w/b	Substrata	f_t (MPa)	Rupture	Age (d)
Obt	1:1:4	sl:mk:s	0.66-0.92	A (E)	0.32 - 0.65	m – s/m	90
Obt	1:1:4	sl:mk:s	0.66-0.92	A (I)	0.17 - 0.44	m – s/m	90
[3]	1:1:4	sl:k:s	--	M (I)	0.05 - 0.15	s	60
[3]	1:1:4	sl:np:s	--	M (I)	0.06 - 0.13	s/m	60
[5]	1:1:4	sl:cc:s	1.32	A (E)	0.03 - 0.05	m	34
Obt	1:1:8 iphan	pc:sl:s	--	A (E/I)	0.19 - 0.39	s/m – s	>28
[9]	1:6	pc:s	1.22	M (E)	0.23 - 0.56	m – s/m	>28
[5]	diversos	lp:cl:s	--	A (E)	0.03 - 0.31	m – s/m	∞

So, in order to be used in restoration works, it is necessary to examine the original mortars and assess the use of mix proportion I for plastering, to avoid

problems of differential stiffness between the mortars and the old substrate. Regarding mix proportions II and III, these had lower values than I, and higher values than those in the literature [3, 5] and the old mortars [5], approaching values of Portland cement mortars, while mix proportion III proved less cohesive. Therefore, mortar II suggests greater potential to be used in restoration, as long as preparation is sufficient.

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IV.10

Compatibility of Repair Mortars with 19th Century Natural Cement Cast Stone from the French Rhône-Alpes Region

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Abstract In the French Alps, near Grenoble, in the middle of the 19th century, natural cements were massively used to produce "cast stone" (concrete block), to simulate natural yellowish to reddish cut stone. In a first project, several ancient concrete buildings were studied and a major decay mechanism was identified: erosion, leading to the loss of the original fake stone appearance. Today, due to a lack of appropriate repair materials, grey Portland-cement-based mortars, combined with paintings are used, leading to a complete loss of the original aspect. Therefore, the aim of this second study was to develop and to test compatible repair materials to conserve the cultural heritage of this region. Based on the results of the first project, specifications concerning the composition and main properties of compatible repair materials were established. Then 4 mortars were selected, 2 of them being specifically formulated. In a second step the intrinsic properties of those mortars were characterised and finally, their mortar/concrete compatibility was assessed.

1 Introduction

The oldest concretes encountered in France date back to the middle of the 19th century and were made with natural cements. These cements were produced in the Rhône-Alpes region and notably used to cast concrete blocks or quite complex

ornaments, which were intended to imitate the colour and the texture of natural stone. One of these is an ochre colour, varying from light brown to red.

In a previous project [1, 2], a preliminary survey revealed that this cultural heritage was, on the whole, quite well-preserved. However, an erosion phenomenon was affecting the majority of the surfaces leading to a gradual disappearance of the concrete skin, which is detrimental to the initial "natural stone aspect." The current rehabilitation techniques consist of the use of gray Portland cement-based mortars combined with a yellow or brownish paint finish. In fact, as the colour and composition of these concretes are very specific, there is a lack of suitable repairing mortars. Therefore, based on the analysis of the composition and properties of several historic concretes in this region, the aim of this study was to formulate and test natural cement-based repair mortars to restore eroded surfaces and to compare their performances to that of the Portland cement-based mortar currently used.

2 Protocol

The protocol of the study was divided into three steps. The first step consisted of the selection of four repairing mortars, two of which were specifically formulated from the specifications established in the first project, based on the analysis of historic concrete.

In a second step, the mortars were characterised in terms of transfer, physical and mechanical properties, microstructure, and performance. The intrinsic properties of the four selected mortars were characterized in terms of shrinkage, water porosity, water vapour permeability, capillary suction, dynamic modulus of elasticity, bending, and compressive strength measurements. The microstructure was characterised by optical microscopy (on polished section) and scanning electron microscopy. The performance evaluation was conducted with visual analysis observations.

The third step of the project was dedicated to the evaluation of the compatibility of the selected mortars with historic concrete and to the assessment of the durability of the repair mortar/concrete system. Therefore, natural cement-based slabs were cast using a 19th century concrete formula and were artificially eroded. After applying the four mortars to the slabs, visual observations and pull-out tests were carried out before (A) and after three sorts of artificial aging (B, C, and D): 10 heating and stormy shower cycles (B), 10 freeze-thaw cycles (C), 10 heating and stormy shower cycles followed by 10 freeze-thaw cycles (D).

3 Requirements and mortars selection

The requirements for mortar selection took into account the main characteristics of the historic concrete, the repair type (fine mortar for erosion) and the monument type [3]. The concrete monuments to be repaired are among the first buildings made of concrete in France, with a specific architecture and in cultural heritage context. As a consequence, criteria such as the preservation of the historic support and the need to use repair material with a colour and a texture close to those of the historic concrete had to be considered.

As quite high alkali contents were measured in the historic concretes to be restored, the use of alkali reactive (even potentially reactive) aggregates had to be avoided. The aggregate size also had to be adapted to the quite small thickness of eroded concrete to be repaired. As a consequence of the high sulphate contents observed in binder of the historic concrete to be restored, the cement to be used had to show a good sulphate resistance in order to be compatible. To assess the durability of the restoration and to avoid further decay of the historic concrete, the properties of the repair mortars had to be adapted to those of the historic support, in terms of transfer properties (water vapour permeability higher than that of the support) or mechanical performances (modulus of elasticity comparable to that of the support). However, the mortars also had to present a good durability and be able to resist the main stresses that repair mortars usually face (low shrinkage, high tensile strength) [4-7]. Finally, to fit with the aesthetic requirements, cements had to be used that exhibited an ochre colour, either combined with mineral pigments or not.

Based on these requirements, two mortars were specifically formulated and two others were selected among repair mortars available on the market (Table 1). It is to be noted that in the Alps region of France, there is a natural cement (so-called Prompt cement) that is still produced using the 19th century industrial process and whose composition is very close to that of the cements encountered in preliminary characterization of the historic concrete. Therefore, this Prompt cement was used in the composition of the two specific formulations and in one of the ready-to-use mortars. Furthermore, this cement has a good sulphate resistance. The fourth mortar selected was a Portland cement-based product containing fibres, which is currently used for rehabilitation operations.

Table 1 Repairing mortars selected

Mortar	Cement type	Mortar type	Comments
1	Prompt cement	Ready-to-use	Available on the market
2	Prompt cement	Ready-to-use	Specially formulated
3	Prompt cement	“On site” mortar	Specially formulated, for skilled operator
4	Portland cement	Ready-to-use	Available on the market

4 Mortars characterisation

4.1 Transfer, mechanical and physical properties

The evaluation of the intrinsic properties of the four selected mortars was presented in a previous paper [8]. The main conclusions are the following:

- concerning the transfer properties, the results of porosity measurements were quite scattered, mortar 4 being less porous (less than 15%) and mortar 1 being excessively porous (more than 40%). Water vapour permeability was quite high for mortar 2 and, on the contrary, very low for mortar 4. Finally, the water capillary sorption tests showed that mortar 2 presented a capillary coefficient that was too high.
- regarding shrinkage after 1 year, mortar 1 exhibited the highest values (0.2%). The best results were obtained with mortars 2 and 3, in which shrinkage was quite low and stable with time. Surprisingly, mortar 4, which contains fibres meant to limit the shrinkage phenomenon, showed values higher than mortars 2 and 3.
- the results of bending and compressive strength indicated very low performances of mortar 2 (even though they were increasing with time). On the contrary, the Portland cement-based mortar (mortar 4) presented much higher bending and compressive strength than the three Prompt cement-based mortars. Finally, the dynamic moduli of elasticity were lower than 27 GPa in all mortars, which is the lowest value measured on the historic concretes. No incompatibility was therefore evidenced.

4.2 Microstructure

Optical microscopy observations performed on polished section after borax attack revealed differences in non-hydrated phases. In mortar 4, which is Portland cement-based, clinker grains presented well-crystallised alite and belite, with no clear separation between C4AF and C3A. In mortars 1, 2, and 3, anhydrous residual grains were poorly crystallised, with small alite and belite crystals and well-separated C4AF and C3A phases.

The hydrated phases observed by scanning electron microscopy also varied depending on the binder:

- mainly calcium silicates hydrates (CSH) and ettringite with fresh portlandite for Prompt cement-based mortar
- and mainly CSH, portlandite, and fresh ettringite for Portland cement-based mortar (mortar 4).

These observations indicated that the microstructure of the Prompt-cement based mortars was quite close to that of the historic concretes; on the other hand, mortar 4 had a clearly different microstructure. Sulphate resistance was undetermined.

4.3 Aestheticism

The colours of the four mortars can be seen in Fig. 1a. Mortars 1 and 3 have an adapted colour but mortar 1 presents pigments traces (Fig. 1b). Mortar 2 is too white, but it is easy to tint. Mortar 4, whose colour is too grey and difficult to tint, is clearly not suitable.

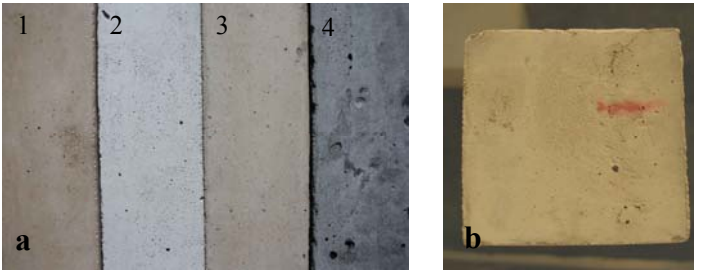

Fig. 1 a) Colours of the mortars and b) Pigment trace on mortar1.

4.4 Slabs manufacture

Twenty slabs (50 cm x 50 cm x 8 cm) were cast for the purpose of mortar/concrete compatibility characterisation. The slabs' manufacture has been presented in a previous paper [8]. A formula extracted from documents dating back to the end of 19th century was used, using Prompt-cement as a binder. To reproduce a surface similar to the most commonly encountered erosion facies, deactivation products were pulverised on the 20 slabs surfaces just after their casting. After manufacture, the slabs were kept in a room at 20°C and 95% RH and dried in the open air for 28 days.

4.5 Mortars application

The four selected mortars were applied to the slabs (four slabs per mortar). In terms of workability, mortar 1 was very fluid, mortars 2 and 3 were easy to apply, and mortar 4 was sticking to the tools and therefore was quite hard to apply (Fig. 2).

Fig. 2 Application of mortars 1 (a) and 4 (b).

After its application, mortar 1 showed immediate shrinkage cracks (Fig. 3a). After setting, white efflorescence appeared on mortar 4 (Fig. 3b).

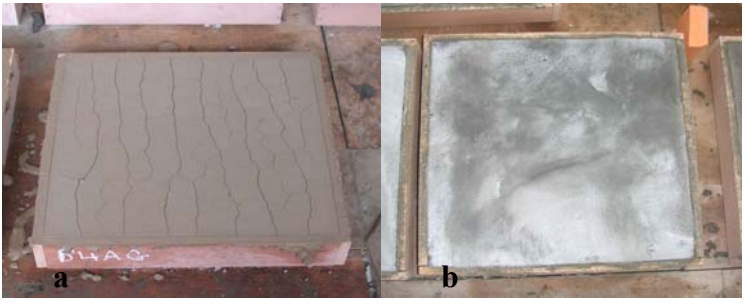

Fig. 3 Shrinkage cracks on mortar 1 (a) and white efflorescence on mortar 4 (b).

After the application of mortars and before the artificial ageing, the slabs were kept for 28 days in a room at 20°C and 65% RH.

4.6 Artificial aging

The artificial aging cycles are presented in Fig. 4.

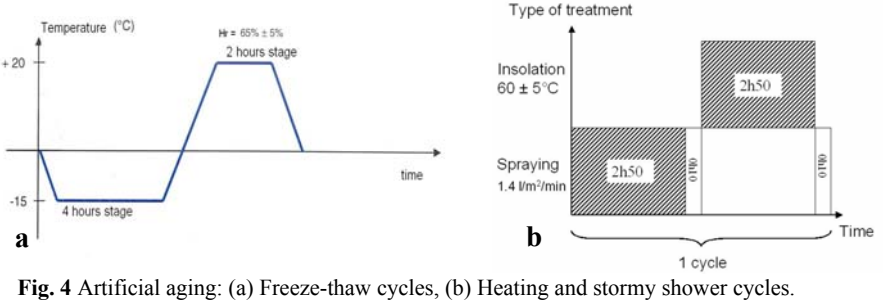

Fig. 4 Artificial aging: (a) Freeze-thaw cycles, (b) Heating and stormy shower cycles.

After artificial aging, visual analysis was conducted, and then the slabs were kept for 7 days in a room at 20°C and 65% RH before the pullout tests. For each type of artificial aging one slab per mortar was tested, and five pullout tests were performed per slab. The pullout tests were performed according to the French standard NF EN 1015-12, which consists of sampling a core through the entire thickness of the mortar and up to 3 mm in the concrete support with a core drill (5 cm inside diameter). Then, circular metal pellets (5 cm diameter) are glued to the mortar surface, and the pullout tests are performed using a 500 daN capacity dynamometer. The load is applied monotonically, increasing to the breaking point. For each test, the breaking load and the breaking site are noted. Finally, the adhesion strength is calculated as ratio between the breaking average load and the pellet surface (the result is expressed in MPa).

In Fig. 5 the adhesion strengths obtained for each mortar before and after the different artificial aging are presented. The breaking sites for each mortar before and after the different artificial aging are given in Table 2.

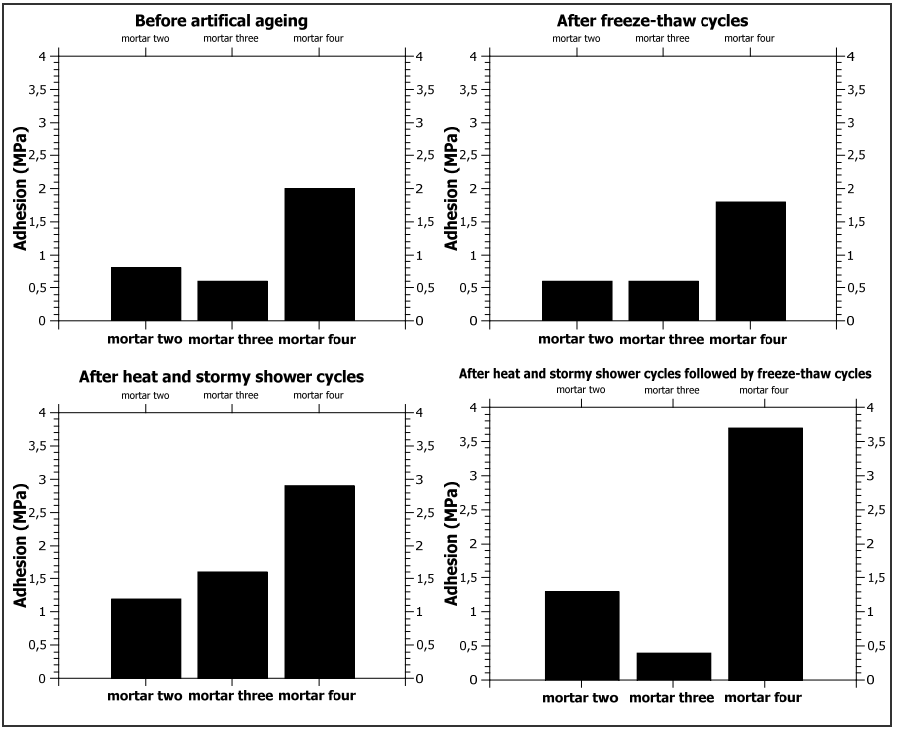

Fig. 5 Adhesion values before and after artificial aging.

Table 2 Breaking sites for each mortar before and after the different artificial aging.

Mortar	A	B	C	D
2	Interface breaking	Interface breaking	Mortar breaking	Mortar breaking
3	Interface breaking	Interface breaking	Support breaking 60% mortar breaking 40%	Mortar breaking
4	Support breaking	Support breaking	Support breaking 60 % mortar breaking 40%	Support breaking 60 % mortar breaking 40%

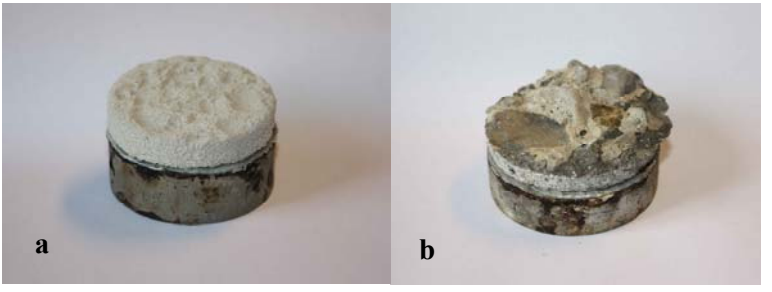

Fig. 6 Interface breaking site (a) and support breaking site (b).

With a simple cure without artificial ageing (A), the adhesion strength was similar for mortars 2 (0.8 MPa) and 3 (0.6 MPa), while the adhesion strength for mortar 4 was much higher (2 MPa). After the freeze-thaw cycles (B), no important adhesion evolution was noticed. After the heating and stormy shower cycles (C), the adhesion values of mortars 2, 3, and 4 increased (respectively 1.2, 1.6 and 2.9 MPa). After the D cycles, the adhesion strengths for mortar 2 (from 1.2 to 1.3 MPa) were similar to the results obtained from the C cycles, although they decreased for mortar 3 (from 1.6 to 0.4 MPa) and increased for mortar 4 (from 2.9 to 3.7 MPa).

Fig. 6 illustrates interface and support breaking sites. With a simple cure (A) and after the freeze-thaw cycles (B), mortars 2 and 3 presented an interface breaking location, whereas mortar 4 presented a support breaking location. After the C cycles, only mortar 2 presented a mortar breaking location, and mortars 3 and 4 presented a break both in the support and in the mortar. After the D cycles, mortars 2 and 3 presented a mortar breaking location, whereas mortar 4 presented a support/mortar breaking location.

To summarise, mortar 4 was too adhesive (with breaking in the support), mortars 2 and 3 showed suitable adhesion properties (adhesion strength higher than the 0.4 MPa threshold of the initial specifications); mortar 1, which shrank immediately after its application to the slabs, could not be tested.

After the freeze-thaw cycles (B), no apparent damage was noted for mortars 2, 3, and 4. After the heating and stormy shower cycles (C), cracking was observed for mortars 3 (Fig. 7) and 4, and no damage was noticed for mortar 2. After the

heating and stormy shower cycles, followed by the freeze-thaw cycles (D), cracking was observed for mortars 3 and 4 and no damage was noticed for mortar 2. Therefore, no additional damage was noted after the (D) cycles.

Mortar 2 showed a good durability whatever the artificial aging, while mortars 3 and 4 suffered degradations after the heating and stormy shower cycles (C), which may be linked to a deformability deficiency.

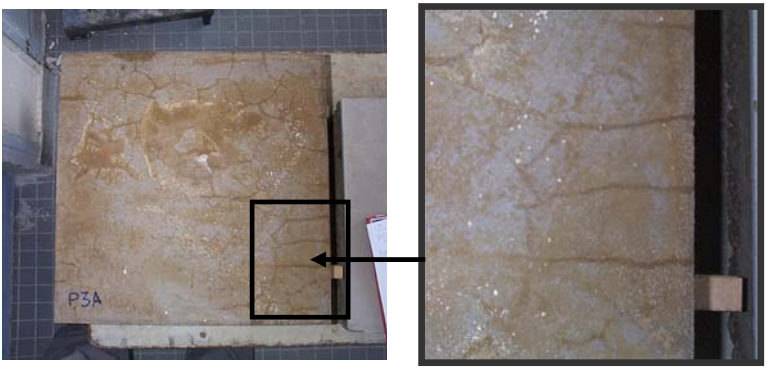

Fig. 7 Cracking observed on mortar 3 after heating and stormy cycles.

5 Conclusions

The aim of this study was to develop and test repair mortar for historic concrete of the 19th century encountered in the French Alps area, which is affected by serious erosion. After a first study focused on these historic concretes analysis [1, 2], a list of specifications was established. Based on these specifications, four mortars were selected, their intrinsic properties were characterised, and the compatibility of the system mortars/concrete was tested.

Firstly, the intrinsic properties tests revealed that some mortars were unable to match the specifications. Actually, shrinkage was clearly too high in mortar 1. Mortar 4, which is Portland cement-based, was clearly too impermeable to water vapor. Its mechanical performances also were much higher than the three Prompt cement-based mortars. Only mortars 2 and 3 (specially formulated) presented transfer and mechanical adaptations. In terms of microstructure, the use of Prompt-cement in the mortars leads to a microstructure close to those of the historic concrete. Only mortar 3 (on site mortar) presented an adapted color.

Secondly, the tests performed on slabs presented some incompatibilities. Mortars 1 and 4 were difficult to apply on the slabs simulating the historic concrete. The adhesion strength for mortar 4 was too high, with breaking sites in the support, which is incompatible with the problem of the support conservation.

For mortars 2 and 3, the adhesion strengths were sufficient, with breaking sites principally at the mortar/concrete interface or in the mortar.

Finally, in terms of resistance to the artificial aging, only mortar 2 (ready-to-use and specially formulated) showed no degradation for all the cycles types, while the heating and stormy cycles caused cracking in mortars 3 and 4.

To conclude, mortars 1 and 4 are incompatible for the repair of the eroded historic concrete of the 19th century of the French Alps area. Mortar 2 corresponds to all the specifications except the colour, but it can be easily tinted. Mortar 3, the "on site" mortar, presents only a deficiency of durability for the heating and stormy cycles. The final step of this study will consist of testing the two best mortars (mortars 2 and 3) on-site in cooperation with skilled operators and with a follow-up in time.

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IV.11

Properties of Lime-Based Restoration Mortars Modified by the Addition of Linseed Oil

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Abstract Linseed oil was one of the most common natural organic additives used in ancient times. Nevertheless the mechanism and the technology, e.g. effects of different dosages, are not clearly explained yet. In the present study, the effect of linseed oil on the properties of six various lime-based mortars has been investigated. Mortar mixtures were prepared in three different versions: unmodified and with 1% and 3% addition of linseed oil by the weight of binder. The effect of linseed oil addition on mortars mechanical (compressive and flexural strength, dynamic modulus of elasticity) and physical properties (open porosity, water absorption through capillarity) have been measured. Mortars´ structure has been studied by means of mercury intrusion porosimetry and scanning electron microscopy. Finally, durability against salt crystallization (NaCl and Na_2SO_4) and freeze-thaw cycles was tested.

1 Introduction

The traditional lime mortar is composed of hydrated lime, sand and water. Besides these constituents it may also contain additives aiming to improve the workability of fresh mortar and/or to improve the strength and durability of hardened mortar.

The idea of improving a mortars properties using various additives is not new, but something which was already known by the first civilizations [1- 2]. Lime-based mortars used in ancient times were sometimes of a poor quality; therefore masons often employed various additives to reach the desired properties. There are records that egg whites, bullock´s blood, fruit juices, keratin and casein were used in Ancient Egypt [3, 4]. Bitumen as the oldest known natural organic additive was used in Mesopotamia some 4000 years ago [1, 5-7]. Romans were known to use pozzolanic materials, which gave hydraulic properties to mortar, but these were

not always available and were costly [8]. Consequently locally available materials increased in use. A variety of substances of different origin were used, such as local agro-products (cereals, juices from trees, fruits and vegetables), oils and fats, milk, eggs, and also blood, dung, urine and other materials such as animal hair [1-6, 8-10]. Besides the additives from the group of proteins, linseed oil seems to be one of the most commonly used organic additives in the past. It was used already in Roman period [1, 2] to reduce the water permeability of a mortar, but was especially used in paving mortars to increase their durability. Unfortunately there is not much information in literature about the ancient technology of mortar preparation. This being their livelihood, masons were scared to write about the things they knew and often such knowledge and experience was buried with them [6].

Recently there's been an increased interest in the use of oil as an additive to mortars. Lime mortars alone sometimes do not meet the requirements of certain types of restoration interventions due to their poor durability whereas a more durable cement mortar is not suitable for the restoration of historical monuments due to its hardness and because of the risk of introducing dangerous salts into historical structures. Therefore the use of additives seems to be a successful way of improving the properties of lime-based mortars. Since the trends in the restoration of historic monuments are to prefer the use of natural materials, linseed oil can be a valid alternative to the synthetic additives. Oil addition may particularly improve a mortar's resistance to salt crystallization and freeze/thaw damage, as it is expected to increase a material's hydrophobicity and thus limit water or salt solution intrusion into the material.

Literature only briefly mentions that oil used to be commonly added into mortars in the past [3-6, 9-11], with little reference to the technology and its actual effect. Nowadays there are only a few works that study the effect of oil addition through experimentation. The effect of oil on some mortar properties (strength, porosity, capillarity) has been tested, but the effect of oil on a mortar´s microstructure and the exact mechanism of is operation is not clearly known. Chandra et al. [5] and Justnes et al. [12, 13] studied the effect of linseed oil on some of the properties of a Portland cement mortar, which has different characteristics than a lime-based mortar. The effect of linseed and whale oil on hydrated lime mortar was tested by Rovnaníková [4] and Santiago et al. [14] respectively. All authors observed decreased capillary absorption of mortars with oil addition when compared to unmodified mortars. The effect of oil addition on the strength of a mortar was ambiguous. Most importantly, the supposed increased resistance of lime-based mortars against deterioration has not yet been verified experimentally.

2 Materials and methods

2.1 Sample preparation

Mortar composition has been selected with respect to the composition of historic mortar [15] (hydrated lime mortar and pozzolanic mortars), and mortars used in modern restoration practise (hydraulic lime mortar, mortars with addition of cement). Table 1 lists the compositions of the mixtures:

Table 1 Composition of tested mortars

Mortar code	L	H	P	B	C1	C2
Lime dry	1	-	1	1	1	1
Hydraulic lime	-	1	-	-	-	-
Pozzolan	-	-	1	0.5	0.9	0.8
Brick dust	-	-	-	0.5	-	-
Cement	-	-	-	-	0.1	0.2
Sand	3	3	6	6	6	6

Oil concentration was 0%, 1% and 3% by the weight of binder. Oil was added into mixed dried components prior to the addition of water. Water was added as the amount needed to maintain a workability of flow value of 14-15.5 cm, the water/binder ratio was then 0.62-0.84.

Specimens (prisms 4x4x16 cm) were stored for 7 days at 95±5% relative humidity (RH), then for 11 weeks at 65±5% RH. Samples of unmodified mortars and mortars with a 1% oil addition were further stored for one year at ambient conditions in an air-conditioned room (20-25°C, 40-80% RH). Specimens were tested after 1, 3 and eventually 12 months of curing (not those with 3% oil addition).

The following materials have been used for the preparation of mortar:

- Lime – dry powder hydrated lime, EN ISO 9002 TUV CERT, content of Ca(OH)2 75% , CaO Hellas.
- Pozzolan – natural pozzolan with very fine particles (<55μm), Dalkafoukis.
- Hydraulic lime – Albaria Calce Albazzana, natural hydraulic lime, BASF.
- Cement – white Portland cement, CEM II/A – LL 42.5N, TITAN.
- Brick dust – Kourasanit.
- Sand – Axios river natural sand, Tratselas S.A.
- Linseed oil – crude natural linseed oil, Mercola.
- Potable (drinking) water.

2.2 Testing methods

This paper will present the results of the following tests:

- *Setting time* - initial and final setting time of all the binding systems (binders were tested in the same proportions as they are in the mortar mixtures) has been determined according to EN 196-3 on the Vicat apparatus.
- *Compressive and flexural strength* was measured according to EN 1015-1:1999. 4-7 and 6-9 specimens were used for testing of compressive and flexural strength respectively.
- *Open porosity through water absorption and pores´ accessibility to water* – procedure described in Čechová [16]. Pores´ accessibility to water was determined as a proportion of water absorption after 48 hours under normal pressure to that measured after another 24 hours under lowered pressure. Two quarter prism specimens of each mortar type were used for testing.
- *Pores size distribution* – measured by means of Mercury Intrusion Porosimetry at CNR-ICVBC, Florence [17].
- *Capillarity* was measured according to EN 1015-18:2002. Two half prism specimens of each mortar type were used for testing.
- *Resistance to salt crystallization* – Two quarter prism specimens of each mortar type were fully immersed into 10 wt% NaCl solution for 6 hours, then dried for 18 hours at 85°C and weighed. 25 cycles were performed.
- *Resistance to freeze-thaw cycles* – Two half prism specimens of each mortar type were immersed into water for 24 hours and weighed. Saturated specimens were then put into a freezer at -20°C for 6 hours. Specimens were allowed to defrost when immersed in water at room temperature before being weighed after 18 hours. 25 freeze-thaw cycles were performed.

3 Results and discussion

3.1 Setting time of binder systems

While the initial setting time of hydraulic binders has not been significantly affected by either a 1% or 3% addition of linseed oil, the final setting time of binders with an oil addition has been retarded. This fact indicates that oil does not play an important role during the initial phase of setting where there is enough water available for the hydration of hydraulic binder, but at later stages as water is consumed and the concentration of oil in the liquid phase increases, the oil might limit water transport and thus slow down the hydration reactions. From this point of view the setting of hydrated lime has not been significantly affected.

3.2 Mechanical properties

The effect of oil addition to a mortars' strength was ambiguous. Addition of 1% of linseed oil generally improved the strength of most of the tested mortars, but the strength of mortars with a 3% addition of oil was dramatically reduced when compared to unmodified mortars.

Addition of 1% linseed oil did not affect the strength at 3 months, but after 1 year of curing pozzolanic mortars (four mortar types with various content of pozzolan, codes P, B and C2) showed a 20%-50% increase in compressive strength (see fig. 1). The strength of unmodified mortars stayed the same or slightly decreased, with the exception of the hydraulic mortar which increased its strength threefold!; nevertheless, the compressive strength of pure hydrated lime mortar (code L) was decreased by 50% with the addition of oil. A 1% oil addition did not affect the hydrated lime mortar´s flexural strength, in fact such an addition seems to slow down the evaporation of water and thus prolong the curing process of hydraulic mortars. For an unknown reason the flexural strength of unmodified pozzolanic mortars decreased (about 60% in average) after 1 year (maybe due to drops in relative humidity and the consequent formation of micro-cracks?), whereas the flexural strength of mortars with a 1% addition of oil, stored under the same conditions, remained the same after the age of 3 months.

When the oil was added in a 3% concentration, both the flexural and compressive strengths (fig. 1) of all mortar types were significantly reduced (65% in average). The reason for this might be that oil is impregnating the surface of the aggregates and thus limiting the contact between the grains of aggregate and the binder phase; alternatively it may be related to the proportion of large pores, as detected by Mercury Intrusion Porosimetry (discussed in Čechová [16]). Phenolphthalein did not prove that an addition of oil would reduce the degree of carbonation – mortars with a 3% oil addition were actually better carbonated than both unmodified mortars and those with a 1% oil addition. This is probably due to the carbon dioxide having an easier access to the pore system once it has been dissolved in water vapour.

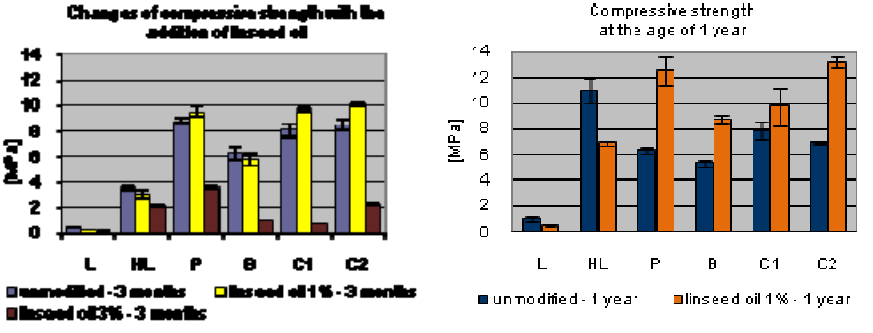

Fig. 1 Compressive strength at the age of 3 months (left) and 1 year (right)

3.3 Physical characteristics

Though there are some differences, open porosity measured through water absorption is not affected significantly by either a 1% or 3% addition of linseed oil.

As expected, oil addition decreases a mortars ability to absorb liquid water; this effect is the most apparent in the results of water absorption through capillarity (as seen in fig. 2). A 1% addition of oil decreases the coefficient of capillary absorption by 55% on average and a 3% addition of linseed oil decreases the value of the capillary coefficient by approximately 90%. Decreased capillarity is probably caused by the hydrophobic effect of linseed oil (mortars with an addition of oil showed an increased water contact angle) but may also be affected by the decrease in the amount of capillary pores (those bigger than 1μm [17, 18]) as detected by Mercury Intrusion Porosimetry.

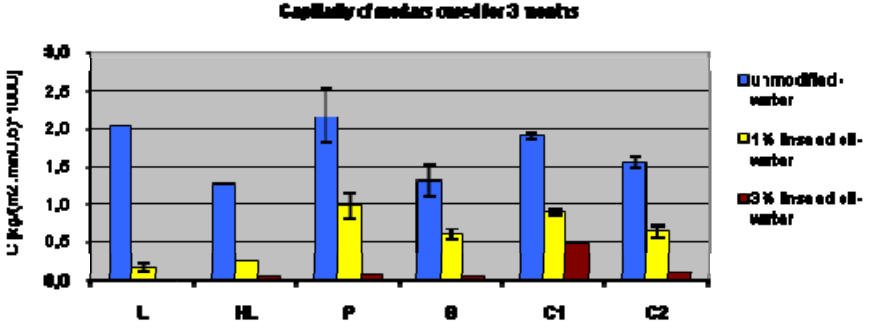

Fig. 2 Coefficient of water and salt solution absorption

Furthermore, the addition of oil into the mortar was found to decrease the amount of pores which are easily accessible to water. The addition of 1% of oil decreased the amount of easily accessible pores from 90% to 80% and the addition of 3% of oil to 30% on average.

Fig. 3 The photograph shows an example of a specimen with a 3% addition of oil (code BO3) in salt solution – the material is hydrophobic and weak, it loses its powdered surface layer

3.4 Resistance to deterioration

Oil addition significantly improves a mortars resistance to salt crystallization as well as to freeze-thaw cycles. In relation to the salt crystallization (see fig. 4), the difference in weight loss between specimens of unmodified mortars and mortars with a 1% oil addition (tested after 1 year of curing) at the moment of breakage (weight loss 100%) or at the end of the testing period was on average 52% (including 0% for hydraulic mortar H). For freeze-thaw resistance the average difference in weight loss was also 52%, though the process of deterioration was different.

Specimens with a 3% oil addition (tested at the age of 1 month) showed improved durability along with those with a 1% addition of oil, despite the fact that they have a very low strength and therefore a resistance which is only due to their total hydrophobicity, as seen in fig. 3. Specimens of unmodified mortars firstly increased their weight due to the accumulation of salts; this lasted until approximately the 20th cycle, after this they started to lose their weight rapidly (approx. 40% in 5 cycles) as the damage proceeded. Mortars with a 3% addition of oil lost weight gradually through the absorption of water or salt solution to a depth of about 2 mm, this therefore meant that they lost their surface layer.

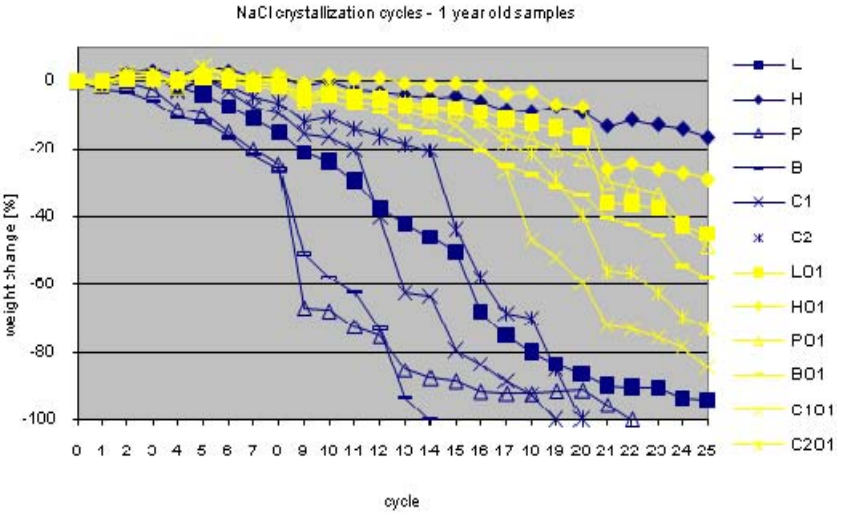

Fig. 1 Resistance to salt crystallization

4 Conclusions

The addition of 1% of linseed oil has proved to have a positive effect on the properties of mortar. It improves mechanical characteristics and limits water absorption into mortar without significantly affecting the total open porosity or decreasing the degree of carbonation. On the other hand, the 3% addition of linseed oil makes mortar almost hydrophobic, but it markedly decreases a mortars' strength. However, all types of lime-based mortars with the oil addition showed a notable decrease in water and salt solution absorption by capillary rise which significantly improved their resistance to salt crystallization and freeze-thaw cycles. On the basis of the obtained results, the addition of 1% of linseed oil can be taken into consideration when designing repair mortars.

5 Acknowledgements

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IV.12

Characterization of Repair Mortars for the Assessment of their Compatibility

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Abstract Compatibility requirements for repair mortars used in restoration works are defined based on the original mortar characteristics, but the quality and the performance of the repair mortars after application on masonry are generally not assessed. From this perspective, original mortars and their repair mortars from three historic masonry structures were characterized to assess their compatibility in terms of chemical, mineralogical, physical and mechanical point of view. A methodology relying on a fundamental approach for a mortar analysis is adopted taking into account the added values and the basic requirements from both practical and scientific point of view. This study is aiming to contribute to the existing knowledge on mortar characterization and to provide new insights on the assessment of the compatibility of the repair mortars.

1 Introduction

In restoration works, design and application of a repair mortar that will closely match with the existing historic materials and that can replace the original mortar requires an extensive and an elaborated work to be carried out within a complete framework: on-site investigation and collecting original/historical mortar samples; characterization of the original mortar within its historical context; a damage analysis to retrieve the basic causes for which a repair mortar is to be applied; defining an optimal intervention strategy; formulation of a repair mortar composition based on above conclusions; and application of the repair mortar by suitable workmanship and technology. This concept brings together a series of interrelated performance requirements to be addressed in terms of authenticity, reversibility, compatibility, retreatability, function and technology [1-3].

One of the fundamental aspects on which the design of a repair mortar should rely is the compatibility of the new mortar with the existing historic materials,

meaning that new mortar to be used does not have negative consequences on the historic materials, and should respect heritage values and authenticity. This will direct the intervention decisions towards the concept of suitable preservation, and will define the boundaries of functional and technical requirements of the repair mortar, which will limit the impact of intervention. Within this strategy different compatibility requirements can be addressed such as aesthetical compatibility, chemical compatibility, mineralogical compatibility, physical compatibility and mechanical compatibility. These requirements will influence each other to certain extents depending on the function of the mortar and on the restoration concept.

After formulating a compatible repair mortar, the information is handed over towards the restoration engineer/architect who outlines the repair mortar recipe within the technical specifications to be used by the contractor. However, a quantitative verification of the actual composition used within the restoration work is seldom performed. The overall judgement of the mortar quality applied on masonry only relies on visual inspection. In this article, compatibility of the repair mortars proposed by laboratory/academic research with those applied subsequently on masonry is assessed. This study is the part of an extensive research on the compatibility of repair mortars used in restoration works, which was studied in a master thesis [4] and will be extended with further research.

2 Case studies

Three case studies in Belgium have been studied taking into account a detailed investigation of the original mortars performed initially by the Reyntjens Laboratory, K.U.Leuven (B). Interviews with all parties involved (contractor, architect, engineer) were performed to get full information on their experience and their opinion on the compatibility performance of the repair mortars used.

Church of Our Lady in Tongeren (B) The monument listed since 1936 is located at the centre of the town as an important landmark for the vicinity. The subsoil below and around the basilica contains traces of 20 centuries of Roman civilization (starting from the 1st century BC) and religious history of the Middle Ages. In the nave of the church an archaeological cellar was constructed in which archaeological excavations up to a depth of 3 m below the present floor level were performed. The archaeological findings were consolidated to enable the exhibition of the site to the public. Repair mortars were formulated taking into account the compositions of the original mortars and their visual aspects to achieve a good aesthetical match with the existing authentic materials. In our research [4], various original and repair mortar samples were collected. In this article, only two mortar types are presented: original brick-laying mortar (T3) dating back from the 1st century after Christ, and its repair brick-laying mortar (T4).

Abbey of Herkenrode in Kuringen (B) Dating back from 1182, the abbey suffered from war and plundering in the period of 1300-1500. It is listed as an

historical building since 1974. Starting from 2003-2004, all buildings on the site underwent a stability and a historical value assessment. The old farmhouses and porter's lodge belonging to the abbey have been restored and are refunctioned as a domain for cultural and recreation activities. In this article, results of the original mortar (H0) and its repair mortar from stables (H2) are discussed.

Table 1 Type and composition of the repair mortars that were prescribed and used in restoration.

Mortar ID	Mortar type	Mortar composition	
T4	Bedding	Prescribed:	Used:
		1 volume part of lime putty	1 volume part of lime putty
		2 volume parts pozzolanic red brick powder and brick parts (< 6mm)	1 volume part Oolitic fine Bath limestone powder (<1mm)
		0.5 parts quartz sand (<0.5mm)	0.5 volume parts pozzolanic brick powder
			0.5 volume parts W50 sand
			0.25 volume parts chalk (<5mm)
			0.25 volume parts brick dust (1-5mm)
H2	Pointing	Prescribed:	Used:
		3 mass parts sand	6 mass (3 volume) parts of white sand
		1 mass part of binder, containing 1/3 mass parts of cement and 2/3 mass parts of lime	2 mass (0.5 volume) parts of yellow sand
			2 mass (0.75 volume) parts of lime
			1 mass (0.25 volume) parts of cement
L3 and L4	Bedding	Prescribed and used:	
		4 volume part white sand; 2 volume parts yellow sand Cantillana; 1 volume part white cement; 1 volume part shell sand; 8 volume parts rolled gravel (0/7)	

Castle ruins Pietersheim at Lanaken (B) This water castle dating back from the 12th century has undergone several subsequent building periods and drastic changes. The masonry of the entrance gate is composed of three-leaf masonry with a sandstone parament and rubble infill masonry. The 16th century defence walls (thickness: 2.0m), were made out of a thick core infill mortar and a thin outer parament of limestone (thickness: 15-30 cm). Overall the limestone parament has disappeared due to the reuse of stones, eroding, degradation by plant growth, freeze-thaw action, etc. The restoration concept was to keep the infill masonry visible and to prevent the underlying masonry from further degradation.

Two types of repair mortars (L3 and L4), which were prescribed in the same mortar composition but applied on masonry in different periods, are studied.

3 Methodology for repair mortar characterization

A systematic approach for the characterization of historic mortars with respect to their repair has been defined by RILEM TC 167 COM which offers a valuable tool to identify mortar components, nature of binder, aggregate, additives, and their relative proportions [2]. Following the same approach, we have adopted a limited set of analytical techniques to characterize the repair mortars. Dedicated site work and laboratory work were followed to achieve an effective characterization in terms of textural, physical, chemical, mineralogical and mechanical point of view. The site work includes sampling, on-site investigation and non-destructive testing of the mortars. The laboratory work covers various analytical and testing methods to characterize the mortar constituents and to define mortar properties in a comprehensive way.

Visual analysis: On-site visual investigation was performed by naked eye and by documentation with colour scale to define colour, texture and surface finishing properties of the mortars. A detailed investigation was further carried out at the laboratory using stereo microscope.
Chemical characterization: Chemical composition of the mortar samples was determined using wet chemical analysis [5] and using X-ray fluorescence (XRF) for the comparison. The latter provides only chemical composition of the mortar constituents. However, wet chemical analysis relies on acid dissolution/separation of the binder from the aggregate, and provides additional information on the chemical composition of the acid-soluble binder and the aggregate, and their relative proportions unless the aggregate is acid-soluble. After separation, particle size distribution of the aggregate fraction was determined. Interestingly, large differences were recorded between wet chemical analysis and XRF results [4].
Mineralogical characterization: Chemical characterization cannot solely yield all the information needed for a complete interpretation. Confirmation of the evidence of identification from chemical composition should be supported by combined methods including mineralogical analysis. To do so, mineral composition of the finest fraction (<80 μm) was identified using X-ray diffraction (XRD) analysis which allows the identification of crystalline phases in the binder. Since the amorphous phases coming from hydration and pozzolanic reactions are very difficult to detect or are even not detectable, XRD was complemented with thermogravimetric analysis (TGA) which can identify these reaction products as well as the degree of carbonation and hydration reactions.
Physical properties: In our study, attention goes to the porosity properties of the mortars such as total porosity, open porosity and apparent density.

Mechanical properties: This was assessed via pointing hardness by pendulum hammer performed as a non-destructive testing at site [6]. Due to the lack of mortar samples in desired quantity and dimensions, mechanical strength via direct testing methods could not be performed.

Table 2 Chemical composition (by wet chemical analysis), physical properties and binder/sand fractions of the original and repair mortars.

	T3 original	T4 repair	H0 original	H2 repair	L0 original	L3 repair	L4 repair
L.O.I. at 540°C (m.%)	3.53	3.58	3.48	4.07	/	2.10	2.87
L.O.I at 1050°C (m.%)	11.92	25.82	17.70	9.61	5.94	10.01	7.92
Insoluble part (m.%)	72.40	27.46	59.61	75.88	86.42	75.12	73.46
Soluble SiO_2 (m.%)	1.50	5.24	1.18	1.86	1.01	1.25	2.59
CaO (m.%)	10.65	38.57	19.41	10.77	5.78	12.03	13.67
MgO (m.%)	0.27	0.06	/	0.12	0.00	0.30	0.24
Fe_2O_3 (m.%)	0.06	0.24	/	0.15	/	0.15	0.12
Al_2O_3 (m.%)	0.60	0.62	/	0.40	/	0.32	0.50
SO_3 (m.%)	0.48	0.98	/	0.70	/	0.56	1.06
Sum (m.%)	97.05	98.99	97.90	99.49	99.15	99.18	98.50
CO_2 (m.%)	9.49	21.89	14.29	7.29	4.09	7.61	4.90
Hydraulicity index	0.20	0.15	/	0.21	/	0.13	0.23
Cementation index	0.44	0.40	/	0.53	/	0.32	0.56
App. density (kg/dm³)	1.428	1.503	1.608	1.861	2.077	1.899	1.953
Open porosity (v.%)	45	42	31	27	21	27	24
Binder/sand-ratio	0.38	2.64	0.43	0.32	0.15	0.23	0.28
Sand (m.%)	72.40	27.46	59.61	75.88	86.42	76.37	73.46
Lime (m.%)	15.20	*	25.6	7.13	11.00	17.28	8.02
Pozzolan (m.%)	2.66	*	/	/	2.00	/	/
Cement (m.%)	/	*	/	7.02	/	/	12.33

*: could not be quantified due to the limestone aggregate fraction

4 From characterization towards compatibility

Original brick-laying mortar T3 is a typical Roman mortar composed of brick dust, brick particles and white inclusions of lime giving crucial information on how the binder was prepared such as the way the lime was slaked. After analyses of this type of mortar by K.U.Leuven, a mortar recipe (T4) was prescribed with a composition of lime putty, brick particles/dust and quartz sand which are compatible with the original materials (Table 1). However, the executed mortar composition of T4 was altered in proportions and in components by the restoration

architect. The fractions of lime putty and sand were kept the same but that of brick particles/dust was replaced by chalk and by limestone powder to duplicate white lime inclusions present in the original mortar. These materials are not compatible with the original materials used and cannot be treated as the part of the binder. The mortar composition of T4 was optimized by the restoration architect for visual reasons to achieve an aesthetical match with the original mortar in terms of colour, texture and structure (Fig. 1). Therefore, a large difference is realized in the chemical compositions of T3 and T4 with the insoluble part referring to the aggregate fraction, the amount of soluble SiO_2 originating from hydration products and the amount of CO_2 related to the calcium carbonate phases (Table 2). The insoluble part in T4 is considerably low because of the presence of chalk and limestone powder being soluble in acid, making the retrieval of the relative proportions of binder and aggregate quite difficult. Higher content of soluble SiO_2 in T4 repair mortar indicates higher degree of hydration reactions due to the pozzolanic reaction between brick particles and lime. This large compositional difference between T3 and T4 is also observed in their mineral compositions (Table 3). TGA results support these findings with different $CaCO_3$ and CO_2 fractions, the latter being very similar to the values obtained from wet chemical analysis (Table 4). Additionally, the presence of $Ca(OH)_2$ in T4 repair mortar is recorded in the XRD and TGA results.

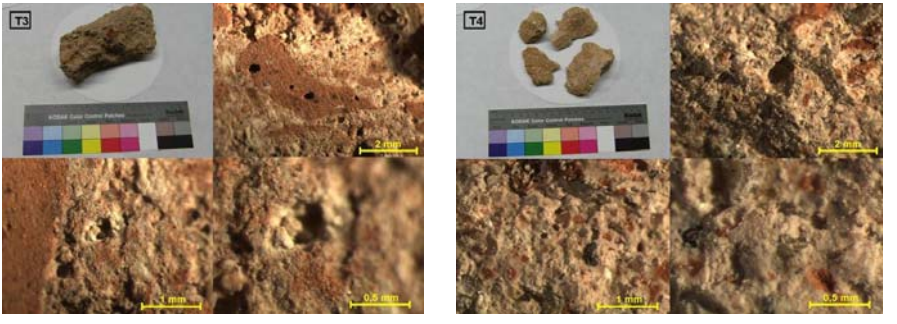

Fig. 1 Left: Original brick-laying mortar (T3). Right: Repair brick-laying mortar (T4).

No visual comparison could be made between the original mortars and the repair mortars from the other two case studies of Abbey of Herkenrode and Castle ruins Pietersheim due to the lack of access to the original mortars in masonry. Similar to the first case study, visual aspect was one of the major concerns for the restoration architect. Sand fraction in the prescribed mortar composition of H2 was replaced with white and yellow sand during restoration to duplicate the visual aspects of the original mortar (Table 1). Although the original mortar H0 is a pure lime mortar, the repair mortar contains a small fraction of cement together with lime to get a faster hardening and initial strength. This has resulted in differences in terms of chemical composition and porosity between H0 and H2 (Table 2),

altering compatibility and authenticity aspects defined initially. Traces of bassanite are found in H2 due to the use of cement (Table 3).

Regarding the third case study of Castle ruins Pietersheim, L3 is the repair mortar applied on masonry during the first phase of restoration of the defence wall. Second phase started after two years when L4 repair mortar was applied. According to the information taken from the restoration architect, in the first phase of restoration the recipe of the repair mortar was altered to get a better aesthetic match with the original mortar as well as a better workability on site. For that purpose, several test areas were mutually assessed both by the contractor and by the restoration architect. The optimal composition was then prescribed in the second phase. An important aspect in this case is the change in function of the repair mortar from bedding to infill mortar which has a protective function for the underlying masonry. Also in this case study, visual aspect was one of the major concerns for the restoration architect. White cement and white sand were used to duplicate the visual aspect of the original lime mortar while achieving faster hardening with cement, which is similar to the previous case study.

Table 3 Mineral composition of the binder fraction of the mortars.

	Calcite [$CaCO_3$]	Quartz [SiO_2]	Portlandite [$Ca(OH)_2$]	Bassanite [$CaSO_4.1/2\ H_2O$]
T3	++	+++	-	-
T4	+++	++	+	-
H2	+++	++	-	+
L3	+++	++	+	-
L4	++	+++	+	+

+++: dominantly present; ++: present; +: traces; -: not detected

Table 4 $Ca(OH)_2$, $CaCO_3$, CO_2 and hydration degree determined using TGA.

	$Ca(OH)_2$ (%)	$CaCO_3$ (%)	CO_2 (%)	Hydration degree (%)
T3	0.00	21.65	9.52	4.39
T4	2.07	60.99	26.83	5.58
H2	0.00	30.27	13.32	19.45
L3	0.00	57.71	25.39	9.29
L4	5.60	35.86	15.78	9.04

Mechanical properties of the mortars were estimated via pointing hardness that measures the quality of the pointing work done [6]. The results are given in Table 5. Repair mortars L3 and L4 indicate relatively similar values. A large difference is recorded between T3 and T4 mortars. Relatively low rebound value of T3, despite its currently sound state, is related to the lack of uniform surface on which the test was performed. It is worth to note that the use of pointing hardness test is limited for the application to lime mortars which can give low rebound values.

This does not mean that the mortar is in a bad condition. The measurements are in fact affected by a number of variables, such as surface roughness, subsurface anomalies (voids, near-surface cracks, or incipient spalls), specimen geometry, vicinity of nearby edges and hammer orientation. Despite this, pointing hardness is a useful means to assess the mortar quality in cases where mortar samples cannot be collected for direct mechanical testing.

Table 5 Pointing hardness of the mortars by pendulum hammer.

Mortar ID	Pointing hardness	Class	Range	Indicated quality
T3	16.00	A	15-25	Soft
T4	51.33	D	45-55	Hard
H2	37.75	C	35-44	Normal
L3	26.20	B	25-34	Moderate
L4	27.50	B	25-34	Moderate

5 Conclusions and final remarks

- Some clear differences are evidenced between laboratory/academic research and restoration practice. Aesthetical/chemical/mineralogical compatibility is the main aspect for the laboratory/academic research while formulating a repair mortar composition. On the other hand, restoration architects seem to be interested mainly in the aesthetical aspects of the repair mortar. This raises the question to what extent compatibility in one aspect is to be merged or sacrificed with/by other compatibility/authenticity requirements.
- Compatibility and authenticity aspects defined for the repair mortar are often compromised by the restoration architect with the concern of achieving faster hardening by introducing cement into the binder composition.
- Assessment of a compatibility of repair mortar via analytical methods is a useful tool but is not always possible in practice. Application of a compatible repair mortar can be ensured by a continuous communication and collaboration among laboratory/academia, restoration architect and contractor.
- Skilled workmanship as a technical input is not considered in restoration works but is essential in the formulation and application of repair mortars [7].

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IV.13

Flexural Strength of Fiber Reinforced Lime Mortars for Historic Masonry Structures

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Abstract The first author of the project is the engineering director of a Temple reconstruction project in Turkey. In attempt to produce mortar similar in composition to that found at the temple site and employ the use of fibers for mortars increased durability and resistance against in-plane loading, the team prepared an extensive experimental program. This program was carried out for the United States National Park Service (NPS), National Center of Preservation Technology and Training (NCPTT). The materials used in this experimental program are two types of masonry units (fired-clay bricks and concrete masonry units), three types of binder matrices (Portland cement-lime, type N; natural hydrated lime 3.5W, and natural hydrated lime 4W), and 8 types of fibers (5 synthetic versions, goat hair, horse hair, and specially treated corn silk fibers). With the variations in matrix preparations and the fiber volume fractions, 80 mixtures are tested for workability, water permeability, compressive strength of mortar and prisms, flexural strength of mortar, bond strength, and shear strength. In this paper only the flexural strength of mortar for 12 of these mixtures are discussed. These selected mortars were chosen because of their composition similarities to the authentic mortar from the temple. This paper assesses the effect of fibers in lime based mortar and provides suggestions on how to determine which mortar most feasible for certain scenarios.

1 Introduction

The first author is currently the engineering director of the reconstruction and rehabilitation of an imperial Roman temple, located on the site of the ancient city of Antiocheia ad Kragum in southern Turkey. The temple has fully collapsed leaving the marble blocks it was once composed of piled on top of each other on

its original platform. Hidden among the piles of blocks are pieces of mortar that are presumed to have been used only in the foundation walls. In the summer of 2008 the team was able to have two companies perform a material analysis on the composition of the mortar from the temple. They found that the composition of the mortar from the temple was 1 part lime to 2.5 parts sand. The results from these analyses can be found in Erdogmus &Armwood HMC 2008[5].

In a preliminary study by the author and her graduate student, micro and macro PVA fibers in Type N mortar were tested at various ratios [6]. The tested Micro fibers were less than 12.7mm [0.5 in.] in length, while the macro fibers length ranged from 12.7 to 63.5 mm [0.5 to 2.5 inches]. The most important finding from this project was that fibers considerably increased the flexural strength, post-crack ductility, toughness, and energy absorption of the material in comparison to plain mortar. It was also observed that the inclusion of micro fibers in mortars did not significantly affect the mortars compressive strength, which is important for producing mortars stronger than the authentic units. It was also concluded that macro fibers are not feasible in mortars specified for reconstruction or rehabilitation purposes. This is because of the protruding nature of the fibers once they are set between units. In addition, a large percentage of the fibers in the mortar were hard to disperse and thus decreased the flow of the mortar. The results of this study are similar to the findings in Mehta (2006) where it was found that fiber reinforced concrete could sustain loads larger than the ultimate flexural strength of plain concrete. The results of this preliminary study were very useful in identifying the potential application of FRMs' in masonry rehabilitation. Though, the need for further study was still apparent, thus leading to the current project.

The mortar analysis and preliminary study of PVA fibers became the groundwork for the author's next project: An extensive experimental program to study the sustainable, synthetic, and organic fibers in mortar binders that most resemble historical mortar. The United States National Park Service (NPS), National Center of Preservation Technology and Training (NCPTT) provided grant money for the author to explore a wider spectrum of FRM mixtures for the rehabilitation and reconstruction of masonry structures. The following materials were studied in various combinations and proportions to give an experimental matrix consisting of 80 mixtures.

Brick Types:

- Standard Clay Bricks
- Standard Concrete Bricks

Binder Types:

- Type N Portland Lime and Sand PL-01
- Natural Hydrated Lime (NHL) 3.5W (ratios: 1:2.5 & 1:3)
- Natural Hydrated Lime (NHL) 5W (ratios: 1:2.5 & 1:3)

(Sand used with the NHL is approved according to ASTM C144-03)[1]

Fiber Types:

(Note-All fibers tested at .25% and .50% by volume of mortar)

- *NyconG- Nano (recycled carpet fibers)
- Poly vinyl Alcohol Fibers (PVA)
    - RECS7- 6mm
    - RECS15- 8mm
    - RSC15- 8mm
- Control 2000- 6mm(100% Multifilament Nylon)
- *†Goat Hair- vary length
- *†Horse Hair- vary length

*†Cornsilk Fibers-vary length

Each mixture was tested for the following properties: Workability, Water Permeability, Compressive Strength of Mortar, and 3-unit-stack Masonry Prisms, Flexural Strength of Mortar, Bond Strength of 5-unit-stack Masonry Prism, and Shear Strength. The full results from this project are shown in the NCPTT report [4].

In this report the flexural strength of a select amount of FRM mixtures will be discussed. Only 12 lime mortar mixtures are presented, 6 NHL3.5W mortars and 6 NHL5W mortars all composed of volume percent ratios of 1 part lime to 2.5 parts sand. Each set of 6 includes a control mortar and 5 FRM of various fibers at .25% volume. Previous literature states that improvements in FRM performance are more significant for lower matrix compressive strengths (Fanella et. al., 1985). Taking this into consideration, the authors used low fiber volume percentages to improve the mortar's properties. The benefits of using the low percentages were that expenses were minimized and the binder matrix was not altered. These mortar samples were tested in flexure using a method similar to that of Drdácký [3]. The results from the flexural strength tests are presented in this paper along with a discussion on how these various FRM mixtures are applicable to masonry reconstruction and rehabilitation.

2 Experimental Study on the Flexural Strength of Mortar

This section will explain the experimental test set up and results from the flexural test of the 12 mortars. The matrix for the mixtures being tested can be found in Table 1. Three samples were tested for each mixture and each cured for 7 days. The specimens cured for 7 days in order to simulate a typical time in which repointed mortar or mortar used for reconstruction would be fully exposed to typical lateral loadings.

Table 1 Mortar Mixtures Tested in Flexure

Mixture	Binder	Binder Proportion (%Volume)	Fiber Type	Percent of Fiber
1	NHL3.5W	1 : 2.5	N/A	0.25
2	NHL3.5W	1 : 2.5	NyconG-Nano	0.25
3	NHL3.5W	1 : 2.5	RECS7-6mm	0.25
4	NHL3.5W	1 : 2.5	RSC15-8mm	0.25
5	NHL3.5W	1 : 2.5	Control 2000	0.25
6	NHL3.5W	1 : 2.5	Horse Hair	0.25
7	NHL5 W	1 : 2.5	N/A	0.25
8	NHL5 W	1 : 2.5	NyconG-Nano	0.25
9	NHL5 W	1 : 2.5	RECS7-6mm	0.25
10	NHL5 W	1 : 2.5	RSC15-8mm	0.25
11	NHL5 W	1 : 2.5	Control 2000	0.25
12	NHL5 W	1 : 2.5	Horse Hair	0.25

2.1 Test Set Up

In this project, an experimental setup similar to the test method performed by Drdácký [3] on non-standard historic mortar specimens was employed. Drdácký [3] determined that testing non-standard size specimens could provide approximations to the results of tests performed on historical mortars. The specimens used for the flexural strength test of mortar are 2" x 2" x 4" in size. This size of specimens were selected for the following reasons: 1) Small size specimens would more closely relate to authentic mortar specimens extracted from the temple, 2) Behavior of the small size specimens will more closely relate to the actual size of mortar joints in masonry, but are still large enough that meaningful flexural testing can be performed, 3) Since multiple specimens made of 80 mixtures for each test are needed, use of smaller specimens reduces the material cost, and 4) Lime mortar specimens with larger volume may have result in uncured parts inside the prismatic specimens.

While 2" x 2" x 4" specimens are feasible for the above reasons, there is need for enough bearing surface and sufficient length over the span for flexural stresses to develop. Therefore, extension with another material (wooden blocks) in the form of the "prostheses" were used (Fig. 1), similar to those suggested in Drdácký's work [3]. It was determined that 3" wooden blocks epoxied to both ends of the mortar block would provide enough extension to test the specimen in flexural behavior. The test set-up and the specimen are shown in Fig. 1.

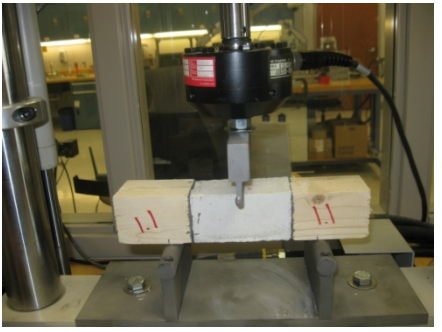

Fig. 1 Flexural Mortar Test Apparatus and Specimen

The load was applied according to ASTM C 293-02 "Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Center-point loading)" [2] and a steady rate of displacement.

2.2 Results

The flexural strength of mortar is important in understanding how the mortar operates under out-of-plane loads. The flexural strength of mortars with fibers has been shown to increase in maximum flexural strength, post-crack ductility, and toughness [6]. The findings in this project agree well with these previous findings. It can be seen in Figs. 2 and 3 how the fibers provide an increase in ductility compared to the plain mortar. For the most part the different types of fibers appear to operate in similar manners in both types of binders. Assessing Fig. 2 the following conclusions were made:

- No FRM mixture provided a higher load capacity than the control mixture.
- The NyconG-Nano and the Horse hair fibers both provided no increase in ductility compared to the control mixture
- The Control 2000 fibers provide the most ductility while still providing an average load compared to the RSC15-8mm and the RECS7-6mm who of which are the only other mixtures to provide any increase in ductility compared to the control
- The RSC15-8mm provided a higher strength than the RECS7-6mm but its ability to hold a higher load longer decreased.

Assessing Fig. 3 the following was concluded:

- The fibers improved the load capacity of all the mortar mixtures compared to the control.
- There is an increase in ductility for all mixtures except the horse hair.
- The horse hair mixture still allowed the mortar to be as brittle as the control mix.

- The mix that provided the most ductility and load capacity was the Control 2000 fiber mixture.
- The RECS7-6mm provided a higher strength than the RSC15-8mm but lower ductility. This could be a result of bad dispersion of the longer fibers which would decrease the load capacity but when the fibers engage they are still able to last longer because they are longer in length.
- Of the six according to the graph the NyconG-Nano fibers and the horse hair performed the worst because of its lack of increase in ductility or load capactiy compared to the control.

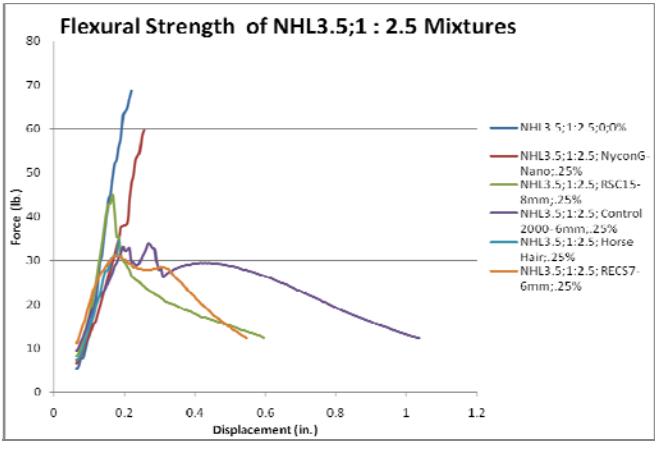

Fig. 2 Flexural Strength of *NHL3.5*; 1 : 2.5 Mixtures

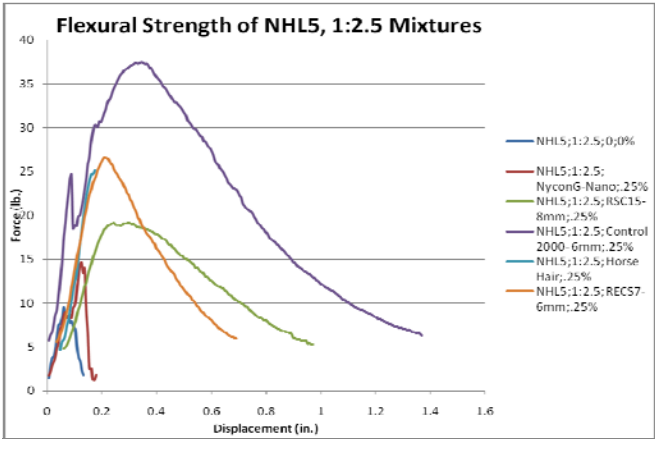

Fig. 3 Flexural Strength of NHL5; 1 : 2.5 Mixtures

Table 2 Flexural Strength of Mortars

Mixture	Maximum Flexural Strength (lb)	Corresponding Displacement (in.)
1	68.69	0.2202
2	59.69	0.2560
3	31.12	0.1726
4	44.99	0.1667
5	33.87	0.2619
6	34.54	0.1845
7	9.55	0.0595
8	15.63	0.1250
9	26.56	0.2083
10	19.19	0.2976
11	37.48	0.3453
12	25.16	0.1726

3 Concluding Remarks

Fiber Reinforced Mortar has proven on more than on occasion that it can increase the strength, ductility, and toughness of plain mortar. This study was not presented just to prove this point. The ultimate goal was to understand how various types of fibers affect the same mortar type and to consider these fibers in binders more closely related to material compositions of historical mortars. Considering the fibers evaluated NyconG-Nano, RCS15-8mm, RECS7-6mm, Control 2000, and Horse Hair, a conclusion can be made to how some of these mortars can be applicable. Of the fibers it was found that NyconG-Nano was the least effective in improving the control. The Horse hair fiber appears to be just as bad as the NyconG-Nano according to Figs. 2 and 3. Though consideration is taken to the fact that the horse hair is non-processed and upon visual interpretation it presumed to be very oily. This oily stage seemed to hinder the hairs ability to bond well with the mortars. It would be recommended that the horse hair be studied future as long as it has been processed to stripe some of the oils away. If the desire of the individual reconstructing or repointing is to have a very ductile mortar more than a large load capacity, it would be suggested that they use Control 2000 fibers. Control 2000 fibers will vary as far as total strength capacity but almost always be the must ductile. The RSC15 and the RECS7 are very similar it is hard to distinguish either's best quality and application but, it is always going to provide in increase in ductility of about .4in or greater compared to the control. The actual load capacity of the two varies but it is predicted just from mechanics of material knowledge that the longer fibers will most likely provide a larger displacement while the shorter fibers will likely proved larger

load capacity. The shorter the fibers the larger quantity needed to reach the desired percentage which means when a crack occurs it will have more fibers engaging to hold that load and keep the crack from increasing as fast. Once the crack has reached the max length of the fibers the mortar will begin to lose its ductility faster. This would seem to be opposite for the longer fibers because the quantity is less there wont be many engaging at the first crack. Though, once the crack continues the longer fibers will carry load longer because the other fibers will begin to engage and the have a longer length to carry the load. It would be useful to test all the fibers except the Nycon-G, in a hybrid mix the results may be very fascinating.

4 References

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IV.14

Effect of Rice Husk Ash Particle Size in Lime Based Mortars

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Abstract This paper presents some preliminary results achieved within the scope of a research programme with the main objective of studying the effect of rice husk ash (RHA) particle size in lime based mortars. A Portuguese commercial RHA was used after being sieved and ground in the laboratory. The influence of the RHA particle size was assessed on fresh and hardened properties of lime based mortars. The results point out: the reactivity of the rice husk ash, the increase in the pozzolanic reactivity with the reduction of the RHA particle size and the possibility of improving lime mortars strength.

1 Lime mortars with rice husk ash

The use of lime based mortars with pozzolanic materials is often recommended as a promising option for replacing mortars due to their use in the past and the recognised incompatibility of cement mortars with old masonry [1]. In terms of worldwide rice production and the waste that the rice husk represents (approximately 20% of the husk production) [2], several studies have been conducted to study the possibility of using this agricultural waste as pozzolanic addition in the formulation of concrete [3, 4] and mortars [5].

When used in concrete production, rice husk ash could lead to a reduction in heat evolution, increase chemical resistance, and decrease permeability and its production cost [2]. Moreover, the addition of rice husk ash to lime based mortars permits the use of these types of mortars in humid environments and increases their mechanical strength and durability [5]. It becomes essential, therefore, to understand the factors affecting the pozzolanic reactivity of rice husk ash in order to maximize the potential of their use in the formulation of mortars.

1.1 Pozzolanic reactivity of rice husk ash

Rice husk, when burned under controlled conditions (temperature, time, and air flow), can be converted into an ash with a high percentage of amorphous silica [3, 4, 6], which, according to Mehta [3], belongs to a superior class of pozzolans.

Besides their chemical and mineralogical composition, the surface area is also an important aspect of the pozzolanic reaction, since it happens between the amorphous silica of ash and lime (calcium hydroxide). Agarwal [7] studied several mortars based on cement with a 10% addition of ashes with different particle sizes and concluded that the addition of ashes with smaller particle size leads to higher values of mechanical strength. The same trend was found by Almeida *et al.* [8] when comparing lime mortars with sieved and ground rice husk ash. However, Paya *et al.* [9] found that ashes with smaller particle size did not maximize the pozzolanic reactivity. Indeed, according to Mehta [3], unlike what happens in pozzolanic materials with low roughness (ex. silica fume), the surface area of rice husk ash depends not only on particle size distribution but also on its roughness, since it has a cellular structure and a rough surface.

The pozzolanic reactivity can be assessed with several techniques [10]: evaluating the rate of consumption of $Ca(OH)_2$ that reacted with pozzolan (EN 196-5 - Methods of testing cement. Pozzolanicity test for pozzolanic cements); measuring the conductivity of the saturated $Ca(OH)_2$ solution with added pozzolan [11, 12]; assessing the mechanical strength of mortars (ASTM C593-06 - Standard Specification for Fly Ash and Other Pozzolans for Use With Lime for Soil Stabilization) and pastes [13]. However, these methods might lead to different conclusions when used to assess the pozzolanic reactivity of the same material [14].

2 Experimental Work

In this paper, the influence of the rice ash size on pozzolanic reactivity was studied by evaluating the mechanical strength of mortars. For this purpose four mortars were studied, all of them with three fixed parameters: commercial rice husk ash, ratio lime/ash, and consistency of 165 ± 5 mm. The commercial rice husk ash was previously prepared in order to obtain different samples of the same rice husk ash with diverse particle sizes. A pure lime mortar was also formulated for reference purposes. Besides the mechanical characterization, porosity and water absorption by capillarity also were assessed to evaluate the influence of rice husk ash particle size on lime based mortars.

2.1 Materials

River sand (grading curve presented in Fig. 1), aerial hydrated lime in powder (CL90), and a Portuguese commercial rice husk ash sold by CINCAS (**Ash**) were used for the production of mortars. The rice husk ash was ground and sieved in the laboratory to study the influence of its particle size.

2.2 Rice husk ash

In the visual observation of the ash, it was possible to identify the presence of particles with different sizes. The larger particles seem to be badly burnt due to their darker colour. The smaller particles present a light grey colour, indicating they were well calcinated. This occurs because the process used by the manufacturer for burnt rice husk does not allow the monitoring of the thermal gradient and the air flow across the material. According to several authors [2, 15], the colour of ash and its chemical constitution show some correlation, since the black colour may be indicative of a high percentage of carbon and lighter colours are associated with higher concentrations of silica. In order to minimize the use of the darker ashes, thereby minimizing the use of ash with high carbon content, the commercial rice husk ash was sieved through the sieve opening 500 μm. At the end of this process approximately 10% of ash (**Ash**) was retained on the sieve opening of 500 μm.

The sieved ash (**AS)** was then ground in a Los Angeles mill to increase its fineness and, consequently, its specific surface [16]. This process has proved effective in reducing the size of the **AS** and led to obtaining ground ash (**AG)** (Fig. 1). Afterwards, **AG** was sieved through sieves 500 μm, 250 μm, 125 μm and 75 μm, and the passing material (designated **A500**, **A250**, **A125,** and **A75**, respectively) was used on the tested mortars formulated with rice husk ash. Figs. 1 and 2 show the grading curves of commercial rice husk ash (**Ash**), ash sieved (**AS**), ash ground (**AG**), and ground and sieved through the sieves mentioned above.

2.3 Tested Mortars

Taking into account what is set down in ASTM C593-06, the mortars with ash addition were formulated with 180 g of hydrated lime, 360 g of rice husk ash, and 1480 g of river sand (ratio by weight 1:2:8 – lime:pozzolan:aggregate). The pure lime mortar was formulated with a lime/aggregate ratio by weight of 1:8. The amount of water used in the formulation of mortars was established in order to ensure a consistency of 165 ± 5 mm, based on the procedures of EN 1015:3 - Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table).

Table 1 presents the tested mortars, the type of ash, and the water/(lime+ash) ratio. In terms of the ratio water/(lime + ash), it was concluded that the addition of ash was responsible for a lower amount of water required to obtain mortars with similar consistency.

For each mortar, six prismatic specimens (40 mm x 40 mm x 160 mm) were prepared in accordance with NP EN 196:1 (Methods of testing cement Part 1: Determination of strength). All samples were demoulded 7 days after their preparation. The specimens of mortars made with ash were stored until their characterisation under controlled conditions of 23±3ºC and 95±5% RH, to ensure their hardening was mainly due to pozzolanic reactions. Since the diffusion of carbon dioxide is very slow in water, the carbonation reactions are reduced in saturated environments. Therefore, the specimens of lime mortar were stored at 23±3ºC and 50±5% RH.

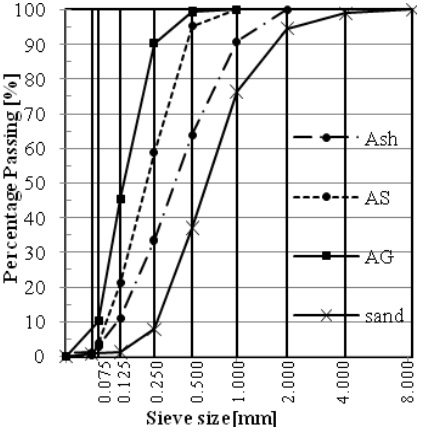

Fig. 1 Grading curves of Ash, AS and AG

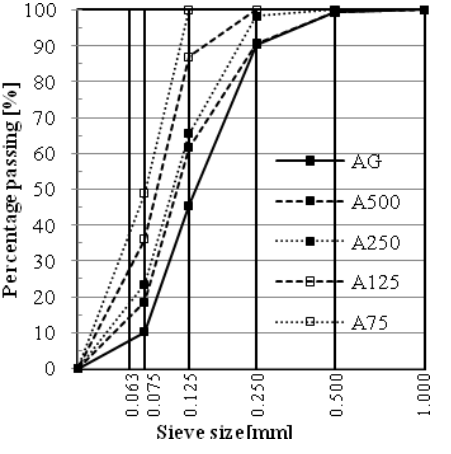

Fig. 2 Grading curves of AG, A500, A250, A125 and A75

Table 1 Tested mortars

Mortar	Type of ash	water/(lime+ash)
L	-	1.83
M500	A500	1.15
M250	A250	1.15
M125	A125	1.14
M75	A75	1.09

3 Mechanical and physical characterization of mortars

Compressive and flexural tests were carried out for each mortar, based on NP EN 1015-11 - Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar, at 14 days and 28 days after their production. The velocity of ultrasound was measured on all the tested specimens with a curing time of 28 days with CNS FARNELL-PUNDIT 6 device with two transducers of 54 kHz and 5 cm diameter.

The physical characterization was done by evaluating the porosity and the capillary water absorption. The open porosity was determined 28 days after their production with a procedure based on EN 1936 (Natural stone test methods. Determination of real density and apparent density and of total and open porosity). The test of water absorption due to capillary action was based on EN 1015-18 (Methods of test for mortar for masonry - Part 18: Determination of water absorption coefficient due to capillary action of hardened mortar) by placing the specimens, previously dried at 60±5ºC for 3 days, in 2 mm of water inside a covered box until the absorption reached an asymptotic value. The specimens were weighed after 5, 10, 15, 30, 60, 120, 180 minutes and 24 hours from the beginning of the test and each 24 hours afterwards. The coefficient of water absorption was calculated for each mortar considering the first 120 minutes of the test, since they were representative of the initial absorption phase. Table 2 presents the characterization of the tested mortars.

Table 2 Physical and mechanical characterization of mortars

Mortar	Porosity (%)	Coefficient of water absorption [$kg/m^2.s^{0.5}$]	Compressive Strength [MPa]		Flexural Strength [MPa]	
			14 days	28 days	14 days	28 days
L	25.2	0.21	0.3	0.5	0.2	0.2
M500	34.1	0.34	2.7	4.7	1.0	2.2
M250	33.8	0.35	3.4	5.6	1.4	2.3
M125	29.7	0.30	3.6	5.7	1.4	2.5
M75	39.5	0.41	3.5	6.2	1.5	2.6

According to ASTM C 593-06, the pozzolanic reactivity can be assessed taking into account the compressive strength. The comparison of the mechanical strength values of the lime mortar and the mortars formulated with rice husk ash allows us to conclude that the ash revealed a considerable reactivity. Increased strength is a consequence of the formation of hydraulic compounds, such as calcium silicates resulting from the pozzolanic reactions.

It also can be observed that all mortars made with rice husk ash have higher values of porosity and, consequently, lower values of density when compared to pure lime mortar. This does not result from the addition of ash, but from the kind

of environment that they were submitted to during their setting. Almeida *et al.* [8], after submitting a mortar made with rice husk ash to dry and saturated environments during their setting, conclude that the latter environment was responsible for higher values of porosity. The same trend was found by Faria [17] in mortars made with different pozzolanic materials. The author explained this trend by the fact that the mortar loses water slowly in the saturated environment, and when part of it is eliminated the mortar is sufficiently hardened, so that the pores may have a larger size and lead to higher values of open porosity [17].

The higher values of porosity obtained for the mortars with rice husk ash are in accordance with the high values of the coefficient of water absorption.

4 Effect of rice husk ash particle size

In Fig. 3, the values of the water/(lime+ash) ratio are graphically represented according to the maximum size of ash. The maximum size of the ash was considered as the mesh size of the sieve through which the milled ash (**AG**) was sieved to obtain **A500**, **A250**, **A125,** and **A75**. The reduction of the maximum particle size of the ashes used reduced the amount of water required to obtain mortars with similar consistency.

The mechanical characterisation points to the influence of the fineness of the ash used, since there was an increase in mechanical strength with the maximum size reduction of the ash used (Fig. 4).

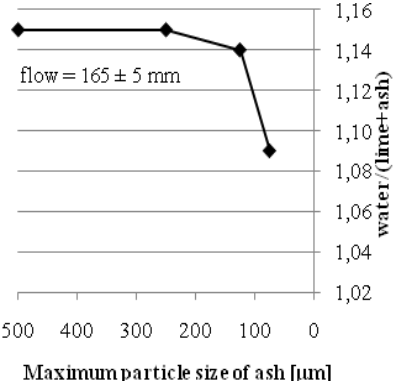

Fig. 3 Relation between water/(lime+ash) ratio and maximum size of ash

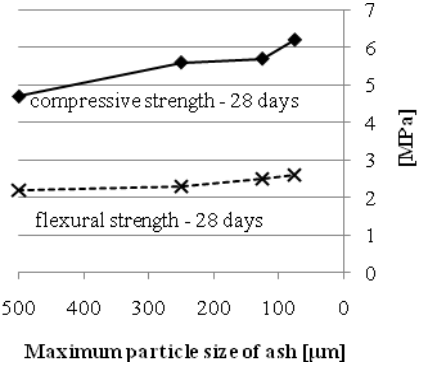

Fig. 4 Relation between flexural and compressive strength and the maximum size of ash

The formation of hydraulic compounds resulting from the pozzolanic reactions are responsible for the differences of the ultrasonic velocity values registered on the mortars formulated with (2600-2700 m/s) and without (1500m/s) rice husk ash.

The porosity values of the tested rice husk ash mortars revealed satisfactory relationship with the velocity of ultrasound and the coefficient of water absorption values (Figs. 5, 6).

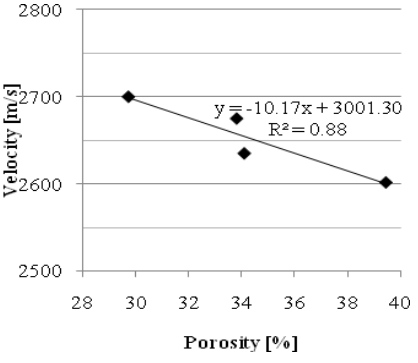

Fig. 5 Relation between porosity and ultrasonic pulse velocity

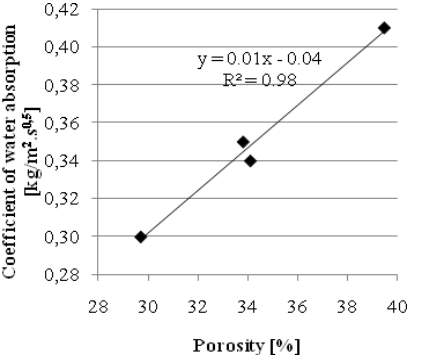

Fig. 6 Relation between porosity and coefficient of water absorption

5 Conclusions

The ashes used, regardless of their finenesses, showed pozzolanic reactivity, as the strength values of mortars made with ash showed a significant increase compared to the value of the reference lime mortar. The mechanical and flexural strength values of mortar M500 were ten times higher than lime mortar values.

When analyzing only the mortars with rice husk ash, it was found that the reduction of the rice husk ash particle size increased the mechanical strength values, and this could be an indicator of a greater pozzolanic reactivity associated with a higher specific surface.

Taking into account some of the recommendations for old buildings [18], the addition of rice husk ash on lime mortars should be performed in smaller proportions, since the formulation used (1:2:8 by weight – lime: rice husk ash: sand) has produced mortars with high values of mechanical strength.

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IV.15

Masonry Repair Options and their Philosophical Ramifications

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Abstract It would be assumed that a survey of a masonry structure would result in the production of an objective report. This situation cannot necessarily be guaranteed as the experience and understanding of masonry deteriorology and repair will vary from practitioner to practitioner. The difference in reporting will clearly determine alterative starting positions for the repair works, with divergence in the project potentially occurring when philosophical tenets are applied. The selection of repairs can be significantly influenced by the different professional's philosophical perspectives that can be broadly categorised as, purist, pragmatist and cynic. These perspectives may direct the approach to repair, placing emphasis of the intervention towards what is of greatest perceived value to the practitioner; for example, honesty over aesthetic integrity and vice versa. This paper investigates how and why projects may start at a subjective point (although perceived as being relatively objective) and be prone to further divergence when building conservation philosophies are applied. This situation would go some way in explaining why two professionals would be confronted with the same structure, yet the outcome of the finished repair project could be significantly different.

1 Introduction

The assessment of a deteriorating masonry structure should lead to an objective evaluation of condition. Whilst traditional visual approaches to survey may have a degree of subjectivity, they are still one of the most commonly adopted methods of inspection. This is ostensibly due to their ease of undertaking, relative low cost and they do not rely upon specialist technical survey equipment. Whatever the method of survey, an objective set of requirements must be established for the building to enable a repair strategy, or more simply an agreed method of work to be established. The repair options available must also be subjected to the application of building conservation philosophy that may result in project divergence.

2 Evaluation of condition & condition surveys

Building survey has been defined as 'a comprehensive, critical, detailed and formal inspection of a building to determine its condition and value' [1]. Condition surveys are one widely adopted form of survey [2], that are assumed to be objective however, they are inevitably subjective in nature, due in part to different surveyor's education and experience in investigating and reporting diagnostics. Straub [3] highlights this situation stating 'the practice of condition assessment by building inspectors yields variable results due to subjective perceptions of inspectors. Surveyor variability is defined as the situation where two or more surveyors, surveying the same building, arrive at very different survey decisions. This variability is caused by a variety of factors such as previous experience, attitude to risk and, heuristics – the use of "rules of thumb" – a leaning towards a particular opinion regardless of the available evidence.' Exacerbating this situation, the evaluation and understanding of stone decay mechanisms is a specialist area and could be surmised to be out-with 'average' professional training. It may therefore be unrealistic to expect the non specialising professionals to evaluate complex masonry projects [2].

Whatever the skill base of the lead professional it has been recognised that tacit investigative protocol is initiated in the formulation of any survey. Douglas & Ransom [4] discuss what they call the 'hierarchy of investigating diagnostics', indicating that this area can be subdivided into, protocols (key defects risk areas and principles for building [5]), testing techniques (destructive and non-destructive) and cognitive branches (critical thinking, problem solving and decision making processes). These cognitive branches can be considered as being the most subjective. Additionally, Ruston [6] has proposed the 'HEIR' (History, Examination, Investigation & Report) method of diagnostics that formalises the survey process, but this still does not reconcile the subjectivity of examination and reporting. In addition to this tacit knowledge, applied university education and aspects of specific professional training are also utilised [2, 7] to form decisions relating to condition. Both the author and Ashurst [2] agree with some of the primary education requirements for surveying such structures (such as an understanding of building pathology, inspection and materials science), however, objectivity is still arguable. The combination of the objective and subjective aspects of diagnostics are reflected by Hollis [8] who states that 'Surveying buildings is an art; verifying the cause of the failure is a science. The surveyor's work involves a combination of both art and science'. As with any 'art' its subjectivity makes commonality in reporting difficult to achieve.

Exacerbating this situation, no standard approach exists for survey work of this nature and as Ashurst [2] indicates; 'Architects and surveyors will create their own approach'. It is the authors' view that an individual approach is acceptable as long as it is logical, well considered, rigorous, and encapsulates the majority of aspects of the hierarchy of building diagnostics and other specific practice based guides.

General best practice has been established within the United Kingdom and many Common Wealth Countries by the Royal Institution of Chartered Surveyors [9] and although the guidance appears relatively comprehensive, it does not include specific, somewhat specialised stone decay mechanisms [10]. An objective initial starting point for any buildings' requirements cannot therefore be guaranteed. This situation may be especially pronounced if the surveyor is not experienced; with significant divergence potentially occurring from other reporters.

3 Philosophical tenets

The way in which we approach any repair project should be underpinned by building conservation philosophy. It is important to realise that almost every technical repair intervention should be assessed against the 'guiding lights' [11, 12] or 'ethics' (those forming the broader issues or key concepts to be considered) and 'principles' (specific criteria upon which conservation works should be based) of building conservation philosophy. These ethics and principles have been summarised by Bell [13]:

Ethics include: Authenticity, integrity**,** avoidance of conjecture, respect for age and historic patina, respect for the contribution of all periods**,** inseparable bond with setting & rights of the indigenous community.

Principles include: Minimal (Least) intervention, legibility (honesty and distinguishability)**,** materials and techniques (like for like materials)**,** reversibility, meticulous recording and documentation & sustainability.

It could be assumed that the importance associated with each of the ethics and principles will vary from person to person, depending on their perspective and what they perceive to be of greater value. It is obviously best to consider them as holistically as possible, whilst comparing and contrasting the individual concepts. A skewed focus, or over reliance on any one of the ethics or principles will lead to a selected repair that may be eminently suitable in one respect, but clearly fails in other aspects. Stirling [14], believes that conservation professionals can be broadly categorised as having one of 3 philosophical viewpoints, namely,

Purists' view: 'the idea that there can be alternative philosophical approaches to the preservation of buildings is seriously misleading. Correctness cannot be watered down'.

Pragmatists' view: 'a sound philosophy is one which points in the right general direction – that of truthfulness. Its precise application must depend on the building and its circumstances. If I am in command of all the facts, then the building itself will tell me what to do.'

Cynics' view: 'conservation is a completely artificial procedure, interfering with natural processes of decay of absolution. Conservation philosophies are therefore necessarily artificial.'

The application of ethics and principles are therefore viewed through the professionals' personal philosophical view point, creating the potential for further divergence. It is however also important to understand that there are no absolutes in conservative repair, only greater levels of defence for selected repairs [15, 16]. The first rule of conservation is that there should be 'no dogmatic rules… each case must be considered on its own merits' [17].

4 Masonry repair options and their philosophical ramifications

Although a client may be specific about initiating repair works to fabric they may not be aware of the need to conform to building conservation philosophy. These issues must be raised by the lead professional who should highlight the implications of repair works set within the context of philosophical ethics and principles [11]. It is obvious that the experience of the practitioner is critical to project success; but it should also be recognised that the inclusion of advice from specialist masonry contractors is also extremely beneficial [2]. Additionally, it is also critical that the lead professional has sufficient knowledge of the range of alternative repair options available for the treatment of deteriorating masonry substrates. Some of these are outlined in the following section, however, it must be emphasised that it is not to be viewed as a comprehensive list of all available techniques.

4.1 Do nothing

Doing nothing can in many cases be a reasonable approach, that has lead to the retention of much historic material. Although a masonry substrate may appear to be in a condition that would warrant intervention this may not be necessarily be the case as many projects may be undertaken to simply restore the aesthetics and integrity of a building [17]. These types of intervention are clearly a deviation from the minimal intervention philosophical tenet and can have a negative influence on the authenticity of the structure. That being said, work that requires a higher degree of intervention could in theory be substantiated if they protect the underlying masonry. Decisions to do nothing must be undertaken by assessing holistic building performance, and understanding the importance and relationship of each associated element and component.

4.2 De-scale

In cases where the removal of friable and loose masonry material is expedient for safety reasons it may be necessary to opt for de-scaling. This process can be a temporary emergency measure or part of a longer term minimal intervention strategy. Descaling entails the simple removal of loose masonry and in excessive cases cutting back decaying stone. This approach, although relatively cheap to execute, is irreversible and clearly leaves a variable aesthetic appearance that can debase the integrity of the building. De-scaling could however be argued to be a reasonable course of action, due to it being relatively minimal intervention in nature. This approach may be considered by many to be insensitive as in many situations the loose and friable surfaces can be saved by using high quality masonry repair techniques, such as pinning, dowelling and consolidation.

4.3 Pinning, dowelling and flaunching

Pinning, dowelling and flaunching techniques are utilised for the consolidation of delaminating masonry surfaces. They require selective holes to be drilled along the affected delaminating surfaces and roughened nylon or high grade stainless steel threaded bars to be inserted into the holes. These are subsequently encased in modified lime grouts, with pigmented lime mortars used to cap the holes. The delaminating layers are also grouted along the failure planes and can also be flaunched with a lime mortar 'skew' along the treated edge. Pinning delaminated stone is least intervention in nature and retains the maximum amount of fabric, but is costly and time consuming to execute. In addition, it is vital that great consideration is given to the selection of any consolidant or grout prior to use as they are difficult to reverse.

4.4 Stone replacement

Stone replacement entails the removal of decaying masonry and replacing with a suitable matching stone. The replacement stone type should be derived from a host of analytical techniques and not simply visual matching [18, 19]. Purists may argue that replacing stone with well matched material does however raise issues of distinguishability of new from existing fabric. This poses the question is well matched stone replacement ultimately dishonest? It is obvious that a 'trade off' occurs with honesty and distinguishability being set against the principle tenets of integrity and like for like materials. Slight variation in tooling effects could go some way to distinguish the repair from existing fabric, but as the finish erodes this would be lost. A professional that places greater emphasis upon honesty over integrity may wish to specify plastic, tile or other distinguishable alternative repairs.

Stones that have eroded to the point that the structural integrity is questionable could warrant replacement. That being said, wholesale replacement of masonry (Fig. 1) should be avoided as this is not minimal intervention, resulting in unnecessary loss of historic material and debasement of authenticity. Conversely, the replacement of isolated stones leads to the retention of a higher degree of original fabric with additional benefits for the authenticity of the fabric.

Fig. 1 Overzealous masonry replacement, Newcastle Upon Tyne

Critics of stone replacement may however, argue that if the structural integrity of the masonry is not in question then lime based plastic repairs may be philosophically more sensitive in nature, owing to a greater potential for reversibility, and retention of more fabric.

4.5 Stone indenting

Indenting masonry is the process of replacing an isolated section of stone and piecing it into the existing (Fig. 2). A good indent should be almost seamless and attached using a suitable mortar. These repairs can be undertaken to carved stone sections or flat faces, and can be considered as being relatively minimal intervention in nature as they are localised. They do however require the removal of a certain amount of stone forming a pocket to house the new material. Stone indenting would initially be honest as the existing and new works would be distinguishable. However, as the stone weathers, and soiling occurs the ability to do so is diminished. The reversibility of stone indenting interventions is questionable as the only real approach is to 'cut out' the repair. Clearly, if a minimal intervention approach was paramount, then plastic (mortar) repairs may achieved better results.

Fig. 2 Stone indent to column, Brandenburgh Gate, Berlin

4.6 Tile repair

Tile repairs are undertaken using clay plain tiles (Fig. 3) or natural stone slips. These are built up in bonded layers and accommodate voids left behind by deteriorated masonry.

Fig. 3 Honest repair in plain clay tiles to limestone and flint substrate

These forms of repair are visually obtrusive and are highly distinguishable and therefore honest. Stone slip repairs can be more subtle and harmonising in the context of stone substrates. Critics [20] of the repairs indicate that they only indicate the philosophical stance that the lead professional has taken, and

ultimately debase the integrity of the structure. The ability to reverse the repairs once executed is high if they are built in relatively soft lime mortars.

4.7 Lime based plastic repair

Plastic repair is the process of removing friable and decaying masonry material and utilising mortar to form new flat or profiled surfaces. The term 'plastic' relates to the plasticity of the materials and not that it contains polymers [21]. These can be attached via suction bonds or armatures depending upon their location and substrate type. Suction bond plastic repairs are relatively reversible as they can be cut out with little damage to the substrate. These repairs can be considered to be minimal intervention when set in a context of replacement stone, but they have a lower life expectancy than other intervention types. The degree of honesty of these repairs is a function of the mortar specification, with a high degree of indistinguishability being achieved if pigments and careful aggregate selection are utilised. Profiled plastic repairs have many advantages over replacement stone in so much as they enable the maximum amount of fabric to be retained whilst being relatively reversible.

4.8 Lime Mortars

The starting point for any mortar for repair should be analysis of the existing material. It could however, be argued that those mortars that best replicate the existing materials are indistinguishable and could be considered as being dishonest. Conversely, those that match the mortar on a performance may tend to be honest, but deviate from the philosophical concept of 'real' like for like materials replacement.

Materials that attempt to replicate historic aged mortars can never be fully achieved, when assessed on a microstructure level. This is due to the texture of a mortar modifying over the life of material. In addition, the complexity of historic mortars is considerably greater than their modern counterparts [22]. The aggregates within these historic mortars can also be more varied than those aggregates available for modern conservation works [23]. The philosophical paradox is that the better the replicating specification, the greater the potential dishonesty. One potential practical answer could be to encourage different surface finish effects on pointing, but this still does not reconcile the problem of honesty once the finish has deteriorated. This situation could therefore be negated by matching the materials properties, whilst using clearly different materials.

5 Conclusions: Divergence of project

A lack of uniformity in the reporting of masonry condition could be argued to create a variable starting position for the selection of masonry repairs. The experience of the professional in masonry repair will have a direct relationship on what strategy is selected. Additional deviation in repair strategies occurs when the subjective application of building conservation philosophy is undertaken. It is clear that alternative surveyors looking at the same building could determine different needs for the structure; one estimating minimal intervention, whilst the others favouring a greater degree of work. It must however be emphasised that these differences are out-with philosophical perspectives with a purist and cynical practitioner determining the same requirements for the substrate.

Upon determination of the requirements the surveyors would then be expected to select suitable repairs of which there are numerous. One of the surveyors may have a better understanding of philosophy and the ramifications of the different interventions, whilst the others may not take this into consideration. The philosophical stance or viewpoint of the lead professional is clearly pivotal as a purist and cynic could lead to significantly different repair types being selected. Purists may favour repairs that direct the observer to their presence and that are to greater or lesser degrees obtrusive (such as tile repairs), whilst pragmatists would place less emphasis upon this and tend towards holistic integrity of the repaired structure. Cynics of building conservation philosophy would in theory pay no attention to the tenets. This would not automatically mean that cynics would undertake poor quality, indefensible repairs as they should still be bound by best practice and an understanding of building performance. The aesthetic appearance of the building has the potential for significant difference and highlights the importance of engaging an experienced practitioner, ascertaining their philosophical perspective prior to project commencement.

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IV.16

Salt Crystallization in Substitution Renders for Historical Constructions

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Abstract Salt damage is one of the major causes of render decay, not only near the sea but also in continental areas. These salts can appear in the walls from different sources: from the ground due to rising damp, carried by the wind as salt spray, flooding or originally present in materials, like unwashed beach sand or due to the salt transport behaviour of the substrate/render and the surrounding ambience severity (temperature and relative humidity) producing salt crystallization. In this paper an experimental laboratory campaign was developed where perforated red bricks rendered on both sides with four different render compositions and different permeability, were submitted to capillary absorption in a sodium chloride solution. Particular attention was given to the influence of different render solutions when contaminated with NaCl and attention was given to the several dissolution-crystallisation cycles: (a) in the location of sodium chloride crystallization in the specimens; (b) crystallization quantification of different specimens. The final goal is to understand the relation between the more or less permeable renders and the damage mechanisms of NaCl dissolution-crystallization cycles, in order to propose possible solutions to stop or slow down the salt decay process in walls contaminated subjected to changes in ambient temperature and relative humidity and contaminated with salt.

1 Introduction

In Portugal, rehabilitation and conservation interventions are assumed of increasing relevance. Renders are used as decorative and protective coats, acting as sacrificial layers that are particularly exposed to climatic actions and mechanical and environmental impact, becoming the most vulnerable constituents of historical buildings. In such buildings conservation renders that are

incompatible with the background and the pre-existing materials, and are inappropriate for the existing conditions, are often adopted, producing new pathologies [1-3].

Rising damp, amongst the sources of moisture present in old masonry, is the most dangerous. Systems based on physical cuts or on the injection of chemical products to prevent moisture in a structure, are often ineffective due to the heterogeneity of the masonry [4]. The high moisture content introduced in the masonry combined with its salt content, can promote the crystallization of such salts [5].

Salt crystallization, is considered one of the major causes of render decay. The extension of this phenomenon is dependent on the salt transport behaviour of the substrate/render as well as on the surrounding temperature and relative humidity. Unfavourable surrounding conditions may cause repeated cycles of dissolution/crystallization, leading to the rapid damage of building materials [6].

Salt damage may occur at the surface or within the render layer. In the first case salt accumulates on the surface as a result of salt moisture transport from inside the wall (rising damp, etc.) or from outside (salt-spray, etc.) and consequent dissolution/crystallization cycles may lead to superficial damage. Salt accumulation inside the render (crypto-florescence) usually causes more serious damage, and may be due to a drying front within the render, changes in porosity due to the co-existence of different materials and the use of water repellents, etc. [7].

In materials contaminated with hygroscopic salts, changes in temperature and relative humidity (RH) may produce dissolution/crystallization cycles of the salt which enhance the damage. In the specific case of sodium chloride (NaCl), cycles of temperature are not harmful, since the solubility of this salt does not significantly vary with temperature; however, a change in RH may lead to dissolution/crystallization cycles which can therefore cause increased damage. Salt damage is rarely a result of a single crystallization event, but rather the consequence of repeated crystallization cycles creating gradients in the salt and in the stress distribution which gradually weaken the material [5].

Recently crystallization damage mechanisms in mortars and plasters have been studied by several authors [4, 7, 8], however a deeper knowledge concerning the influence of the whole system (brick masonry + render) is often lacking.

In this study the entire system (brick + render) is taken into consideration and tested in the laboratory. For this experimental research has been developed to study the location and type of sodium chloride crystallization in rendered brick masonry when submitted to dissolution/crystallization cycles.

2 Experimental Work

Experiments were conducted in the laboratory. The samples, specially designed for the purpose of the work were composed of red perforated bricks (300×195×40mm) with a 1.5cm render on either both sides or one side (in the case of L and CRes specimens), to simulate internal plaster and external render on brick masonry. The samples were submitted to the same conditioning (temperature and relative humidity) and to a similar salt concentration solution.

2.1 Sample preparation

Four different renders were used: L and LMet - permeable lime based mortars; C and CRes - very hydraulic almost non-permeable mortars. The renders' compositions are described in Table 1. All mortars were prepared according to standard procedures – EN1015-2.

Table 1 Mortars formulation

Render	Formulation	Volumetric formulation
L	Slaked lime putty and Tagus River sand	1:3
LMet	Slaked lime putty, metakaolin and Tagus river sand	1:0.2:3.5
C	Cement and Tagus river sand	1:4
CRes	Ready-to-use cement mortar with acrylic addition	Ready-to-use

The samples were carefully executed to reduce workmanship problems (fig.1). They were cured in a conditioned environment at 20ºC and 65% relative humidity (RH) and were wetted twice a day during the first 7 days, with the exception of specimens of pure lime putty, which were cured in dry conditions (23ºC and 50% RH). Table 2 describes the sample compositions and curing conditions.

After curing, the samples were partially immersed in NaCl solution (fig. 2).

Fig. 1 Sample preparation

Fig. 2 Partial immersion in NaCl solution

Table 2 Sample preparation and curing

Specimen	Side A		Side B		Curing time
	Render composition	Curing conditions	Render composition	Curing conditions	
L	L	23ºC/ 50% RH	-	-	4 months
L-L	L		L	23ºC/ 50% RH	
L-LMet	L	20ºC/ 65% RH	LMet	20ºC/ 65% RH + Wetted with water twice a day during the first 7 days	
L-C	L		C		
L-CRes	L		CRes		
LMet-LMet	LMet	20ºC/ 65% RH + Pulverized with water twice a day during the first 7 days	LMet		
LMet-C	LMet		C		
LMet-CRes	LMet		CRes		
C-C	C		C		1 month
C-CRes	C		CRes		
CRes-CRes	CRes		CRes		
CRes	CRes		-	-	

2.2 Dissolution/Crystallization Cycles

After curing, four dissolution/crystallization cycles were carried out over a total period of 4 months. The samples were partially immersed in NaCl solution (27g/L – similar to sea content) to allow capillary rise through them, reproducing in the laboratory the conditions seen in rising damp. After each wetting cycle the samples were dried at 40ºC in a ventilated oven. The samples were not brushed between cycles.

The salt crystallization was evaluated by visual monitoring and by weighing the specimens daily. The wetting and drying phases in each cycle were prolonged until a constant mass was reached.

3 Results and Discussion

3.1 Salt Crystallization – visual observation of efflorescence

Visual observations of sodium chloride crystallization were made at the end of the 4th dissolution/crystallization cycle (Table 3). These observations allowed the determination of crystallization patterns due to the different render compositions, which simulated internal plaster and external render in the same testing conditions. At this point almost no material loss was found.

Some differences were observed in the crystallization between the different samples at the end of the 4th dissolution/crystallization cycle:

- On C-C, L-CRes, LMet-CRes, C-CRes, Cres-CRes and CRes, where at least one render coat was based on cement, the salts formed a dense crust on the top of the brick, although variations between the samples did occur. On CRes render's surface almost no salt crystallization can be seen, while on C, L and LMet render's surface there was some salt accumulation. On samples with CRes render on one or both sides higher crystallization on the top of the brick and/or on the surface of the more permeable renders of the same specimen (C, L and LMet) was observed, probably because the transport through the CRes render is reduced.
- On L, L-L, L-Met, L-C, LMet-LMet and LMet-C, salts appear as "hair crystals" on the top of the brick, but some differences can be observed. On the surface of the renders, salt crystallization appears as generalized "hair crystals" although for L, L-L, LMet-LMet these crystals were less generalized. On the surface of L-LMet, L-C and LMet-C samples, the salts appear as generalized "hair crystals" on the upper part of the render, appearing higher than those with the same render formulation on both sides, as L, L-L or LMet-LMet.

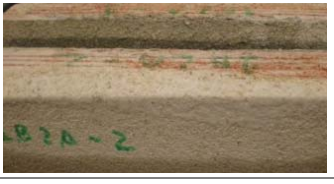
Table 3 presents a synthesis of the observations of salt crystallization. Table 3 shows that the renders with a high and/or medium permeability, L-L, LMet-LMet, L-C and LMet-C, are subject to concentrated crystallization, preventing damage to the brick. These renders should therefore be more favourable in protecting old masonry from salt damage where rising damp is prevalent.

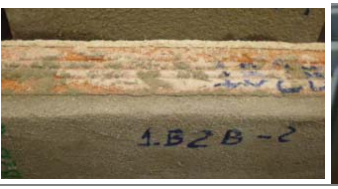
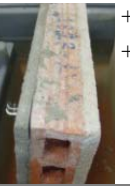
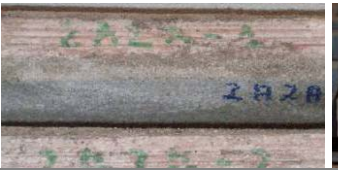
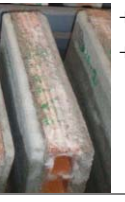
3.2 Salt Crystallization – quantification during the 4 cycles

The quantification of crystallization (%) in each specimen is presented in Figure 3. This quantification is obtained by calculating the weight difference of each specimen by subtracting the weight before the beginning of the crystallization/dissolution test cycles from that at the end of each cycle. The crystallization at the end of each cycle is the crystallization in the referred cycle

added to the crystallization of the previous cycles. Until the end of 4th cycle almost no material loss was found.

Table 3 Visual evaluation of surface crystallization (4th cycle)

Specimen	Specimen crystallization		Crystallization evaluation	
			Mortar	Brick
L			++(L)	+++
L-L			+++(L) +++(L)	++
L-LMet			+++(L) +++(LMet)	+++
L-C			+++(L) ++(C)	++
L-CRes			+++(L) +(CRes)	+++
LMet-LMet			+++(LMet) +++(LMet)	++
LMet-C			+++(LMet) ++(C)	++

LMet-CRes			++(LMet) +(CRes)	++++
C-C			+++(L) +++(L)	+++
C-CRes			++(C) +(CRes)	+++
CRes-CRes			+(CRes) +(CRes)	+++
CRes			+(CRes)	++++

* The evaluation range: (+) almost no crystallization is observed; (++) some crystallization located as “hair crystals”; (+++) crystallization generalized as “hair crystals”; (++++) dense crust crystallization.

Some differences were observed in the crystallization % between the different specimens:

- An increase in crystallization amount after each cycle was found for all samples. This increase is higher for cement based renders in all cycles. The highest difference in crystallization is found from the 2nd to 3rd cycles in all samples.
- Samples with lime based renders on both sides (L-L, LMet-LMet) showed less crystallization in each cycle, than samples with cement based renders on both sides (C-C, CRes-CRes).

- L-L and LMet-LMet showed a small difference between them at the end of 4th cycle; for the cement based samples C-C and CRes-CRes, a higher difference between them was found.
- At the end of 4th cycle, sample L had the lowest crystallization amount. The highest crystallization amount corresponds to CRes-CRes and C-CRes.
- Among samples with at least one render based on lime, the highest crystallizations at the end of 4th cycle were found on L-CRes and LMet-CRes.
- LMet-LMet and LMet-C showed a lower weight gain (even a small weight loss), which is being interpreted as lower crystallization in 4th cycle compared when compared to the 3rd cycle. However, this weight loss maybe due to some material loss.

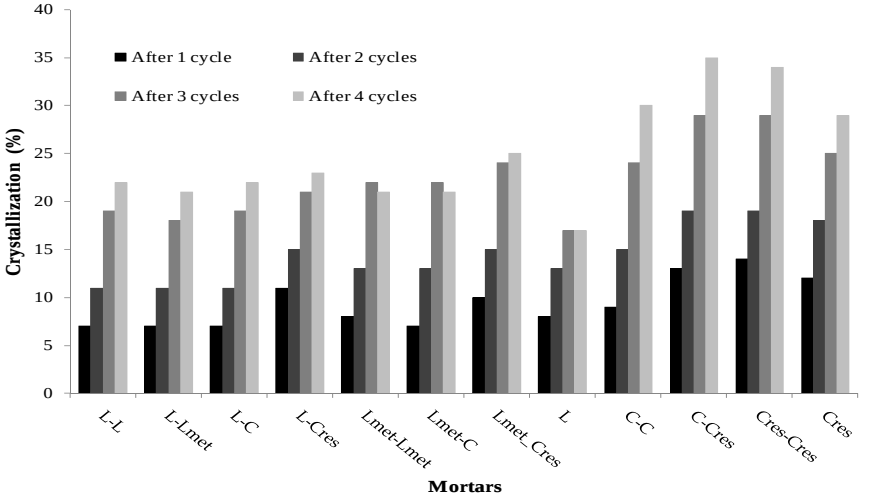


Fig. 3 Crystallization (g/kg) of samples

4 Conclusions

The present experimental work demonstrates that accelerated dissolution/crystallization cycles with sodium chloride, favour the accumulation of NaCl salt efflorescence on the render and/or on the top of the brick with different samples showing different crystallization accumulation patterns.

The study of crystallization and damage localization and evolution is crucial for their understanding in brick masonry.

The main conclusions that can be drawn from this experimental work are:

- The samples specially designed for this experimental work were able to simulate brick masonry with internal plaster and external render.

- With the adopted testing methodology, the main differences in crystallization, considering a whole system (brick masonry + render more or less permeable), could be understood.
- The visual evaluation of specimens' surface crystallization (Table 3) and the quantification of crystallization gave consistent results.
- Relevant differences can be found in final salt distributions between samples with cement based render (less permeable) and only with lime based (permeable) render. For the latter, there is a similar distribution of salts on the surface of renders and on top of the brick; for less permeable specimens there is a higher salt concentration on the top of the brick when compared to render's surface.
- The samples with a high heterogeneity between the internal plaster and external render show the highest damage, namely those rendered on one single side, and those with a lime render (L or LMet) on one side and CRes on the other.
- The low permeability render CRes showed the highest crystallization on the brick, especially on CRes-CRes samples. Apparently CRes render acts as a barrier, restricting the evaporation of the water through the render, allowing a higher crystallization on the top of the brick, where the evaporation occurs. This behaviour indicates a tendency of cement renders of low permeability to favour crystallization in the masonry, increasing damage inside the wall.
- The samples with high and/or medium permeability renders L-L, LMet-LMet, L-C and LMet-C, concentrate crystallization on the render, preventing high damage in the brick. These results point to the conclusion that these referred types of systems are to be preferred in the conservation of old walls, considering that the objective is to increase the durability of the masonry, to the detriment of the render if necessary.

Based on these main conclusions, investigations must be carried out using scanning electron microscopy (SEM) to better understand the deposition of the salts in greater detail and the influence of render formulations on salt crystallization and possible decay.

It is also important to study the porous structure of the bricks and of the mortars applied, and to compare them, in order to establish a link to the degree and localization of salt damage.

5 Acknowledgements

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IV.17

Hydration of Roman Cements Used for Architectural Restoration

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Abstract Roman cement was extensively used to decorate facades during the nineteenth and beginning of twentieth Century. The interest of this material has been revisited recently in the field of conservation of architectural cultural heritage. This article gives preliminary results on the characterization of the raw materials and main reactive phases (using XRD, SEM, selective dissolution and isothermal calorimetry) of a roman cement recently produced from the Lilienfeld marlstone (Austria), in comparison with a commercial roman cement (from Vicat, France). The mineralogical composition of the two cements strongly differs according to the presence of sulphate minerals in the marlstone and the temperature of calcination. Isothermal calorimetry and in-situ XRD carried out on cement paste allow the identification of the AFm and AFt type phases as early age hydration products responsible of the flash setting typical to roman cements. The composition rich in alumina and the crystallinity of dicalcium silicates strongly differs in the Lilienfeld cement and influence their reactivity at the later ages.

1 Introduction

Patented in England by James Parker in 1796, roman cement was extensively used in civil engineering structures [1-3] before the invention and development of Portland cement. From the first half of the 19th century, roman cement was also used as binder for stone repair mortars and façade decoration of historical buildings all over Europe [4-6]. Since the last decade, the properties and durability of historical roman cement mortars and their compatibility with stone substrates have been demonstrated by many studies [4,7-9]. The main advantages of roman cements for stone restoration can be summarized as followed: low energy consumption resulting from low calcination temperatures (800-1100°C), durability even in highly polluted environment (urban exposure and aggressive solutions),

compatibility with historical building materials (aesthetical, chemical and transfers properties), and versatility of mortar formulations and applications techniques.

Roman cement is produced from raw marlstone rather than from a mixture of different source materials as for traditional cements (ordinary Portland cements, calcium aluminate cements, calcium sulfo- aluminate cements, belites cements…). Furthermore no gypsum is added during the grinding process to regulate the workability of fresh roman cement mortars. The raw marlstones have a wide range of chemical composition and are calcined at temperatures where sintering and melting would not occur (800-1100°C). The "clinker" is then finely ground and usually no further product was added. According to the literature [8], it was difficult to control the composition of roman cements due to the various compositions of marlstone calcined with heterogeneous process in shaft kilns. Vicat (France) was a major company producing roman cement throughout the last two centuries and remains the only producer in Europe. Vicat Prompt cement, used alone or mixed with hydraulic lime, provides technical solutions for historical masonry repair [10,11]. The use of roman cement has been recently revisited in the frame of Rocem project [5] which aimed at investigating historic roman cement mortars to provide compatibility criteria for repair mortars [4], to select appropriate raw materials and optimize the calcination process in laboratory and pilot scale kilns [12-14]. Based on Rocem project, the new Rocare project aims at making roman cement as a compatible and sustainable product as alternative solution to available products (lime, hydraulic lime and commercial roman cements) and adapted to local needs of restoration market in Europe. This necessitates the fundamental understandings of the mineralogical development during the calcination process and the subsequent hydration reactions once mixed with water, aggregates and chemical admixtures. This article presents new results on the characterization of two different roman cements, a commercial cement (Vicat prompt cement) and a roman cement produced in the frame of Rocem project (2003-2006) resulting from the calcination of the Lilienfeld (Austria) marlstone in a pilot scale rotary kiln (920°C for 300 min), as reported in [15]. The hydration was studied from the first minutes up to three months. The main challenge of this study is the characterization of reactive amorphous phases resulting from the calcination of marlstone at low temperatures. Combined techniques for anhydrous cement characterization (selective dissolution, XRD, EDS mapping) allow the discrimination of intermixed and non crystalline phases responsible for the workability and long term performances specific to these cements.

Cementitious notation: C- CaO , S- SiO_2 , A- Al_2O_3 , $\overline{C}$ - CO_2 , $\overline{S}$ - SO_3 , H- H_2O

2 Materials and methods

The oxide composition of the Lilienfeld and Vicat cements is given in Table 1.

Table 1 Oxide composition of the Lilienfeld and Vicat cements

	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	TiO_2	LOI
Lilienfeld	30.08	8.97	44.42	3.81	2.44	0.13	1.81	0.54	0.38	7.79
Vicat	18.70	7.51	54.8	3.35	3.90	3.36	1.08	0.30	0.29	6.97

The characterization of the cement reactants used selective dissolution methods according to the works of Stutzman *et al* [16]. The Salicylic Acid/Methanol Extraction (SAM) dissolves alite C_3S, belite C_2S, and free lime. The KOH/sugar solution dissolves the interstitial phases of aluminate and ferrite leaving a residue of silicates and minor phases.

Isothermal calorimetry is a technique to study the kinetics (heat flow is expressed in $J.h^{-1}.g^{-1}$ of cement) and the total heat ($J.g^{-1}$ of cement) generated by exothermic reactions occurring in controlled conditions. Five to ten grams of fresh cement paste were cast in a glass vial placed in the calorimeter (TAM Air calorimeter and thermostat 3114/3236 from Thermometric). In-situ mixing experiments were done using a specific device equipped with paddle, allowing the measurement of heat flow from the very start of the reaction [17].

The cement paste was prepared by adding water to cement (mass ratio W/C of 0.65) and mixed with a paddle mixer for 1 minute at 1100 rpm. The fresh cement paste was cast in plastic vial, demoulded after 24 h and cured in de-ionized water. A slice of specimen was cut for each test time. The hydration of the cement pastes was stopped by solvent exchange. The paste slices were cut and immersed in isopropyl alcohol for 6 days and then dried in desiccators.

XRD was carried out with an X'Pert Pro PANAlytical diffractometer (Cu tube, λ=1.54 Å). The crystalline phase identification in anhydrous cements and cement paste used the powder method (after 100 micron sieving).

Scanning Electron Microscopy (SEM, Philips Quanta 200) was used to study the microstructure of anhydrous cement powder. Pelletized raw cement and cement pastes were impregnated with epoxy resin and polished to obtain cross sections. The microanalysis of phases was done with Energy Dispersive Spectroscopy (EDS, Bruker AXS Quantax). Quantitative elemental mapping was performed using ultra-fast spectral imaging acquisition for 15 min. The Esprit software (from Synergie[4] PGT) allows the acquisition of images with a simultaneous spectral accumulation in a database for each pixel. The set of acquired images were then treated to normalize the intensity of each chemical element with respect to its quantity determined by accumulated EDS spectra. Finally the atomic Ca/Si and Al/Si ratios were calculated from the intensity of quantitative images (using routines developed with Matlab) and mapped inside the most representative grains of the respective cements.

3 Results

3.1 Characterization of the anhydrous roman cements

3.1.1 XRD and selective dissolution

Fig.1 shows the XRD patterns of the Lilienfeld and Vicat cements before and after selective dissolution. The main crystalline phases present in the Lilienfeld cement originate from the incompletely calcined marlstone, e.g. quartz and calcite in relatively high amounts and albite and muscovite as secondary phases from clayey fraction. Other crystalline phases result from the calcination of the minerals in the temperature range 800-900°C. Among these phases, the diffraction peaks related to calcium silicates β or α'-C_2S show a relatively low degree of crystallinity in the 31-34°2θ range, compared to the well crystalline β-C_2S present in Vicat cement (Fig. 1). Secondary phases are identified as Portlandite, CH, presumably from pre-hydration of free lime. After extraction of the silicates phases by the SAM method, the XRD pattern reveals small amounts of gehlenite C_2AS and a calcium silicate carbonate, tilleyite $C_3S_2.2C\overline{C}$, occurring as a natural mineral whose formation has not been reported during the manufacture of cements [18], in contrast to spurrite $(C_2S)_2.C\overline{C}$, a carbonated form of C_2S [19] identified as traces in the Lilienfeld cement but in greater amounts in Vicat cement. One interesting result is in the strong similarity of the XRD patterns before and after the KOH/sucrose dissolution. The overlap of these two patterns indicates that the Lilienfeld cement contains no significant crystalline aluminate reactants. These results were already reported in [20].

The mineralogy of Vicat cement differs strongly from that of the Lilienfeld one and is composed of a wider range of silicates and aluminates reactants. Due to higher temperature of calcination (up to 1200°C), the crystallization of β or α'-C_2S is enhanced, as illustrated by the diffraction peaks in the 31-34°2θ range and much less quartz remains compared to the Lilienfeld cement. The selective dissolution methods seem more suitable to the Vicat cement to discriminate the different phases. The main aluminates phases, identified after SAM dissolution, are $C_{12}A_7$, C_3A, C_4AF and $C_4A_3\overline{S}$ and the main silicates phases identified after KOH/sucrose dissolution, are β or α'-C_2S and spurrite $(C_2S)_2.C\overline{C}$.

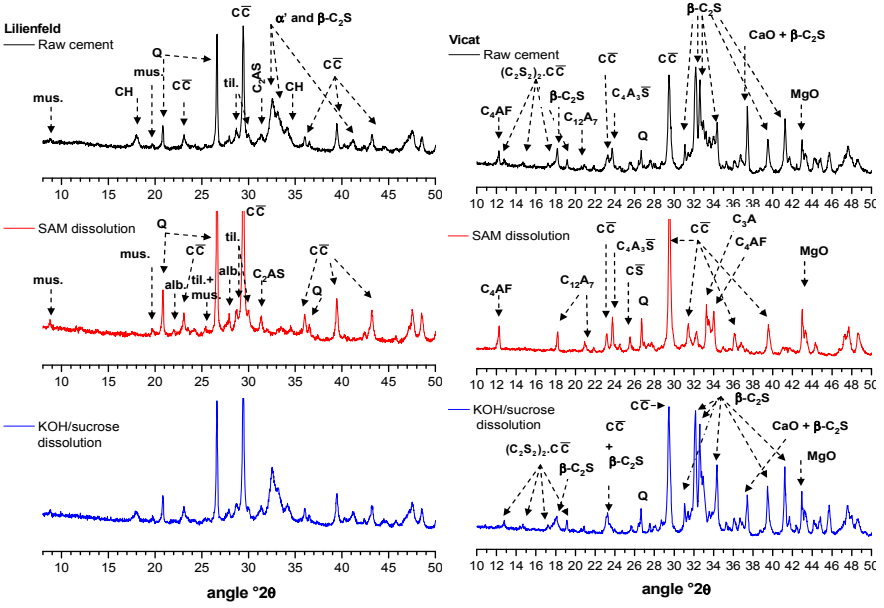

Fig. 1 XRD patterns after SAM and KOH/sucrose selective dissolutions of the Lilienfeld and the Vicat cements (Q-quartz; mus- muscovite; alb- albite; til- tilleyite)

Traces of calcium sulphate $C\bar{S}$ were also identified in the XRD pattern of the raw Vicat cement. Compared to the Lilienfeld cement, the Vicat cement contains higher amounts of sulphate (Table 1) crystallized under the form of anhydrite $C\bar{S}$ and ye'elimite $C_4A_3\bar{S}$ which both contribute to significant changes in the hydration products (Fig. 8). The presence of calcium sulphate $C\bar{S}$ can be explained by the release of sulphur from the weathered sedimentary pyrites included in the limestone grains, as illustrated in Fig. 5. Another source of sulphur is seldom observed in the cement grains under the pattern of calcium monosulphide CaS. This phase plausibly originates from the reaction between free lime or calcite and gaseous sulphide under local reducing conditions of calcination.

3.1.2 SEM and EDS-mapping analyses of the Lilienfeld cement

Polished cross-sections of pelletized Lilienfeld cement powder were prepared prior to SEM examinations illustrated in Fig. 2. The morphology and composition of the nodules appear to be uneven in the sample, but some general features can be identified. As already suggested by XRD, many quartz and calcite grains remain in the nodules, surrounded by a reactive phase appearing whiter grey in BSE mode. This phase presumably results from the diffusion of calcium and silicate ions during the calcination process of marlstone. However the EDS mapping (Fig.

3) suggests that alumina is systematically present in significant amounts in this phase which is consequently referred to as C-A-S reactant in this paper. Fig. 3 shows the EDS mapping on a nodule containing quartz, calcite and K-feldspar ($KAlSi_3O_8$ as endmember) grains surrounded by the C-A-S reactant. The elemental analysis gives a Ca/Si ratio evenly distributed in the grain and close to 1. K-feldspar is source of silica and alumina which changes the Al/Si ratio ranging 0.2-0.4 in this specific grain. The non stoichiometric composition of this phase can explain the difficulty to relate the diffraction peaks in the 31-34°2θ range to actual β or α'-C_2S.

From Fig. 2, it is noteworthy that the morphology of cement grains remains unchanged after selective dissolution methods. First, the intragranular porosity, already observed in the raw cement, does not increase significantly after. Furthermore, SAM and KOH/sucrose dissolution do not affect the C-A-S phase surrounding quartz and calcite.

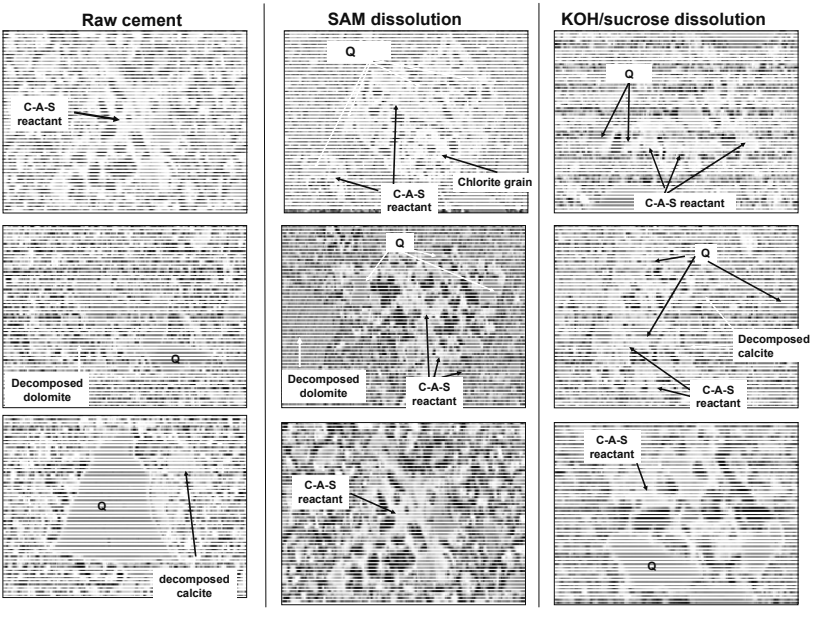

Fig. 2 Microstructure of the Lilienfeld cement grains (left: raw cement – middle: after SAM dissolution – right: after KOH/sucrose dissolution)

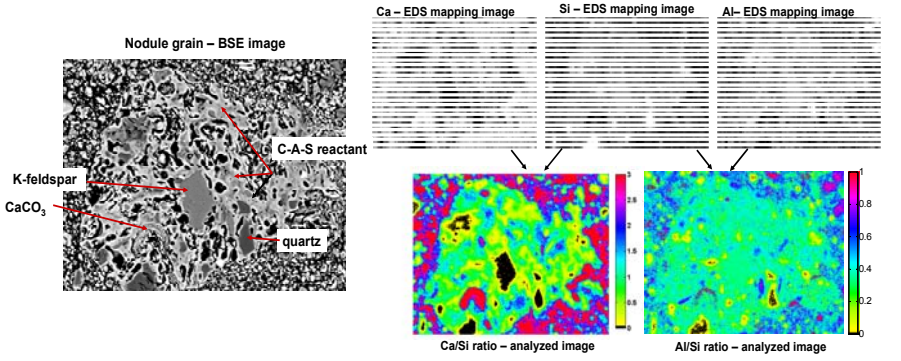

Fig. 3 EDS mapping of the raw Lilienfeld cement

3.1.3 SEM and EDS-mapping analyses of the Vicat cement

In contrast with the Lilienfeld cement, the Vicat cement is manufactured at higher temperature and consequently better crystallized and discriminated phases are observed in Fig. 4. A typical grain is composed of C_2S grains surrounded by a solid solution of C_3A, $C_4A_3\overline{S}$ and C_4AF. Some clusters of periclase MgO, resulting from the decomposition of dolomitic materials, usually appear as dark areas in BSE mode. As already mentioned from the XRD results, little quartz remains in the cement and some porous nodules resulting from incomplete calcination are seldom seen. The morphology and composition of these porous nodules (bottom left image in Fig. 4) are comparable to those present in the Lilienfeld cement (Fig. 2). The XRD results on samples after selective dissolution are confirmed by BSE images (Fig. 4) in which the rounded C_2S grains are removed by SAM solution and C_3A and C_4AF are dissolved after KOH/sucrose dissolution.

The EDS images for the Vicat cement (Fig. 5) show the suitability of the technique to map the silicate and the aluminate phases inside the most representative grains. Contrary to the Lilienfeld cement (Fig. 3), the C_2S grains (blue in Fig. 5) have a stoichiometric Ca/Si ratio of 2 and are well differentiated from the aluminate phases (C_3A, $C_4A_3\overline{S}$ and C_4AF) illustrated in red according to the arbitrary scale bar related to the Al/Si ratio.

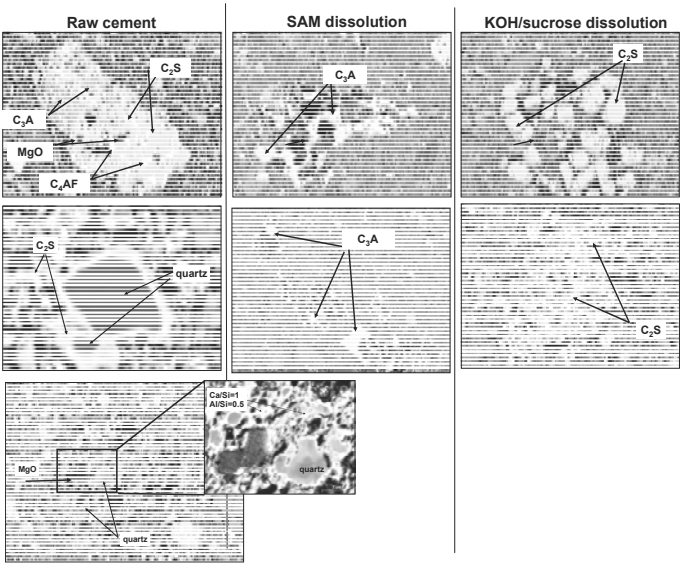

Fig. 4 Microstructure of the Vicat cement grains (left: raw cement – middle: after SAM dissolution – right: after KOH/sucrose dissolution)

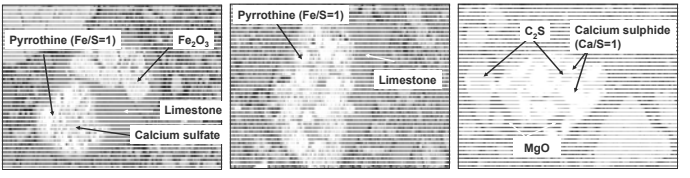

Fig. 5 Specific sulphate phases in the raw Vicat cement grains

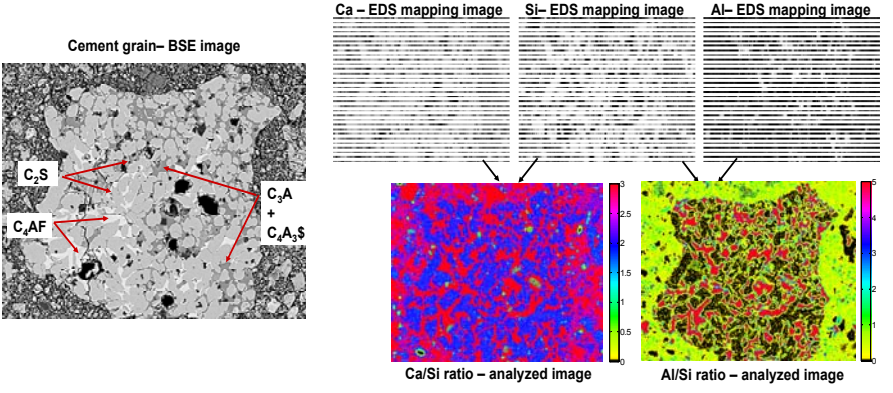

Fig. 6 EDS mapping of the raw Vicat cement grains

3.2 Hydration of roman cements

3.2.1 20°C isothermal calorimetry

Fig. 7 shows the heat generation during the hydration of the Vicat and the Lilienfeld cements at very early age (with in-situ and ex-situ mixing). The rapid hydration of both cements is characterized by a single heat flow peak with comparable acceleration rate and intensity. For both systems, the initial heat flow peak corresponds to the dissolution of reactive phases and both the precipitation of hydration products.

The identification of crystalline hydration products was studied by in-situ XRD analysis for the first 15 hours. From the beginning of hydration, there are very different phase assemblages in the two cements. While ettringite $C_6A\overline{S}_3H_{32}$ and hemicarboaluminate $C_4A\overline{C}_{0.5}H_{12}$ both precipitate from the first minutes of hydration in the Vicat cement, the first phase identified in the Lilienfeld cement is $C_4A\overline{C}_{0.5}H_{12}$. This phase dissolves after 5 hours hydration and reacts with carbonate ions from the pore solution to precipitate monocarboaluminate $C_4A\overline{C}H_{11}$, which predominates after 24 hours (Fig. 8).

Regardless of the nature of hydration products, the reaction levels off after 8 to 10 minutes of hydration for the two systems. This age also corresponds to the end of the workable time of the cement pastes. At later ages, the right graph (low Y-axis scale) shows significant discrepancies in the calorimetric response between the systems. In the Vicat cement, a very sharp peak is observed from 18 hours with a maximum after 36 hours. According to XRD (Fig. 8), this peak would correspond to the precipitation of monocarboaluminate $C_4A\overline{C}H_{11}$. In the Lilienfeld cement, a much smaller and broader peak is seen from 2-3 days of hydration which extends over several days, and would match with the hydration of C-A-S phase as suggested by XRD (Fig. 8). The total heat curves show that the rapid formation of $C_4A\overline{C}H_{11}$ contributes to the higher heat generated by the Vicat cement. However the hydration rate of the C-A-S phase is greater in the Lilienfeld cement in comparison to the slow hydration of well crystallized C_2S in the Vicat cement.

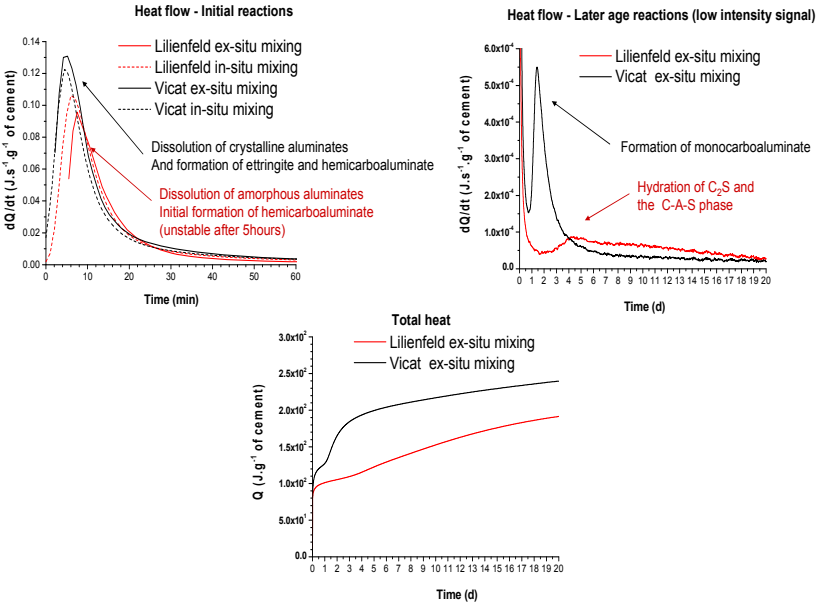

Fig. 7 Heat flow and total heat during early age and long term hydration of the Lilienfeld and the Vicat cements

3.2.2 XRD analysis of hydrated cement pastes

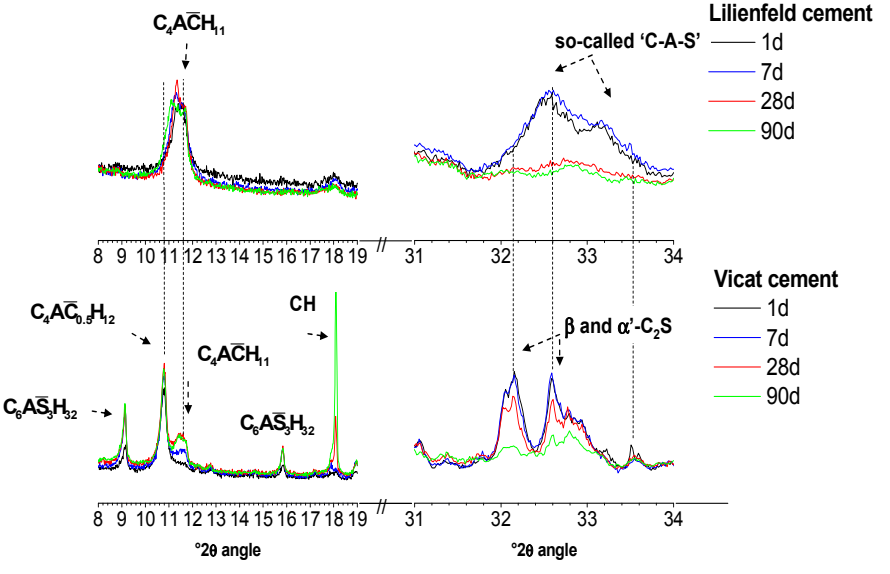

Fig. 8 XRD patterns of hydrated Lilienfeld and Vicat cement pastes

Fig. 8 shows the XRD patterns of cement paste cured for 90 days under water. In the Lilienfeld cement, $C_4A\overline{C}H_{11}$ predominates after 24 h but with a relatively broad diffraction peak which could indicate a solid solution with initial hemicarboaluminate $C_4A\overline{C}_{0.5}H_{12}$, as already suggested by [20]. After 90 days, the hydration of the C_2S and the C-A-S phase seems well advanced but no crystalline hydration products were identified. In the Vicat cement, the ettringite originally formed and hemicarboaluminate $C_4A\overline{C}_{0.5}H_{12}$ remain stable for 90 days. The precipitation of monocarboaluminate $C_4A\overline{C}H_{11}$ is initiated after 24 h and levels off after 28 days of curing under water. Compared to the C-A-S reactant in the Lilienfeld cement, very little C_2S reacts before 28 days. The hydration of C_2S is well advanced after 90 days and leads to the precipitation of calcium hydroxide CH co-precipitating with amorphous calcium silicate hydrates C-S-H.

4 Conclusions

This paper compares the mineralogy and hydration of two types of roman cements used for historical masonry. Due to the differences in the raw materials and the calcination process, the Lilienfeld and Vicat cements have different mineralogy and hydration mechanisms. These two cements rapidly hydrate and require retardation admixture for practical applications. The higher calcination temperature in the Vicat cement leads to the formation of crystallized belites, partly carbonated to form spurrite at high CO_2 partial pressure in the shaft kiln, which are relatively low reactivity phases. The presence of sulphates (pyrites) in the raw marlstone leads to formation of calcium sulphate and ye'elimite which rapidly hydrate to ettringite. After a few minutes, the sulphate concentration rapidly becomes undersaturated with respect to ettringite precipitation and the calcium aluminates hydrate to hemicarboaluminate. This phase is unstable in presence of calcite and monocarboaluminate slowly precipitates during curing under water.

During the calcination of the Lilienfeld marlstone, incomplete crystallization of calcium silicates occurs within nodules containing significant amounts of calcite and quartz. A few grains of stoichiometric C_2S are formed and were locally observed in a rim around the quartz grains. Remaining clay materials provide aluminate ions leading to the formation a non stoichiometric C-A-S phase. The XRD and SEM results after selective dissolution indicate that silicate and aluminate are intimately linked in this poorly crystalline C-A-S phase. The diffusion of ions seems to be incomplete under these conditions of calcination to form purely crystallized C_2S. The XRD pattern of this C-A-S phase would suggest a disordered structure for which the reactivity is enhanced compared to the crystallized β and α'-C_2S. However crystalline hydrates as calcium hydroxide, which is the usual product of C_2S hydration, were not detected after 90 days of curing.

5 Acknowledgements

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IV.18

Two Views to Deal with Rain Penetration Problems in Historic Fired Clay Brick Masonry

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Abstract In this paper a comparison is made between two views to solve rain penetration problems in solid historic fired clay brick masonry. The first one aims at protecting the masonry against rain penetration ("rain coat" concept). In the second approach the penetration of rain in the masonry is accepted and the measures taken are focused on improving the *capillary* moisture transport in the masonry and on the application of materials with favourable drying characteristics and/or the enhancement of the drying conditions ("breathing" concept). It is shown that the often preferred protection approach may result into deterioration of the rain penetration problem instead of diminishing it. Also is shown that the second approach generally leads to a significant drying of the walls, thus providing a sound solution for rain penetration problems in solid historic fired clay brick masonry.

1 Introduction

Water leakage in historic solid masonry walls regularly occurs and is a major source of damage: in masonry it causes frost and salt damage; in timber it may lead to rot. Moreover, humidity may have negative effects on the living conditions in historic buildings.

From practical experience and from the literature [1-3] various causes for moisture problems like leaking can be deduced:

- inadequate material properties of the applied fired clay brick and masonry mortar; incompatibility between brick and mortar properties
- cracks in masonry
- inadequate design
- poor ventilation
- negative effects of a number of inadequate restoration measures

- poor workmanship of the builders during construction and/or restoration

This paper is based on a study of rain leakage problems studied in particular in historic masonry of wind mills in the west of the Netherlands. These are ideal objects for such a study as wind mills are intentionally exposed to wind and rain (to optimize their functionality) and often show leakage problems. The problems observed in this study are also applicable to historic solid masonry of towers, churches, castles etc.

Before discussing the different measures that may be taken to solve leakage problems some further thought is given to different types of moisture transport in solid masonry.

2 Rain penetration and porosity

Brick and mortar are porous media, which means that moisture absorption in these materials is governed by capillary action and drying by evaporation. For the separate materials moisture transport is easy to understand, for the composite material *masonry* this is more complicated.

Capillary water transport

Optimal contact between mortar and brick is the result of (i) the correct choice of brick and mortar (compatibility) allowing the formation of a dense mortar-brick interface and (ii) the skill of the mason: the brick should be fully surrounded by mortar (no cavities). Under these conditions, the two capillary systems of brick and mortar are smoothly connected.

Moisture transport from mortar to brick and vice versa are dependent on differences in pore dimensions and pore distributions of the two separate materials. The transport of moisture from brick to mortar may be hindered if the porosity of the mortar is much finer than that of the brick: in that case the mortar acts as a barrier and slows down or even stops moisture transport through the masonry.

Liquid moisture transport may take place in the case of connected capillary pore systems as a result of pressure differences (e.g. wind pressure, drying, ventilation) if the moisture content in brick and mortar are higher than the critical moisture content (at the critical moisture content the capillaries are covered by a thin layer of water). This may lead to leakage.

“Free water transport”

Apart from capillary action (in fact moisture transport through capillary pores of porous materials) moisture transport can as well occur as a form of “free” water transport. With this is meant water that travels through a wall along “canals” formed by interconnected fissures, hollows, cavities, cracks etc. (“canal” porosity more than 100μm in diameter). Pressure differences, especially wind pressure do

have a significant effect on the moisture transport velocity for this type of porosity: water may pour out of the wall as a jet of water.

This is a far more unfavorable condition for leakage than capillary moisture transport: as the capillary water transport velocity is much slower than the "free" water transport velocity

It seems obvious that creating or reinstating conditions of capillary water transport (by filling up the cavities) may significantly improve the water tightness behavior of the wall,

Grout injection may be the proper way to realize this change in water transport behavior in a wall.

3 Two views to solve water leakage problems

Basically to solve leakage problems in solid masonry two different ways of approach are applied. The first one aims at protecting the masonry against rain penetration ("rain coat" concept). In the second approach the penetration of rain in the masonry is accepted and the measures taken are focused on (i) if necessary, improving the *capillary* moisture transport in the masonry (ii) the application of materials with favourable drying characteristics and/or (iii) the enhancement of the drying conditions, e.g. improvement ventilation ("breathing" concept).

The potential and limitations of both views are discussed hereafter.

3.1 Protection against rain penetration

In case of leakage the most logical and promising way to solve this problem seems to be, the protection of the masonry from the penetration of rain (rain coat solution). In practice a number of solutions are applied in which this approach is chosen, such as the application of:

- render
- tar
- thatch on masonry
- tiles
- ivy
- etc

render

tar

ivy

tiles

ferrocement

Fig. 1 Examples of protection measures against rain water leakage

Apart from protecting the underlying masonry against rain penetration these solutions have the disadvantage that they significantly alter the visual appearance of the object. This is often unacceptable if the structure has a cultural heritage value.

Water repellent

In that case protection against rain penetration is often headed for by the application of water repellents, as they are transparent. The assumption then is that the application of water repellent causes (i) rain water to be warded off and (ii) the wall to be dryer and dryer in the course of time.

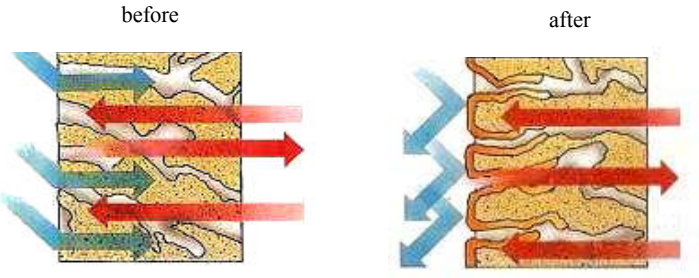

Fig. 2 Idealized graphic presentation of the effect of a water repellent [5]

Fig. 2 shows that the water repellent coats the pores and penetrates for some mms in the wall and allows vapor transport after application of the water repellent. The graph idealizes drying as only vapor transport, which is not hindered by the water repellent. In most cases also liquid transport plays a role. Water is then stopped by the water repellent and only can evaporate from the pores some mm's within the wall: a slow process (see Figs. 2 and 3).

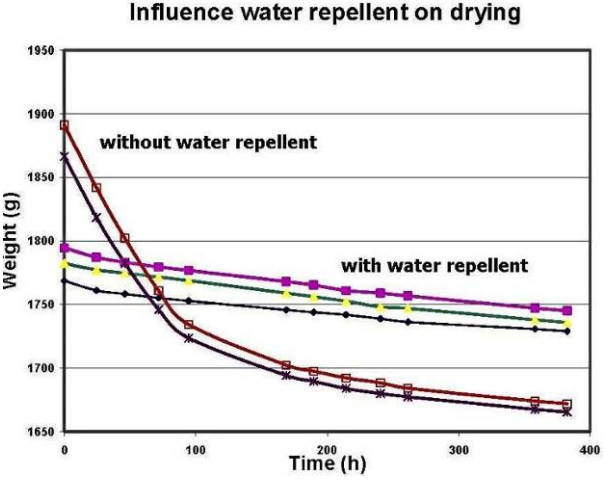

Fig. 3 The application of a water repellent significantly slows down the drying of a wall.

Inspection of more than 25 masonry wind mills, where water repellents were applied, showed that the leaking problems in stead of diminishing always increased. An important reason is that wind mills may develop micro-cracks in the masonry as a result of the heavy dynamic oscillations of the sails.

So rain water may enter through these micro-cracks in the wall instead of being warded off. Also other moisture sources like occasional flooding, continuous rising damp, recurrent inside condensation and hygroscopic moisture uptake may be causes of moisture absorption into the wall. With moisture inside the wall the

applied water repellent turns out to be a disadvantage as already shown: drying is significantly slowed down.

There is as well another strong motive to refrain from the application of water repellents in the case of historic masonry. The reason is that very often historic masonry contains salts. Drying leading to salt crystallization just under the repellent layer may cause substantial damage (see Fig. 4)

Fig. 4 Salt damage as a result of the application of a water repellent

It can be concluded that protection against rain penetration ("rain coat" concept) may be rather tricky: one should be well aware of possible other moisture sources (which may be unavoidable) and as well take into account possible side effects.

3.2 Accept rain penetration and focus on the realisation of capillary moisture transport in the masonry and enhance drying

Intuitively this view ("breathing" concept) seems to be less promising as the promotion of drying is normally aimed at through materials which as well significantly absorb moisture.

However as well the following should be considered:

- if the water leaking is caused by "free water transport" measures taken (e.g. injection) to create or reinstate *capillary* moisture transport have the effect that the moisture transport significantly slows down. Experience has learned that well-made solid masonry, having capillary moisture transport, generally is water tight.
- in sound masonry the mortar acts as a barrier; and as been shown in [6], the penetration of rain water in the wall during a shower is limited to a depth of 1.5 brick length; more water will drain from the outer face of the wall; so, the amount of absorbed water is limited.

- In the Netherlands 1 hour of rain shower is counter balanced by 15 hours of drying.

Case: rain penetration problems in the Windmill at Maassluis

In a number of consulting projects this view has been chosen as a guidance to solve rain penetration problems; this appeared to be successful. One of the cases the windmill at Maassluis showing serious rain penetration problems. Will be elaborated.

Starting conditions

The starting conditions of the masonry were as indicated in Fig. 5. From this figure can be deduced that an attempt was made to protect the wall against moisture penetration: at the outside face of the wind mill a water repellent was applied; the repointing consisted of a dense cement mortar, showing interface micro-cracks as a result of shrinkage, at the inner face a dense cement plaster.

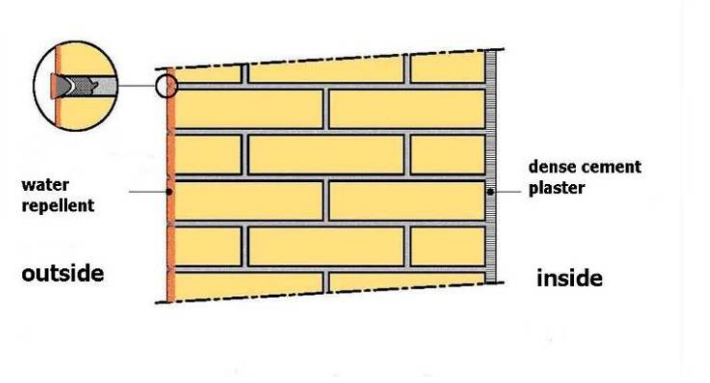

Fig. 5 Cross section of the wind mill wall before intervention: at the outside face a water repellent was applied, at the inside a dense cement plaster, the pointing consisted of a dense cement mortar.

It is clear that if the wall absorbs through e.g. micro-cracks moisture, this moisture is more or less entrapped as drying is hindered at the inside face and is very slow at the outside face.

In order to obtain data on the moisture content situation in the wall moisture profiles were determined at two places in the wind mill wall, using powder samples.

Fig. 6 shows that the moisture content in the wall, in spite of the protecting measures (water repellent, dense plaster layer) is very high.

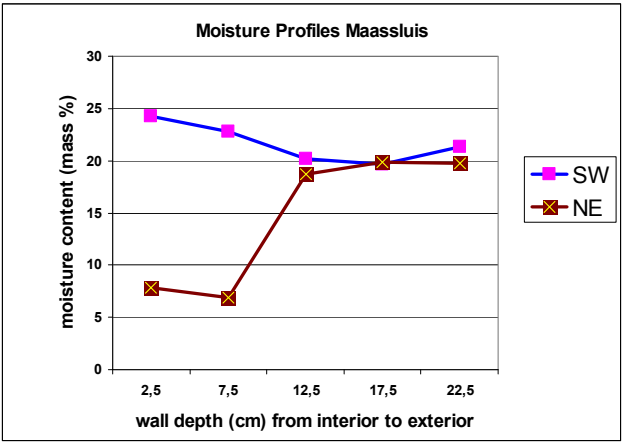

Fig. 6 Moisture content profiles at the south-west side (rain side) and the north-east of the wind mill wall [7].

Drying measures

In a process of more than 2 years measures were taken to change the situation from moisture absorbing to drying; to this end the following was done:

- removal of the plaster
- 2 years of drying
- meanwhile,
    - application of a simple ventilation system inside de wind mill
    - removal of pointing mortar and replacement by an open good drying mortar, compatible to the substrate
- After 2 years: application of a new restoration plaster with high porosity and good drying properties.

Monitoring moisture content over the years in wall of wind mill wall at Maassluis

In order to verify the effectiveness of r the measures taken were moisture content measurements were performed over the years. To this end a TRIME sensor was used [8].

The TRIME technique (Time Domaine Reflectometry with Intelligent Micromodule Elements) enables the measurement of a reflection of a pulse that travels in a material. Instrumental to the introduction of the pulse into the material are two antennas at the side of the probe (Fig. 7). These antennas are by means of expansion springs in contact with a tube that is glued to the material.

The travelling time of the pulse up and down the conduction rods and into the material provides information about the presence of water in the material, as the travelling time is a function of dielectric properties of the material.

The tube remains in the wall; the moisture content in the wall is monitored by taking measurements from time to time in the course of the years.

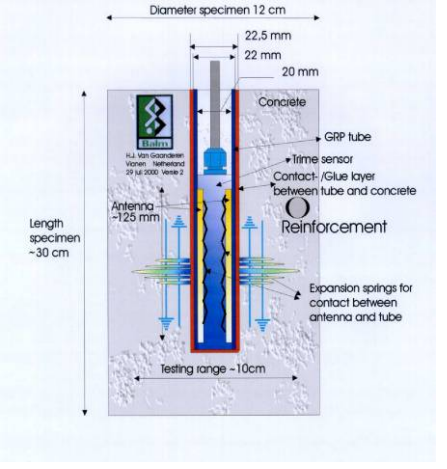

Fig. 7 Left: graphic presentation of TRIME sensor

The measurements showed that a significant drying of the wall took place in the course of a period of several years.

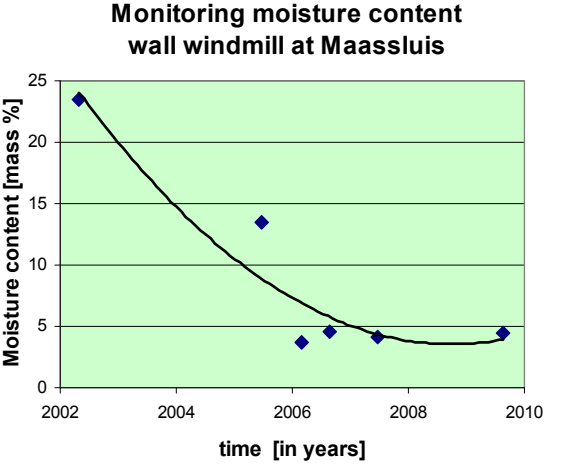

Fig. 8 Drying over the period 2002-2010, monitored using a TRIME sensor.

4 Conclusions

From study of field cases and the execution of several test cases the following could be concluded:

Protection against rain penetration ("rain coat" concept)

Many measures (render, tar, thatch, tiles, ivy etc) to realize the "rain coat" concept are not suitable in cases of historic masonry where change of visual appearance is not acceptable.

Protection of the outside face of the masonry by a transparent water repellent and a dense plaster on the inside has often unexpectedly resulted in a significant *increase* of moisture in the wall.

Specifically in historic masonry possible salt damage as a result of the application of water repellent should be considered.

Accepting rain penetration, promoting drying ("breathing" concept)

In the "breathing" concept rain penetration is accepted and drying is aimed at through the skilful application of materials with good drying characteristics and improving drying conditions (ventilation). A basic condition is that there is capillary moisture transport (preliminary injection may be needed).

It was proven in test cases that this approach resulted in a significant drying of walls; even in case the outside face of the wall still contained water repellent and only the pointing was replaced by adequate good drying repointing material and at the inside of the wall the dense plaster was replaced by high porous restoration plaster.

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IV.19

Durability to Salt Decay of Commercial Ready-Mixed Mortars for the Conservation of Cultural Heritage

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Abstract The durability of some commercial ready mix mortars used for repair of historic masonry to salt crystallisation was studied using the salt crystallisation test produced by a RILEM TC. The mortars were previously characterised by chemical and physical tests and some wallettes were made by the same type of bricks and the studied mortars. The specimens were submitted to the crystallisation test and their damage memorised by visual inspection and y the use of a profilometer. The results of the durability tests are reported and discussed with a comparison to the pore size and distribution of the mortars.

1 Introduction

There is no doubt that salt decay is one of the most dangerous phenomena which can seriously compromise the conservation of historic materials of the cultural heritage, especially in Mediterranean countries. The related decay mechanisms have already been investigated and discussed in several studies, as well as the influence of many factors affecting salt movement, crystallization location and degradation rate [1, 2]. Among others, researchers have pointed out the great importance of the compositional and microstructural features of porous materials for the evaluation of their salt-decay attitude and the need for further experimental work on different substrates.

The present work reports the investigation on NHL binders and on commercial ready-mixed mortars for the conservation of cultural heritage. A considerable number of these products are currently available in the market and their use is increasing, as they may represent a convenient alternative to the preparation of traditional lime-based mortars. Nonetheless, a thorough knowledge of their

characteristics and durability is still missing. It is therefore quite difficult to predict their behaviour at work, especially when new materials are introduced in a heterogeneous system, as masonries of built heritage almost always are. A complete characterization of the compositional, mineralogical and mechanical features have been performed by means of a wide range of techniques, including optical microscopy, XRD, FTIR, SEM. As the relevance of salt-induced decay is known to be strongly related to the microstructure of porous materials, porosity measurements have been carried out as well.

RILEM MS-A1 pre-standard procedure has been strictly followed for the evaluation of salt resistance to sulphates of tested commercial materials. Damage evolution of wallettes has been monitored by visual observation and by quantification of material loss from the surfaces after several imbibition/drying cycles. Remarkable differences in the damage extent and in the decay patterns have been observed, depending on the characteristic features of the different mortars.

The results of the experimental investigation are reported in the following sections together with a comparison between the durability of the studied mortars.

2 NHL Mortars characterisation

Four ready-mixed commercial mortars and two commercial binders were selected. All products are intended to be employed for restoration purposes, are classified as cement-free, with a minimum content of soluble salts and are based on NHL binders. Samples MA, MB, MC, MD refer to the ready-mixed mortars, while samples LA and LB refer to the commercial binders. Materials characterisation of each product was performed both on anhydrous raw materials and on hardened mortars samples by means of: stereomicroscopy; X-ray diffraction; FT-IR spectroscopy; ionic chromatography; optical microscopy of thin sections observed under visible light and UV light; SEM+EDX analysis. The related results have been thoroughly reported in previous works [4, 5] and are here only summarized.

Concerning the powdered raw materials, the main binder phase in most of the analyzed samples is Larnite. It is a di-calcium silicate (Ca_2SiO_4) analogous to C_2S, which is typical of NHL compositions and responsible for the hydraulic behaviour of the binders. Larnite is associated to portlandite ($Ca(OH)_2$) in the composition of all samples, expect for MD. Sample MA, differently from all others, only shows the presence of portlandite while no Larnite is traced. Aggregates of the ready-mixed products are quite heterogeneous: quartz and calcite are the most diffused mineral phases, which are present together with plagioclase, mica and dolomite. MC has a predominant carbonatic aggregate.

Analyses of samples from the hardened mortars provide further compositional and micro-structural information. Mortar MA has residual non hydrated C_2S

grains uniformly dispersed within the matrix and a high amount of fine grained calcite is present as carbonatic filler. The hardened matrix of MB is very compact and very rich in partially reacted slag fragments which contribute to the hydraulic behavior. Therefore, this mortar should be properly defined as a slag-lime mortar, rather than a NHL-based one. C_2S is the main hydraulic phase traceable in the binding matrix of mortar MC, but few C_3S grains are present as well. The presence of an air-entraining additive in this mix leads to a peculiar microstructure with small and regular rounded shape pores. MD has a compact binder with only few residual not hydrated C_2S grains dispersed in the matrix. Samples LA and LB, which are prepared mixing together commercial binders and standard quartz-siliceous aggregate, show predominant C_2S and few C_3S grains in the hardened mortars. Moreover, in LB binder composition a carbonatic filler is present.

On the hardened mortar specimens porosimetry analyses were carried out by mercury porosimeter. In Table 1 the total porosity and the average pore radius in volume are reported.

The initial salt content of the commercial products was assessed before the crystallization test. Soluble salts content is very low for MA and MB, it increases respectively for MB, MC, LB and reaches the maximum value for LA. Sulfates are the prevalent ionic species detected and LA alone shows a predominance of chloride.

Table 1 Porosity and Median Pore Radius (Volume)

Type of mortar	Porosity [%]	Median Pore Radius (Volume) [µm]
MA	30.37	0.05
MB	26.48	0.16
MC	27.08	0.43
MD	34.26	0.66
LA	22.59	0.27
LB	21.42	0.20

3 Experimental

The adopted crystallisation test is useful to verify in laboratory the performance of brick/mortar systems, such as re-pointing mortars or surface treatments on a masonry support, reflecting the site situation. The aim of the test is also prevention, design and quality control of jointing and pointing, or even control of surface treatments. This means that it can be carried out to choose compatible mortars for repair and for pointing or the right surface treatments but also to control the jointing and pointing execution on samples cored on site. Different types of bedding mortars can be tested with the same types of brick, in order to choose the most appropriate ones.

3.1 Test procedure

The test was carried out according to the Recommendation RILEM MS A.1 of RILEM TC 127-MS. [6]. The wallettes (approx. 250x200x120 mm) (Fig 1a), were put in contact with their back side with a 10% (w%) Na_2SO_4 solution (anhydrous Na_2SO_4 reagent grade, Fluka) and then stored over a layer of dry gravel in a plastic container (open at the top, sealed along the borders) with the upper face exposed to the environment (controlled laboratory environment of 20°C and 50% R.H.).


a)

b)

Fig. 1 Wallettes: a) out of the container; b) adding de-mineralised water

After four weeks the first crystallization cycle was concluded, wallettes were subjected to a) visual inspection, b) cleaning from efflorescence and detached materials with a soft brush and a vacuum cleaner, c) photographic survey, d) description of the observed damage, e) reading of the surface profiles by means of a laser profilometer which allowed to quantify the damage. De-mineralised water was then added and new 4-weeks cycles began. (Fig. 1b)

3.2 Materials choice and preparation of the specimens

Each wallette consisted of three courses of bricks with two horizontal bed joints and a vertical one (Fig. 1a). A red soft-mud brick of high porosity, used for restoration was selected.

Commercial NHL binders were mixed with clean standard aggregate with a 1:3 B/A ratio (w/w) and then added with pure water. Anhydrous ready-mixed products were just added with the correct amount of pure water according to the indication of technical data sheets. All mixing operations were conducted under controlled conditions with the aid of a mortar mixer.

3.3 Damage measurement by laser profilometer

A laser profilometer was used to monitor the damage (Fig. 2) [7]. The use of the laser profilometer allows to measure, with a very good resolution, the loss of material from the exposed surface calculated at subsequent times.

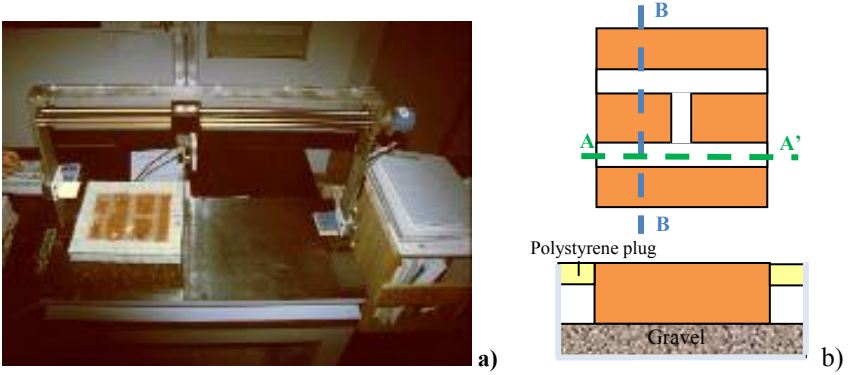


Fig. 2 Damage measuring device: a) lasers profilometer, b) scheme of the measurement.

Profiles recorded at the end of each 4-weeks cycle show how the surface is changing during time due to the progress of the decay and the loss of material can be measured [8]. The results can be also used for probabilistic interpretation of the progressing damage for prevention [9].

4 Discussion of the Results

Visual inspection continuously made during the tests revealed some common behaviour of the mortar joints. Since the first days soft efflorecences in the shape of needles appeared on the surface of MA, MD (Fig. 3a). In other cases efflorescence appeared at the interface brick-mortar joint (Fig. 3b). Later on, one month after the test beginning some bricks suffered delamination (Fig. 3c).

During the first and the second cycle of the test the highest loss of material as powderingor crumbling occurs. At the end of the second cycle the damage seems to stabilise; in fact a phenomenon of local spalling and delamination takes place.

Fig. 3 Distribution of efflorecences on different wallettes during the first cycles

The most critical situation is represented by the MA specimen, on which the spalling appears to be the most evident even at visual inspection (Fig. 4). This

behaviour could also be measured monthly by the laser profilometer as shown graphically in Fig. 5.

Fig. 4 Surface of MA wallette after 4 weekly cycles: before (a) and after (b) brushing (c) detail of MA wallette after 4 weekly cycles: severe scaling of the mortar can be observed**.**

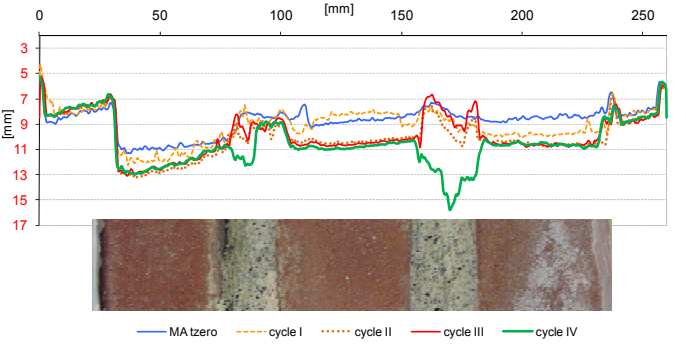


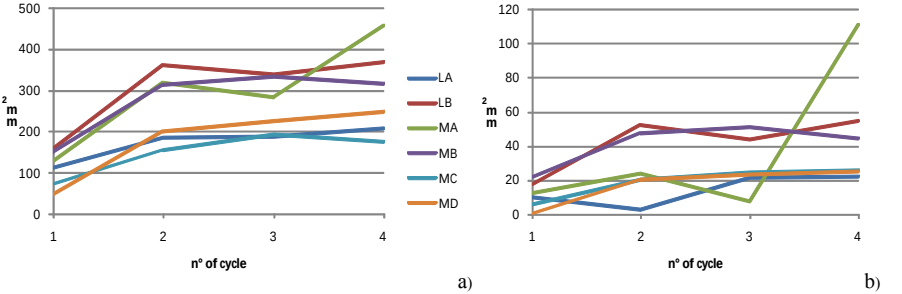
Fig. 5 Damage evolution of the wallette MA during the test: progressive loss of material recorded by laser profilometer at the end of each 4-weeks cycle

The loss of the area recorded by the profilometer can be assumred as a parameter of the continuous damage and even be used for the implementation of deterministic or probabilistic mathematical models to predict the material behaviour under salt crystallisation damage [9]. In Fig. 6b, two damage diagrams (area lost at each measurement in mm^2). The values were obtained by elaborating the data given by the profilometer for the brick-mortar profile and for the mortar joint. The curves show that the specimen MA was the most damaged.

In the diagrams, apparent increase in the measured areas corresponds to bulging of the surface at the starting of delamination and spalling.

The damaged caused by the salt crystallisation is due to the fatigue caused to the material by the repeated cycles which induce a damage to the microstructure of the material itself. The mortar is a porous material and its decay mechanisms induced by the salts crystallising into the pores are influenced not only by the porosity characteristics, but also by the pore distribution which varies from material to material.

In Fig. 7 the pore size distribution measured by mercury intrusion is shown; it can be easily observed that only for the specimen MA the pore size distribution occurs between 0.002 and 0.6 µm



a) b)

Fig. 6 Damage evolution: loss of material recorded at the end of each 4-weeks cycle: a) from brick and mortal profile; b) from the mortar joint (mm^2)

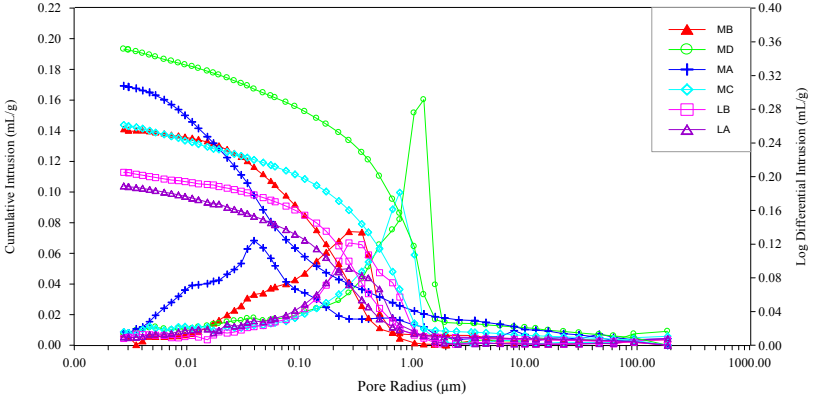


Fig. 7 Cumulative intrusion and pore size distribution by mercury intrusion

5 Conclusions

Binders and premix products based on hydraulic natural limes put on the market as "mortars for restoration" represent a large interesting field for the conservation of historic masonry. The studied mortars were chosen on the base of the so called Technical Forms prepared by the producers. The mortar characterisation by laboratory tests revealed the differences between the studied products. These differences cause in the hardened mortars composition, microstructural and mechanical properties highly variable between the products.

As a consequence the durability of the mortars and their influence on the durability of the wallettes prepared in laboratory is highly variable.

The evaluation of the mortar durability remains a complex objective as it is a function of a high number of parameters for which it is difficult to define a priority order.

The possibility of defining guidelines based on technical requirements commonly chosen also with the producers and able to address a compatible choice of the mortars, is the aim of the research which is still under development and has already given some reliable results.

6 Acknowledgements

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IV.20

Design of Jointing Mortar Compatible with the Masonry of the Villa Maheddine of the "Ottoman Era"

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Abstract The estate villa Mahiédinne is a historical monument belonging to the municipality of Sidi M'Hamed (Wilaya of Algiers) which dates back to the Ottoman era. The field of villas is in a state of advanced degradation, with defects in the plaster, cracks, the use of poor jointing mortar and the use of coating with cement, being apparent. This work aims to address some of the damage by making a jointing mortar compatible with the masonry used. The basic mixes are composed of sand (0/3), tuff (the percentage of which is calculated to have a continuous size distribution of mixed sand + tuff), air lime (CL90), and a series of mortars based on mixed hydraulic lime NHL2 and NHL5, and a series of mortars based on cement CPJ-CEM II 32.5 and 42.5. Mortars were prepared with super-plasticizer (MEDAFLOW 30). The consistency of the mortars, setting time, compressive strength and flexural strength where all analysed and compared. Following the results, the mortar made from air lime seems to be the most appropriate or closest to the historic masonry, although it has a relatively low mechanical strength. This handicap can be improved by adding to the composition a certain percentage of hydraulic lime; the content of which varies depending on the environment and characteristics specific to a building.

1 Introduction

The mortars used for new construction are not suitable for old masonry due to their high content of Portland cement, which confers on them a density, compressive strength and relatively high hardness; properties which do not allow them to act as mixtures compatible with the old materials, hence the need to use a

softer mortar offering less resistance to compression and more flexibility than the masonry units, therefore allowing the mortar to accommodate minor movements of the building. In the case of important movements, a soft mortar will support the disorders and will sacrifice itself for the benefit of maintaining the integrity of the masonry units. It is easier and cheaper to repair the mortar joints than to replace a deteriorated stone. It is under this perspective that the authors have undergone work to design a jointing mortar compatible with the old masonry.

The estate villa Mahiédinne also called Djenane Mahiédinne belongs to the commune of Sidi M'hammed of Algiers, which dates back to the Ottoman era. The whole villa consists of three elements: A house and its annexes situated around a courtyard, a group of two houses with shared access to a courtyard bordered by a double portico with a sea view, and a house located in the space between the previous two groups of houses. Fig. 1 shows the ground plan of the Mahiédinne villa. The houses dating from the Ottoman era are built in a traditional system with supporting walls; they are built from masonry with a mortar made of clay and lime (fig. 2).

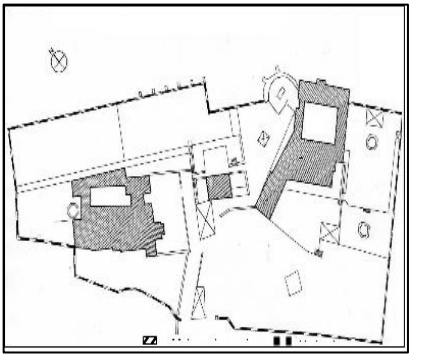

Fig. 1 Ground plan of Mahiédinne

Fig. 2 Construction system of brick with lime mortar

The two villas are in an advanced state of deterioration with defects such as coatings and cracks in many of the mortars. In most of the restoration work required, the first step was to remove the old mortar, which makes the existing masonry more vulnerable and weakens it further.

The use of cement mortar (from earlier work) on the old masonry was not compatible and made the wall vulnerable to degradation (figs. 3 and 4). The primary factor in the degradation of the masonry of the villa Mahiédinne is moisture (figs. 5 and 6). Moisture infiltration was in one of three formats;

- 1) Rising damp from the ground up by capillary action in the masonry walls and the floors.
- 2) The humidity caused by the infiltration of rainwater which is most prevalent in the walls exposed to the prevailing winds. On the edge of the sea, this action

is compounded because the rain is responsible for removing the salt spray on the masonry, the walls then become hydrophilic and hold water.

- 3) Moisture infiltration through accidents or lack of maintenance on the roof (eaves, gutters or downhill) or pipes (risers, falling water, etc.); such infiltration is often not immediately detected. This moisture is also the source of algae, moss and vegetation.

Fig. 3 Use of cement mortar

Fig. 4 Detachment of cement mortar

Fig. 5 Lichen on the external wall

Fig.6 Moisture in the external wall

2 Materials testing methods

2.1 Sampling

Samples were collected as fragments of mortars from the ground floor and first floor of the villa (figs. 7 and 8). The following figures were calculated from the samples:

pH: Direct measure of free (H +) ion concentration in aqueous solutions with a pH meter with a precision of 0.01.
μv: Apparent density (g/cm3), following the standard (NF P98 250-6)
μs: specific density (g/cm3), measured by the pychnometer method
AA (%): water absorption percentage (wet weight-dry mass) / dry mass (%)
P (%): calculated open porosity percentage
The mineralogical composition was determined using the powder method with X-ray diffraction (XRD) (philips, type PW1710).

Figs. 7 and 8 Sampling of mortar

2.2 Characteristics of sand and tuff used in these formulations

The module fineness and percentage of clean sand and tuff was calculated according to the procedure outlined in the standard NF P 18598; the results are given in table 1. The mixing curve, as determined by the standard, was deemed suitable for the sands used in mortars.

Table 1 Fineness and clean sand and tuff

Module of Fineness		Clean sand and tuff	
Sand	2.92%	Esp sand	92%
Tuff	1.22%	Esp tuff	74%
Mixture	2.67%	Esp mixture	86%
Results	average sand	Result : satisfied	

2.3 Preparation of mortar compositions

The base mixes are composed of sand 0/3, tuff (the percentage is calculated to have a continuous size distribution of mixed sand + tuff) and hydrated lime; one mixture was made with NHL 2 (composition CA) and another with NHL 5

(composition CB), with a further series of compositions being based on the cement CPJ-CEM II 32.5 (composition CC) and CPJ-CEM II 42.5 (composition CD). The composition of mortars prepared for analysis and study are given in tables 2, 3 and 4. The optimal dosage of dry super-plasticizer added (MEDAFLOW 30), to the compositions was 0.40 %.

Table 2 Composition of NHL 2 based mortars

	Composition in volume	CL 90 (%)	NHL 2 (%)	Sand (%)	Tuff (%)
CA	CA 01	33	-	57	10
	CA 02	23	10	57	10
	CA 03	15	17	58	10
	CA 04	5	25	60	10
	CA 05		30	60	10

Table 3 Composition of NHL 5 based mortars

	Composition in volume	CL 90 (%)	NHL 5 (%)	Sand (%)	Tuff (%)
CB	CB 01	23	10	57	10
	CB 02	15	17	58	10
	CB 03	5	25	60	10
	CB 04	-	30	60	10

Table 4 Composition of mortars based on cement

	Composition in volume	CPJ-CEM II 32.5 (%)	CPJ-CEM II 42.5 (%)	CL 90 (%)	NHL 2 (%)	Sand (%)	Tuff (%)
CC	CC 01	33	-	-	-	57	10
	CC 02	-	33	-	-	57	10
CD	CD 01	22	-	11	-	57	10
	CD 02	22	-	-	11	57	10
	CD 03	-	22	11	-	57	10
	CD 04	-	22	-	11	57	10

3 Results and discussion

3.1 Physical Proprieties and Mineralogical results of collected mortars

The physical proprieties are given in table 5 and the mineralogical composition given in table 6.

The XRD analysis shows that the composition of the mortar is: calcite, quartz, albite, muscovite and potasum tectosilicate. The constituents of the raw materials that have made this mortar are: air lime, sand, ground bricks and clay. The nature of composition and method of preparation influenced the apparent density, specific density, water absorption, pH and open porosity of the mortars.

Table 5 Physical proprieties of mortar

Samples	Mv (g/cm3)	Ms (g/cm3)	Po(%)	AA(%)	pH
Sample 01	1.93	2.64	23.12	18.72	9.12
Sample 02	1.81	2.52	21.75	17.94	8.86
Sample 03	1.69	2.34	22.85	18.42	8.92
Average	1.81	2.50	22.57	18.36	8.96

Mv: Apparent density (g/cm3), *Ms*: specific density (g/cm3), *P* (%): calculated open porosity percentage, *AA* (%): water absorption percentage (wet weight-dry mass) / dry mass (%).

Table 6 Mineralogical analyses of mortar

Samples	Minerals
Sample 01	Quartz, muscovite, calcite, albite
Sample 02	Quartz, potassum tecto alumino silicate, calcite
Sample 03	Quartz, muscovite, calcite, albite, rutile

3.2 Measurement of the consistency of mortars

The consistency or spreading the mortar is measured by the shaking table, following the standard (NF P15-437). The mortar, after being introduced and removed from the mould, receives 15 shocks in 15 seconds. Measurement of the diameter of the wafer is thus obtained.

3.3 Measurement of setting time

Table 7 Setting time of samples

Composition with superplasticizer	Setting time	
	Initial setting time	Final setting time
CA (CA 01)	7h	12 h
CB (CB 04)	2 h 40 min	5 h 45
CC (CC 01)	2 h 30 min	3 h 45
CD (CD 01)	2 h 40 min	3 h 55

For the measurement of setting time the standard NF 48062 was followed. A single composition per set (representative of the series) was chosen for analysis; the results are given in table 7.

3.4 Measurement of shrinkage

For withdrawal measurements the standard NF P 15 6433 was followed. A single composition for each series was analysed, the results are shown in table 8

Table 8 Measurement of shrinkage

Composition studied	Shrinkage (with adjuvant %)	Shrinkage (without adjuvant %)
CA (CA 01)	0.006	0.4
CB (CB 04)	0.007	0.6
CC (CC 01)	0.014	0.9
CD (CD 01)	0.008	0.7

3.5 Measurement of mechanical properties

3.5.1 Measurement of the flexural and compressive strength of collected samples

The mortar samples taken from the villa were reduced to a standard form (4cm x 4cm x 16cm). The flexural strength was determined by three-point loading to failure. The fragments obtained after the flexural tests, were used for test cuts. The results are given in table 9

Table 9 Mechanical proprieties of site samples

Sample	Flexural strength (N/mm2)	Compressive strength (N/mm2)
1	12.2	17
2	10.1	10
3	14.6	12
Average	12.3	13

3.5.2 Measurement of flexural strength and compressive strength of samples made in the laboratory

For the compositions studied, a super-plasticizer with a dry dosage of was selected to reduce the spread to 100% (decrease of E / L to 0.3) to get the best qualities of the mortar.

The results obtained are shown in tables 10 and 11. The mechanical strength of the mortars studied evolves over time to reach a maximum value after 90 days. However, the hydraulic mortars reached more than 80% of their resistance before 28 days.

Table 10 Changes in value of flexural strength (bar) over time

Mortar Compositions	7days	28days	90days
CA 01	11.12	26.50	59.20
CA 02	15.30	34.80	55.25
CA 03	00.0	7.50	14.80
CA 04	00.0	11.40	18.20
CA 05	05.80	21.18	25.20
CB 01	00.0	12.10	20.00
CB 02	00.0	02.50	26.15
CB 03	06.8	28.10	32.50
CB 04	10.12	30.15	35.10
CC 01	29.12	30.12	35.10
CC 02	31.50	38.45	49.15
CD 01	30.10	35.10	41.10
CD 02	34.15	40.00	48.15
CD 03	49.10	50.00	54.10
CD 04	40.00	54.15	55.10

Table 11 Changes in value of compressive strength (bar) over time

Mortar Compositions	7days	28days	90days
CA 01	11.10	28.10	49.15
CA 02	15.20	35.10	55.20
CA 03	18.15	39.15	59.70
CA 04	23.80	55.20	70.10
CA 05	34.85	81.10	95.50
CB 01	24.50	49.50	54.35
CB 02	25.10	90.10	112.20
CB 03	30.15	125.10	150.15
CB 04	48.10	165.15	199.10
CC 01	280.15	380.10	430.10
CC 02	390.10	480.15	510.35
CD 01	180.15	280.25	300.00
CD 02	200.00	320.95	330.20
CD 03	350.10	380.20	390.25
CD 04	300.25	390.25	395.35

Mortars based on CPJ-CEM II 42.5 (CD) have the greatest resistance to compression followed by those based on CPJ-CEM II 32.5 (CC) and those containing hydraulic lime (the NH5 (CB) and NHL2 (CA)). These mortars have a hydraulic jack and an air outlet according to the percentage of lime they contain.

If the difference in compressive strength between the different compositions is in favour of those based on hydraulic binders; with the resistance to flexion they are all equal.

3.6 Imbibition and capillary porosity

To observe the effect of mortar joints on the continuity of hydraulics, cylindrical bricks of collected mortars (D = 40mm H = 80mm W=5mm), prepared using a core drill, were cut into two parts following of same height (H = 40 mm).These samples (after 90 days of ripening) were placed in a sealed tank in which the level of distilled water was kept constant throughout the test. At increasing time intervals, samples were weighed and the height of the capillary absorption measured with a digital calliper. The results are presented at the Table 12.

Table 12 Summary results of tests of imbibitions and capillary porosity (AFNOR B10-613)

Mortar Compositions	A1 ($g.cm^2.min^{1/2}$)	B1 ($cm.min^{1/2}$)	A2 ($g.cm^2.min^{1/2}$)	B2 ($cm.min^{1/2}$)	Capillary Porosity	
					1st zone	2nd zone
CA 01	0.054	0.299	0.045	0.248	18.06	18.01
CA 02	0.055	0.292	0.030	0.184	18.39	16.02
CA 03	0.051	0.281	0.024	0.156	18.15	15.23
CA 04	0.072	0.306	0.024	0.151	23.53	16.03
CA 05	0.054	0.298	0.017	0.128	18.12	13.19
CB 01	0.060	0.301	0.032	0.171	19.93	18.53
CB 02	0.063	0.283	0.030	0.146	22.26	20.42
CB 03	0.055	0.288	0.021	0.138	19.10	15.26
CB 04	0.060	0.302	0.014	0.093	19.87	14.78
CC 01	0.050	0.280	0.0002	0.010	17.86	02.33
CC 02	0.063	0.302	0.0002	0.010	20.86	02.02
CD 01	0.056	0.295	0.0038	0.044	18.98	08.54
CD 02	0.065	0.310	0.0023	0.032	20.97	07.22
CD 03	0.054	0.284	0.0031	0.039	19.01	08.03
CD 04	0.064	0.304	0.0019	0.029	21.05	06.61

The imbibition coefficients A and B correspond to the slopes of the weight gain and capillary rise from the front according to the square root of time. If the imbibition front is homogeneous (horizontal well), the two coefficients A and B may be related to the porosity accessible to water by capillary rise (Nc) which is the volume occupied by water compared to volume of material during imbibitions, as seen by:

$$A = \rho_{water} B N_C$$

The results show that there is a dispersion in the properties of imbibitions between the samples. Nevertheless, hydraulic continuity is created between the modified parts of the cylindrical sample of interest.

The water begins to rise in the first zone of the brick drawing a line that reflects the homogeneity of the material. There is then a discontinuity more or less acute depending on the composition of the mortar studied. The kinetic capillarity is less strong if the mortar contains more hydraulic binder and water conditions of the latter.

4 Conclusion

The results show that the air lime mortar seems to be the most appropriate, even if it has a relatively low resistance. This handicap can be solved by varying

the percentage of hydraulic lime, depending on the circumstances and characteristics.

The CA01 composition (33% air lime CL90) shows the best value of flexural strength after 90 days. The CA05 composition with 30% hydraulic lime (NHL2), the CB02 composition with 15% air lime and 17% hydraulic lime (NHL5), and CB04 composition with 30% hydraulic lime (NHL5), show a compatible value of compressive strength with old masonry.

Following the results and comparisons with the collected mortar, CA01, CB02 and CB03 compositions are recommended for restoration purposes.

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IV.21

Water Transport between Mortar and Brick: the Influence of Material Parameters

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Abstract This article deals with the parameters and governing mechanisms of the early water transport between mortar and brick. Two bricks with different transport parameters were used in combination with two different mortars: a lime hydrate mortar and a cement mortar. Water transport was monitored during the first two hours after contact using X-ray imaging and modelled using the finite element code Hamfem. The amount of desorbed water after two hours depends more on the mortar than on the brick. The rate of flow across the interface shows a complex behaviour in the experiments, which is not entirely captured by the model: there is an overshoot in flow, followed by a reversal of flow direction. The accuracy of simulations is also limited by the importance of over-capillary effects in the bricks near the interface. It appears that this over-capillary water is only partly distributed over the brick, and partly reabsorbed by the mortar.

1 Introduction

The importance of early water transport from mortar to brick for the workability during bricklaying and the mortar-brick bond of the hardened masonry has been reviewed and discussed in [1]. A mortar should lose some water in order to be compacted and gain stiffness, but at the same time this shouldn't go too fast because in that case correct placement of the brick could become difficult. If too much water is desorbed, the left-over quantity may be too low to provide for complete hydration of the binder [2].

Recent research has focused on water transport across interfaces in hardened masonry [3, 4] as well as in the fresh state of the mortar [1, 5-7]. Moisture profiles have been recorded either by neutron transmission [1], NMR [3, 6], or X-ray

radiography [2, 4]. X-ray radiography was demonstrated to give reliable results with a sufficient moisture content resolution and spatial resolution [8].

The numerical solution of the problem can be done using discretised transport equations in a FEM or CVM solver, or by simplifying the problem to a sharp-front analysis. The latter is successful when capillary uptake from a liquid surface is studied [4], but it cannot predict cases where the water supply is limited and more smooth moisture contents gradients can be expected. Discrepancies between observations and model results are often observed in the interfacial zone.

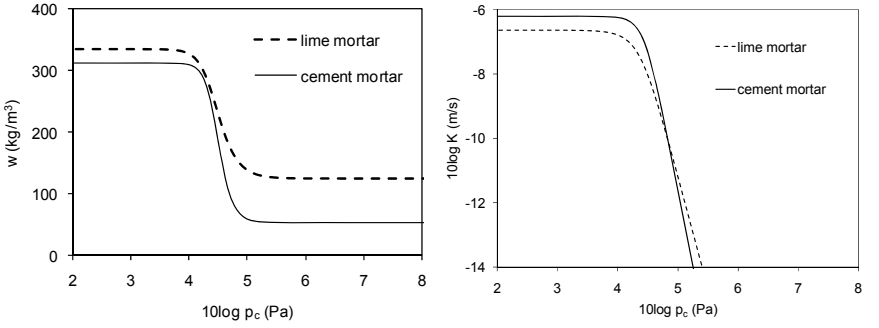
Up to day the lack of a reliable experimental method to measure the water retention curve and permeability of fresh mortar has limited the possibilities for model calculations [6]. This has lead to rather speculative analyses based on observations on the hardened material. It has been demonstrated recently that a combination of pressure plate tests, suction tests and permeameter tests can provide the required data [9]. This article starts from these data to extend the discussion of the transport over interfaces to the fresh state of the mortar, in observations as well as simulations.

2 Materials: mortars and bricks

Two types of mortar were combined with two types of brick. The mortars are a lime hydrate mortar (Tradical 98, CL 90S, EN 459-1) and an ordinary Portland cement mortar (Schwenk, CEM I 42.5R, EN 169-1). The sand is a rather fine and fairly rounded siliceous sand of grading 0/0.5(0/1) according to EN 13139 (sieving procedure EN 933-1). The mortar compositions were derived from practical experiments with masons. Mix ratios and initial water content are given in Table 1. The origin of these data is documented in [2, 9]. Figs. 1 and 2 give the water content w [kg/m³] (water retention curve) and permeability K [m/s] as a function of capillary suction p_c [Pa]. The important difference between both mortars is that lime mortar retains more water, which is reflected in the smaller slope of the curve and higher residual water content.

Table 1 Properties of the mortars.

Composition parameters	*Lime mortar*	*Cement mortar*
Binder to sand mass ratio (kg/kg)	0.112	0.218
Initial water to binder mass ratio (kg/kg)	2.016	0.907
Initial water content (kg/m3)	334	313
Residual water content (kg/m³)	124	54

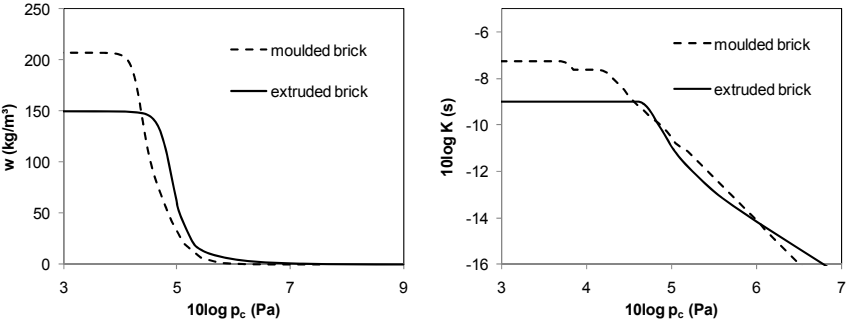


Figs. 1, 2 Water retention curves and permeability curves of fresh mortars.

The bricks are one extruded and one moulded fired clay brick. The extruded brick is custom made by Wienerberger. It is the least porous and medium absorbing (Table 2). The moulded brick is of type 'Spaans rood' by Wienerberger and has higher porosity and faster absorption. Determination of the hygric properties was done by vacuum saturation, mercury intrusion porimetry (water retention curve) and X-ray radiography (diffusivity, recalculated to permeability). These experimental techniques are documented elsewhere and will not be treated here [10, 11]. The water retention curves and liquid permeabilities are plotted in Figs. 3 and 4. The extruded brick has lower porosity but exerts higher capillary suction than the moulded brick, which is due to its finer pores. The permeabilities are comparable over a certain range of capillary pressure, but the capillary saturated permeability of the moulded brick is considerably higher. Permeability of the moulded brick was validated with a moisture uptake experiment.

Table 2 Properties of the bricks.

	Extruded brick	Moulded brick
Vacuum saturated water content w_{sat} (kg/m³)	209	323
Capillary saturated water content w_{cap} (kg/m³)	150	207
Capillary absorption coefficient (kg/m²s$^{0.5}$)	0.19	0.53



Figs. 3, 4 Water retention curves and permeability curves of bricks. Note that both quantities are given as a function of capillary pressure, which is the potential used in the numerical code, and that permeability is in units of time, corresponding to a description in mass fluxes.

3 X-ray observations

The test principle consists of placing a specimen between an X-ray source and a detector, which records the intensity of the transmitted radiation first in dry state (I_{dry}) and then in wet state (I_{wet}). The difference between the actual water content at time t and the initial water content is calculated from the difference in intensities according to [12]:

$$w = -\frac{\ln(I_{wet} / I_{dry})}{\mu_w d} = -\frac{\ln I_{wet} - \ln I_{dry}}{\mu_w d} \tag{7}$$

with μ_w [1/m] the attenuation coefficient of water, which was measured separately for cement water and lime water for these experiments, and d the thickness of the specimen. Details of specimen geometry, experimental setup and procedures can be found in [2].

The 2D array of moisture content points was converted to moisture fronts in the brick or the mortar by averaging over a band of not less than 100 pixels. The results of one out of two tests for each combination were selected and are plotted in Fig. 5. The image is limited to the brick; treatment of the mortar data is more complex and beyond the scope of this article. It can be observed that the moisture content near the interface is larger than the capillary saturated water content, whereas in the bulk of the brick, the moving moisture front does not reach this level. The movement of the front as a function of time is qualitatively similar for all cases, but it can be observed that the early fronts for the moulded brick are slightly ahead of those for the extruded brick. This is not the case for the later profiles. The transferred water amount is comparable for both mortars. This points however at very different behaviour, because the lime mortar has a much higher initial water content: it retains relatively more water. The zone of high water

content near the interface decreases over time: this is partly due to diffusion inside the brick, but possibly also to reverse water flow back towards the joint.

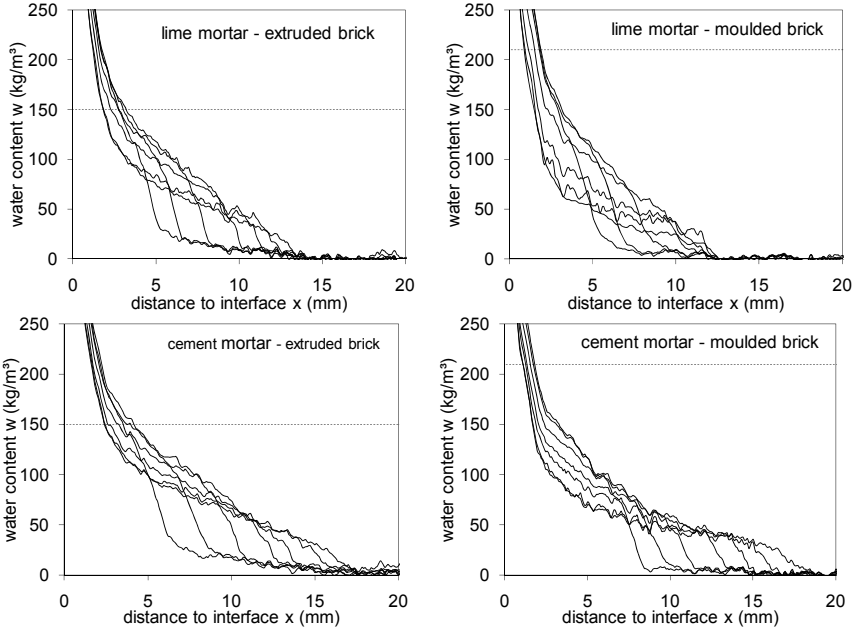


Fig. 5 Moisture fronts in the brick for four combinations of mortar and brick. The capillary water content is indicated with a dotted line. The curves are taken at t=1.5, 3, 6, 15, 30, 60 and 120 min.

4 Numerical modelling

Capillary liquid water transport was modelled using the FEM software Hamfem [13]. Vapour transport is neglected. The transport equation solved for each node is:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}(k \frac{\partial p_c}{\partial x})$$

with k the mass-formulated liquid permeability in [s] (K=k/g). A free capillary absorption test was simulated to validate the material parameters. Initial boundary conditions were: dry state for the brick and initial water content of the fresh mix for the mortar.

The results are plotted for all combinations in Fig. 6. They give a full view of the evolution in the mortar, which is difficult to derive from the measured images. Clearly visible water content gradients are developed within the lime mortar, but not within the cement mortar, which has a too high permeability. In the initial

stage the extruded brick gets loaded with water up to capillary saturation, but already after 1.5 min a decrease starts. The moulded brick does not reach capillary saturation, because of its high permeability (or rather diffusivity), which leads to the faster diffusion of the water. The moisture front proceeds faster and the maximum is lower.

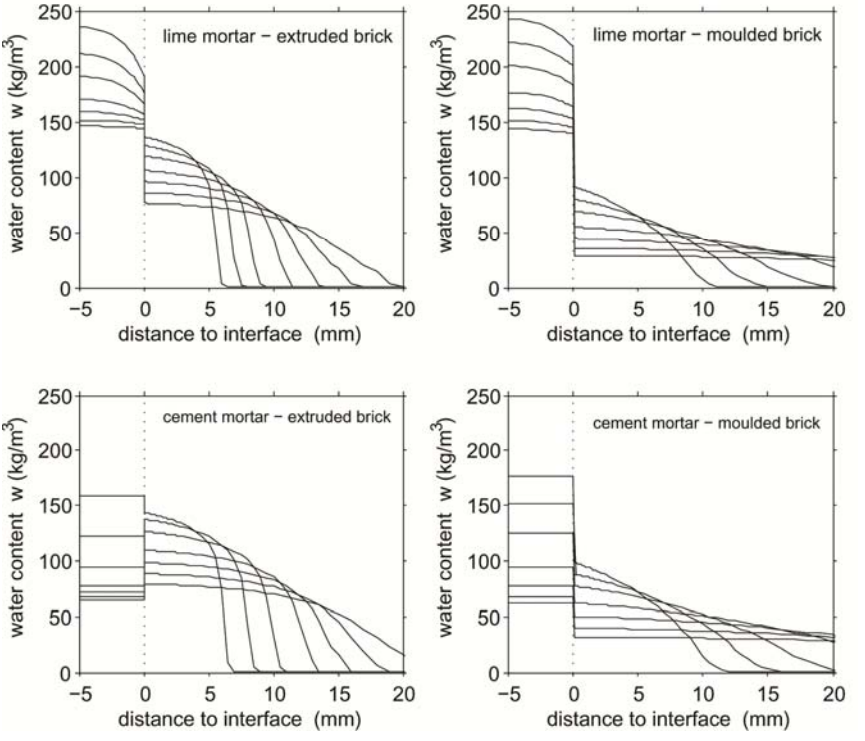


Fig. 6 Numerical calculations of moisture content in mortar and brick. The dotted line indicates the position of the interface.

Fig. 7 displays the calculated cumulative fluxes over the interface for all measurements and model calculations. Experimental fluxes were calculated as the integral of the moisture content curve in the brick, truncated at capillary water content. Two important differences between model and experiments can be noted:

- The observed over-capillary behaviour near the interface (see also Fig. 5) is not covered by this simulation tool. In most natural situations of water uptake the entrapment of air hinders full saturation, but in this case, with a mortar layer in direct contact with the brick and some pressure exerted on it, higher water content can easily be reached. It is exactly this over-capillary water which in the early observations lead to an overshoot, and in the later phase to an apparent reversed flow. Indeed it seems that, when the mortar develops an

increasing capillary suction, this over-capillary water (at very low potential) is available for backward flow.

- The diffusion within the bricks is slightly overestimated, especially in the moulded brick. In this context it can be noted that the permeability of the moulded brick is determined by using data from uptake, which explains why moisture uptake is more accurately modelled than redistribution.

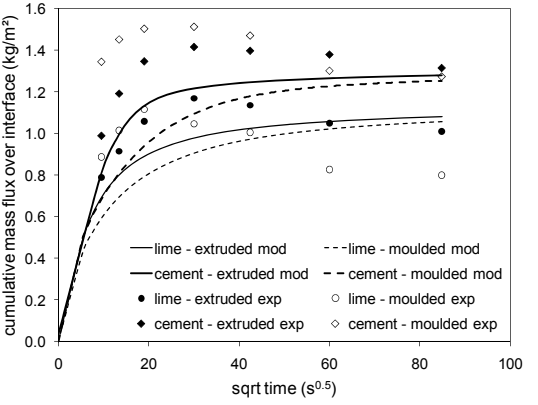


Fig. 7 Overview of water mass fluxes over the mortar-brick interface for all combinations measured and numerically calculated.

5 Discussion and conclusions

Experimental data of moisture transport properties of two fresh mortars and two bricks were used for the numerical calculation of early water transport between both. The results were verified with observations by X-ray radiography. The most important conclusions are:

- The model and the measurements agree fairly well on the shape of the moisture profiles and on the 120 minutes water content. This can be considered as a validation for the use of the selected material parameters, measuring procedures and model code.
- Some discrepancies between model and observations are related to over-capillary behaviour.
- The left-over water content in the mortar joint after 120 minutes depends mostly on the water retention properties of the mortar: the lime mortar retains some 60% of its initial water amount, the cement mortar only 30%. The influence of the type of brick is smaller.
- The modelled and measured fluxes across the interface are comparable in magnitude: it can be assumed that the interface resistance is small or non-existing. This is an important conclusion, which leads to the assumption that

interface resistances in hardened masonry are only developed during the hydration or carbonation reactions of the binder, upon the development of the capillary pores in the binder matrix. It is logical that there is no real discontinuity in porosity in the mortar's fresh state, while in the hardened state this will be the case.

6 Acknowledgement

Hans Janssen is kindly acknowledged for providing the parameters of the extruded brick and for his advice in using Hamfem software.

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IV.22

Roman Cement for the Production of Conservation Mortars

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Abstract Roman cement was patented in 1796 and used extensively throughout European architecture of the 19th and early 20th centuries before the domination of Portland cement and new architectural styles became established. It was characterised by a brown colour and a fast setting time, typically ~15 minutes. However, conservation of this architecture has received little attention and the former rich palette of cements is no longer available. Companion studies of historic mortars and the laboratory calcination of various raw materials have been undertaken. The historic mortars have been found to be both richer in cement than many modern mortars and generally utilised fine sands. Optimal cements have been produced at low temperatures, typically 750°C, and characteristic microstructural features of sub-optimal, optimal and super-optimal calcinations are described. Observation of these within the historic mortars indicates that the control of kiln temperatures was poor. Additionally, grinding of the historic cements did not always yield the grain sizes contained within contemporary specifications. The criteria for the production of Roman cements have been successfully re-established.

1 History of Roman cements and their mortars

1.1 Roman cement production

Roman cement was patented in 1796 [1] by James Parker in England and marketed under various brand names often related to its geographical location of

production. Indeed, Pasley [2] was particularly scathing of the use of the term Roman cement although the terminology was used throughout Europe. Production soon spread to France and then more widely across Europe and the USA. The British production was frequently in coastal regions using septaria or cement-stones won from the cliffs and beaches or dredged offshore; in contrast, most continental European raw material was mined from stratified marls. Suitable marlstones could be found in different geologic formations, including Eocene, Jurassic and Cretaceous. The key feature of Roman cement manufacture was that the source of calcareous and argillaceous minerals (typically some 25% clay) was found within the single source raw material rather than being blended to optimum proportions from separate sources, as occurs in the production of modern Portland cement. In this sense they share the same attribute as natural hydraulic limes. As a consequence, each cement reflected both the mineralogy and morphology of the source material yielding a wide range of compositions and properties as acknowledged by Hauenschild [3].

The marlstone was crushed to fist-sized pieces and usually fired in continuously operated shaft kilns with alternate layers of coal or coke; Hoffmann kilns are also reported to have been in use. Time and temperature of calcination was controlled empirically, and it was known that some marls, especially those containing elevated amounts of fluxing agents such as feldspars or iron oxides, needed shorter times and lower temperatures [3]. The calcination temperatures had to be high enough to largely enable the decomposition of calcite, but on the other hand sufficiently low to prevent sintering. The rate of cooling of the calcined clinker was slow as it was often allowed to cool in the kilns. Subsequently, it was ground to a fine powder before being packed into 250kg barrels or 60kg sacks. A short time of storage prior to packing was sometimes recommended to achieve slight retardation of the cement without any loss of quality.

Roman cement was characterised by its warm brown colour of various hues and a rapid setting. Most authors draw a distinction between rapid (<7 minutes), medium (7 – 15 minutes) and slow (>15 minutes) setting Roman cements. The invaluable Austrian standard of 1880, modified in 1890, specifies that the 28 day compressive strength of a quick (<15 minutes) cement to be > 6MPa and a slow (>15 minutes) cement to be >8MPa [4, 5].

1.2 Roman cement usage

By the second half of the 19th century Roman cement was in wide-spread use in both architectural and engineering construction in Central Europe as well as some northern countries. Its major application was in facade decoration as cast decorations or ashlar stones and in-situ applied renders or run elements (see Figs. 1 and 2). In addition to external stuccos, it was used for internal hardwearing plaster, particularly in cellars or areas of buildings to which the public had ready access [6].

Various volumetric compositions are recommended in the contemporary UK literature for stucco use, covering the range 1:0.25 to 1:1.5 of the cement to aggregate ratio [6 – 11]. By way of contrast, recommendations for the use of the French Vassy cement [12] are for leaner mixes in the range 1:1.5-2.5. Specifications for cast elements are less common and are confused by a lack of clarity in the literature as to whether the ratios are by weight or volume. However, typical compositions are located at the richer end of the spectrum cited above.

Fig. 1 Palais Epstein, Vienna (1868-72) Unpainted facades combine Roman cement renders & ornaments with terracotta elements

Fig. 2 Original cast decoration and rusticated ashlar blocks: private house, Vienna

Across Europe, there was variation in custom of either painting the facade surface or leaving it in imitation of natural stone. The English Harwich cement was a dark chocolate brown and was often covered by a light coat of limewash or oil paint. The imitation of terracotta or natural stone was a frequent intention when Roman cements were used in many of the Gruenderzeit facades in Central European cities and towns, where eventually uncoated cast elements were surrounded by painted renders. Towards the decline of this architectural style on the eve of World War I, even those elements seem to have been painted more frequently.

1.3 Decline of Roman cement

The decline in production of Roman cement occurred for various reasons, often related to local conditions. In the UK, over-zealous collection of the septaria from beach sources led to concerns about coastal erosion. This coincided with significant improvements in the performance of Portland cement in the mid 1850s. However, in the Austro-Hungarian Empire, Roman cement only went into decline in the years before the First World War as changes in architectural style towards a modern functionalism, with the absence of ornaments, became prevalent.

The conservation of Roman cement-based architecture has not received the same level of attention as that of lime-based construction. Only one natural cement has remained in production in Europe; that being Prompt produced by the

Vicat cement company in Grenoble, France. Hence, the once rich palette of materials is not available to modern conservators and compromises must be made. In response, the EU has funded two projects in order to re-establish the technology of production and use of this important range of materials.

2 Investigation of historic mortars

2.1 Condition of the facades

Despite over a century of urban pollution and generally a number of refurbishments, many examples of facades in good condition may be found in which even the finest of original detail has been retained. Where the surface has not been painted, a network of fine micro-cracks is frequently observed. These are probably a result of early age drying shrinkage and do not represent a structural threat to the facade.

In cases of the failure of drainage systems, e.g. guttering, or rising damp, decay of the facade may occur as a result of associated frost or soluble salt action. Additionally, inappropriate application of renders can be a cause of distress, e.g. application of Roman cement mortar on a substrate of softer and more porous lime mortars.

2.2 Mortar analysis

Samples (~50) of unweathered mortar from buildings in 6 European countries were taken with the intention of obtaining a better understanding of the aggregate mineralogy, mortar composition and mechanical properties. A further aim was to develop an insight into the composition of the binder phases in order to interpret the historic processes of cement production. This investigation was performed in parallel to a laboratory study of the calcinations of marls from various locations of 19th century Roman cement production. The details of analytical techniques and laboratory production of Roman cements may be found elsewhere [17 – 19].

2.2.1 Physical properties

A wide range of mortar composition was identified. However, there was a differentiation between cast mortars and renders with the typical aggregate weight being 20 – 25% and 40 – 50% respectively. After accounting for the likely hydration and carbonation of the cement over a period of some 150 years these equate approximately to 1:0.25 and 1:0.7, by volume, respectively which tend towards the richer end of the composition spectrum referred to earlier.

A wide range of aggregate grading was observed with those from the cast elements being coarser than those from renders; the general trend was for the use of fine sands. Whilst it is rare to find reference to sand grading in the contemporary literature there are some recommendations for the use of fine sand with Vassy cement and hydraulic lime and coarse sand for non-hydraulic lime [20, 21]. An interesting feature is the observation of bi-modal size distributions in some large cast elements. These particles were well-rounded; this contrasts with particles ranging from very angular to round for renders and small casts; similar variability in the mineralogy of aggregates was observed reflecting the local geological origins of the sands.

Weber et al [17] report a range of physico-mechanical properties of mortars from two casts and three renders. Whilst comparison with mortars using other binders is complicated by the lack of standardisation in curing, sample preparation and the influence of the substrates upon which the renders have been applied, it is apparent that Roman cement mortars are relatively strong and brittle; strengths of some 44MPa were measured on cast elements (40mmx40mmx20mm). Water vapour permeabilities of 3-4x10^{-10}kg/m^2sPa have been measured. These mortars are much stronger and possess higher vapour permeability than would be expected of a natural hydraulic lime mortar under comparable conditions.

2.2.2 Mineralogy and morphology of binders

As part of the EU funded ROCEM project, laboratory calcination of marls from several sources was undertaken [19]. Optimal calcinations, determined by rapid setting and maximum strength performance, were encountered at low temperatures; typically in the region of 750°C measured within the charge of marl. Sub- and super-optimal cements showed slower setting and lower strengths. The hydration and strength development of the cements are characterised by a two-step process. Firstly, rapid setting correlates with the formation of calcium aluminium oxide carbonate (or carbonate hydroxide) hydrates [22]. Secondly, after a varying dormant period, depending on the source of the original marl and calcination conditions used for cement production, further strength development occurs as result of belite hydration. Strengths at ages of 6 hours and 1 year of up to 4MPa and 20MPa respectively have been recorded for 1:1 mini-cylinders of pastes at w/c = 0.65 [19].

Optimal cements are characterised by maximum α'-belite content, a high content of an amorphous phase and residual calcite and quartz indicating incomplete calcination; the latter is in line with historic comments that the best cements were not completely de-carbonated [e.g. 23]. Carbonated belite, spurrite, was observed in some cements at low temperatures. As the calcination temperature is increased, the α'-belite converts to the β-belite form observed in natural hydraulic limes and Portland cement; spurrite was also reduced. Additionally, aluminosilicate as gehlenite is observed. These developments are accompanied by a reduction in the amorphous phase and residual calcite and

quartz. Brownmillerite was observed in cements with a high iron content. Sub-optimal calcinations yield relatively coarse grains of silica and quartz embedded in a groundmass which exhibits features inherited from the marl. Whilst the quartz grains in optimal cements display reaction rims resulting from the inward diffusion of calcium ions this reaction is not observed in sub-optimal cements. A full description of the morphology, mineralogy and hydration of the laboratory cement may be found elsewhere [18, 19, 23, 24]. This work permits a confident interpretation of historic mortars.

The pore structure of historic mortars has been determined using mercury porosimetry. A bi-modal distribution is frequently observed with fine pores less than 0.2μm being associated with well hydrated cement and coarse pores up to 1μm, characteristic of mortars in which the hydration was halted at early ages. The total porosity accessible to water is high (30-40%) and illustrated in Fig. 3.

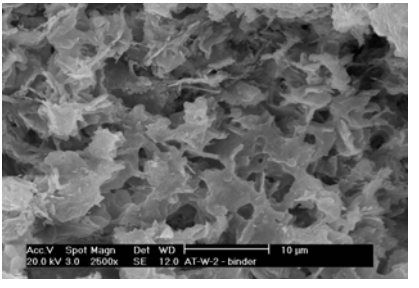

Fig. 3 Historic mortar showing open porosity.

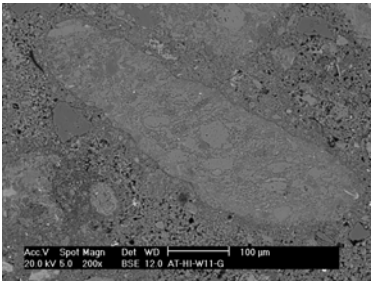

Fig. 4 Sub-optimal calcination

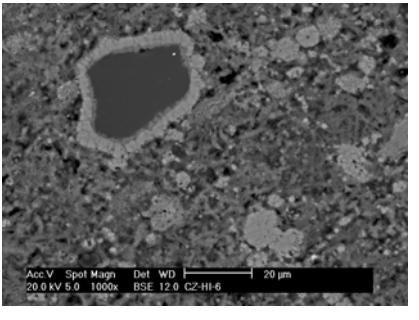

Fig. 5 Optimal calcination

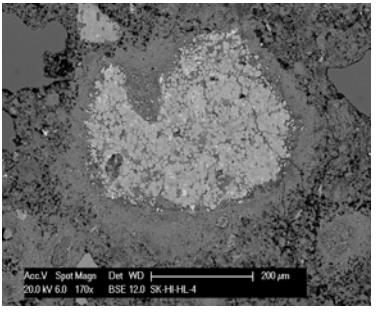

Fig. 6 Super-optimal calcination

A typical historic Roman cement mortar contains evidence from a substantial proportion of mostly un-hydrated clinker of all three categories of calcination in nearly equal proportions. This is a function of several factors: (1) natural inhomogeneity within the source marls, (2) inhomogeneous temperature profiles both within the kiln and the marl fragments and (3) the intentional inclusion of super-optimally calcined material as a means to control the rapid setting. Fig. 4 shows sub-optimal calcinations in which the structure of the original source

material has been maintained; in some mortars fossil remnants remain. There is little evidence of calcium diffusion into the quartz grains. However, belite is formed from reactions between intimately mixed siliceous and calcareous components within the "groundmass". Optimal calcination (Fig. 5) is distinguished by two types of substantial grains i.e. non-reactive and fully hydrated. The former is characterised by a reaction rim surrounding a silica core; the composition of the bulk of the rim approximates to belite whilst a narrow inner band of wollastonite is sometimes apparent. This grain is surrounded by a fully hydrated matrix. The fully hydrated grains comprise a dense calcium silicate hydrate which often shows cracks within the grain but not the surrounding groundmass. Within zones of super-optimal calcinations (see Fig. 6) large grains of coarse belite, wollastonite or gehlenite are observed. Holes are often noted in these grains as a result of local melting from either high temperatures or the presence of fluxing agents.

The use of back-scattered electron imaging reveals many of the unreactive grains as an internal aggregate and very well bonded into the hydrate structure. The size of some of the grains (up to 1mm) also suggests that these cements were not always well ground, despite the requirements of contemporary specifications.

3 Conclusions

Despite being produced from a wide range of source materials and being produced in inefficient kilns using a variety of fuels Roman cements have been shown to exhibit a number of significant common features associated with sub-, optimal and super-optimal calcination conditions. Whilst, the compositions tend to be rich in cement they contain "internal aggregate" which should be accounted for in the mix formulations. This "aggregate" is well bonded into the hydrated matrix unlike conventional aggregates. It is probable that, had the contemporary grinding technology been as efficient as now demanded, the benefit of these inclusions would have been lost. The historic mortars have the unusual attributes of being both strong and 'breathable'. To date, two critical aspects of conservation have been addressed: (1) the knowledge of material properties and decay mechanisms has been enhanced and (2) the technology to produce quality Roman cements and mortars has been re-learned.

4 Acknowledgements

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IV.23

Design and Production of Repair Mortars for Historic Masonry Taking into Account the Characteristics of Old Mortars

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Abstract This paper focuses on the design and reproduction of crushed brick/lime mortars for the repair of historic masonry. The research presented involves an analytical study of lime mortar samples collected from various archaeological sites and historic buildings in Cyprus. The results of this study are used to determine the physical, mineralogical and petrographical characteristics of these old mortars. Based on the results of the analytical study, a series of compatible repair crushed brick/lime mortars are prepared in the laboratory. The physicomechanical characterisation of these mortars reveals the most important factors which determine their strength, workability and durability. These are: the type and degree of fineness of the ceramic powder, the water/binder (w/b) and binder/aggregate (b/a) ratios and the type of mould. The performance efficiency of the experimental mortars is evaluated through pilot applications on several substrates.

1 Introduction

The weathering and deterioration of traditional mortars is an international problem, particularly affecting monuments and historic buildings. Since mortars play a vital role in the structural integrity and durability of masonry construction, their repair or replacement is unavoidable after several years in use. Taking into account the fact that old mortars have proved to be fully compatible with traditional masonry materials through the centuries [1], the design and production of repair mortars should be carried out in such a way so as to ensure that the characteristics of the final product are similar to those of the original materials. The characterisation and study of the production of traditional mortars is,

therefore, very important since it helps to reveal the material culture and the philosophy and principles of the construction technology of the past.

This paper describes an effort to design and reproduce repair lime mortars in the laboratory taking into account the characteristics of similar old mortars. The work is part of a wider project aiming at the physicochemical characterisation of old mortars from Cyprus and the evaluation and assessment of new mortars for conservation purposes. The systematic research approach presented here leads to the identification and interrelation of basic parameters of mortar design. Furthermore, the good performance of the experimental repair mortars is testified in pilot applications on several substrates.

2 Materials and Methodology

The methodology adopted in this study involved initially the analysis and characterisation of a number of lime mortar samples collected from various archaeological sites and monumental buildings in Cyprus belonging to different historical and even pre-historic periods of use. Macroscopically, some of the samples, which were taken with hammer and chisel, were intact, while others were in small pieces and looked very friable. Furthermore, the samples were different in colour, texture, grain size and surface roughness.

Part of each sample was ground and used for X-ray diffraction (XRD) analyses to identify mineral constituents. The XRD analyses were performed within the angle range 2θ=2-70° using a step size of 0.020°. A slice from each specimen was used for the preparation of a thin section which, in turn, was used for petrographic examination. The open porosity and bulk density of the samples were also measured using the vacuum saturation technique with water as the wetting liquid.

The analytical study of the old lime mortars was followed by the design and laboratory preparation/testing of experimental mortars with similar compositions (Table 1). In all the experimental samples, the aggregates comprised of local crushed calcareous sand (0-4 mm). The mixing of the aggregates and binder (hydrated lime and crushed fired clay ceramic $\leq$ 150 μm in equal quantities w/w) with tap water was mechanical and always uniform. The workability of the fresh mortars was tested using a flow table. Compaction was carried out in accordance to EN 196-1 [2]. It is worth noting that it was considered critical to use the same batch preparation (i.e. mixing and compaction time) for all specimens to avoid potential differences between batches. Such differences have been known to exist for mortars in previous studies [3].

Most of the samples were prepared using standardised prismatic steel moulds with dimensions 40 x 40 x 160 mm. To prevent the mortar from sticking, the sides of the moulds were prepared with oil prior to placing the wet mix in them. After casting, the moulds were covered with a glass plate to prevent loss of water by evaporation and they were placed in a curing chamber operating at 23°C and

60%RH. Specimens were removed from the moulds after 7 days. A number of specimens were prepared using moulds fabricated from limestone (Fig. 1). These moulds were lined with damp filter paper prior to placing the wet mix in them in order to allow for the set mortar to be removed from them without inhibiting the transfer of water from the wet mix to the absorbent mould material.

Table 1 Mix designs for repair mortars, workability (spread) and 28d mechanical properties (Note: in samples 22-25 a different type of ceramic powder was used).

Sample	w/b	b/a	Spread (mm)	f_c (MPa)	R (MPa)	E_{dyn} (GPa)
11*	0.800	0.33	134	3.97	1.13	0.55
22	0.800	0.33	130	1.49	0.55	0.27
23	0.800	0.25	100	1.32	0.44	0.25
24	0.800	0.50	182	1.09	0.55	0.27
25	0.800	1.00	233	1.22	0.53	0.20
26	1.000	0.33	200	0.94	0.53	0.22
27	0.875	0.33	169	1.50	0.68	0.36
28	0.800	0.33	143	2.10	0.92	0.49
29	0.750	0.33	118	2.57	0.96	0.52
34**	0.800	0.33	150	3.81	0.88	0.44
35***	0.800	0.33	146	3.34	0.86	0.42
36****	0.800	0.33	120	2.16	0.81	0.29

* Ceramic powder fineness 0-63 μm

** Ceramic powder fineness 63-75 μm

*** Ceramic powder fineness 75-150 μm

Fig. 1 Prismatic moulds fabricated from limestone

The performance efficiency of all the experimental mortars was evaluated by a series of standardised and non-standardised testing procedures designed to measure their physical and mechanical properties. The tensile (R) strength of the samples was determined by 3-point bending of the 40 x 40 x 160 mm prismatic samples using a Mecmesin (MWD 800-003) manual test stand. The compressive

strength (f_c) was measured on the half-samples emerging from the 3-point bending using a 250 kN test-frame and a loading rate of 2400 N/mm^2/sec. Dynamic modulus of elasticity (E_{dyn}) was also determined using resonant frequency apparatus. Last but not least, the open porosity, bulk density and capillary water absorption of a number of experimental samples were measured.

One of the experimental mortar mix designs was applied on wallets constructed of fired clay brick and limestone. The adhesion strength of the mortar was estimated using a pull-out test according to EN 1015-12 [4]. The wallets were monitored regularly for 12 months.

3 Results and Discussion

3.1 Characterisation of old mortars

The XRD analyses (Fig. 2) of the old lime mortars revealed that calcite was the main mineralogical constituent of these composites. Quartz and other accessory minerals were additionally present in many samples. Salt crystallisation was observed in some cases where halite and/or gypsum were evidenced. The presence of gypsum, which can be formed from calcium hydroxide present in the mortars and sulphate in the air, is probably the result of secondary salt formation with atmospheric pollution.

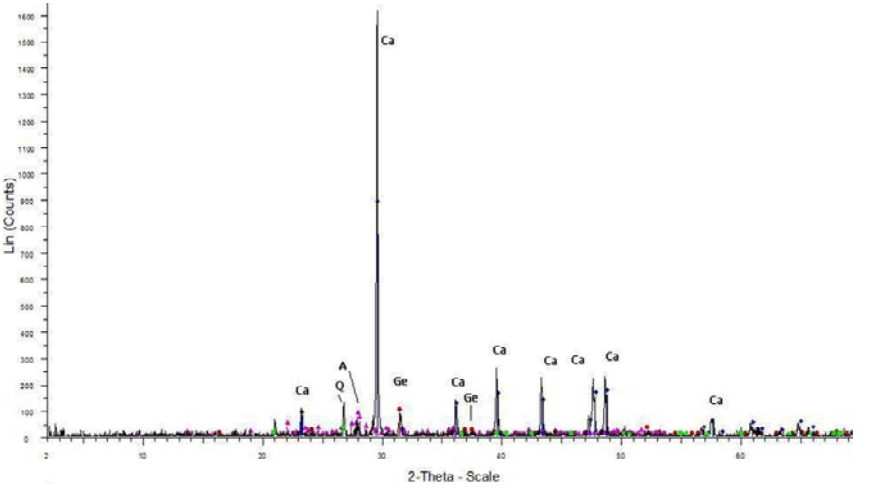

Fig. 2 Characteristic XRD pattern for an old lime mortar showing the presence of calcite (Ca), quartz (Q), anorthite (A) and gehlenite (Ge).

Gehlenite ($Ca_2Al_2SiO_7$) was also found in some of the old lime mortars. This is characteristic of the use of natural hydraulic lime burnt at low temperatures (<1200°C) [5] and/or ceramic fired at 800-1060°C. The use of the latter is also confirmed by the presence of anorthite in some samples [6, 7].

Crushed fired clay ceramic, in the form of small (angular, sub-angular and rounded) reddish inclusions of size 1-3 mm in a compact (fine-grained) matrix, was also evidenced in petrographic observations (Fig. 3). The latter also provided evidence of the use of fine to medium bioclastic aggregates and aggregates of a reef limestone nature in the mortar mix designs. Traces of feldspars were also observed in some cases.

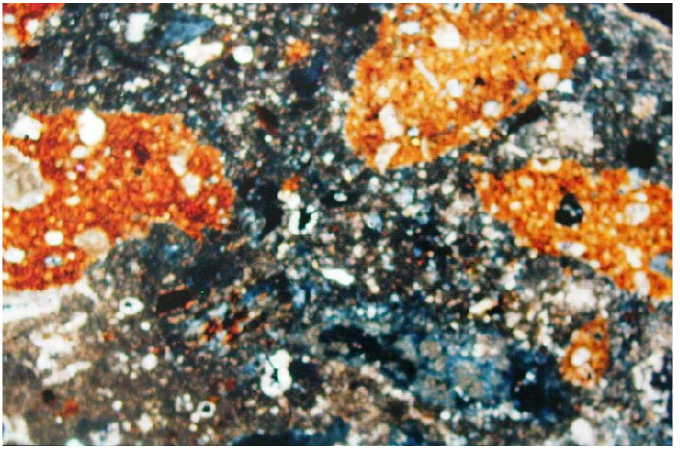

Fig. 3 Photomicrograph of an old mortar taken from a water mill showing evidence of fired clay ceramic in the form of reddish inclusions. Crossed nicols (65x).

The open porosity and bulk density of the old lime mortars ranged between 30-52% and 1.1-1.8 g/cm^3 respectively. These values agree well with results found in the literature [8]. It is worth noting that the porosity and microstructure of mortars depend significantly on the quantity and type of binder, the aggregate gradation and grade of compaction.

3.2 Experimental mortars

From the results (Table 1) of the physicomechanical characterisation of the experimental crushed brick/lime mortars, it became obvious that the type and degree of fineness of the ceramic powder played a very important role in the strength development of the end product. Ceramic powder proved to be more active with a decrease in its particle size (see samples 34-36). According to evidence found in the literature [9, 10, 11] the grain and fragments size of the

ceramic powder influences directly its hydraulic reactivity and, consequently, the physicomechanical properties of the hardened mortar.

The experimental results also showed that the workability of the fresh mortars improved by increasing their b/a ratio (see samples 22-25). The highest compressive strength was achieved by mortar sample 22 which had a b/a ratio of 0.33 (w/w).

While the w/b ratio of the fresh mortars also seemed to play a vital role in their strength development (see samples 26-29), experimental results (Table 2) showed that the compressive strength of the hardened mortars increased significantly over time. The porosities and capillary water absorptions of the same samples were reduced over the same period of time. However, their values did not fall outside the range of respective values estimated for the old lime mortars.

Table 2 Experimental results at 28, 90 and 180 days.

Sample	w/b	b/a	Spread (mm)		f_c (MPa)	R (MPa)	E_{dyn} (GPa)	P (%)	S (mm/min$^{1/2}$)
30	0.800	0.33	145	28d	1.95	0.70	0.42	36.3	2.40
				90d	2.67	0.90	0.51	36.0	2.36
				180d	2.64	0.54	0.46	35.6	2.33

The mortars cast in the limestone moulds (see sample 11 in Table 1) exhibited significantly higher compressive strengths than those cast in the steel moulds. This is clearly because the former had sufficient water abstracted in the wet state to lower their water/binder ratio and therefore increase their strength. It is worth noting that, while mortars placed in steel moulds remained soft for several days, similar mixtures placed in limestone moulds had set within 24 hours. This is consistent with the behaviour of the mortar mixture used in the plastering of the brick and stone wallets (Fig. 4).

Fig. 4 Pilot applications of repair mortars on wallets constructed of stone (front row) and fired clay brick (back row).

The latter showed absolutely no evidence of cracking or efflorescence (salt growth on their surface) 12 months after their construction. Pull-out tests resulted in adhesion strengths exceeding the minimum requirement of Eurocode 6 (i.e. 0.2 MPa) and well over $1/30^{th}$ of the compressive strengths of mortars. Adhesion strengths were significantly improved along joints.

4 Conclusions

Following the physical, mineralogical and petrographical characterisation of a number of old lime mortar samples from Cyprus, compatible repair mortars were prepared in the laboratory. These mortars consisted of raw materials (crushed fired clay ceramic, hydrated lime and aggregates) which were locally available. Examination of the physicomechanical characteristics of the experimental mortars revealed the most important factors (i.e. type and degree of fineness of the ceramic powder, w/b and b/a ratios and type of mould) which determine their strength, workability and durability. The good performance of the experimental repair mortars was testified in pilot applications on several substrates.

5 Acknowledgements

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IV.24

Stress Rate Sensitivity of Masonry Units Bound with Hydraulic Lime Mortar

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Abstract It is well established that most construction materials behave differently under static and dynamic loading. The stress-rate sensitivity of concrete, steel and rock has been intensively investigated. However, the literature on the time-dependent response of masonry joints is scarce, particularly with regard to bond behaviour in historical stone masonry. This paper describes the dynamic response of sandstone masonry units bound with hydraulic lime mortars. A drop weight impact machine was used to generate stress rates in the range of 1kPa/s to 10^7kPa/s. The dynamic impact factor and stress rate sensitivity were evaluated for the flexural strength of the mortar and for the bond strength and further, the pattern of failure was noted for each mix and loading rate. Based on a related study, polypropylene micro-fibres were incorporated at 0%, 0.25% and 0.5% volume fraction into the mortar. Results show that although hydraulic lime mortar is stress rate sensitive, the dynamic impact factor is overestimated by existing CEB-FIP models. Further, the stress rate sensitivity of the bond strength decreased with an increase in the fibre content. Also, where as the mode of failure in the masonry units under quasi-static loading was through fracture at the mortar-block interface, the failure plane transferred to within the mortar under dynamic loading, particularly with fibre reinforcement.

1 Introduction

Many old stone masonry structures are located in areas of seismic activity. The proper rehabilitation of such buildings requires a quantitative knowledge of the dynamic response of the masonry unit and its components. In particular, the bond between the stone blocks and the binding mortar is of concern [1]. In the restoration of heritage stone masonry in Canada, hydraulic lime mortar (HLM) is preferred over Portland cement mortar [2]; for the former is intentionally weaker

than the stone blocks and also allows for their movement over the first few months. The quasi-static response of masonry joints is well established [3, 4]. It is known to depend upon the type of mortar and possess a post-peak residual bond strength [5]. However, very little is known as to the rate sensitivity of masonry joints. Burnett et al. [1] conducted the first such study using clay bricks bonded with lime-Portland cement mortar and found a dynamic impact factor of 3. Subsequently, Hao and Tarasov [6] quantified the response of similar mortar and clay bricks under dynamic compression. To the authors' knowledge, the present study is the first on the dynamic response of the flexural bond in a masonry unit, particularly with sandstone blocks and hydraulic lime mortar.

That fibres enhance the energy dissipation in concrete is well known [7, 8]. Short, discrete polymeric fibres improve the energy dissipated by concrete under impact loading, sometimes exceeding in rate sensitivity over steel fibres [7]. While fibres enhance the aggregate-paste interface [9], in a stone masonry joint it is not just the strength but also possible changes to the failure mechanism which define the composite response. In this paper, plain and fibre reinforced hydraulic lime mortars were characterized under compression to establish reference mechanical properties. Commercially available polypropylene microfibers were introduced at 0.25% and 0.50% volume fraction to render three mortar mixes together with a reference plain mix. The stress rate sensitivity of the flexural response of such mortars was established, followed by an examination of rate effects on the flexural bond in masonry units. An instrumented drop-weight impact tester was utilized to generate the high stress rates, upto 10^7 kPa/s. The stress rate sensitivity was investigated via CEB-FIP formulations [10] generated for Portland cement composites.

2 Experimental Details

2.1 Materials and Composition

Sandstone from the Paskapoo formation (Fig. 1a) was used to prepare the masonry units. A natural hydraulic lime (NHL-2) with a targeted compressive strength of 2 MPa (at 180 d) was sourced from France. Its chemical composition is shown in Table 1. Polypropylene microfibres with properties as listed in Table 2 were introduced as the discrete reinforcement at dosage rates of 0.25% and 0.50% by volume fraction (V_f). The plain mortar was prepared as per CAN/CSA A 179-04 [11] and the mix design for both plain and fibre reinforced mixes is shown in Table 3. For the plain mortar, the water-to-binder ratio was suitably adjusted to achieve a flow between 100-115% in order to meet the workability criterion per CAN/CSA A 179-04 [11]. No change was made to the mix design to adjust slump

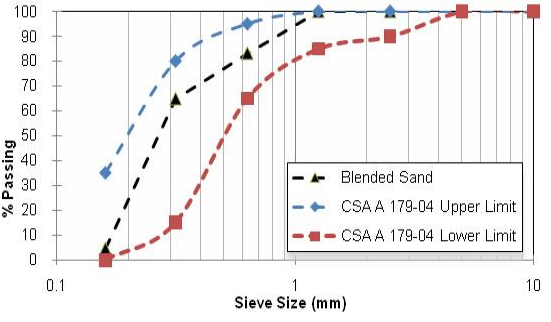
flow with fibres, so as to maintain proportions. A blended sand was used as the fine aggregate, to meet the grading criterion as shown in Fig. 1b.

Table 2 Chemical Composition of NHL-2 (percentages related to original dry lime (%)) [12]

CaO	LOI	SiO_2	MgO	Al_2O_3	SO_3	Al_2O_3	Fe_2O_3	Na_2O
54.26	15	12.57	7.65	5.42	2.13	1.35	1.16	0.34

Table 2 Properties of Polypropylene Microfibres used in this Study

Specific Gravity	0.91
Fibre Length (mm)	20
Density (kg/m^3)	910
Tensile Strength (MPa)	450
Modulus of Elasticity (MPa)	3450
Denier	3

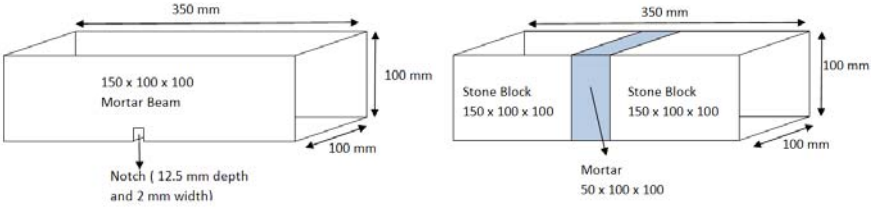


a) b)

Fig. 1 a) Sandstone Block; b) Grain Size Distribution of the Fine Aggregate in Mortar

Table 3 Mix Design of Hydraulic Lime Mortar

Mix & Designation	Fibre Volume Fraction (% V_f)	NHL-2 (kg/m^3)	Sand (kg/m^3)	Water (kg/m^3)	Slump Flow (%)
V_f=0.00% (F0)	0	400	1200	400	103
V_f=0.25% (F1)	0.25	400	1200	400	48
V_f=0.50% (F2)	0.5	400	1200	400	39



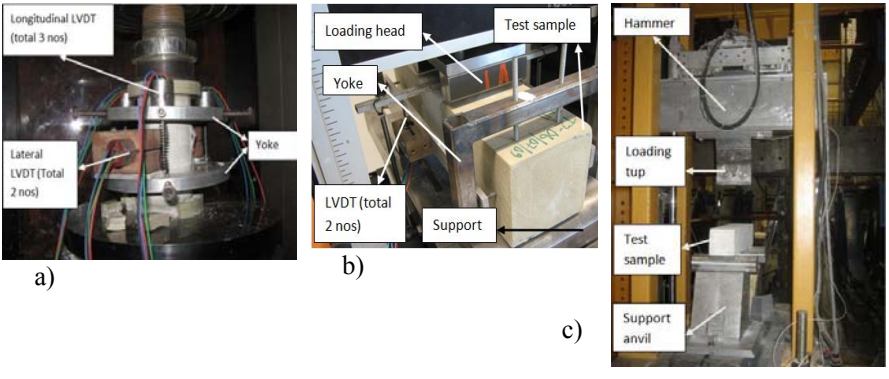
a) b)

Fig. 2 Schematic of Prisms for Flexural Testing of a) Mortar and b) Masonry Unit

Cylinders (100 mm x 200 mm), mortar prisms and masonry units (100 mm x 100 mm x 350 mm) were made from the same batch of mixture to ensure uniformity of test results. Two sandstone blocks (100 mm x 100 mm x 150 mm) were joined with HLM to produce each masonry unit. Three specimen replicates were tested for each data point. Further, three sandstone cylinders (50 mm x 100 mm) were also cored to evaluate their compressive response.

2.2 Test Setup

The cylinders were instrumented as shown in Fig. 3a for compression tests as per ASTM C469 [13]. Quasi-static flexural tests (Fig. 3b) were conducted as per ASTM C 1609 [14]. Linear variable displacement transducers (LVDTs) were used to get the displacements data in both cases. In order to ensure a known failure path, the mortar prisms were sawn to create a notch 12.5 mm wide and 2 mm wide at mid-span. The data acquisition system obtained load, stroke and LVDT recording at 5 Hz.



a) b) c)

Fig. 3 Test Setup for: a) Compression; b) Quasi-Static Flexure; c) Dynamic Flexure

An instrumented drop weight impact tester (Fig. 3c) was employed to generate the higher rates of flexural loading. For each of the mixes in Table 3, three mortar

prisms and three masonry units were examined under impact from two separate heights namely, 250 mm and 500 mm. The striking edge of the impacting hammer, i.e. the loading tup was instrumented with eight strain gauges to form the load cell. A piezoelectric accelerometer was attached below each specimen at mid-span (adjacent to the notch in case of mortar prisms) to gather the acceleration history. Data from the load cell and the accelerometer was recorded at 100,000 Hz. The inertial effects associated with a suddenly applied load must be accounted for to evaluate the true stressing load experienced by the material [15]. For a beam subjected to 3-point bending under impact, the stressing load, Pb(t), is obtained by subtracting the generalized inertial load on the specimen, Pi(t), from the tup load, Pt(t), represented by [16]:

$$Pb(t) = Pt(t) - Pi(t) \tag{1}$$

$$P_i(t) = \rho A a_o(t)\left[\frac{1}{3} + \frac{8(ov)^3}{3l^2}\right] \tag{2}$$

where, a0(t) is the acceleration at midspan of the beam at time, t; ρ is the mass density for the beam material; A is the cross-sectional area of the beam; l is the clear span of the beam and, ov is the length of the overhang of the beam.

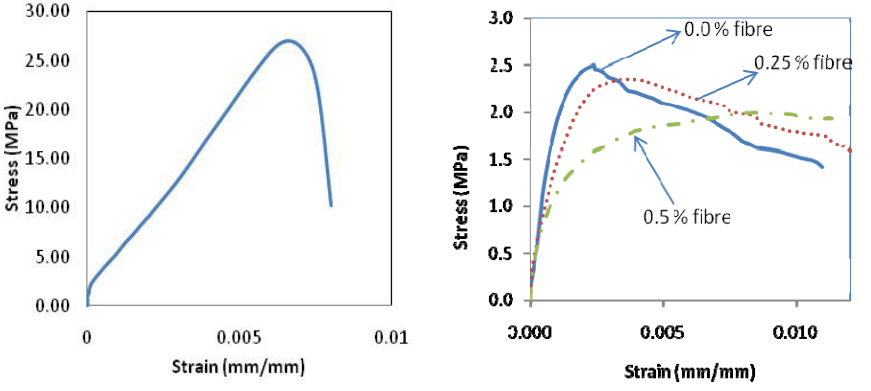
3 Results and Discussion

3.1 Compressive Response

The compressive strength of sandstone and its elastic modulus were 27 MPa and 3800 MPa respectively (Fig. 4a). The stress-strain responses in compression for plain and fibre reinforced HLM are shown in Fig. 4b, with the mechanical properties listed in Table 4. The data indicates a drop in elastic modulus with fibre reinforcement.

Table 4 Compressive Response of Plain and Fibre Reinforced Hydraulic Lime Mortar

Mix & Designation	f'_c (MPa)	E_c (MPa)
V_f=0.00% (F0)	2.5	1930
V_f=0.25% (F1)	2.4	1380
V_f=0.50% (F2)	2.0	1320



a) b)

Fig. 4 Compressive Response of a) Paskapoo Sandstone and b) Hydraulic Lime Mortar

3.2 Flexural response

3.2.1 Mortar

The quasi-static response of plain and fibre reinforced HLM is shown in Figure 5a, while their dynamic response is shown in Figs. 6a and 7a for drop heights of 250 mm and 500 mm, respectively. As expected, a post peak residual strength capacity was witnessed in fibre reinforced mortars. The addition of fibres increased the flexural strength of the mortar at quasi-static loads, but where as dynamic loading resulted in an increase in the flexural strength for all mortars, the role of fibres is not clear. There was an optimum fibre dosage, (in this case = 0.25% V_f), that resulted in maximum flexural strength for higher drop heights.

3.2.2 Masonry Unit

The quasi-static flexural response of the masonry units is shown in Fig. 5b, while the response under impact loading is shown for a drop height of 250 mm and 500 mm in Figs. 6b and 7b, respectively. Note that the addition of fibres led to higher flexural bond strength at quasi-static and low impact loads. However, for the 500 mm drop, the strongest bond performance was with the plain HLM. The role of fibres may be explained through an examination of the failure mode as illustrated in Fig. 8. Where as the mode of failure in the masonry units under quasi-static loading was through fracture at the mortar-block interface (Fig. 8a), under dynamic loading the failure plane transferred to within the mortar (Fig. 8b), particularly with fibre reinforcement.

3.3 Rate Effects

The stress rate sensitivity was expressed in terms of the dynamic impact factor (DIF) and is shown in Fig. 9. Note that the addition of fibres led to a decrease in rate sensitivity for both the flexural strength of the mortar and the flexural bond strength of the masonry unit. Significantly, the sensitivity of the flexural bond was higher than the sensitivity of the flexural strength of the mortar alone. The authors note that the constitutive laws [10] formulated for regular concrete vastly overestimate the stress rate effects for HLM.

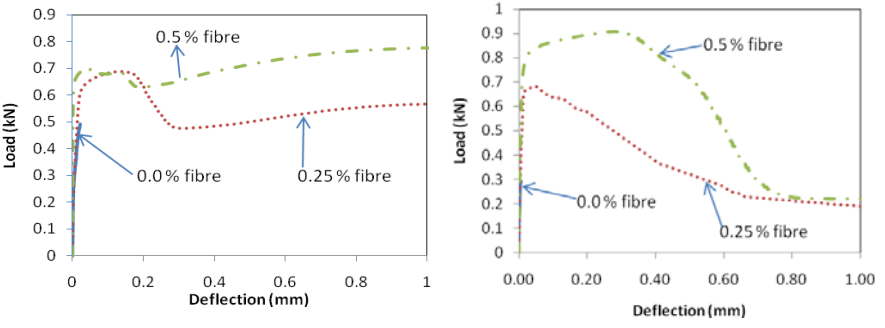
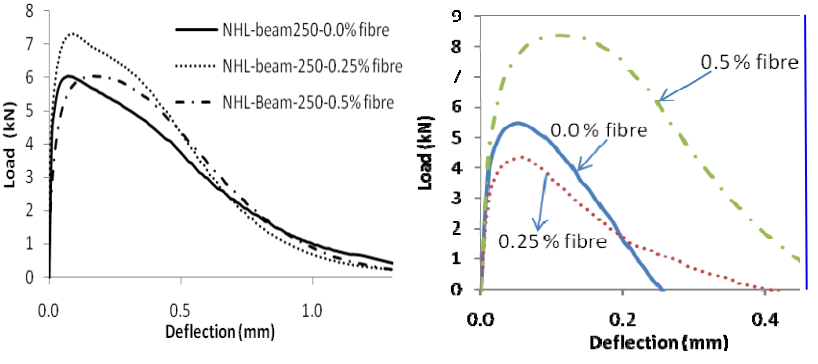
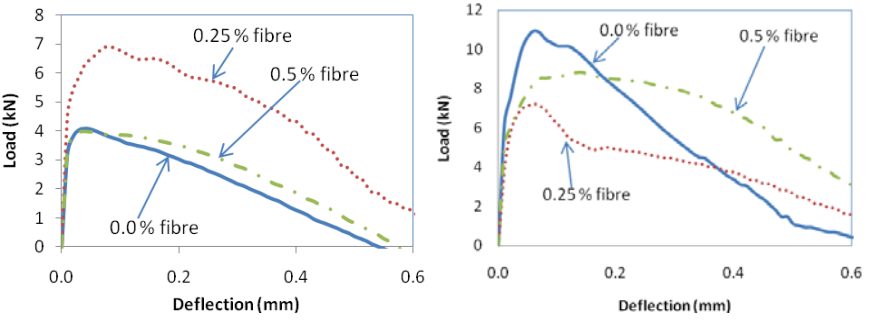


Fig. 5 Load-Deflection Response under Quasi-Static Flexure for a) HLM and b) Masonry Unit



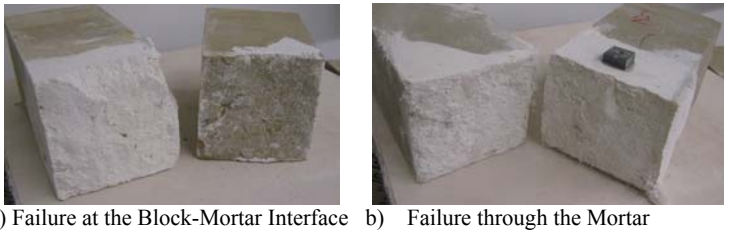
a) Hydraulic Lime Mortar b) Masonry Unit

Fig. 6 Flexural Load-Deflection Response under Impact from 250 mm



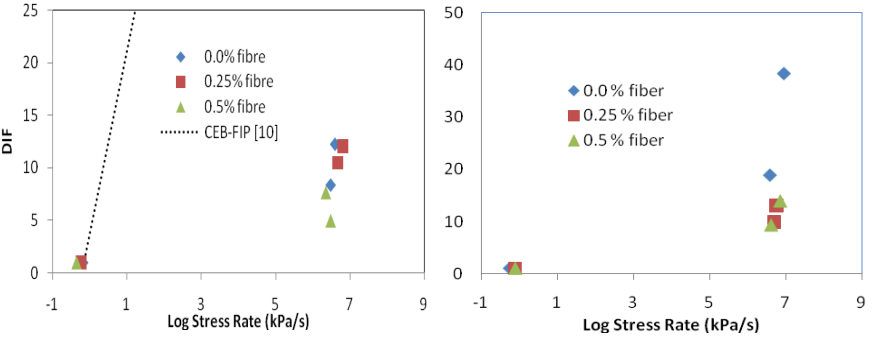
a) Hydraulic Lime Mortar b) Masonry Unit

Fig. 7 Flexural Load-Deflection Response under Impact from 500 mm



a) Failure at the Block-Mortar Interface b) Failure through the Mortar

Fig. 8 Modes of Failure in Masonry Units: a) Quasi-Static Loading (All Specimens) and b) Dynamic Loading (Fibre Reinforced HLM)



a) Flexural Strength of HLM b) Bond Strength of Masonry Unit

Fig. 9 Stress Rate Sensitivity for Various Fibre Contents

4 Conclusions

1. Polypropylene fibres in HLM improve the flexural bond at quasi-static loads.

2. Under dynamic loads, adding polypropylene fibres to HLM transfers the mode of failure from the stone-mortar interface to fracture within the mortar.
3. Hydraulic lime mortar is sensitive to high stress rates under flexure, but the CEB-FIP expression overestimates the dynamic impact factor.
4. The flexural bond strength was more sensitive to stress rate than the flexural strength of the mortar at similar rates of loading. However, the addition of polypropylene fibres consistently decreased their rate sensitivity.

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IV.25

The Design and Use of Repair Mortars for Historical Masonry in Australia

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Abstract For the first 150 years of European settlement in Australia, masonry buildings were constructed largely using the techniques brought from Europe (particularly Great Britain) by the immigrants. Lime for mortar was made by shell burning until limestone deposits were worked from the mid 19th century. Contamination of the source and the wood–fired burning process ensured that the resulting lime was at least feebly hydraulic, as shown by testing. As in so many parts of the world, lime in mortar was displaced by Portland cement after World War II. Even the available Australian Codes lost sight of the role of lime and became quite misleading in giving guidance to users. As heritage restoration became important from the 1970s, there was increasing interest in lime, but architects and engineers had no guidance and made many mistakes which are still being perpetuated. Following experience in masonry conservation in buildings dating from the 1790s onwards, the author has been instrumental in developing a synthetic hydraulic lime mortar which is now being used successfully throughout Australia.

1 Introduction

1.1 Lime mortar use in Australia

The first European masonry buildings in Australia were built in the 1790s using bricks made in clamp kilns. Lime was made by burning shells gathered from aboriginal "middens" (waste dumps), but large quantities of this material were not available due to kiln shortages and deficiencies, and many early buildings were almost entirely built with soil bedding and even had soil plaster with the little lime available used for lime–wash paint to give some durability. As the colony developed, kilns were set up in many places along river and harbour foreshores,

but it was not until the mid 19th century that limestone deposits were first used for a more consistent supply of lime. These deposits, unfortunately, were generally well away from settlements and easy transport, and the use of lime from shells was continued for some time [1].

Many lime mortars found in older buildings, particularly those from the many built in the late 19th century, such as inner city terrace houses, are now found to be a powder which falls from the joints when the outer crust has broken. This observation has led to many architects and engineers, even those with some conservation experience, gaining a distorted impression of the quality of all lime mortar. On the other hand, very sound mortars were made from the earliest times when knowledgeable people were employed, particularly on government works.

A possible explanation for the poor mortar of the late 19th century has been found in the reporting of a customs duty dispute in which the New South Wales (NSW) colonial government classified imported New Zealand hydraulic lime as Portland cement and levied the same duty on it [2]. This would have been a disincentive to the local industry using hydraulic lime and the increasingly pure "fat" limes made from the local limestone deposits would have made poor mortar without use of pozzolan.

1.2 Current practice

Since the middle of the 20th century Portland cement has taken over as the cementing agent in almost all mortar; lime, if used at all, is usually in the form of hard–burnt dry slaked material, which adds little to the mix apart from workability. The situation has been exacerbated by a lack of understanding on the part of the Australian Masonry Code committee [3], which has effectively banned lime for new work in any mix "weaker" than 1 part lime: 2 parts cement: 3 parts sand; the issue is further confused by simply referring to the "Limes in building" code [4] and not distinguishing dry slaked lime from lime putty from quicklime, etc. in volume batched mixes. Further problems are caused by the Code not designating sand grading requirements, which results in unworkable mixes made from single–sized sands, which are then made workable by the bricklayer using additives ranging from household detergent to fireclay.

The situation in conservation works is little better, particularly when the conservation specialist's back is turned.

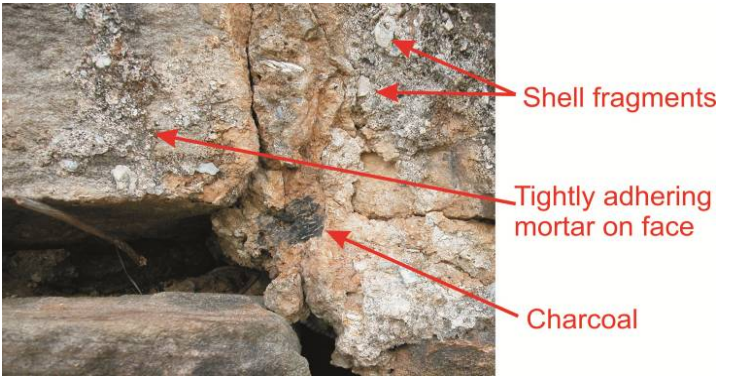

Fig. 2 Photo showing characteristics of mortar found in place at 1840

2 Research on early lime mortars

2.1 Examples

The properties of some of the early lime mortars have been investigated in detail and it is useful to set out the findings. The two samples used for illustration purposes are a c.1840 mortar used for construction of a stone reservoir and an 1859 mortar used for a brick–arch railway bridge.

2.2 c.1840 mortar

A reservoir wall and adjacent "cattle tank" were built around 1840 at Campbelltown, near Sydney, using convict labour gangs. Sandstone was quarried nearby and lime was sourced from shells. Samples of the original mortar were subjected to analysis using a scanning electron microscope (SEM) and X–ray diffraction (XRD). Fig. 1 shows the mortar in place and Figs. 2 and 3 show the SEM results, including spot energy dispersive spectrographs indicating the compositions.

XRD results have been found of minimal use as the calcite and silica peaks tend to hide the smaller peaks of components critical to classification; this may not be a problem if the work was done in a laboratory with a good database of similar materials by an operator versed in mortar materials.

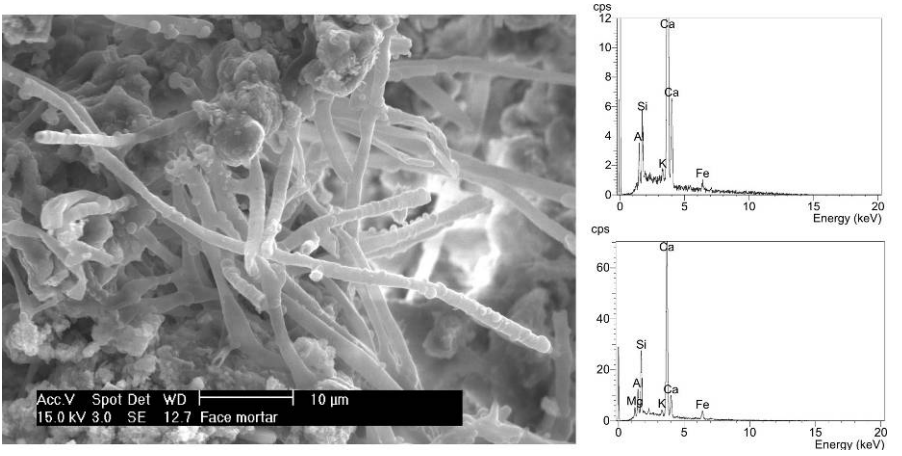

Fig. 3 Characteristic C-S-H crystal SEM picture and corresponding spot energy dispersive spectrographs for crystals which seem to be found mainly in old hydraulic lime mortars.

The principal finding has been that the mortars have significant quantities of calcium silicate hydrate (C-S-H) crystals indicating hydraulicity. Of interest has been that the long thin "birds nest" crystals are, in fact, tubular and the bore of the tube was able to be measured as 0.5 µm.

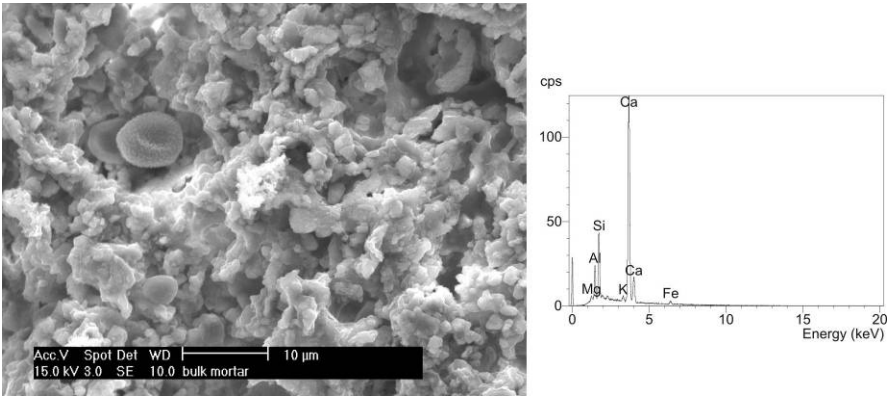

Fig. 2 SEM picture of another form of C-S-H, "fluffy paste" crystals similar to those found in modern Portland cement based mortars together with the spectrograph.

2.3 1859 railway bridge mortar

This was the first mortar for which the author was able to obtain an analysis and, as well as the SEM results, a chemical analysis was undertaken showing that

the mortar had 12% clay mineral content and so was "feebly hydraulic" under the Vicat classification [5].

The quality of this mortar throughout the joint had first been demonstrated when a pair of bricks was removed from the structure for analysis. When these bricks were prised apart, the fracture occurred in the face of a brick, not at the joint, indicating the strong bond obtained. It was this example which led the author into investigating old lime mortars, as it clearly showed that they were not all as poor as those frequently found in buildings.

Test results to date have not been able to show whether the mortar was made from lime which was deliberately or accidentally hydraulic and no documents have been found which can assist this determination; petrographic examination might help, but has not been fundable within the project budgets.

2.4 Other results

The need to repair and strengthen a number of 19th and early 20th century railway structures has required determination of the flexural properties of the brickwork. Whilst the Australian masonry code [6] does not allow the mobilisation of tensile strength under gravity and live loading, it does under intermittent loads from wind and earthquake actions. To determine the flexural strength of existing brickwork, cores have been taken and the cylinders tested under four–point bending. Characteristic flexural strengths in excess of 1 MPa have been determined, with individual cylinder bending tests exceeding 6 MPa flexural tensile strength: the maximum flexural tensile strength allowed under the code [7] for modern mortars is 1 MPa.

2.5 The problem of sand

Early mortar makers living near the coast had unlimited supplies of beach and dune sands, but these tended to be neither sharp nor well graded. Observations suggest that coarser particles, giving better sand grading, were introduced by using crushed shell, either unburnt material from the kiln or deliberately added separately as seen by the lack of signs of burning on some fragments.

In the modern masonry industry, poor sand grading has continued as noted above. Another problem found in conservation practice is that sand is chosen often for its colour, not its physical properties.

Rediscovering the importance of sand grading and interpreting the writings of such as authors as Vitruvius [8] and Palladio [9], together with 19th and early 20th century writers on this subject, has been an important part of the author's journey.

3 Replacement mortars

3.1 Design criteria

The design criteria used for replacement mortars in buildings have nominated an adequate, but not too strong, compressive strength and permeability greater than the bricks or stone. The latter requirement, which is critical to limiting salt damage, has been the most neglected and hardest to achieve. Most unfortunately, many practitioners have ignored both requirements with mixes made from powdered slaked lime, white or off–white cement for appearance and single sized dune sands; workability agents or even clay are often added. The resulting mortars have given none of the key properties, but they seem to look satisfactory, at least for sufficient time for the continuing problems not to be ascribed to the faulty work.

3.2 The first new mortar

The 1827 church in Port Macquarie, NSW, about 300 km north of Sydney, was built with convict labour using sandstock bricks made from local clays and fired in clamp kilns. The author was engaged for major conservation works on the masonry in 2002.

The first requirement was to design a suitable mortar for repointing the brickwork which was of suitable strength (i.e. not too strong) and with permeability greater than or equal to the bricks. The church is very close to the coast and salt damage was widespread, particularly where Portland cement–based mortars had been used for past repair work. Severe damage had also been caused by an ill–fated attempt to control rising damp by cement rendering the outside of the walls to window sill level: not only were the bricks damaged and had to be reversed or replaced, but the trapped moisture caused severe damage to the internal timber panelling.

The mortar design was based on aged lime putty, graded sharp sand and a blast–furnace slag pozzolan at 5% of the lime by volume.

To determine permeability matching, samples of bricks were cored to produce 38 mm x 13 mm discs and mortar samples were made up to the same dimensions. The samples were mounted using resin in PVC tube and tested with water using a controlled pressure differential of 20 kPa: permeability (in m^2) was then determined from the volumetric flow rate using a form of Darcy's law (see Figs. 4 and 5).

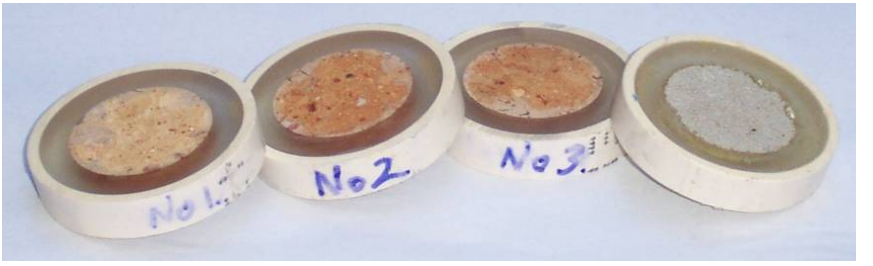

Fig. 4 The one mortar and three brick samples set within their respective resin and PVC tubing sleeves.

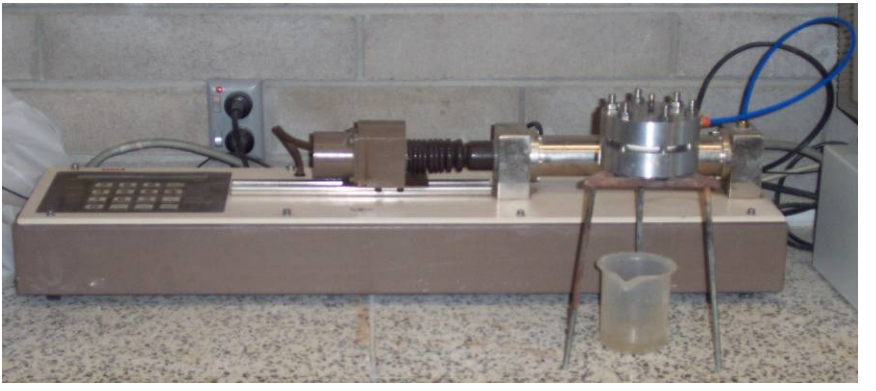

Fig. 5 Permeability testing equipment including a GDS pressure/volume controller connected and pressure gradient apparatus containing masonry core.

The initial test, of what was thought to be a reasonable mortar design, resulted in a mortar having a permeability 1/10th of that of the bricks, showing how wrong one can be if testing is not undertaken. A suitable mortar was found after adjusting mix proportions and sand grading.

The undertaking of this test was a valuable part of the mix development process and showed that a mortar mixed using all the criteria normally recommended did not necessarily produce the desired result.

3.3 The next phase in development of synthetic hydraulic lime mortars

Further study of the literature and old specifications made it clear that there was a clear distinction between the practices followed by plasterers and masons in their use of lime: stories of plasterers' aged supplies of lime putty had been generally interpreted as applying to masons also, and this confusion also seems to have been common in other English–speaking countries until work undertaken by members of the Building Limes Forum was better known [10]. Study of 19th century

specifications in Australia also indicated that quicklime (sometimes referred to as rock– or stone–lime) was the normal material for masonry, that it was to be used with the "hot" lime process and that "fat" lime was not desirable for masonry, as illustrated in a typical specification used in Australia in the early 20th century [11]. This latter requirement appears, however, not to have been followed because of the general unavailability of hydraulic limes in Australia.

Manufacturers of lime in Australia produce more than 90% of their product for uses other than masonry. In most cases purity is required and reactivity is not an issue for buyers when the product is to be used for such industries as chemical manufacture and water treatment, where the bulk of sales are made. There is, however, one non–mortar use where reactivity is important and that is the stabilisation of clay soils in road construction: at least two production plants (in the whole of eastern Australia) are known to make soft–burnt lime thanks to the requirements of road construction. The lime is available in granulated form, rather than the coarser particles of traditional rock lime: the smaller particles give a material with a greater bulk density, which needs to be accounted for in the mix design.

Having found suitable sources of quicklime, it was necessary to determine the best available pozzolan. The blast furnace slag used in the early mixes was only available in bulk quantities and with little control over quality. Brick dust from demolished buildings was not available in sufficient quantities from older buildings with low–fired bricks. Metakaolin was determined to be the best choice and, although imported, had consistent quality. Sand was specified in accordance with the grading in the British code [12], and some washed, coarse river sand, produced for compacted paver bedding, was found to comply with the requirements without further treatment.

Mixes have been made successfully for different structures with lime:sand proportions of between 1:3 and 1:4, by volume, and with metakaolin pozzolan added at between 5% and 15% by volume of lime.

Strength testing of the mortars has given further problems as the first cubes moulded and placed in a laboratory "fog" room failed to gain any strength from carbonation, due to saturation resisting the diffusion of carbon dioxide. The most recent test results have been obtained by placing the cubes prior to testing in a chamber controlled at 70% relative humidity and 20°C, as nominated for the testing of "historic" mortars by the ASTM method [13].

4 Where to from here?

There is still resistance to the use of properly formulated lime mortars in Australia, not just for new works but for conservation of historical buildings. For example, one of the major specifiers of conservation works on 19th century sandstone in government and other buildings in Sydney is still recommending a

mix by volume of one part Portland cement: 1 part dry slaked lime: 6 parts sand, and with no sand grading requirements. At the time of writing the author was engaged in what appeared to be an unwinnable dispute with this group over adopting lime mortar, and the elimination of epoxy fastenings, for the replacement of a sandstone cladding on a major public building.

Industry may be less resistant and a major manufacturer of lime which is already producing the best "soft burnt" material is interested in making progress with the manufacture of hydraulic lime as it may help the "ticking of green boxes" in its corporate profile.

5 Conclusions

The struggle to bring Australia up to "world's best practice" (a term loved by politicians), in its use of lime mortar has started, but has a long way to go before all involved can be convinced that modern Portland cement is not an appropriate material for use in historical masonry. The author has made a start and now the resulting "hot lime" mixes are being used in projects throughout Australia.

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IV.26

The Effect of Relative Humidity on the Performance of Lime-Pozzolan Mortars

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Abstract The development of strength in conservation mortars is of particular significance for new synthesized lime-based mixtures, in terms of practical application, performance requirements and renovation cost of built monuments. In this work, the effect of relative humidity (RH %) on the strength characteristics of lime-natural pozzolan mortars was studied, in three groups of specimens, cured at different humidity conditions (45, 65 and 95 RH %). The compressive strength of the specimens was determined at preset time periods, from 7 days to one year. At the same time periods, the setting products and the microstructure of the mortars were monitored by thermal analysis (DTA/TG) and scanning electron microscopy (SEM/EDX). The results highlight the beneficial effect of elevated humidity on the strength of lime-pozzolan mortars and at the same time some issues related to the reliability and reproducibility of laboratory performance in field works are addressed.

1 Introduction

The study of lime-pozzolan systems is of particular significance for modern renovation mortars, since the addition of either natural or artificial pozzolans in lime putty enhances the strength and durability of the produced mixtures. This is achieved through the formation of calcium silicate hydrates (CSH), calcium aluminum hydrates (CAH) and calcium aluminum silicate hydrates (CASH) [1, 2]. Study of the above systems contributes towards the improvement of traditional building techniques, and in addition, towards the optimisation of the performance characteristics and durability of the produced mixtures. To this direction, it is necessary to understand the effect of the different parameters that affect the performance characteristics of lime-pozzolan mortars, to determine the optimum

conditions for laboratory tests (in order to ensure reliability and reproducibility of the results in field) and finally, to highlight any parameters that may affect the performance of such mortars in field applications. The latter poses both structural and economic impacts, since it affects the structural and decorative integrity of architectural monuments, as well as the total conservation/renovation cost.

In this paper, the effect of curing conditions of lime-pozzolan mixtures on the setting process and the mechanism of strength development at an early stage are studied in three groups of mortars each cured at a different relative humidity. The development of their mechanical properties was determined at preset time periods, along with the formation of setting products and the resultant changes in microstructure. The understanding of the influence of relative humidity on the above parameters (setting mechanism, microstructure and strength) is essential for enhancing the durability and field performance of lime-pozzolan mixtures. Finally, this work contributes to the identification of weaknesses in the comparison and interpretation of the laboratory and field performance of lime-pozzolan mixtures.

2 Experimental

2.1 Preparation and curing of test specimens

The binary pastes were prepared by mixing equal parts (w/w) of one year matured lime putty, made of laboratory grade calcium hydroxide powder, and a commercial ultra-fine (0-35 μm) natural pozzolan of volcanic origin. By mixing equal parts of calcium hydroxide powder and water (w/w) the real density of lime putty was set to 1.400 kg/m^3, while the real and apparent density of pozzolan were 2.400 and 430 kg/m^3 respectively. Diffraction analysis of the pozzolanic material revealed that it consisted of an amorphous, glass-like material, accompanied by some secondary crystalline phases such as quartz, illite/muscovite, kaolinite and Na-feldspars (albite, anorthoclase).

The pastes were prepared by mixing all the constituents with de-ionised water up to a standard consistency [3] for 5 minutes [4]. The water to solid constituents' ratio for all pastes was set at 0.28. In addition, mortar mixtures were prepared by mixing lime, pozzolan, standardised sand (EN 196-1) and water in the ratio described in EN 196-1 [4]. Both the pastes and the mortar mixtures were initially cured for seven days at 98-100% RH. Then, they were divided into three groups (A, B and C) and stored at 20 ± 2°C, at three different RH % levels, namely 95 ± 3% for group A, 65 ± 5% for group B and, 45 ± 5% for group C.

2.2 Monitoring of setting process

The setting process of the binary mixtures was studied at preset intervals (1, 3, 7, 14, 28 days) after applying a hydration - stop procedure [5] by immersing the samples in acetone and then, in di-ethyl-ether solutions. This was followed by the drying of the specimens in a ventilated oven at 70°C for 22 h. The phases formed during setting were determined by X-ray powder diffraction (XRD) and differential thermal analysis (DTA/TG). XRD was carried out in a Siemens D500 diffractometer, with a beam step of 0.03°/ 5 s. Thermal analysis was performed in a Perkin-Elmer Diamond Pyris thermal analyser, in static air conditions from room temperature up to 1.000°C, using a heating rate of 10°C/ min. The development of the hydration process and its effect on the microstructure of the specimens was examined in a FEI-Quanta Inspect scanning electron microscope, coupled with energy dispersive X-ray analyser (SEM/EDX). Finally, the compressive strength was measured in three cubic specimens from each group of mortar mixtures [6]. The specimens were tested in an Instron 1195 testing machine, using a displacement rate of 109 μm/s.

3 Results and discussion

3.1 Microstructure and setting products

Soon after the mixing of the pozzolan with lime, the formation of different hydrated phases, such as calcium aluminium hydrate (11-203), calcium mono-carboaluminate hydrate (41-219) and calc. aluminium oxyhydroxide hydrate (33-255), is initiated. Other phases detected in the binder fraction include calcite ($CaCO_3$) and portlandite ($Ca(OH)_2$) coming from carbonated and unreacted lime, respectively. The above hydrated phases were formed through the reaction of lime with pozzolan into the pore-solution, and were identified in the diffraction patterns at different curing periods. Their formation is evident after the first 24 hours and their peaks are more intense in specimens cured at high humidity levels (groups A and B), while there is a delay in specimens of group C. For the same time period, the ratio of the relative intensity peaks of the hydrated phases over the intensity of the portlandite main peak, increases as the humidity levels of curing conditions becomes higher (Fig. 1).

Although calcium silicate hydrates (C-S-H) are very poorly crystallised materials of varying stoichiometry, their formation was also evidenced in the diffraction patterns by the presence of two faint peaks in the area of 32 ° 2θ and 50 ° 2θ, along with a third one in the area of 29 ° 2θ, which is obscured by the shoulder of calcite [7]. Similarly to the aluminum hydrates, their relative amount increases with the relative humidity levels during curing.

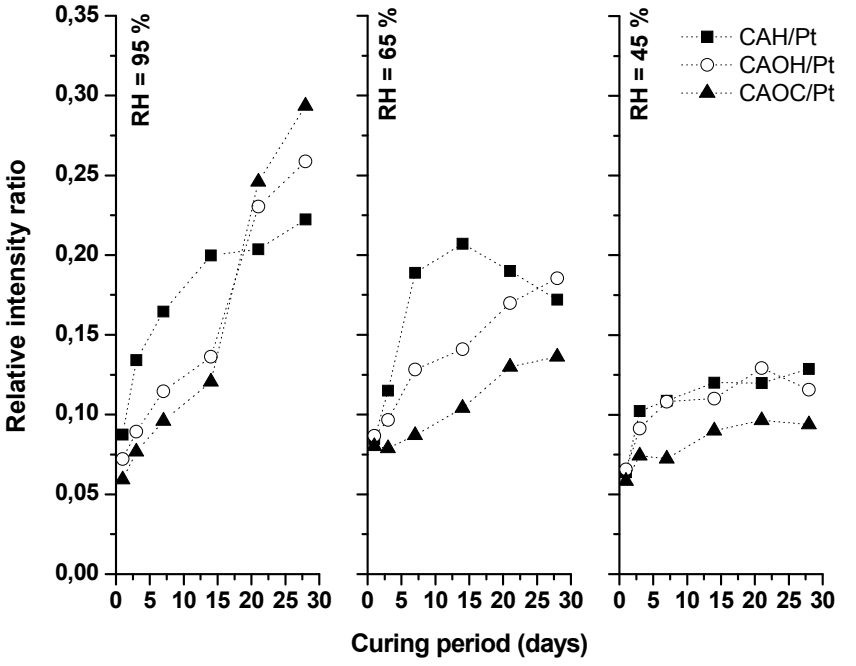

Fig. 1 Relative intensity ratios of calcium aluminium hydrate (CAH), calcium mono-carboaluminate hydrate (CAOC) and calc. aluminium oxyhydroxide hydrate (CAOH), over portlandite (Pt) for mixtures cured at different humidity conditions.

Aiming to further quantify the total amount of the hydrates formed during the setting, thermal analysis results concentrating on the thermal transformations in the range of 90°C – 200°C were investigated. The endo-thermal peaks that appeared in this range are attributed to the formation of both C-S-H and C-A-H phases [8]. The results indicated that there is no significant difference in the amount of hydrates formed in mixtures cured at 65% and 95% RH. However, the mixtures cured at high RH levels, exhibited a clear trend towards increase of the amount of hydrates, compared to those cured at medium RH conditions. In contrast, the pastes cured at room conditions presented no further development of the hydrated products after an initial period of seven days (Fig. 2).

The examination of the mixtures in the SEM proved that the formation rate and evolution of the above-described hydrated products strongly influenced the development of microstructure of lime-pozzolan pastes. The initial mixing of the solid constituents with water, created a uniform microstructure for all pastes, which was characterized by the presence of inter-granular macro-pores (Fig. 3a), filled with water. During the evolution of setting and curing, the new setting products were formed on the surface of the pore channels and started to fill up the available empty space (Fig. 3). SEM examination of fractured surfaces revealed that during the initial setting period (1-3 days), both pozzolan and calcium

hydroxide (lime) particles can be easily distinguished, while the hydration products formed can be hardly detected. Consequently, the amount of hydrated phases was considerably increased for groups A and B (Fig. 2), reaching an upper limit at 180, 120 and 28 days for groups A, B and C respectively.

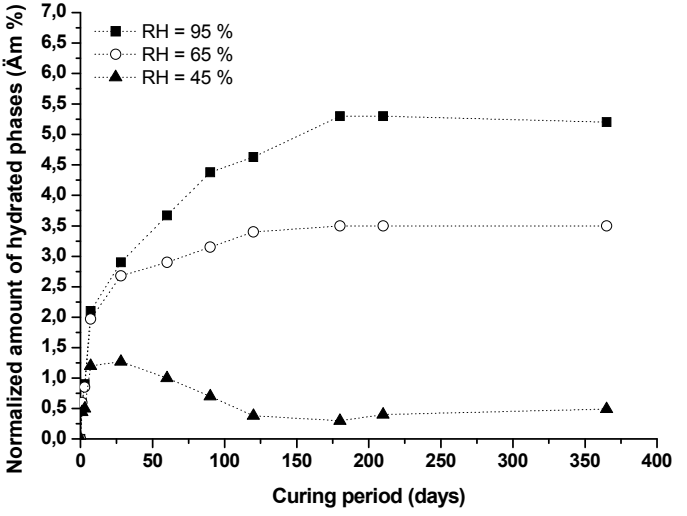

Fig. 2 Evolution of hydrated phases in lime-pozzolan mixtures cured at different humidity conditions, based on DTA/TG analysis.

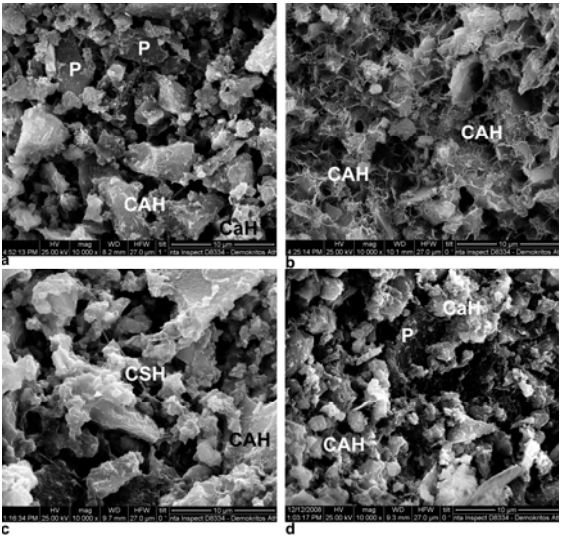

Fig. 3 Microstructure of mortar specimens from group A, after 7 (a) and 28 (b) days of setting, along with groups B (c) and C (d) after 28 days setting period. (P = pozzolan, CaH = calcium hydroxide, CAH = calcium aluminium hydrates, CSH = calcium silicon hydrates).

After this period, the evolution of hydrates, and consequently the modification of the microstructure, was strongly influenced by the curing conditions and the available water participating in the hydration reactions. As a result, after 28 days it was easy to distinguish between the three groups on the basis of the developed microstructure (Fig. 3): Group A seems to have a denser microstructure, while its macro-porosity (large capillaries) diminishes due to the enhanced formation of hydrated products. Group B also shows a decrease in the amount of large capillary pores, but it still contains a considerable amount of macro-pores and therefore presents a coarser texture. On the contrary, Group C exhibits the same microstructure in seven days, with pozzolan particles still visible and a large amount of macro-pores. This, along with X-ray diffraction and thermal analysis results, indicates that hydration is much slower in group C, where the carbonation process dominates.

3.2 Strength development

The interpretation of the compressive strength values of all specimens (Fig. 4) indicates that the development of mechanical properties is closely related to the curing conditions of the mixtures. After the first 7 days of setting, the mixtures develop only part of their potential total strength, while all specimens present very similar compression values.

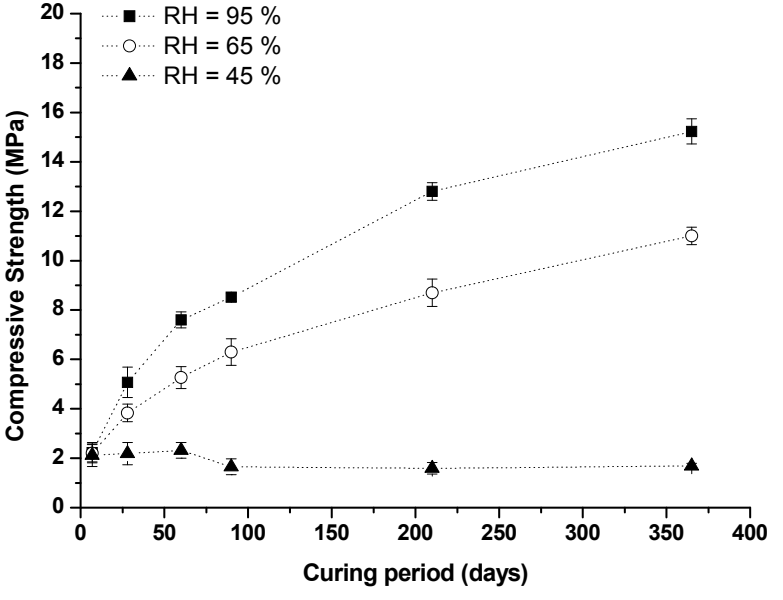

Fig. 4 Development of strength in mortar specimens cured at different humidity conditions.

Consequently, up to 28 days (which is the setting period proposed by standards [3, 4, 9] for assessing in laboratory the mechanical properties of mortars) the obtained strength values greatly depend on the curing conditions. For humidity levels ≥ 65% RH (standard conditions) a considerable strength development is observed (groups A and B), which increases further by increasing the humidity up to 95% RH. In contrast, samples of Group C present strength values considerably lower, reaching a decrease between 50-60%. The monitoring of the compressive strength values for a setting period of one year shows that the mixtures cured at an elevated humidity (groups A and B) continuously increase their strength; at this time-scale the differences between the two groups become significant. In contrast, the specimens of group C present no further evolution of their mechanical properties. This pattern (group C) fits better to the field conditions in the majority of conservation projects in the Mediterranean basin and describes the gap between the laboratory and field application performance of lime-pozzolan mortars.

4 Conclusions and recommendations

The laboratory monitoring of the setting process and strength development indicates that the initial 28 day period is very critical for the formation of microstructure and the future performance of lime-pozzolan mixtures. Thus, it is important to avoid, the introduction of any microstructure defects in this period, thus ensuring the acceleration of the hydration process [10].

At the early stage, after the consumption and/or evaporation of the initially added water, the hydration process is controlled by the hygric properties of the mixtures, their water retention capacity and therefore, the humidity levels of the surrounding environment.

The humidity conditions during setting have a major impact to the process that will dominate. At high RH % levels, when capillary condensation takes place inside the pore network, carbonation is inhibited and hydration processes dominate. The increased humidity results in the solubility of lime, which creates a highly alkaline environment and favours the lime-pozzolan reactions towards the formation of hydrated products. Moreover, capillary condensation blocks the diffusion of CO_2 inside the pores and carbonation is avoided.

The optimum humidity conditions for capillary condensation depend each time on the type, granular distribution and mix proportions of raw materials.

From the elaboration of the results it is indicated that the amount of hydrated products are limited in mixtures cured bellow 65% RH, while in contrast, the amount of calcium carbonate is increased bellow this limit.

Finally, although the different groups of specimens present a similar strength during the first seven days, the extension of curing period at humidity levels above 65% RH, multiply the compression strength values of mixtures up to 3 times in contrast to those that are left to set in open air conditions.

In the above context, the following parameters could contribute towards better practice and performance of lime-pozzolan mortars, especially in field applications:

- The use of a standardized quality matured lime putty instead of dry hydrated lime powder [11],
- The use of an optimum amount of pozzolan, in order to achieve maximum lime consumption within the first few days [12].
- The fineness of the pozzolan should be set below 63 μm, to accelerate the hydration rate [13].
- The use of water retaining agents, in an attempt to ensure that a water supply is retained within the mortar mass for a prolonged period [14].

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IV.27

The New Groups of Formulated Limes (FL) of Lime Standard EN 459 - Bane or Boon?

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Abstract Lime is the most commonly used binder for the preparation of mortars for restoration purposes. In the near future the reviewed EN 459 will standardise a new group of limes, the Formulated Limes (FL). Formulated Limes are limes with hydraulic properties mainly consisting of air lime (CL) and/or natural hydraulic lime (NHL) with added hydraulic and/or pozzolanic material. According to EN 459 the mixing of FL allows the blending CL or NHL with the following main constituents: Portland cement including Portland cement clinker, natural pozzolana, natural calcined pozzolana, limestone and/or granulated blast furnace slag. The available lime in FL in the form of $Ca(OH)_2$ should be between 15 to 80% by mass, which means that vice versa, it is possible to prepare standardised limes with a huge amounts of natural and artificial hydraulic components. These FL allow a very dedicated mix design of mortars and plasters with custom-made properties though their interactions between historic substrates remain unpredictable.

1 Introduction

In Europe limes are standardised in EN 459 [1], which is currently under review. It is state of the art that lime mortars were mixed by using air lime (CL), hydraulic lime (HL) or natural hydraulic lime (NHL) acc. EN 459. There is indepth knowledge about these limes and the chemical-mineralogical and mechanical-physical properties of mortars prepared using CL, HL or NHL. Furthermore, there is a lot of literature published dealing with the interaction between lime based restoration mortars and the historic substrate to be restored.

Nevertheless, there is no knowledge of the properties of fresh and hardened mortars that will be prepared using the new Formulated Limes.

The use of lime for the preparation of building materials as well as for the construction of monuments and buildings has a long tradition and can be traced back until the 7th century B.C. [2]. Today there is a widespread application of lime mortars due to the advantages of its processing and use as well as the natural origin of lime. The European norms are submitted in the agreed time intervals of a review and if necessary, a revision. The preliminary version of the actual revised standard EN 459-1 was published in August 2008 [3]. In the revised EN 459-1 a new class of lime has been recorded, the so called Formulated Limes (FL). FL are limes, which consist of normative predetermined limits of definite additive amounts of components chosen according to the specific properties required; for example the added inorganic-mineral components act predominantly hydraulically. Inorganic fillers as well as organic additives are considered in the standard. From this component variety results a huge number of mixture possibilities which must fulfill the given properties of the standardized Formulated Limes. The standard provides the required content of free lime and the values of compressive strengths after 7 or 28 days. Based on these demands 9 different FL classes can be defined; however no regulation in regards to the possible mixing proportions of the Formulated Limes results from it.

Lime mixtures similar to the FL mixtures were used up to now exclusively by a few manufacturers in France and Italy. Hence, knowledge of the material characteristics of these mixtures is solely internal and is not published. Within the scope of the European standardization, every manufacturer has the right to insert his tested product into the corresponding norm. At the moment there is no knowledge of FL by German lime producers; nor is there any understanding of the interaction between the components of the corresponding mixtures within the normative set of chemical and physical limits or the mix design and the mixing proportions of the FL substances.

2 Formulated Limes – an Overview

The mixture components of the Formulated Limes are different binders and supplementary cementitious materials (SCMs [26]) from the building sector which are included in the standard prEN 459-1(Table 1) [3]. The hydraulically effective mixture components of the FL are plotted in the Rankin diagram (Fig. 1). In this representation the huge variation in the composition of the FL becomes clear.

In total, 9 different classes of Formulated Limes are possible; each differ in the chemical composition and the physical properties of the mixed mortars (e.g. setting time, compressive strength). The standardized limitations of the FL are listed in Tables 2 - 4.

Table 1 Accepted components of Formulated Limes according to EN 459-1 (Single components of less than 5 % by mass are acceptable without declaration. If the total amount of different minor components is higher than 10 % by mass, all minor components have to be announced).

material	as main component	as minor component	additives	comments
lime (CL and NHL)	X			acc. EN 459-1
cement (CEM I, II, III)	X			acc. EN 197-1
OPC clinker	X			acc. EN 197-1
natural pozzolan	X			acc. EN 197-1
natural calcined pozzolan	X			acc. EN 197-1 (Q)
lime stone	X			acc. EN 197-1 (L, LL)
granulated blast furnace slag	X			acc. EN 197-1 (S)
calcium sulphate		X		acc. EN 197-1 (G)
micro silica		X		acc. EN 197-1 (D)
organic additives			X	declaration > 0.2 % by mass
mineral additives			X	declaration > 1 % by mass

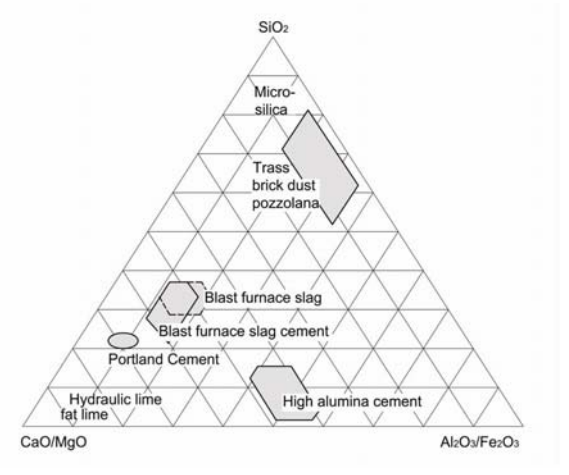

Fig. 1 Hydraulic active FL components plotted in the Rankin diagram

Table 2 Chemical requirements of FL according to prEN 459-1

FL	SO_3 [% by mass]	available lime as $Ca(OH)_2$ [% by mass]
FL A	≤ 2	≥ 40 and < 80
FL B		≥ 25 and < 50
FL C		≥ 15 and < 40

Table 3 Physical requirements of FL according to prEN 459-1

FL	compressive strength [MPa]		setting time [h]	
	7 days	28 days	start	end
FL 2	-	> 2 to ≤ 7	> 1	≤ 14
FL 3.5	-	> 3.5 to ≤ 10		≤ 10
FL 5	≥ 2	> 5 to ≤ 15		≤ 1

Table 4 FL classes and requirements according to prEN 459-1

compressive strength [MPa]	end of setting time [d]	available lime[% by mass]	40 – 80	25 – 50	15 – 40
		FL	A	B	C
28 d: 2 – 7	≤ 14	2	FL A 2	FL B 2	FL C 2
28 d: 3.5 – 10	≤ 10	3.5	FL A 3.5	FL B 3.5	FL C 3.5
28 d: 5 – 15 7 d: ≥ 2	≤ 1	5	FL A 5	FL B 5	FL C 5

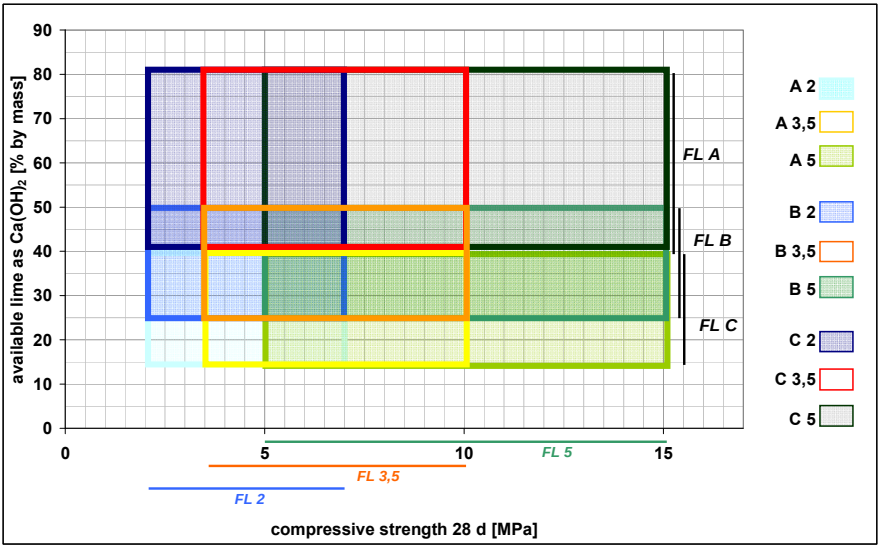

Fig. 2 Diagram of the different FL classes acc. prEN 459-1 [3]

The requirements of the standard prEN 459-1 allow the overlapping of FL classes that relate to the content of available lime and compressive strength after 28 days. This interrelation is shown in Fig. 2., which also shows that the different FL classes can be mixed using different binder mixtures and that the FL classes are not unambiguously separated from each other. As a result, the same FL can be mixed with different components and vice versa; a FL can also be assigned to several classes. From these degrees of freedom, together with the high complexity of the mixture composition, the sensible FL class limits of the partly complicated FL mixtures are determined as a function of their application.

The properties of the single mixture components of the FL are already known from the application of both lime and cement. Indeed, the properties of possible binder combinations, contents and requirements for FL which are possible in prEN 459-1 are more or less unknown. Further extensive mixing proportions and compositions presumably arise from the use of FL mixtures in mortar and plaster.

3 Historic Mortars with Lime

In 2003, the US-American Getty Conservation Institute published an extensive literature review of the numerous publications that deal with historic mortars; however, the main focus of this literature review was the repair of historic buildings. Hughes & Válek [4] have also published a review about mortars and their behavior in historic buildings and the properties of lime mortar in postpositive historic mortar systems as well as the use of natural hydraulic limes

in such scenarios have been discussed by Pavía and Treacy [6]. A summary of the mineralogical and technological properties of hydraulic lime in mortars for the restoration of natural stone was completed by the Institute of Stone Conservation (IFS) [5].

The consideration of mortar properties is often limited to a single parameter, e.g. workability, durability or structural performances in application. Among the well known properties of mortar, it is the high water vapour diffusion values and the adsorption ability of lime mortars that can positively influence the indoor climate and adsorption of air pollutants; the high water retention capacity can also improve the indoor climate [7, 8]. Thomson [9] describes the advantages of the workability of lime mortars and points out their high plasticity, high water retention capacity and their high porosity, as well as their good water vapour diffusion capacity. The high water retention capacity of fresh lime mortars is also evidenced by comparative studies between cement-sand mixtures and lime-sand mixtures [10]. Arandigoyen and Alvarez [11] confirm a positive correlation of the water retention capacity of fresh mortars as a function of the lime content. Investigations regarding the influence of lime on the fresh mortar properties of a cement based mortar have shown that the viscosity of the cement lime paste is influenced more by the morphology of the lime rather than by its chemical composition [12]. Further experiments have shown that an appreciable amount of cement must be substituted by lime to significantly influence the microstructure of the mortars [13].

The mechanical properties of lime mortars have been examined by numerous authors, however, only a few have correlated the strength with other relevant parameters. The setting and the increase in strength were examined by Baronio et al. [14]. It was stated that with increasing relative humidity the compressive strengths of lime mortars with HL 5 as well as with CL 90 increased. Stefanidou and Papayianni [15] and Lanas et al [16] correlated the strengths with the amount of aggregates and concluded that in HL 5 and CL 90 mortars the porosity increased with a rise in binder content, which promoted both the carbonation and post-hardening of the mortars. Henriques and Charola [17] studied the influence of the mix procedure of CL mortars on the strength and concluded that changes in the mix procedure have no effect on the mechanical properties. However, the compressive and bending tensile strengths, as well as the dynamic modulus of elasticity (E-modulus) of HL mortars increase with a longer mixing time.

According to Groot [18], the bond strength is one of the most important properties of hardened mortars because it ensures the structural strength of masonry and joints, thus providing a resistance to weathering. Furthermore, it is shown that the water retention capacity decisively influences both the bond and the adhesive tensile strength. The dynamic of moisture transport between brick and mortar is considered to be important because it controls the development of hydration and the adhesive bond. Additionally, a fine, uniform pore structure improves the strength of lime mortars whereas an irregular structure of pores in the boundary layer leads to a reduction in strength [19].

The relation between the bond strength of NHL with the water content, water retention capacity, workability and water vapour permeability has been studied in Hanley and Pavía [20]; these studies are incomplete and are currently in progress. However, Maurenbrecher et al. [21] have shown that the main cause for the loss of bond strength in masonry is the action of frost.

A direct relation between porosity and mechanical strength was detected for mortars with binder/aggregate-ratios below 2:1 [22]; a relationship which is evident in modern lime mortars [23]. In general, a rise in capillary porosity increases both the absorption and suction whilst subsequently reducing the strength and the frost resistance of a mortar. Nevertheless, it is possible not to affect the frost resistance if a mortar contains a sufficient amount of air pores, which act to reduce the stress resulting from the action of frost; as can be verified by the measurements of the water saturation coefficient [6].

In NHL based mortars the capillary suction, which is independent of the hydraulic strength of the lime, is seen to rise in proportion with an increasing flow diameter [20]. As shown by Baronio et al. [14] the properties of moisture transport are not dependant on the curing of the mortar.

Concerning rheological properties, several associations are pointed out in the current literature. For instance, Hanley and Pavía [20] studied the relationship between the workability and strength of NHL mortars and have determined, for each hydraulic lime, the optimum flow diameter required to reach the optimum strength. Sébaïbi et al. [12] have used the viscosity of cement lime pastes to determine water binder ratio's, to enable working with mortars of the same consistency, assuming that viscosity is rather influenced by the morphology of the lime than by the chemical composition.

Winnefeld and Böttger [24] have showed that shrinkage is heavily dependent on the amount of hydraulic binder and Knöfel and Schubert [25] have suggested that a maximum linear shrinkage of 0.30 mm/m is the minimum requirement for lime mortars for to resist freeze-thaw.

A high water retention capacity is a desirable property in air lime mortars and hydraulic lime mortars. Therefore the workability (plasticity) is improved while a sufficient amount of water is retained to enable the development of hydrates in hydraulic limes and to improve the carbonation of calcium limes. Fine lime particles improve the water retention capacity of a mortar whilst at higher water-binder ratios; clay has been shown to reduce the water retention capacity of a mortar [24]. The higher the specific surface area of the lime, the higher is the water retention capacity.

4 Conclusion

With the establishment of the new lime group FL it is assured that only limes whose single components are well known will be used for the preparation of

mortars for the restoration of historic masonry. Because of this, chemical-mineralogical knowledge of the binder compounds and any unforeseen damaging reactions between FL restoration mortars and historic materials should be excluded in the future.

There is an abundance of literature relating to the single components of FL but in regards to the interactions between the main component lime and the normative admitted mixing proportions, data is only deductive from mixtures similar to FL. To use the complex lime group of FL in a controllable trial, specifically when using mortars with defined qualities, the present knowledge must be increased and FL mortars with the typical positive lime mortar properties must be developed.

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IV.28

Impact of historically inspired processes of lime mortar preparation on its properties

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Abstract The aim of the paper is to present and discuss selected results of research concerned with historically inspired techniques of nonhydraulic mortar preparation. The research offers results that may be useful both in conservation practice as well as in improving the methodology of lime mortar specimens preparation for testing purposes. The paper presents the results of an impact of water to binder ratio, time of fresh lime mortar mixing and maturing and over rapid drying on lime mortar specimens properties in the course 90 days of formation of calcium carbonate matrix. Methodological specification of the preparation of lime mortar specimens is dealt with in the paper more in detail.

1 Introduction - compatibility and lime mortar preparation

In taking care of historical masonry and its surface coatings, great emphasis is laid on material and aesthetic compatibility of the historic mortars and new mortar. Yet the material and aesthetic compatibility issues are often reduced to composition, texture, colour, and structure correspondence of the historical and the new mortar. The fact that the properties of the mortars are also affected by the techniques of mortar preparation, application, and curing is well known [e.g. 1-5], however the problem is still disregarded by the scientists.

The research of the impact of historically inspired preparation techniques of lime mortar on its chemical and mechanical properties has been the aim of PhD theses [6]. The results are useful in the revitalization of historical techniques of lime mortar preparation and curing in conservation practice [7, 8] and for improving the methodology of lime mortar specimens preparation for testing purposes. The preparation processes – if neglected – can strongly affect the durability of the lime mortar and results of lime mortars testing.

2 Experimental work

2.1 Mortar components and mortar composition

To preclude the influence of mortar composition on the research results, only nonhydraulic lime mortars with a binder to aggregate ratio of 1:3 by volume were studied and will be discussed. Volume proportions of components have been converted to weight proportions to ensure precision in the proportioning process.

Powder calcium hydroxide aged under water for two years in the form of lime putty was used as the binder; natural quartz-based sand was used as the aggregate. Table 1 gives bulk density and chemical composition of the mortar components; Table 2 shows the gain size distribution of the aggregate. Table 3 details the mortar composition.

Table 1 Bulk density and chemical composition of used components

Components	I.L. [%]	SiO_2 [%]	CaO [%]	MgO [%]	Fe_2O_3 [%]	Al_2O_3 [%]	SO_3 [%]	CO_2 [%]	CaO free [%]	Na_2O [%]	K_2O [%]
Lime putty Bulk Density 1375 kg.m^{-3}	23.3	0.20	96.66	0.57	0.04	0.03	0.19	1.37	91.2	-	-
Sand Bulk Density 1380 kg.m^{-3}	1.5	82.00	1.30	0.45	R_2O_3 9.50		<0.10	-	-	0.13	2.30

Table 2 Gain size distribution of the aggregate

Gain size [mm]	5.0	2.5	1.0	0.5	0.25	0.125	0.063	below 0.063
Passing [%]	100	98.9	78.1	35.4	9.1	3.4	2.1	0.2

Table 3 Composition of fresh mortars

Influences on mortars properties	Mortar	Components	Weight (g)	W/B ratio*	B/Ag ratio
D, E, F,REF – Influence of W/B ratio	D	Water	360	1.92	1:3
		Lime putty	400		
		Aggregate	1200		
	E	Water	270	1.58	
		Lime putty	400		
		Aggregate	1200		

	F	Water	0	0.54
		Lime putty	400	
		Aggregate	1200	
G, REF – Influence of over drying of fresh mortar (TD) Q, REF – Influence of fresh mortar maturation (TM) M, N, REF – Influence of mortar mixing time (MM) H, I, REF – Influence of water treatment (WT)	G, Q, M, N, H, I, REF	Water	180	1.23
		Lime putty	400	
		Aggregate	1200	

* W/B ratio more precisely W/$Ca(OH)_2$ ratio has been calculated from mass of dry $Ca(OH)_2$ presented in lime putty, lime putty containing 65 % solids by mass

2.2 Methodology of the mortar preparation

Fresh lime mortar was inserted into a prism mould measuring 20 mm by 20 mm by 100 mm. The specimens' dimensions were chosen to reduce the volume of the mortar and to ensure a representative range of the mortar carbonation after 90 days. A minimum of six prisms for every type of mortar (D, E, F, G, Q, M, N, and REF) were prepared.

2.2.1 Water to binder ratio

For water to binder weight ratio (W/B ratio) of every type of mortar (D, E, F, G, Q, M, N, and REF), see Table 3.

2.2.2 Time of mixing

Apart from the mortars N and M, the time of mortar mixing was 5 min. Time of the mortar M mixing was 1 min and 15 min for the mortar N.

2.2.3 Time of mortar maturation

Apart from the mortars Q, the time of mortar maturation was 0 days. The time of the mortar Q maturation was 30 days. While maturing, the nonhydraulic lime mortar was protected from the air to prevent water evaporation.

2.2.4 Temperature of drying

Apart from the mortar G, mortars were dried in the moulds for three days at RH 60 ± 10% and 20°C. The mortar G was overly rapidly dried for three days, at RH 60 ± 10% and 50°C immediately after moulding.

2.3 Testing methodology

2.3.1 Shrinkage

Shrinkage was measured in the longitudinal dimension after the specimens were dried (after 3 days), according to EN 12808-4 [9]. The average value of a minimum of six specimens is presented.

2.3.2 Carbonation process

The carbonation of nonhydraulic lime binder is the transformation of calcium hydroxide into calcium carbonate in the presence of carbon dioxide and water. The carbonation process leads to an increase in weight of the binder of 35 percent.

To observe the binder carbonation process nondestructively under different conditions, the specimens were weighed regularly over the course of 90 days [10]. The average percentage of binder weight gain after 90 days due to carbonation in a minimum of six specimens is presented.

2.3.3 Flexural strength

The four point flexural test was carried out using a Testatron compression machine at the loading rate of 0.15 mm/min. The results of the flexural strength after 90 days are the average values of a minimum of six specimens.

2.3.4 Compressive strength

The compressive strength tests were conducted on fragments of the specimens resulting from the preceding flexural test, according to EN 1015-11 [11]. The compressive strength testing was performed on a Testatron. The loading rate was 0.3 mm/min. The results of the compressive strength after 90 days are the average values of a minimum of three specimens respectively.

2.3.5 Porosity and pore-size distribution

Mercury intrusion porosimetry (MIP) was used only for matrix porosity and pore size distribution of the mortars after 90 days in diameters varying from ca. 1 μm to the order of 0.01 μm. The porosity and pore structure of the mortars in pores with diameters varying from ca. 1 μm to the order of 1000 μm has been specified by means of optical microscopy combined with digital image analysis of polished sections of the mortars after 90 days [12]. Both values are presented in the Table 4.

3 Results and Discussion

The results of the experiments are in the Table 4 and in the Fig. 1.

3.1 Water to binder ratio

It was verified that decreasing water to binder ratio (W/B ratio) reduced the shrinkage of mortar after its setting. Decreasing the W/B ratio also tends to reduce the porosity of mortar in the range of pores in sizes up to ca. 1 μm. At the same time there was no accompanying decrease in the mortar carbonation due to porosity reduction. This corresponds with the fact that decreasing the W/B ratio increased the strength of the lime mortar, especially the compressive strength.

Unfortunately, the water to binder ratio is often missing information in practice recommendations as well as in the studies on lime mortars, though it affects large scale of mortar properties.

Traditionally, no extra water was added to mortar made from very stiff lime putty and aggregate [3-5]. This mortar has a W/B ratio of approximately 0.5 (mortar F in the experiment).

Table 4 Experiments results

Mortar: specification	Shrinkage/SD (stand. dev.) [%] *	Carbonation [%]**	Flexural Strength/SD [MPa]**	Compressive Strength/SD [MPa]**	Porosity (>1μm / ≤1μm) [%]**
1. Influence of water/binder ratio on mortars properties (W/B)					
D: W/B=1.92	2.49/0.26	37.17	0.23/0.03	0.44/0.03	25.5 / 10.3
E: W/B =1.58	1.96/0.18	46.97	0.22/0.04	0.52/0.03	21.3 / 11.4
REF: W/B=1.23	1.99/0.18	46.91	0.34/0.03	0.77/0.04	23.3 / 12.1
F: W/B =0.54	0.31/0.17	47.27	0.36/0.02	2.1/0.19	15.0 / 11.8
2. Influence of mortar mixing on mortars properties (MM)					
M: MM=1 min	1.92/0.38	52.42	0.37/0.03	0.85/0.04	-
REF:MM =5 min	1.99/0.18	46.91	0.34/0.03	0.77/0.04	-
N:MM =15 min	1.85/0.31	55.65	0.38/0.04	0.84/0.04	-
3. Influence of mortar maturation on mortars properties (TM)					
REF: TM=0 days	1.99/0.18	46.91	0.34/0.03	0.77/0.04	-
Q: TM =30 days	2.18/0.35	67.23	0.45/0.03	1.45/0.03	-
4. Influence of over-rapid of drying on mortars properties (TD)					
G: TD=50°C	2.01/0.40	45.05	0.33/0.03	0.74/0.02	-
REF: TD=20°C	1.99/0.18	46.91	0.34/0.03	0.77/0.04	-

* tested after 3 days; ** tested after 90 days

3.2 Time of mixing

Time of mortar mixing had no essential impact on the mortars' properties under study after 90 days. However, it is important to mention that lime putty and lime mortars are thixotropic materials [3, 5, 13], and an intensive or long time spent mixing the mortar can convert stiff coarse stuff into smooth and workable mortar with a very low water to binder ratio [1-5]. Regrettably, this is not a standard approach to mortar preparation in current practice, when mortar workability is compensated by adding too much water. From this point of view, the length and method of mortar mixing have an important place in the process of lime mortar preparation, as part 3.1 demonstrates.

Traditional techniques of mortar mixing generally involved beating, chopping, and ramming on a wooden board or trough for at least an hour until the mix was sticky and workable [5].

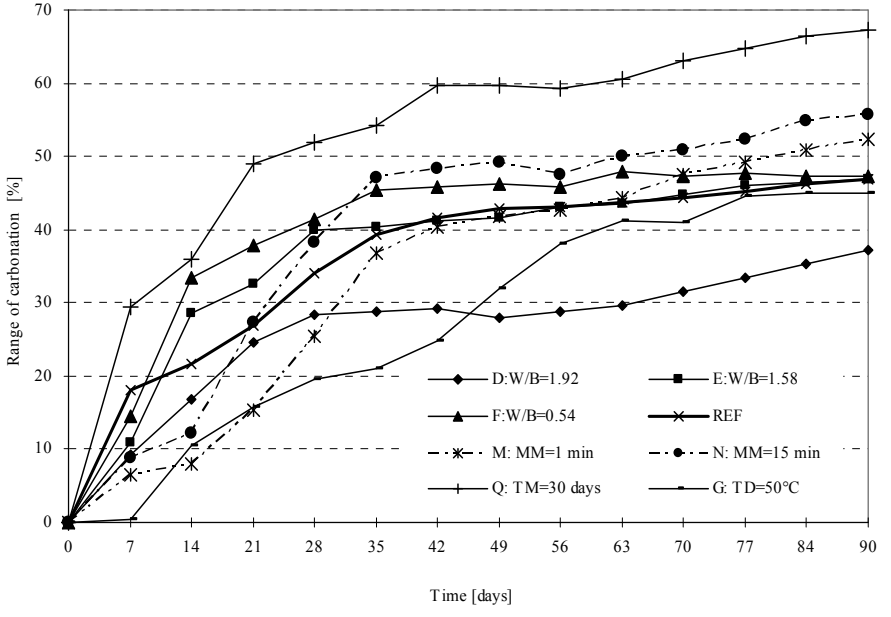

Fig. 1 Range of mortars carbonation in the course of 90 days. Mortar REF:W/B=1.23; MM=5 min; TM=0 days; TD=20°C.

3.3 Time of mortar maturation

Maturation (aging or storing) of fresh nonhydraulic lime mortar is also a historically inspired process of lime mortar preparation [1-5].

During testing, it was determined that nonhydraulic lime mortar that had been allowed to mature for 30 days before use (mortar Q) carbonated more quickly than unmatured mortar REF. The maturation (aging or storage of fresh nonhydraulic lime mortar) increases the strength of the mortar, especially compressive strength. At the same time, as lime mortar matures, shrinkage and porosity increase (similar to the maturation or aging of lime putty [14, 15]).

Traditionally, maturation happened after cold or hot mixing or after quicklime and aggregates slaking in the mixtures [4, 5]. Where possible, mortar should be mixed and matured at least three months before required on site [5].

3.4 Temperature of mortar drying

Often the over-rapid drying of fresh mortar is associated with shrinkage. In the experiment it was noted that after over-rapid drying mortar G, shrinkage was not affected. Serious retardation of mortar G carbonation, however, occurred as a result of over-rapid drying in the first 7 days. Carbonation continued after a return to normal conditions in the following weeks, and over-rapid drying basically did not affect the properties under study after 90 days.

4 Conclusion and recommendations

On the basis of the acquired results, it is possible to draw the conclusion that to prepare lime mortars specimens with reproducible properties or to prepare an experiment evaluating the explicit impact affecting mortars properties, it is profitable to consider that lime mortar properties are affected to a large extent also by techniques of mortar preparation. The processes of mortar preparation affect not only chemical but also mechanical and structural properties of lime mortar.

The improved methodology of nonhydraulic lime mortar specimens preparation for testing purposes should include the specification of:

1) the properties of mortar components (aggregate, lime, additives, water);

2) lime mortar composition, including water to binder ratio, which affects fresh mortar behavior as well as properties of lime mortar in the course of carbonate matrix formation;

3) time and way of stiff mortar mixing (in connection with lime putty thixotropy);

4) time and conditions of fresh lime mortar maturation before use;

5) method of mortar moulding;

6) time of mortar specimens exposition before testing;

7) temperature and humidity of the environment in the course of mortar setting and carbonate matrix formation.

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IV.29

Mortars for Conservation-Restoration of Wall Painting Support in Rupestral Churches

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Abstract The paper presents the laboratory research of lime base mortars for conservation-restoration of mural painting support situated in severe microclimate conditions. The repair mortars were analyzed from the point of view of chemically (soluble salts content), physically (water absorption, coefficient of saturation in water, adherence at support), mechanically (compressive strength) and resistance to the freeze-thaw phenomenon. The mortar test panels were then applied in situ inside of the Corbii de Piatra rupestral church (14th century), Arges County, Romania. Their behavior has been studied over a period of 6 months. The hardening of the mortars was observed by X-ray diffraction and loss on ignition. The adherence of the mortars to the mural painting support and their behavior in relation to the degradation factors (excessive humidity, the migration of soluble salts, biological attack) was also observed.

1 Introduction

Preliminary researches [1] of mural painting support from rupestral church Corbii de Piatră, Arges county - Romania have showed that original mortar (14th century), from the walls and nave arch and altar, is a mortar rich in lime reinforced with straw. The mortar has a porosity of about 19%, possible due to degradation of vegetal aggregate under influence of temperature, humidity and salts from walls. The mortar from iconostasis (19th century) is a mortar based on lime of which composition is of about 97% lime and about 3% fine siliceous aggregate.

In order to find a solution for monument conservation series of mortars based on lime were tested in laboratory. These were then applied in situ and their behavior was followed on the period of next 6 months.

2 Experimental

2.1 Materials

Hydrated lime (CL 80) was used as binder and different types of aggregates: finely ground limestone (content of $CaCO_3$ of 97.20%), river sand (grain size 0-1 mm), sandstone – similar with that of church walls (grinded up to a grain size of 0-1 mm) were used. Taking into account the conditions of microclimate specific to rupestral church, in some compositions pozzolanic additions were used as follows: silica fume (content of about 92% SiO_2), volcanic tuff (content of about 62% SiO_2 reactive).

Raw materials have a low content of soluble salts, expressed as SO_3, Cl^-, Na_2O, respectively K_2O (table 1). Soluble salts were determined on chemical way, from the solution resulted as consequence of maintaining 18 hours in distilled water of 2 g of grinded mortar.

Table 1 Content of soluble salts in used materials

Raw materials	Soluble salts (%) is it weight %			
	K_2O	Na_2O	SO_3	Cl^-
Hydrated lime	0.00	0.00	0.00	0.000
Limestone	0.00	0.00	0.00	0.017
Volcanic tuff	0.00	0.00	0.00	0.017
River sand	0.00	0.00	0.00	0.034
Sandstone	0.00	0.01	0.09	0.025

Mortars carried out from these raw materials were noted from C1 to C6 and are within compositional systems: C1 lime-limestone (1:1.86); C2: lime-limestone (1:2.70); C3: lime-sandstone (1:2.70); C4: lime-silica fume-sandstone (1:0.05:2.85); C5: lime-silica fume-river sand (1:0.05:2.85); C6: lime-limestone-volcanic tuff-river sand (1:0.86:0.62:2.92). The ratios are expressed as weight parts.

2.2 Experimental conditions and methods of testing in laboratory

In laboratory, evaluation of mortars characteristics was performed on prismatic specimens (40x40x160mm) prepared and kept in accordance with EN 1015-11 [2]. The water content for preparation of specimens was established according to a consistency of 140±10 mm, determined on flow table (EN 1015-3 [3]).

The mortars were characterized from point of view: physically (apparent density, water absorption; coefficient of saturation in water, adherence at support), chemically (content of soluble salts), mechanically (compression strength) and sustainability (freeze-thaw resistance).

Values of the apparent density were obtained by ratio of the weight and volume of the dry mortar samples. Water absorption was performed in accordance with the method of immersion in water from STAS 2414/91 [4]. Saturation coefficient was determined making the ratio between absorbed water at room temperature and that absorbed at boiling [5, 6]. For the adherence at support the mortar was applied on full burnt brick, in a layer with thickness of about 6 mm. Testing was performed with DYNA Z16 apparatus, at the age of 56 days. Content of soluble salts was determined as in case of raw materials. Mechanical resistance (compressive strength) was tested in accordance with SR EN 1015-11 [2] at age of 28 and 56 days. Resistance at freezing-thawing consisted of keeping the mortar prisms immersed 8 hours in distilled water, then 8 hours in air at -15 to -17°C. Determination was considered complete when specimens was recorded a weight loss of over 5% or were destroyed by cracking.

2.3 Experimental conditions and methods of testing of mortars applied in situ

The mortars were applied in situ in two areas of the monument, such as:

- - on iconostasis, to north, the brick wall, area without mural painting. The mortars being noted: C1-C, C2-C, C3-C, C4-C, C5-C and C6-C;
- - in altar, on northern wall, lower register, direct on sandstone wall, without mural painting. The mortars being noted: C3-Z, C4-Z, C5-Z.

Conditions of microclimate inside church, in the moment of mortars application (at the end of March), were temperature about 5°C and relative humidity of the air 70%.

Behavior of the mortars in situ was remarked from the application moment and on a period of 6 months from application. Temperature and relative humidity of the air in this period were registered minimum values of 5.8°C and 42% of RH and maximum of 21.7°C and 95%.

To evaluate the behavior of the mortars the following characteristics were taken into consideration: *workability*, *capacity of modeling* – expressing the possibility to confer to material the desired relief; *mural aspect* – representing chromatic tonality of mortars in relation to the original, *adherence* of mortar at support, *phenomena of contraction* – which may be manifested through detachments of support and appearance of some cracks in puttying field; *reversibility* – expressing material quality to be removed without difficulties and without entrain support damaging; *resistance at environment factors* – modifications as consequence of

humidity, temperature; *resistance at bio-degradation factors* – counting units forming of colonies from mortar samples; *appearance of saline efflorescences*.

The hardening process was evaluated soon after application and after 6 months of curing by determination of loss on ignition at different temperatures (450°C, 1000°C) and through X-ray diffraction.

3 Results and discussions

3.1 Results obtained in laboratory

Results of physical-mechanical determinations are presented in the table 2. It is noted that mortars have low apparent density which was considered as an advantage for the works of restoration because they do not add supplementary weight at original materials. The mortars C1 and C2, which have a very fine granulation and contain limestone as aggregate, present values of water absorption higher than the other mortars that have as component river sand or sandstone as aggregate. From the last ones, the mortar C6 has a higher water absorption (17.7%) in comparison with C3, C4 and C5 (15.3-15.9%) because of presence in its composition of the tuff and a lower proportion of aggregate (river sand). The mortars present a good adherence at support and the detachment takes place through breaking in mortar mass. Of all the mortars, those containing river sand and sandstone (C3…C6) have higher values of adherence. The explanation may be the larger grain size and aggregates nature, which make the composition of the mortar closer to that of the altar's wall and iconostasis.

Table 2 Physical-mechanical characteristics of mortars

Mortar code		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Apparent density (g/cm^3)		1.49	1.53	1.64	1.70	1.73	1.70
Water absorption (wt. - %)		24.9	23.5	15.6	15.9	15.3	17.6
Water absorption by boiling (wt. - %)		25.55	24.04	16.92	16.78	17.33	18.17
Coefficient of saturation with water		0.97	0.98	0.92	0.95	0.88	0.97
Adherence at support (N/mm^2)		0.06	0.06	0.09	0.07	0.13	0.11
Compression strength (MPa)	**28 days**	0.7	1.2	0.9	2.0	2.2	2.7
	56 days	0.5	1.1	0.9	2.7	2.6	3.1
Freeze-thaw resistance (nr. cycles)		1	1	2	7	9	15

Obtained values of mechanical strength demonstrate that all tested mortars have a low compressive strength (0.5-1.0 MPa) and moderated (max. 3.1 MPa), that make them compatible with conservation state of mural painting support of

the monument. The values of coefficient of saturation with water are between 0.88 and 0.97. In literature [5, 6] is mentioned that as much coefficient of saturation with water is closer of 1 as lower is freezing resistance of the samples. Consequently, in accordance with the data from table, all tested mortars are susceptible to not have frost resistance. Nevertheless, because of different mechanical strength at compression, mortars behavior at frost is different. Thus, for same coefficient of saturation (0.97) in case of the mortars C1 and C6, the most resistant at frost is the mortar C6 (min. 15 cycles) because has a higher mechanical strength (3.1 MPa in comparison with 0.5 MPa in case of the mortar C1). Also, from the mortars with comparable mechanical strengths (1.1 MPa for mortar C2 and 0.9 MPa for mortar C3), more resistant to freeze-thaw process is the mortar C3, because its lower coefficient of saturation (0.92 in comparison with 0.97 for mortar C2). The mortars C4 and C5 have the same behavior with mortars C2 and C3.

From chemical point of view, it may be considered that the mortars not contain soluble salts.

3.2 Results obtained in situ

From the evaluation of the mortars in fresh state it can be said that they have presented a good behavior, assuring a sufficient working time for application. Also, they have presented a good modeling capacity, and also a good adherence at support. From point of view of the mural aspect, the mortars which contain sandstone as aggregate (C3, C4) are closer as chromatic tonality of the iconostasis or altar's wall. The mortars with limestone (C1 and C2) are closer as chromatic tonality of the lime mortar of mural painting support. Below (Fig. 1 a, b) presents the areas with applied mortars.

a. b.

Fig. 1 Mortars applied on iconostasis (a) and on sandstone wall (b)

At the end of observation period, the adherence of mortars was tested through mechanical removal with scalpel, of a part from these. It was observed that there was no separation of mortars to the interface with the support, which means a

good adherence of these to substrate. Mortars are reversible, because their mechanical removal occurred easily without producing deterioration in the area on which these have been applied.

The mortars C1 and C2 which contain fine calcareous aggregate, present on their surface micro-cracks of contraction (Fig. 2a). In case of the mortars C3 to C6 which contain aggregate with 0 -1 mm granulation not presented cracks of contraction (Fig. 2b).


a.

b.

Fig. 2 Images where micro-cracks of contraction on mortar surface C1 are remarked (a) and their lack on the mortar C4 (b) applied on iconostasis

From chromatic point of view the mortars which contain sandstone as aggregate (C3 and C4) or river sand (C5 and C6) have tonalities compatible with the support. All mortars proved a good resistance at environment factors (temperature, humidity) during the observation period (summer and autumn). On mortars surface, saline efflorescences were not remarked and X-ray diffraction not put into evidence the presence of salts and degradation products, in detectable limits. Also, at the end of observation period, the lime was not completely carbonated: the XRD patterns revealed small quantities of portlandite (see cap. 3.3).

Microbiological analysis of samples taken from the surface of mortars did not put in evidence any contamination with bacteria or fungi. It could be due to inorganic material content of the mortars and presence of portlandite which makes an alkali pH which inhibits the growth of micro-biodeteriogens. We did not find photoautotrophic microorganisms or any organic deposits which could act as nutrients for heterotrophic microorganisms (bacteria and fungi).

3.3 Evaluation of hardening process

Hardening process of performed mortars takes place either as carbonation reaction only (mortars C1, C2, C3), or as carbonation and pozzolanic reaction between lime and pozzolanic additives –silica fume or volcanic tuff (mortars C4, C5, C6).

Following the determinations for all terms and in case of all mortars it was found diminishing loss on ignition at 450^{o}C, simultaneously with an increasing

values of loss on ignition at 1000°C in comparison with the initial one, which means transformations of calcium hydroxide in calcium carbonate as consequence of carbonation process of the lime (Fig. 3).

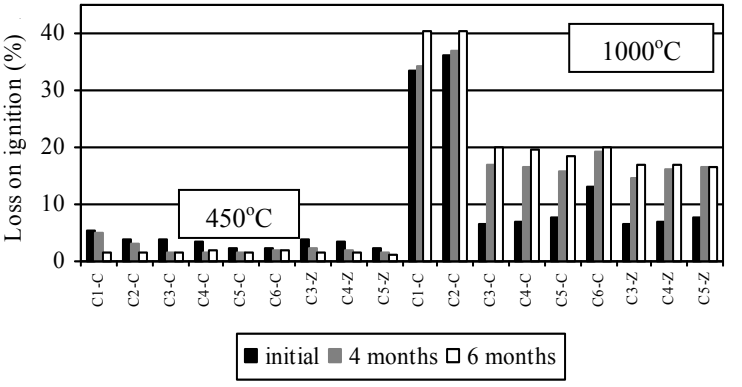

Fig. 3 Loss on ignition at 450°C and 1000°C of the mortars applied on iconostasis (C1-C – C6-C) and on sandstone wall (C3-Z – C5-Z)

Through diffraction analyze same evolution of hardening process was stated, being more pronounced at the term of 6 months. In the figure 4 the diminishing of the peaks specific to portlandite and increasing of those specific to calcite at the term of 6 months in comparison with the initial term is remarked.

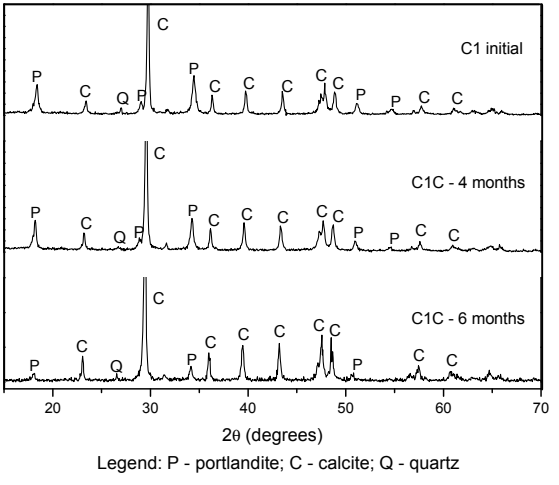

Fig. 4 X-ray diffraction patterns of mortar C1-C at different terms

The X-ray diffraction analysis of the mortars with pozzolana (C4 to C6) were not put into evidence the presence of pozzolana reaction compounds in detectable limits.

4 Conclusions

Obtained mortars, tested in laboratory, have characteristics which sustain their use in the activity of conservation and restoration of historical monuments: low apparent density, low mechanical strength at compression (0.5 MPa) up to moderate (max. 3.1 MPa at 56 days), good adherence at brick support, resistance at freeze-thaw phenomena (especially mortars C4, C5, C6).

After 6 months of monitoring of behavior and esthetic aspect, under mentioned conditions of temperature and humidity, it was stated that all mortars have maintained an appropriate adherence at support, efflorescences have not appeared on mortars surfaces, are reversible and may be removed without danger to damage the area where these have been applied.

Mortars with aggregate of river sand or sandstone (C3…C6) have not presented cracks of contraction at hardening. From point of view of composition and chromatic tonality these mortars are more compatible with the masonry of the iconostasis and with the sandstone wall.

Mortars with limestone (C1 and C2) have a composition and a tonality more compatible with lime mortar of the mural painting support.

Modifications because of temperature and humidity variations have not stated. Chemical composition of mortars does not sustain biological growth respectively biodegradation.

Evaluation of the compatibility for the mortars applied with original support will be finished after a period of minimum 2 years.

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IV.30

Strengthening of Pure Lime Mortars with Nanoparticles of Calcium Hydroxide

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Abstract CaLoSiL E25 is a suspension of nanoparticles of calcium hydroxide in ethanol, which has been developed as a consolidant for lime mortars. As a preliminary study, the behaviour of the product was evaluated on laboratory samples before on-site testing. Pure lime mortars were produced with different aggregate/binder ratios, in order to obtain cured mortars with different pore-size distributions and different strengths. After full carbonation, these lime mortar specimen were consolidated with several cycles of CaLoSiL E25. The changes in water transport were evaluated according to the number of cycles applied. The consolidation effect of the treatment was measured by three techniques developed in our laboratory for determination of flexural, compressive and tensile strengths on small samples.

1 Introduction

Renders are the most common coats of masonry buildings. Their first function is to protect the masonry, but for some important buildings they also have a decorative function. However they are exposed to aggressive physical, mechanical and chemical actions inducing a lot of damage. Their main decay pattern is the loss of cohesion, which is a loss of mechanical strength of mortar's layers due to loss or alteration of the binder joining the aggregates, causing crumbling, desegregation, sanding or powdering.

In the past renders were replaced by new ones when severly damaged, thus, losing the materials history and construction technology. During the 19th and beginning of the 20th centuries, lime mortars were replaced by cement-based mortars, presenting "better" properties, such as quicker setting, higher strength, increased resistance to freeze/thaw cycles and salt crystallisation [1]. But it often induced more damage to the masonry due to a mismatch between the materials and their strength [2].

Since the second half of the 20th century, a regain of interest for the lime technology in the field of historic building conservation has been observed through research in traditional techniques and use of compatible repair materials [3, 4].

The maintenance of old renders often implies to restore the strength of the materials (consolidation) and to re-attach layers by grouting. It is frequently followed by other conservation operations to prevent further degradation.

Several products mostly used for the consolidation of stone have been experimented to restore cohesion to old mortars like limewaters or ethylsilicate [5, 6]. Limewater is considered to a more traditional consolidant, as the loss of binder within the mortars is replaced by the same chemical component but it shows a poor cementing action [7], unless applied in hundred of cycles. With the improvement of technology, new materials were developed and can be used as an alternative for limewater: nanoparticles of calcium hydroxide, $Ca(OH)_2$, (or nanolimes). The particles size range between 50 and 200nm. The dispersions of $Ca(OH)_2$ in solvent can be highly concentrated (up to $50g.L^{-1}$), thus limiting the number of applications, which is an important drawback of limewater treatment.

2 Materials and Methods

2.1 Preparation of the mortars specimens and application of the treatment

The binder used was a lime putty, and the aggregate a river silicate sand, called Borek. The lime putty was prepared by slaking a quicklime (CaO, class A, produced by Lhoist) and the slaked lime was stored for 3 years under water. The matured lime putty was properly mixed before use and its bulk density determined ($1350kg.m^{-3}$). Lime mortars were prepared with different binder/aggregate ratios: 1:4, 1:6 and 1:9.

Three types of specimens are prepared: prisms (100mm x 20mm x 20mm), plates (60mm x 40mm x 5mm) and rings (height: 30mm, inner diameter 35mm, outer diameter 40mm). The specimens are cured during two months, with light spraying with water every 2 or 3 days. Afterwards, they are sprayed only once a week for another four months.

After carbonation, the specimens were treated with CaLoSiL, which is a new consolidant based on colloidal suspensions of lime nanoparticles in various solvents. For this study, Calosil E25 is selected: colloidal calcium hydroxide dispersed in ethanol (the concentration of $Ca(OH)_2$ is $25g.L^{-1}$).

The product was applied by dropping on the surface of all three types of mortar specimens until full saturation. 2, 4, 6 and 10 cycles are applied, after waiting for the evaporation of the solvent between each application.

Full saturation of the specimens is obtained by applying 10mL on the beams, 5mL on the rings and plates.

2.2 Testing

2.2.1 Porosity

The porosity accessible to water N_t [%] was determined by the following test I.1 in the Rilem recommendations [8]. The measurements are done on three different samples taken from prisms and the result presented in this paper is the average of the three values.

The pore size distribution of the non treated specimens was determined by mercury porosimetry. Samples of prisms specimens (less than 1cm^3) were dried in the oven at 60°C. The data were collected by the Quantachrome porosimeter model Poremaster PM-60-13, with pressure range of 0.005 – 413MPa. The mercury parameters were set to values of 480 erg/cm^2 for the surface tension of mercury and 140 degrees for the contact angle. For each samples, two measurements were done.

2.2.2 Water uptake coefficient [9]

When a porous material is put in contact with water, the capillary tension allows the fluid to penetrate inside the pores of this material. This phenomenon can be followed by the change in weight, which is directly linked to the volume of water absorbed.

Before hand, the samples are dried to constant mass at 60°C. The samples are immersed to a height less than 2mm. At time intervals, initially very short and then longer, the samples are slightly wiped with a dampened cloth and quickly weighed, then put back in the tank. The time t [h] that has elapsed from the beginning of the test is noted just like the mass M [kg].

The tests are performed on three prisms and the result presented in this paper is the average of the three values.

2.2.3 Mechanical tests

Bending strength is the common 3 point bending strength tested on prisms (100mm x 20mm x 20mm). The two other tests, compressive and tensile strength are carried out on non standard specimen and specially developed for the purpose of testing the relatively low strengthening effects [10]. The compressive strength is performed on rings. The shape of the specimens allows increasing the surface-to-cross-section area ratio, and thus it intensifies the measurable strengthening effect. Tensile strength is performed on small plates. The sizes of these samples

also allow improving the product penetration and the curing conditions. The result is the average value of measurements on five specimens.

3 Results

3.1 Water transport properties

Lime mortars were prepared with different binder/aggregate ratios: 1:4, 1:6 and 1:9, in order to obtain lime mortars with different pore-size distributions and different strength. The mortar with ratio 1:9 represents a very weak, degraded mortar. Mortars 1:9 and 1:6 have a high amount of pores with a diameter of approximately 100µm, while the mortar 1:4 has smaller pores. In mortar 1:4, two main groups can be distinguished: from 0.02 to 1µm and from 7 to 50µm (Fig.1).

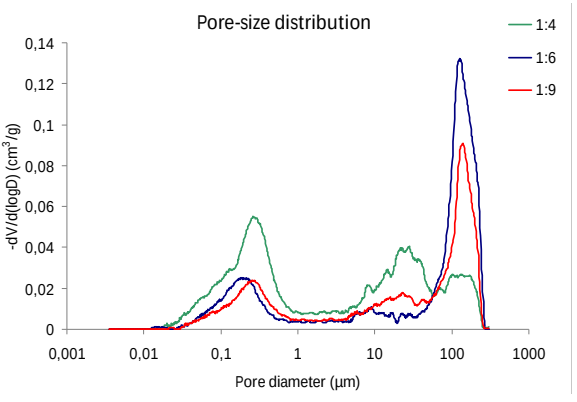

Fig. 1 Pore-size distribution determined by Mercury Intrusion Porosimetry.

Table 1 Water accessible porosity (v/v %)

	Mortar 1:4	Mortar 1:6	Mortar 1:9
Reference	**28.3**	**30.1**	**31.9**
2 cycles	28.4	29.9	30.7
4 cycles	27.3	29.3	30.5
6 cycles	27.7	29.0	29.4
10 cycles	26.6	28.5	28.8

The results of water accessible porosity measurements are presented in Table 1. The porosity of the reference mortar 1:4 is lower than the one of the mortar 1:6

and 1:9. This confirms that the porosity of the lime mortars increases as the binder/aggregate ratio decreases, as it was previously shown by Jornet [11].

For each type of mortars, there is a decrease of the porosity observed when the number of application cycles increases. A higher decrease of porosity after treatment is observed on the weak mortar with a binder/aggregate ratio of 1:9. After ten cycles of application, the decrease is of 1.7% and 1.6% for mortars 1:4 and 1:6, while the porosity decreases of 3.1% for mortar 1:9. After 6 and 10 cycles, mortar 1:9 shows similar porosities as mortar 1:6.

The charts of water absorption test for mortar 1:6 are displayed in Fig. 2. A decrease of the speed of absorption is noticeable after treatment, by calculating the coefficient of water absorption W:

$W_{reference} \sim W_{2cycles} > W_{4cycles} \sim W_{10cycles} > W_{6cycles}$.

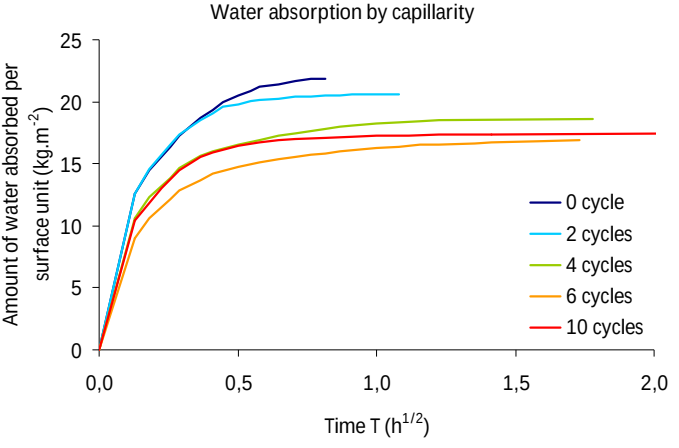

Fig. 2 Water absorption by capillarity on specimens of mortar 1:6.

There is also a decrease of the total amount of absorbed water (Table 2).

Table 2 Total amount of water absorbed (w/w %)

	Mortar 1:4	Mortar 1:6	Mortar 1:9
Reference	**9.7**	**12.7**	**14.4**
2 cycles	9.2	12.3	9.2
4 cycles	8.4	10.7	5.8
6 cycles	8.6	9.7	5.0
10 cycles	8.2	9.5	3.5

The changes in water absorption follow the changes observed on the porosity of the specimens after treatment.

The changes in water transport properties observed after treatment are small and correspond to an increase in binder within the mortars.

3.2 Mechanical strength

The results of measurements of the compressive strength on rings specimens are displayed in Fig. 3. For the reference specimens, the mortars strength is higher when the binder/aggregate ratio is high: $\sigma_{1:4} > \sigma_{1:6} > \sigma_{1:9}$.

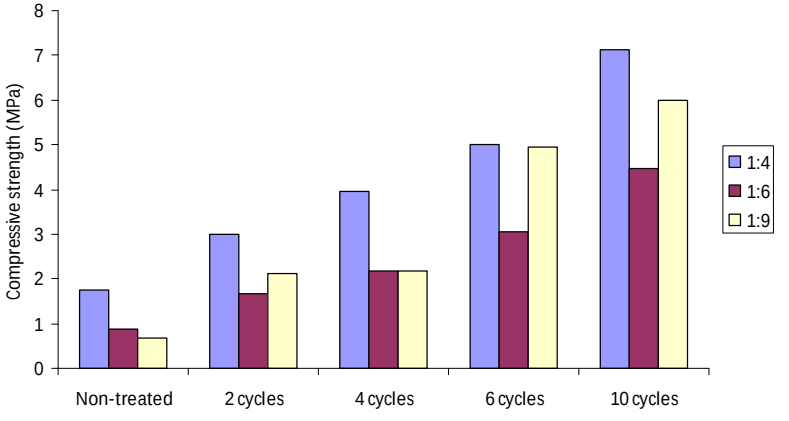

Fig. 3 Compressive strength on rings specimens.

For the treated specimens, we observe that the compressive strength increases with the number of application. The changes are, like for the porosity, more noticeable on the weak mortar. After 10 cycles of application, the strength increases 3 times for the mortar 1:4, 4 times for the mortar 1:6 and 8 times for the mortar 1:9. Moreover, after 4 cycles of application, the specimens from 1:6 and 1:9 show the same compressive strength, and after more application, the treated mortar 1:9 is stronger than 1:6.

Besides, looking at the chart from Fig. 3, we can notice that the compressive strength does not seem to reach a maximum value yet. It would need a higher number of applications.

The other results of mechanical test are presented in Table 3. Similar observation can be made: for untreated specimens, the mortars strength is higher when the binder content is high, and the bending and tensile strength increase with the number of applications cycles.

Table 3 Bending and Tensile strength (MPa)

	Bending strength			Tensile strength		
Mortars	1:4	1:6	1:9	1:4	1:6	1:9
Reference	**0.9**	**0.7**	**0.4**	**0.5**	**0.3**	**0.2**
2 cycles	1.3	1.0	0.5	0.8	0.7	0.4
4 cycles	1.5	1.3	0.9	0.9	0.5	0.7
6 cycles	2.1	1.6	1.1	1.0	0.6	0.8
10 cycles	2.8	1.9	1.6	1.2	0.9	0.9

3.3 Side effect: whitening of the surface

A whitening of the surface is visible on all type of mortars, increasing with the number of cycles, as can be seen on the Fig. 4. It is also visible, on sample P-9-41, after 10 cycles of application, that there is a whiter part on the edges of the plate, probably due to the concentration of particles.

Fig. 4 Change of colour of the specimens (mortar 1:9) after treatment.

4 Conclusion

When conservation work is required on a historic building, the decayed renders are often replaced. Since the second half of the 20th century, a lot of research has been done in order to characterise the old mortars and produce new ones with similar characteristics. A new alternative is the consolidation of the decayed mortars by colloidal suspensions of calcium hydroxide nanoparticles, allowing conserving the historic mortars. Its first asset is the chemical compatibility: the nanoparticles of calcium hydroxide restore the cohesion of the lime between the aggregates.

In the present work, the results from laboratory tests on lime mortar specimens show high strengthening potential of the commercial product CaLoSiL E25. The consolidating effect depends on mortar composition (binder/aggregate ratio) and

thus on its pore-size distribution. The tests also demonstrate that the strength can be adjusted by applying a determined number of applications cycles (or using different concentration of the product). Optimal treatment procedure with suspensions of calcium hydroxide nanoparticles should be determined before on-site application to decayed renders, according to their pores characteristics and the needed strength values.

Special attention must be paid to the possible whitening of the treated surface, which in some case can cause a visual alteration of the conserved renders.

To conclude, colloidal suspensions of calcium hydroxide nanoparticles appear as a promising consolidant for ancient lime mortars with loss of cohesion.

5 Acknowledgment

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IV.31

Grouts for Injection of Historical Masonries: Influence of the Binding System and other Additions on the Properties of the Matrix

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Abstract Grouting of historical masonries has been a widely used technique for regaining their integrity or strengthening them. Since cement-based grouts proved very strong and in some cases destructive for these old masonries, grouts based on a lime-pozzolan binding system have been developed by researchers as an alternative, meeting compatibility issues required for repair interventions. In this paper a number of grout compositions based on lime and other traditional binders are studied with and without additions of limestone filler and nano particles of silica. In some, a small quantity of white cement (15%w.t) was incorporated into the system. Apart from the different constituents of the binding system, the addition of admixtures was used for improving the properties of grouts. Rheological properties, such as flowability, volume stability and penetrability of the grouts were measured in the fresh state. Mechanical properties of dried grouts as well as of grouted sand were checked. Volume changes due to drying shrinkage of grouts were recorded after demoulding and up to 28 days. The microstructure of the dried grouts of the control mixture and that with silica nano particles was examined by stereoscope, image analysis and DTA-TG methodology.

1 Introduction

Injecting grouts into masonry is a widely used repair technique for consolidating and strengthening old structures. It has a long history, but the first systematic work started in the 1980s [1-6]. Since then the technique of grout manufacture has been improved by introducing high speed or ultrasonic wave mixers and establishing criteria for designing a suitable grout for each case study grout. The first applied grouts were rather cement-based, modified with organic or inorganic additives. As experience has accumulated and compatibility issues in the

repair of monumental or historical structures have gained acceptance by the scientific community, many efforts have been made to develop softer grouts. In these experiments, cement was partly replaced with lime and pozzolanic materials, since the cement–based mixtures were very strong and changed the behaviour of the old structure. By testing not only the grout mixtures but also the response of grout-repaired masonries to different types of loadings, ternary binding systems of grouts are proposed and experimentally justified [7].

The need for relatively early strength development of high water/binder grout mixtures does not allow a large percentage of cement to be substituted by softer binders. However, modern advanced admixtures, in which the water/binder ratio can be substantially reduced for the benefit of strength in combination with higher reactivity of fine grains of traditional binders, have created new opportunities for designing a compatible and effective grout.

Nanotechnology tools and nanoscale materials are very promising items with which the properties of microstructure can be steadily modified. According to literature, nanosilica particles decrease the Ca/Si of C-S-H compounds and increase the mean silicate chain length, leading very possibly to a C-S-H matrix of long-term stability [8-10]. In general, nanoparticles of Si are believed to possibly reduce portlandite leaching and increase strength and durability by enhancing the matrix-aggregate interface and C-S-H gel formation.

Since the grain size of the solid constituents of grout is of paramount importance for its penetrability, very fine limestone filler and nanosilica particles were chosen as additions for improving the strength capacity and performance of lime-pozzolan grouts. Therefore, the scope of the research is to find the potential of lime-pozzolan mixtures for well-defined pozzolans and additions.

2 Experimental

The intent of this experimental work was to study lime and pozzolan-based soft grouts and to attempt to improve their properties by adding fine limestone filler and nanoparticles of silica fume. This lime-pozzolan binding system was selected because it has been found in the majority of old mortars of the Roman and Byzantine period. Two natural pozzolanic materials were used after milling to increase their fineness, including a volcanic material from the island of Milos and a diatomite. Brick dust from modern fired bricks was also added as pozzolanic or inert material. Its particle size was smaller than 0.2 mm. In one group of mixtures 15% of white cement was added to replace pozzolan. Some of the characteristics of the binders and additions used are shown in Table 1. The proportions of the grout mixtures are given in Table 2.

Table 1 Characteristics of the constituents of the grouts

Constituents	App. Specific density	Specific surface area m^2/g	Pozzolanicity index ASTMC311:77 (MPa)	Particle size analysis Percentage of grains (μm)	
				d(0.9)	d(0.5)
Lime powder	2.471	2.250	-	10.8	3.09
Milos pozzolan	2.403	1.820	10.5	11.6	4.3
Diatomite	2.425	1.070	9.0	59.8	13.9
Cement	3.100	1.030	-	57.9	17.0
Brick dust	2.851	0.225	2.5	454.4	129.0
Limestone filler	2.846	0.408	-	152.9	47.5
Silica fume (14nm)	2.20	200.0	-	-	-
Hydrophilic nanosilica (150nm)	2.20	170-230	-	-	-

Table 2 Composition of the grout mixtures

	Parts by weight						Nanoparticle % by mass		
Code Nr	Lime powder	Milos Pozzolan	Diatomite	Brick dust	White Cement	Limestone filler	Hydrophilic	Silica fume	w/b
1a	1	1	-	-	-	-	-	-	1.09
1b	1	1	-	-	-	0.5	-	-	0.86
1c	1	1	-	-	-	-	1	-	1.18
1d	1	1	-	-	-	-	-	1	1.43
2a	1	0.6	-	0.4	-	-	-	-	0.90
2b	1	0.4	-	0.6	-	-	-	-	0.95
2c	1	0.2	-	0.8	-	-	-	-	0.90
2d	1	1	-	-	-	-	-	-	0.85
3a	1	-	1	-	-	-	-	-	0.86
3b	1	-	1	-	-	0.5	-	-	0.71
3c	1	-	1	-	-	-	1	-	1.03
4a	1	0.7	-	-	0.3	-	-	-	0.97
4b	1	0.7	-	-	0.3	-	-	-	0.83
4c	1	0.7	-	-	0.3	-	1	-	1.04

The quantity of water was adjusted to keep flow time measured by Marsh cone (ASTM C939-87) 9-11 sec, which was previously defined as adequate based on

in-situ experiments in old masonry. The flow time was measured immediately and one hour after mixing. Special attention was given to make high performance grout mixtures of acceptable fluidity, penetrability, and stability. Therefore, a mix of superplasticizer of polycarboxilic basis and retarder 1.5% by mass of binders was added to all grout mixtures. A high speed mixer (up to 8000 rpm) was used. The admixtures were added into a small quantity of water, which was part of the total added quantity.

Nanoparticles of Si were also pre-mixed with water before their addition to the mixture. The mixing started with low speed and was gradually increased up to 8000 rpm. The total mixing time was 5 min for grout mixtures without nanoparticles and around 8 min for those with nanoparticles. Penetrability of the fresh mixtures measured by using sand-column test (NORM NFP 18-891,1986) filled with sand 2-4 mm. The grouted sand of the column of each test was immediately cast into 4 cm x 4 cm x 4 cm steel moulds for testing compressive strength.

Volume stability of grouts was measured after 24 hours from mixing by using cylindrical containers, according to DIN 4227 Teil 5 standards. The test results concerning fluidity, penetrability, and 24 hour bleeding are shown in Figs. 1, 2, and 3. Three triplets of 4 cm x 4 cm x 16 cm steel moulds were sealed and filled with fresh grouts and cured at climatic chamber of 90% RH and 20°C up to testing date.

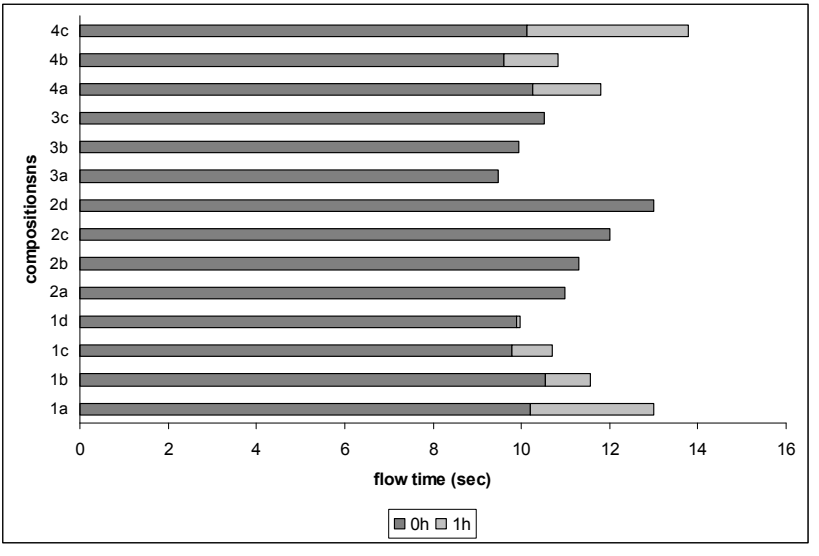

Fig. 1 Flow time of lime-based grouts

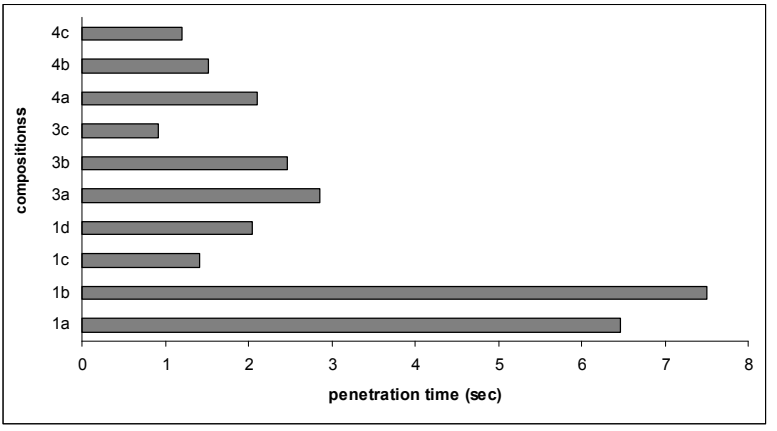

Fig. 2 Penetrability of lime-based grouts

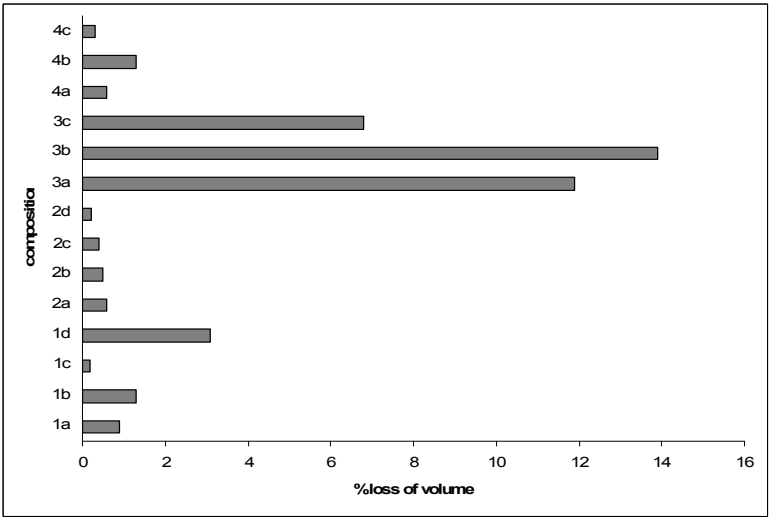

Fig. 3 Bleeding water volume after 1h of lime-based grouts

3 Results and Discussion

The tests of fresh grouts showed that the water/binder ratio, flow time, and penetrability all decrease in the grout mixtures to which extra limestone filler is added, while volume loss after 24 h seems to increase. On the contrary, the extra addition of nanosilica particles 1% by mass of binders, without changing the percentage of the admixtures, clearly increases the water/binder ratio to keep the flow time limits. Furthermore, penetrability is significantly improved by reducing

the required time for penetrating the sand column. The volume loss of nanosilica modified grouts is also considerably reduced, except in the case of nanosilica fume added-grout for which the water/binder was very high in comparison to the control grout. Considering only the basic properties of the fresh grouts, it seems that the nanosilica addition influences them positively. That is very important for the good performance of grouts. The addition of brick dust, which reacts both as pozzolanic agent and inert filler, seems to decrease the water/binder ratio, but flow and penetrability time are unacceptably increased, while the volume stability is improved. The volume loss of lime-diatomite mixtures is also very high, a negative point for this combination of binders. After demoulding (1-2 days after casting), the prismatic specimens were placed in a room of relative humidity below 60% and temperature around 20°C, and deformation as volume change percentage were recorded for 25 days. Volume changes were measured, instead of length changes as mentioned in DIN 52450:1985 standard, as it is considered more representative for drying shrinkage deformation in lime-based mortars. In Figs. 4 and 5, the measurements are given for the best two compositions 1a, b, c, d and 4a, b, c. It is obvious that drying shrinkage deformations are higher when nanosilica is added, while the extra addition of limestone filler does not differentiate them so much.

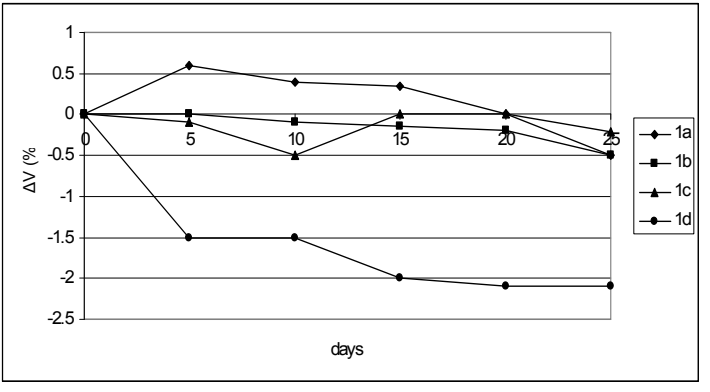

Fig. 4 Volume changes with time after demoulding of grout mixture with code Nr1

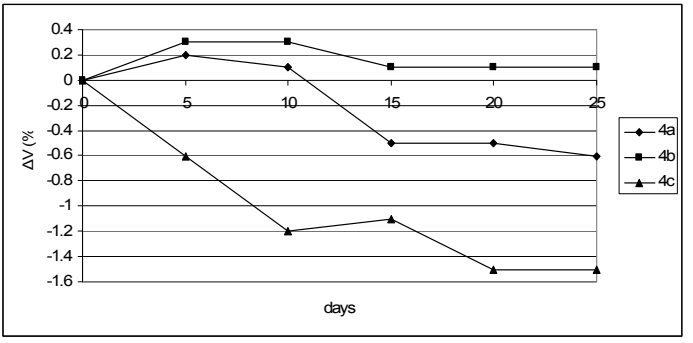

Fig. 5 Volume changes with time after demoulding of grout mixtures with code Nr4

The stereoscopic examination (magnification 10X) of the sections of these specimens with nanosilica showed the characteristic pattern of very intensive cracks, as indicated in Figs. 6 (a, b) and 7 (a, b).

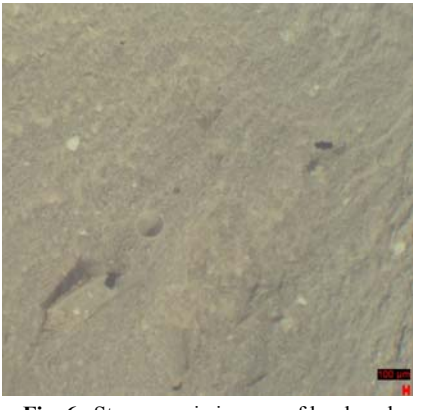

Fig. 6a Stereoscopic images of hardened grout without nanoparticles. Composition 1a

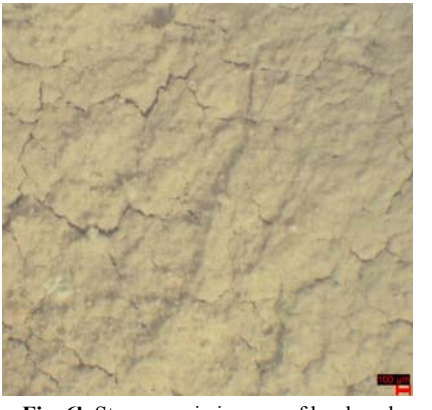

Fig. 6b Stereoscopic images of hardened grout with nanoparticles. Composition 1d

Fig. 7a Stereoscopic images of grout with cement without nanoparticles. Composition 4a

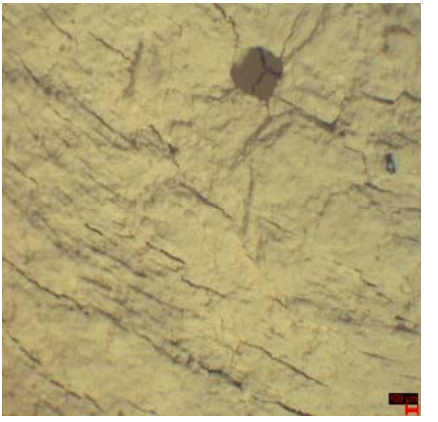

Fig. 7b Stereoscopic images of grout with cement with nanoparticles. Composition 4b

The compressive and flexural strength of prismatic specimens and the crushing value of grouted sand cubes were tested at 28 days age after continuous curing in moist conditions. As mentioned above, the results representing the mean value of three prismatic (4 cm x 4 cm x 16 cm) and three cubic (4 cm x 4 cm x 4 cm) specimens are included in Table 3. In addition, the dynamic modulus of elasticity was measured using ultra sonic wave sonometer. The results for the compositions of group code Nr1 and Nr 4 are depicted in Fig. 8.

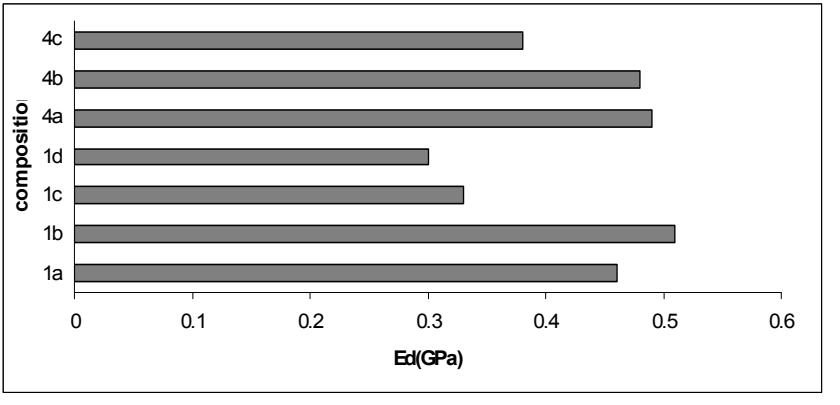

Fig. 8 Dynamic modulus of elasticity of grouts of code Nr1 and 4

Furthermore, the porosity of hardened grout mixtures was measured and listed in Table 3. The values mentioned are the average of 4 samples.

Table 3 Strength and porosity of grouts

Code Nr	Compressive strength 28-d MPa specimen:prism	Flexural strength 28-d MPa specimen:prism	Compressive strength 28-d MPa (grout sand) specimen:cubes	Porosity 28-d %
1a	2.24	0.76	1.15	41.07
1b	2.48	1.03	1.37	39.8
1c	1.96	0.74	0.7	42.3
1d	1.40	0.67	0.59	50.53
2a	3.35	1.23	-	-
2b	2.33	0.88	-	-
2c	.52	0.62	-	-
2d	0.87	0.51	-	-
3a	1.16	0.58	0.90	36.55
3b	0.86	0.46	1.40	39.60
3c	0.72	0.51	0.68	43.99
4a	2.63	1.09	1.64	39.3
4b	2.33	0.97	1.48	31.5
4c	1.45	0.70	0.99	42.68

Results indicate that limestone filler contributes to higher strength development of lime-pozzolan grout, while there is either no such increase in lime-diatomite and lime-pozzolan-cement or the strength is almost of the same level. When brick dust replaces pozzolan the 28 days strength is considerably lower, proving less pozzolanic capacity, although the water/binder ratio was lower than the control mixture 1a. When nanosilica is added, the strength and dynamic modulus of elasticity is decreased significantly. This could be attributed to higher water/binder ratio and higher values of porosity in comparison with control mixtures, but it needs further investigation because it is a negative unexpected issue. Additionally, the thermogravimetric analysis (DTA-TG) of the control 1a and 1c, 1d matrices at 28 days and 3 months showed there was a reduction in $Ca(OH)_2$ and an increase of $CaCO_3$ (Table 4). Significant reduction of $Ca(OH)_2$ was recorded for 1c (43.6%), and the increase of $CaCO_3$ for that sample was 24.5%.

Table 4 Content of $Ca(OH)_2$ and $CaCO_3$ measured by DTA-TG method at 28-d and 3-months age

Code Nr	$Ca(OH)_2$ (%)		$CaCO_3$ (%)	
	28-d	3months	28-d	3months
1a	8.37	7.24	30.75	31.11
1c	7.19	6.44	23.59	28.70
1d	6.10	3.44	25.09	31.25

4 Conclusions

Net lime-pozzolan grouts of acceptable fluidity, penetrability, and volume stability develop strength 2.3 MPa. Replacing 40% of pozzolan by brick dust, the strength increased (from 2.3 to 3.3 MPa) but fluidity is decreased. If 15% of pozzolan is replaced by cement, the properties of fresh grout are good and the strength is slightly increased (from 2.3 to 2.65 MPa). The limestone filler improves the strength of lime-pozzolan grout but influences negatively the performance of fresh grouts. Diatomite as pozzolanic material does not contribute to the improvement of the grout properties in the fresh and hardened states. The addition of nanosilica particles (hydrophilic and silica fume) under the defined terms, without using higher percentages of admixtures to manage the extra water demand, proved very positive for the fluidity, penetrability, and volume stability of grouts. However, it was clearly detrimental to strength development, resulting in a drop in strength from 2.24 to 1.96 MPa for Nr 1 series and from 2.64 to 1.46 MPa for Nr 4 series. Further investigation is necessary.

5 Acknowledgments

The authors would like to thank students Lemonia Apostolaki and Anna Gontia for their assistance in the laboratory work.

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IV.32

Influence of Sand Fines on the Mechanical and Physical Properties of Lime-Based Renders and Plasters

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Abstract Lime–based mortars of adequate workability are used for repairing coating mortars on old masonry in historical buildings. The analysis of a great number of old plasters and renders made by the Laboratory of Building Materials at Aristotle University of Thessaloniki (AUTH) during the last twenty years showed that these mortars are rich in fines (aggregate with size less than 0.063mm). In the present paper, mortar samples with different binders and different sands were prepared and tests to assess the influence of fines on their mechanical and physical properties were performed. Apart from standard sand, three other sands were used as there are many building sands whose content in fines is relatively high. In addition, many ready mixed mortars contain a high percentage of fines. Based on the results, it is obvious that the fines can significantly reduce the strength and increase the volume shrinkage of the mortars. Furthermore, the porosity was increased and capillarity was also increased. Additionally, the type of fines also seems to play a role in their behaviour in relation to the basic binder. This research work contributes to improving the design of mortar mixes for lime-based plasters and renders.

1 Introduction

Renders and plasters constitute the protective and often the decorative skin of structures composed of stone, brick masonry or even adobe [1]. The technique of covering the structural surfaces with renders is known since the pre-historic era where adobes were rendered with clay or lime-based mortars (Fig. 1).

Fig. 1 Render applied to protect mud brick.

During the classical and Roman period, renderings were the only way to seal cisterns (Fig. 2).

Fig. 2 Render in cistern at Olynthos 4th century B.C.

Since then, renders based on lime were continuously used until know. This simple material elaborated with special care was used as a base for wall-paintings or wherever there was direct contact with humidity. Much later and during the 19th century, renders were also artistic materials as they were used to decorate mansions (Fig. 3).

Fig. 3 Building of the 19th century in Thessaloniki.

Specific materials and techniques were often used for renders and plasters in order to fulfil their functional and aesthetic requirements. The analysis of a large number of old renders (more than 500 samples) based on the recording of the chemical, microstructure, mechanical and physical properties showed that they were rich in fines, the binder/aggregate content ranges from 1:1 to 1:2 while the aggregates could be classified as sand of different maximum size (2mm, 4mm or even 8mm) [2, 3]. Additionally, inclusions such as straw and chips of wood were often added in order to increase their stability and durability and minimize their cracking tendency (Fig. 4) [4].

Fig.4 Chips of wood in a render of the Byzantine period.

In some cases pigments were added in order to give a colourful result (Fig. 5) [5].

Fig. 5 Red render from the Roman period.

The thickness of historical renders ranged from 3-7cm (Fig. 6) to less than a centimetre. The different layers generally showed very good adhesion with the masonry substrate. The usual practice was to apply renders in three layers. The first one was used to cover the rough wall and coarse sand was used for that purpose while the second had a thickness of 5mm and was applied after the first layer was dry. The sand used for the second layer was fine. In order to ensure the

cohesion of the two layers, the roughness of the first layer was increased by forming grooves by hand or by a special instrument [6, 7]. The outer layer was 3-5mm thick and contained fine sand. Old renders where usually multilayer systems, with increasing porosity and decreasing radius of pores from the interior to the exterior layers. This constitution promoted wicking of water to the outer face, preventing moisture accumulation inside masonry and at the interfaces. These renders allowed water absorption but also favoured quick drying. In the mortar layers of the external coverings of stone masonry that were in contact with drainage channels, a reactive soil acting as pozzolanic material has been used [8]. The analysis showed that the insoluble residue of their composition as well as the content in soluble SiO_2, Al_2O_3 and Fe_2O_3 is relatively high. These mortars with pozzolanic material are dense in structure and it seems that they were purposely manufactured to resist moisture.

Fig. 6 Thick render in a wall during the Roman period (Olynthos 4th century B.C.).

The sand used could be a fluvial deposit with rounded particles or a terrestrial deposit with sharp-shaped sand. The properties of the selected sand were dependent on the type of application and thus the type of mortar but also on the availability and level of knowledge. The size distribution was usually well sorted (Fig.7).

The problem encountered in restoration works is how to protect the existing remains of the old renders and complete the missing parts with a compatible mortar which ensures the safety of the existing materials and the continuity of the masonry. On the other hand, it should be considered that the repair mortars (renders mostly) will be exposed to severe climatic conditions and to moisture and salt damage mechanisms. Substrate and render properties, environmental conditions (e.g. changes in relative humidity) and application technique are important parameters with regards to durability.

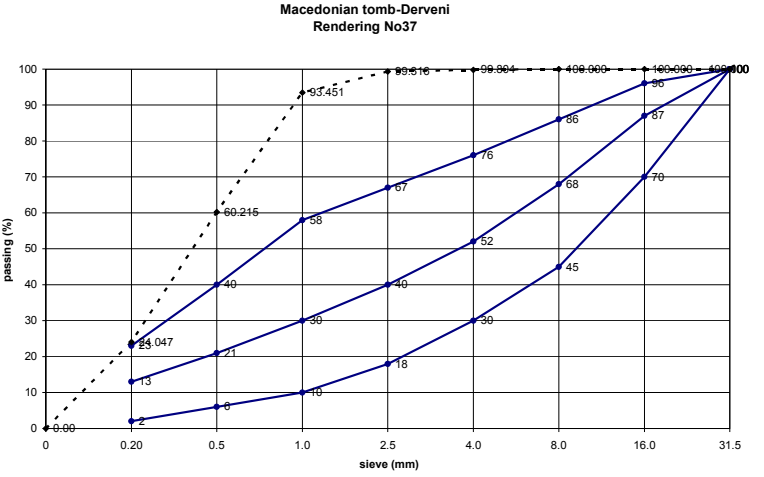

Fig. 7 Gradation of sand from a render in a Macedonian tomb near Thessaloniki.

In the present paper special interest is given in the parameter of fines in the mixture of renders as this parameter has an important role on the properties of fresh mortars but also on the hardened ones. The type and amount of fines added in a mixture influence the fluidity and workability but also the porosity, the shrinkage and the strength of the final product.

2 Experimental

The parameters studied were:

Four binding systems: lime (L), lime-pozzolana in 1:1 proportion by weight (P), lime-pozzolana-brick dust in 1-0.5-0.5 (B) and lime-pozzolana- white Portland cement (C) in 1:0.8:0.2. The fineness of these materials is shown in Table 1.

Table 1 Fineness of binders measured by particle size analysis.

	d(0.9) μm	d(0.5) μm	d(0.1) μm	Specific surface area m^2/g
Lime	10.8	3.0	1.2	2.25
Pozzolana	11.6	4.3	1.5	1.83
Brick dust	454	110.8	12.5	0.225
White cement	57.9	17	2.1	1.03

Four types of sand standard (1) AFNOR, and three commercial mortar sands which were enriched in different in natural fines: sand coded (2) contains silica fines <10%, (3) a sand which contains clay fines 10-15% and (4) a sand with 10-15% limestone fines. Fig. 8 shows the gradation of sands used. The sand with limestone fines is the finest sand.

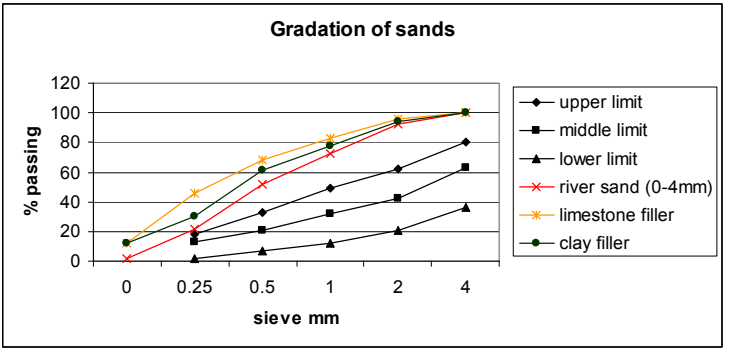

Fig. 8 Gradation of tested sands.

Table 2 Composition of mortars with different sand (parts by weight).

	L	P	B	C	Standard sand	River sand fines 10%	River sand Limestone filler 10-15%	River sand Clay 10-15%	w/b	Flow table cm
L1	1	-	-	-	1.5	-	-	-	0.65	18
P1	0.5	0.5	-	-	1.5	-	-	-	0.76	18.5
B1	0.5	0.25	0.25	-	1.5	-	-	-	0.55	17.6
C1	0.5	0.4	-	0.1	1.5	-	-	-	0.63	17
L2	1	-	-	-	-	1.5	-	-	0.87	18.8
L3	1	-	-	-	-	-	-	1.5	0.58	17.3
L4	1	-	-	-	-	-	1.5	-	0.76	16.3
P2	0.5	0.5	-	-	-	1.5	-	-	0.72	16.4
P3	0.5	0.5	-	-	-	-	-	1.5	0.60	17.6
P4	0.5	0.5	-	-	-	-	1.5	-	0.87	17.5
B2	0.5	0.25	0.25	-	-	1.5	-	-	0.83	16.8
B3	0.5	0.25	0.25	-	-	-	-	1.5	0.51	17.3
B4	0.5	0.25	0.25	-	-	-	1.5	-	0.72	17.8
C2	0.5	0.4	-	0.1	-	1.5	-	-	0.71	16.8
C3	0.5	0.4	-	0.1	-	-	-	1.5	0.53	16.5
C4	0.5	0.4	-	0.1	-	-	1.5	-	0.80	17

The binder aggregate ratio was 1:1.5 for all mortar mixtures and workability measured by the flow table (EN 1015-3:1999) was 16-18cm (Table 2). The measured properties at 28 days using 4x4x16cm mortar specimens were flexural and compressive strength and dynamic modulus of elasticity according to EN1015-11:1999. Also, absorption according to CPC11.3, capillarity according to EN1015-18:2002 and volume deformation were measured for one month after demoulding.

From Table 2 it is seen that the mixes with less added water in order to achieve the required workability are the ones with clay fines. Generally the mixes with limestone and river fines seem to acquire more water. The results of the mechanical and physical characteristics are shown in Table 3.

Table 3 Mechanical and physical characteristics at 28 days.

Compositions	Compressive strength MPa	Flexural strength MPa	Edyn GPa	Specific gravity	Porosity %
L1	0.38	-	9.55	-	-
P1	4.30	1.66	117.28	1.56	30.6
B1	3.11	1.60	119.05	1.67	29.8
C1	5.90	2.35	149.09	1.71	21.8
L2	0.34	0.09	3.87	-	-
L3	-	-	-	1.65	44.1
L4	0.47	0.25	15.79	1.61	41.7
P2	3.14	1.05	96.04	1.61	27.5
P3	3.30	1.41	71.65	1.43	34.9
P4	3.00	1.42	93.65	1.50	38.0
B2	3.01	1.39	112.97	1.50	35.9
B3	1.19	0.70	40.79	1.44	41.2
B4	2.55	0.85	85.09	1.71	16.3
C2	5.76	1.92	137.02	1.55	31.5
C3	2.64	0.98	78.35	1.65	31.9
C4	3.65	1.66	109.66	1.42	35.8

Fig. 9 shows the maximum value of compressive strength is achieved in mixes with standard sand. As expected, the compositions with cement present the highest strength. In this binding system the addition of clay causes reduction of strength (C3) which is more than 2MPa. For the lime-pozzolan-brick dust binding system, compositions with clay show reduced strength (B3) which is almost 1MPa while in the lime-pozzolan binding system the lowest strength is observed when limestone filler is used. For pure lime mortars, the strength for all compositions is below 1MPa but the composition with limestone filler seems to give the best results (L4).

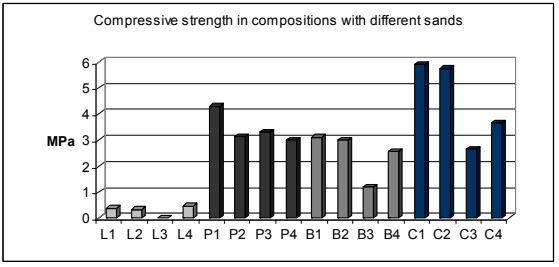

Fig.9 Compressive strength at 28days.

Regarding porosity, samples made from mortar mixes with standard sand have the lowest porosity values while the highest values are observed in mortar samples with fine limestone filler (Fig. 10). For lime mortars L1 and L2 it was impossible to measure porosity at 28 days because the samples disintegrated under water

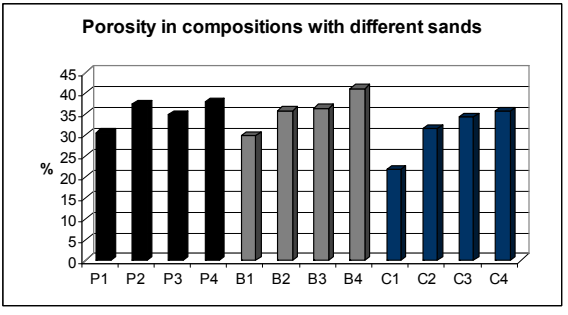

Fig. 10 Porosity of mortar samples at 28 days.

Shrinkage of the mortar samples was measured for 30 days after demoulding, measuring the volume of the samples daily (Fig. 11). The maximum shrinkage is recorded in mortars with fine materials especially with clay and limestone filler.

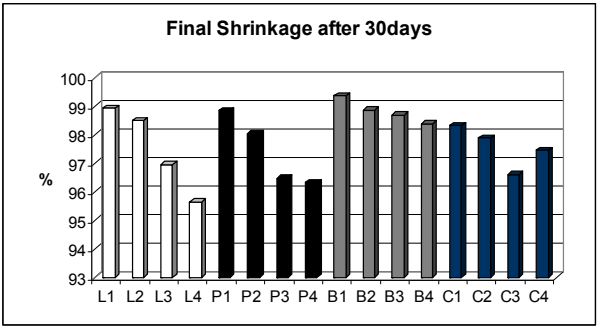

Fig. 11 Decrease of volume in mortars with different sands.

The rate of water absorption (capillary suction) for the lime-pozzolan mortars is shown in Fig. 12. The mortar samples containing standard sand and sand with low fines content have a similar rate of water absorption which is faster than the mortars with sand with higher percentages of fines. The behaviour of the other binding systems was similar.

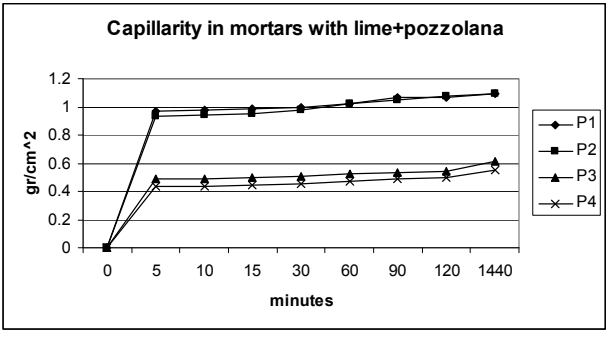

Fig. 12 Typical capillary curves for mortars with different sands

3 Results

The addition of fines to the aggregate in lime-based mortars can cause considerable alterations to the properties of the mortars.

The optimum properties were recorded in mortars with standard sand but also the sand with low percent in fines presented comparable results. Significant differences are observed when the percent of fines is 10-15% in all properties tested. The origin of fines is also an important factor that influences different properties. For example, the strength is decreased in compositions with clay fines while porosity is affected mainly by limestone fines. When shrinkage was measured in mortars with cement the presence of clay fines had the greatest effect, and limestone fines had the greatest effect in mortars with the other binders. Capillarity also seems to be affected by the type of fines as the compositions containing fines 10-15% presented low absorption probably due to the fact that fines block capillary pores. In these samples the absorption and the rate of absorption are low.

The results show that parameters such as the type of binder and the sand grading, in this case affected by the fines, are important to the properties of mortars. The role of fine materials in mortar compositions is crucial for their strength and durability. Regarding renders which have increasing demands in porosity properties and resistance to humidity rather than compressive strength, the percentage of fines in sand should not be more 10%.

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IV.33

Long-Term Effectiveness of Renovation Plasters in Jevíčko Castle

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Abstract Use of renovation plasters on historical buildings has its specifics. This type of plasters does not have a historical tradition, due to its composition. By this reason renovation plasters are perceived negatively by representatives of conservation and their use on historical buildings is strictly regulated. With historically valuable buildings it is often also difficult to realize some very effective renovation measures, such as undercutting, grouting, electro osmosis and others. The causes often lie in preservation of monuments, as well as technical and economical problems. Therefore it is not very often possible to prevent the ground dampness penetration into bearing structures really consistently. That means we must count with the fact that dampness will appear in the masonry again and again and will influence the function of the renovation plasters. If we want the renovation system to work as long as possible, the access of ground dampness must be at least radically limited.

1 The Castle's location and history

The renaissance castle, located in the former royal city Jevíčko, was built in 1559 originally as a fortress by Prokop and Jetřich Podstatský from Prusínovice. From the original structure only the tower remains. The castle was rebuilt in its present form at the end of 18th century. At the time of socialism (1948-1989) the building was used as a school building.

2 Condition of the building before redevelopment in 2001

The building is built from brick with a foundation of stone and stone-brick masonry. The surface of the surrounding terrain was made from stone-block paving which sloped towards the building. The facade has not been repaired and

maintained for a long time and masonry in the basement was damp up to the ceiling. The building was constructed above the level of groundwater but is exposed to a strong onslaught of surface moisture and rainwater from the adjacent terrain. Measured moisture levels in the masonry were up to 17% in some areas. All measured moisture values from a sample room are seen in table 1; these were recorded using a digital hygrometer (UNI 2).

Fig. 1 Castle in Jevíčko – the facade is not covered by renovation plaster

Fig. 2 The original condition of the wall in the interior of the library before renovation actions in 2001

Table 1 Values of the moisture content of a brick masonry wall in the library-determined by hygrometer UNI 2 in 2001

Values of moisture by hygrometer UNI 2 in 2001								
Height of measurement (cm)	Measured value of masonry moisture in % Identification of vertical axes							
	1	2	3	4	5	6	7	8
250	4.5		3.8					
200	11.1		4.4					
150	17.1		12.2		2.1	2.1	6.9	
100	13.1		11.1		3.4	10.5	9.8	
50	15.6		10.3		8.2	15.6	10.5	

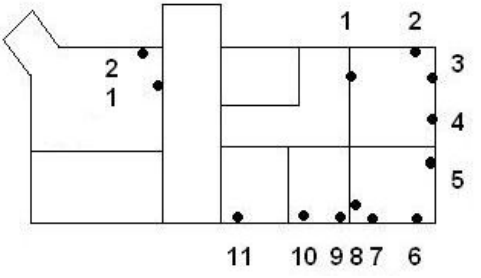

Fig. 3 The plan of the Castle - identification of places of measurement

3 Technological process and redevelopment

The first and most important task was to implement a functional drainage system that would substantially solve the rainwater and surface water issues. Without these technical measures redevelopment plasters would not work even in the short term. It was also recommended that a gutter sidewalk, made of rough river gravel of fraction 35 – 120 mm, be installed by the wall to provide a non-absorbent cover to the contact between the soil and gravel and to reduce rain splash on the facade.

The interior walls and details in contact with the floor were cleaned with pressurised water after the plasters were removed. All replacement materials were provided by the local producer – Hasit. The mortar SANIER-Porenausgleichsputz 208 (for missing masonry and large joints) was used in conjunction with the spray SANIER – Vrospritzmörtel 205 which was applied fresh. Adjustment of masonry unevenness was made using the screening grout SANIER – Porenausgleichsputz 208 with a second layer of redevelopment plaster SANIER – Wandputz 210 at a thickness of 20 mm. After drying the surface was coated with a finishing plaster -

Feinputz 212. Prior to applying plaster close to the floor, Seattle Dichtungschlämme, was applied to a height of 50 cm to provide a permeable seal. Final plaster adjustment in the interior was done using the silicate color SILIKAT 760 which is abrasion resistant and doesn't create layers when repeatedly applied. Existing exterior skirting plaster was removed and replaced using the newer renovation plasters.

4 The condition of the building 6 years after the redevelopment

Building reports for the evaluation of the redevelopment in 2001 were divided into two parts: the offices and the current library. The same procedure was also selected for current surveys. The building is in an excellent technical condition, as is confirmed by visual inspection and by many measurements; some of which are shown in this paper. Wall surfaces, both exterior and interior, are without signs of moisture and disorder. The castle is partially cellared and a survey of the basement, which is ventilated from time to time, was also done. Breakdowns of sewerage were removed and no source of moisture has been found anywhere.

A very effective system of rain gutters to conduct surface water and rain water away into sewers was constructed around the building. The troughs are located approximately 80 cm from the castle walls so that the water drains away from the walls and water from the surrounding terrain doesn't get close to the building. Instead of the recommended gravel pavement, paving made of stone blocks fitted into a sand bed were installed allowing ventilation of the backfill.

The interior of the library was dealt with according to the recommendation of the remediation technician, with open backed shelves being used for housing books to allow for a sufficient flow of air in the room (Fig.6).

Table 2 Values of the moisture content of the brick masonry wall in the library-determined by hygrometer UNI 2 in 2007

Values of moisture by hygrometer UNI 2 in 2007								
Height of measurement	Measured value of masonry moisture in %							
(cm)	Identification of vertical axes							
	1	2	3	4	5	6	7	8
250								
200			1.0		1.4	1.3		
150	1.3	1.4	1.0	1.2	1.4	1.3	1.4	1.4
100	1.6	2.8	1.0	1.3	1.6	1.4	1.5	1.6
50	2.0	1.6	1.5	1.4	1.6	1.5	1.5	1.6

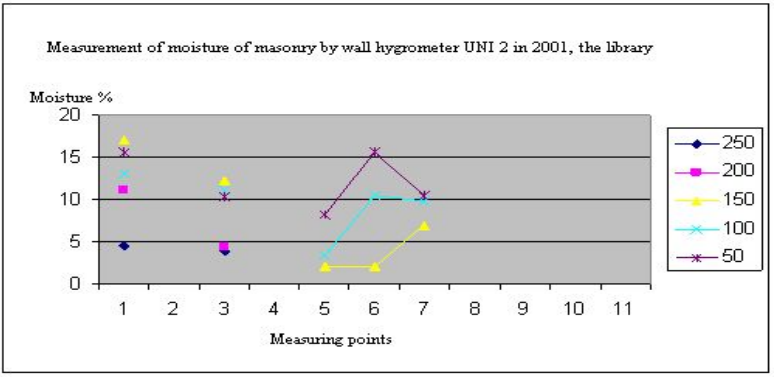

Fig. 4 Value of moisture by hygrometer UNI 2 in 2001, in the library

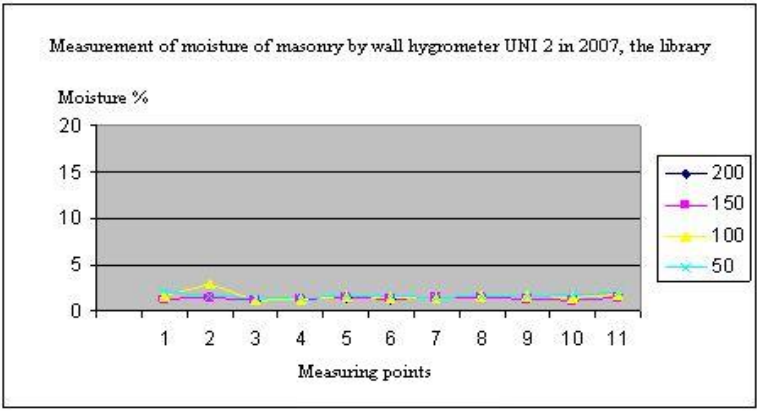

Fig. 5 Value of moisture by hygrometer UNI 2 in 2007 in the library

Fig. 6 Current status – suitable open shelves without a closed back are used in library

Fig. 7 System for the reduction of surface water and rain water with drainage to a rain water sewer

Fig. 8 System for the reduction of surface water and rain water to a rain water sewer

5 Conclusion

The redevelopment of Jevíčko castle provides an example of a renovation system which meets all the wanted requirements and demonstrates a high efficiency solution for a historic building. Humidity levels within the construction were decreased by more than 10%. The excellent technical condition of the building is not only due to a successful redevelopment system but also to continuous, consistent maintenance by the building manager.

IV.34

Mortars from Roman Cement and their Properties

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Abstract A new fast-setting cement, called Roman cement, appeared recently in the market. To identify the possibilities of using it in the field of cultural heritage, it is important to know as much as possible about its properties. In the Czech Republic, one of the possible uses is as jointing and plastering materials for spongilite walls (spongilite is a highly heterogeneous material with an anisotropic character, this sedimentary rock consists of calcite and different forms of SiO_2), as well as a repair material for spongilite architectural details. The first part of our research, presented in this work, studies effects of the addition of various proportions of lime hydrate on the properties of fresh and hardened mortar from Roman cement. First of all, properties of fresh mortar such as water/binder ratio, speed of setting, volume stability and volume density were measured on the different mixes prepared. After 28 days of setting, the hardened mortars were characterized. Volume density, open porosity and pore size distribution were all determined. Then, the samples were subjected to testing: compressive and bending strength and resistance to salt crystallization. In order to characterize the components in the Roman cement, XRD, XRF, infrared spectroscopy and Raman spectrometry were used. The future work will focus on comparing the properties of Roman cement mortars to those of spongilite, in order to determine a mortar based on Roman cement suitable for the use in spongilite restoration work.

1 Introduction

Roman cement is a natural high-hydraulic binder. It is manufactured from marlstones and from not very high-purity limestones naturally enriched with a clay component. Roman cement differs from the conventional Portland cement particularly by its lower firing temperature, which is 600–1200°C [1] and is lower

than the sintering temperature. Roman cement possesses an ochre colour, which is the deeper the higher the cement hydration degree. This makes for shading of the hardened surface. At sites where the surface is wetted, the binder continues to hydrate after setting. Typical of Roman cement is a very fast start of the setting process, from 7 to 20 minutes [2]. Its workability period depends on temperature and on the amount of setting retarder added [3].

Hydrated lime (lime putty) is an air binder obtained by slaking calcium oxide (lime) obtained by calcination of limestone. The setting process for mortars from hydrated lime consists of 2 phases: (1) drying of the colloidal gel of the lime binder and (2) carbonation in suitable conditions, i.e. in the presence of atmospheric carbon dioxide and some amount of water in the mortar. The mortar drying mechanism includes evaporation of water and absorption of the mix water from the mortar by the underlying material. The setting time is long as compared to other building materials and depends on the resulting layer thickness. The setting time is long due to the low carbon dioxide concentration, and only starts after a partial evaporation of water from large pores. Carbon dioxide dissolves in water and reacts with the lime binder giving rise to calcium carbonate [4, 5].

This work studies effects of the addition of various proportions of lime hydrate on the properties of fresh and hardened mortar from Roman cement. Combination of the two binders results in a higher mortar strength than that achieved with hydrated lime alone; in addition, the strength is attained sooner and the workability time of Roman cements is longer [3].

2 Experimental

2.1 Materials

Hydrated lime (CL90-S Vápenka Čertovy schody a.s., Czech Republic) and Roman cement (Prompt cement, Vicat, France) served as the binders, and pure silica sands (AQUA obnova staveb s.r.o., Czech Republic) were used as the filler (Fig. 1). Citric acid (Tempo setting retarder, Vicat, France) was added in order to slow down the mortar setting process.

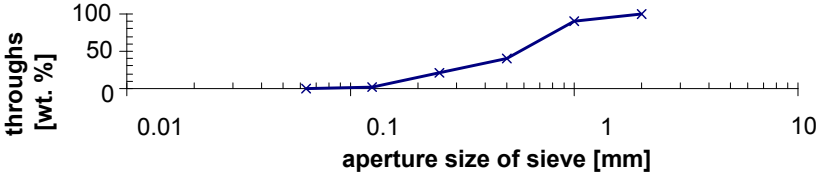

Fig. 1 Sand particles size distribution (1:2:1, fraction 0.1-0.3:0.3-0.8:0.6-1.2 mm).

2.2 Binder properties

Binder mixtures were prepared using variable hydrated lime-to-Roman cement weight ratios, i.e. from 0:10 to 10:0, with an addition of 0.6 wt.% of the setting retarder with respect to the Roman cement fraction. The setting times and volume stability were determined for the mixtures.

Volume stability is characterized by the quantity

$$\Delta l = l_2 - l_1 \qquad (1)$$

where l_1 … is the sleeve feet distance before boil [cm]
l_2 … is the sleeve feet distance after boil [cm].

2.3 Mortar and test specimen preparation

Mixtures were prepared in the 1:3 binder-to-filler ratio. The binder composition encompassed the weight ratio span from 0:10 to 10:0, with an addition of 0.6 wt.% of the setting retarder with respect to the Roman cement fraction. After addition of water, the mixture was stirred with an electric stirrer at a slow speed for 3.5 minutes.

Cubes (4×4×4 cm), beams (2×2×10 cm), and disks (6.7×1 cm) were prepared from each mixture.

The samples were wetted periodically for 28 days from the mortar preparation. Subsequently, carbonation and hydration were discontinued by drying the samples to constant weight at 60°C. The samples so prepared were used to examine their physico-chemical properties (following 24 h acclimation to room temperature and RH).

The mortars were labelled xC + yV where x and y were the weight fractions of Roman cement (C) and hydrated lime (V).

2.4 Properties of the hardened mortars

The mortar carbonation depth was measured by using an acid-base indicator (0.5% phenolphthalein in ethanol) spread over a fresh specimen section.

Compressive strength was determined on 10 cubes (see above) of each mortar, bending strength was determined on 10 beams of each mortar.

For water absorption capacity experiments, the test specimens, dried to constant weight, were placed in a container, and water was added to one-half of their height. During the first hour, water was added to fill three-quarters of the specimen height, and in another hour, additional water was added to submerge the specimens completely. In this condition the specimens were allowed to stand for 48 hours. Subsequently, the specimens were placed in a desiccator and evacuated with a water pump. The specimens were weighed, both in the 48 hours and following evacuation, i.e. hydrostatically and in air. The weight data provided

water absorption under atmospheric pressure in 48 hours and after evacuation, as well as the open porosity and bulk density of the hardened mortars. Mortar pore size was determined by mercury intrusion porosimetry.

The standard test method described in EN 12370 *Natural stone test methods. Determination of resistance to salt crystallization* was modified to determine resistance to salt crystallization. Two specimens of each mortar were submerged in a 14% Na_2SO_4 solution for 2 hours. Then the specimens were placed in a drier at 60 °C and a high initial relative humidity. The specimens were dried to constant weight and subjected to the next cycle.

Water vapour permeability was determined as described in EN 1015-19 *Methods of test for mortar for masonry. Determination of water vapour permeability of hardened rendering and plastering mortars* (saturated KNO_3 solution – maintains RH at 93% and LiCl – maintains RH at 12% (20°C)).

The internal structure of the binders in the mortars was examined by scanning electron microscopy, the phase composition of the hardened mortars was characterized by X-ray diffraction. The hydration process in the mortar prepared from Roman cement was examined by measuring changes in the intensities of the characteristic peaks in the Raman spectrum.

3 Results and discussion

In the binding mixture setting speed measurements, only the mixture containing 9 wt. part of lime hydrate set appreciably more slowly than the remaining mixtures (Fig. 2). The result is basically similar to the slow drying process of pure lime mortar. Although setting at a rate similar to that of the remaining mixtures, the 2C+8V mixture exhibited markedly inhomogeneous properties.

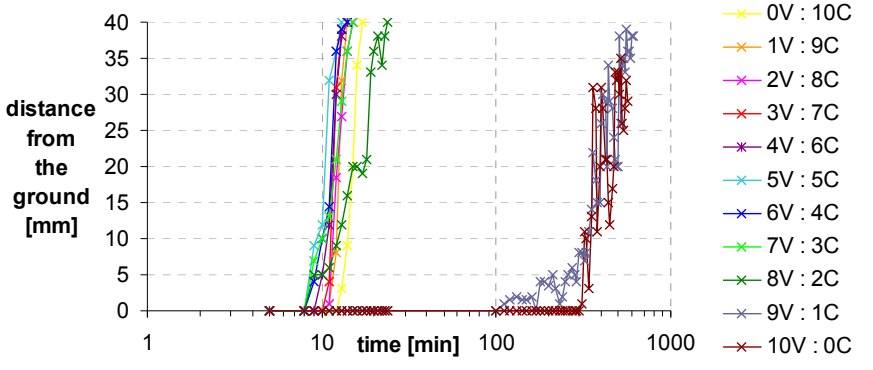

Fig. 2 Time of binders setting.

In the hardened mortars, the presence of hydrated lime affected both the bending strength and the compressive strength (Fig. 3). The 5C+5V mixture

possesses compressive strength twice as high as a pure lime – or less than one-half the strength of pure Roman cement mortar. As regards bending strength, as little as 4 parts of hydrated lime reduced the resultant strength to the level of pure lime mortar. Those results are supported by SEM photographs (Fig. 4), clearly displaying two different homogeneously mixed structures, viz needle of AFm phase, globular particles of C-S-H phase and calcite and portlandite crystals from the hardened lime mortar. This is in agreement with the XRD results (Table 1).

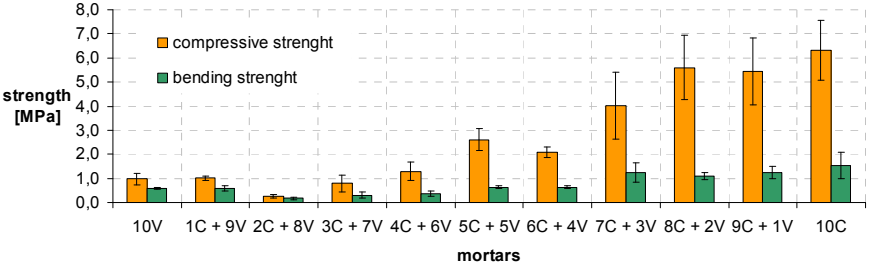

Fig. 3 Graph of compressive strength and bending strength.

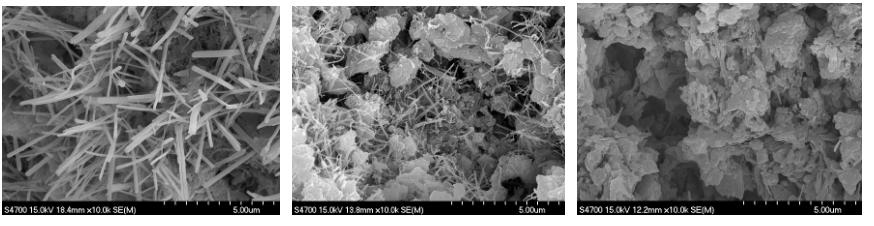

Fig. 4 SEM images of mortars, from the left: 10C, 5C+5V, 1C+9V.

Table 1 Composition of some mortars from XRD in relative percentage weight.

Formula	Name	Roman cement	1C+9V	5C+5V	10C
$CaCO_3$	calcite	-	59	45	37
$Ca(OH)_2$	portlandite	-	18	6	-
SiO_2	quartz	3	5	8	25
$CaCO_3$	aragonite	-	18	13	-
Ca_2SiO_4	bellite	80	-	27	38
$Ca_2(FeAl)_2O_5$	brownmillerite	17	-	-	-

Porosity, water absorption and vapour permeability measurements clearly demonstrate the effect of hydrated lime on Roman cement mortar (Table 2). Although exhibiting lower water absorption and porosity and hence, water vapour permeability, mortars with an appreciable fraction of Roman cement do not differ markedly from pure lime mortar. This is also demonstrated by resistance to salt

crystallization (Table 3), where no unambiguous trend in dependence on the hydrated lime fraction is observed. The pore size distribution in the mortars is also similar, only, perhaps, mortars with a predominant fraction of Roman cement possess rather fine pores as compared to the pure lime mortar.

Table 2 Porosity, water absorption and vapour permeability.

Mortar	Porosity (mercury porosimetry) [%]	Open porosity [%]	Water absorption [%]	Vapour permeability [$g.h^{-1}$]
10V	25.0	30.5	16.7	0.017
1C+9V	25.4	28.5	15.2	0.016
2C+8V	26.1	29.7	16.4	0.016
3C+7V	23.1	31.0	17.3	0.017
4C+6V	24.3	26.5	14.3	0.016
5C+5V	21.6	24.8	13.1	0.014
6C+4V	25.9	24.6	13.2	0.013
7C+3V	22.4	24.4	12.9	0.013
8C+2V	21.5	25.5	13.3	0.013
9C+1V	20.6	24.5	12.7	0.012
10C	21.8	23.1	12.0	0.012

Table 3 Determination of resistance to salt crystallization, cycles of destruction samples.

Cycle	Mortar which was destroyed
1.	2C+8V
2.	3C+7V, 6C+4V
3.	3C+7V, 7C+3V, 10C
4.	2C+8V, 4C+6V, 4C+6V, 5C+5V, 5C+5V, 6C+4V, 8C+2V, 8C+2V, 9C+1V, 10V, 10V
6.	1C+9V, 10C
7.	1C+9V
15.	didn't destroy 7C+3V, 9C+1V

The Raman spectra show how the bellite (dicalcium silicate) and C-S-H gel peak intensities vary during the Roman cement hydration process (Fig. 5). This process of hydration can be expressed by its predominant chemical reaction:

$$C_2S + H_2O \rightarrow \text{C-S-H} + Ca(OH)_2.$$

As a result of this process, we can observe that bellite´s relative peak intensity decreases while C-S-H gel´s relative peak intensity increases.

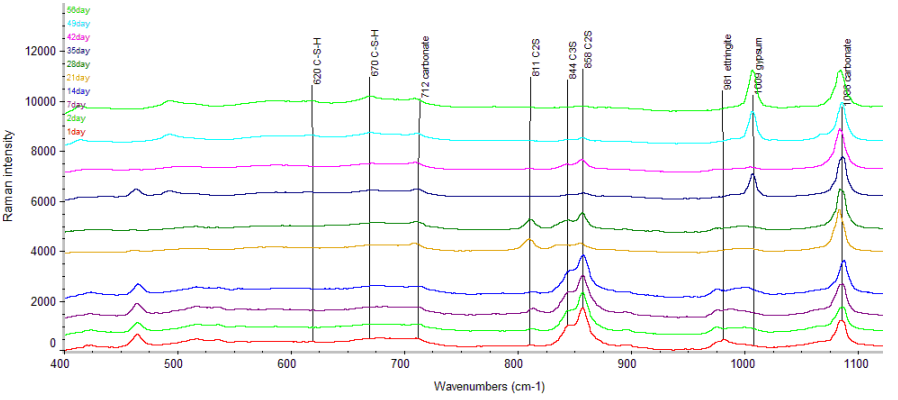

Fig. 5 Raman spectra of the 10C mortar hydration.

4 Conclusion

Mixed mortars prepared from Roman cement with a fraction of hydrated lime behave similarly to mortars prepared from pure Roman cement in terms of setting. This process is only slowed down if the fraction of hydrated lime predominates over that of Roman cement. As expected [3], the strength of hardened mortars grows with increasing proportion of Roman cement. An appreciable increase as compared to hydrated lime mortar, however, only occurs if the fraction of Roman cement is the same as or higher than that of hydrated lime.¨

5 Acknowledgement

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IV.35

Nano-Lime as a Binder for Injection Grouts and Repair Mortars

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Abstract Lime water, esters of silicic acid and plastics are common materials used for the conservation of historic mortars. Injection grouts containing cement or hydraulic lime are also employed. In recent years, the usage of hydrated lime has increased; however, the mechanical properties of the repaired material are often unsatisfactory. In many cases, due to the large particle sizes of the lime used, only loose connections with the sub-surface are obtained. The availability of materials containing lime [$Ca(OH)_2$] nano-particles offers the possibility of creating injection grouts and repair mortars with extremely small particle sizes. All systems suggested in this paper are characterised by solids with particle sizes smaller than 6µm. They can be used to consolidate mortars and to fill voids. An important feature is that the injection grouts are able to migrate into the space between loose particles and to stabilise these areas. The materials developed are aqueous with a high stability. The solids formed by their use are characterised by having a high porosity and demonstrate good capillarity. They are hydrophilic. Typical properties of solids formed from an injection grout are: 36% porosity, 4.3 N/mm² compressive strength after 30 days, 1.1 N/mm² flexural strength, 23 wt.% water uptake and 0.4% shrinkage. This paper summarises the design and development of injection grouts and repair mortars and presents results from initial applications. The concept developed allows the adjustment of the properties of the injection grouts and repair mortars to the properties of the mortars that have to be consolidated.

1 Introduction

Lime based mortars, plasters and stuccoes have been used for centuries. They are amongst the most common binding materials and are found at archaeological sites as well as in historical buildings. Their conservation and restoration is carried

out progressively, requiring different types of materials and different techniques. One main requirement is that the materials used are compatible to those originally used. During pre-consolidation, loose particles and surfaces that exhibit "sanding" have to be fixed. Consolidants must, therefore, be able to penetrate deep into the damaged zones. If necessary, this process can be followed by the removal of soluble salts by for example, poultices. Injection grouts with free flowing properties are required to fill voids and fissures. A porous transition zone allowing capillary transport from intact masonry through the mortar to the surface should be formed.

Repair mortars are used for the replacement of lost parts but also for the filling of open voids and cracks in mortars, plasters and frescoes. In many cases, the use of repair mortars is also necessary as a first step to stabilise historic mortars and plasters before the fundamental conservation process can begin. For that purpose, materials which can be varied in composition and concentration are necessary.

Until recently, the following materials were available [1, 2]:

- Lime suspensions,
- Lime water,
- Injection grouts and repair mortars based on lime hydrate and / or cement,
- Lime or cement based filling pastes and slurries,
- Hydraulic lime mortars, plaster and injection grouts,
- Silica sols, water glass solutions,
- Esters of silicic acid and
- Organic resins.

The application of lime mortars and lime water is well known [3, 4]. However, difficulties may arise when lime particles with a large size are present. Similarly, the application of lime water as a pre-consolidant can result in the full saturation of the treated material with water, which may cause additional and/or new deterioration. The use of cement based materials can often result in structures which are too hard and the use of silicon-based organic consolidants and binders are unsatisfactory due to the formation of hydrophobic surfaces [5].

A main consideration for successful conservation is that the materials used in the different working stages are fully compatible among themselves. It is the aim of this paper, to demonstrate that a set of fully compatible conservation materials can be prepared using nano-lime and natural fillers.

2 Materials

2.1 Materials for pre-consolidation

Strength profiles of weathered historical mortars and plasters have shown that the weathered zone often extends to a depth of several centimetres; peeling, flaking and detachment of murals can commonly be observed. Before using injection masses or repair mortars, a pre-consolidation of loose particles and deteriorated zones is therefore often necessary. For this, a material that can migrate into the space between the sand grains and the mortar constituents is required.

The investigations summarised in Drdácký et al. [6] and Maryniak-Piaszczynski et al. [7] have indicated that the nano-lime product CaLoSiL can be used as a pre-consolidant. It contains synthetic calcium hydroxide particles with sizes between 50 and 250 nm which are stable when dispersed in ethanol, n-propanol or iso-propanol. The sols formed have a shelf live of three to five months and typical concentrations are between 10 and 50 g/L. CaLoSiL is a product of IBZ-Salzchemie GmbH&Co.KG, Germany.

The nano-sol is able to migrate deeply into the mortar and fine nano-particles of calcium hydroxide are deposited in the treated areas after evaporation of the alcohol. Subsequent carbonation by reaction with atmospheric carbon dioxide results in strengthening and consolidation. In most cases the moisture present in porous systems is more than sufficient to allow complete carbonation, even at depths of several centimetres. XRD investigations (fig. 1) have demonstrated that the two calcium carbonate modifications, calcite and vaterite, are formed. These components also form in conventional lime based mortars.

The use of a water free consolidant is of great importance, especially in situations in which the presence of water can cause additional deterioration, for example during the consolidation of frescos or vaults.

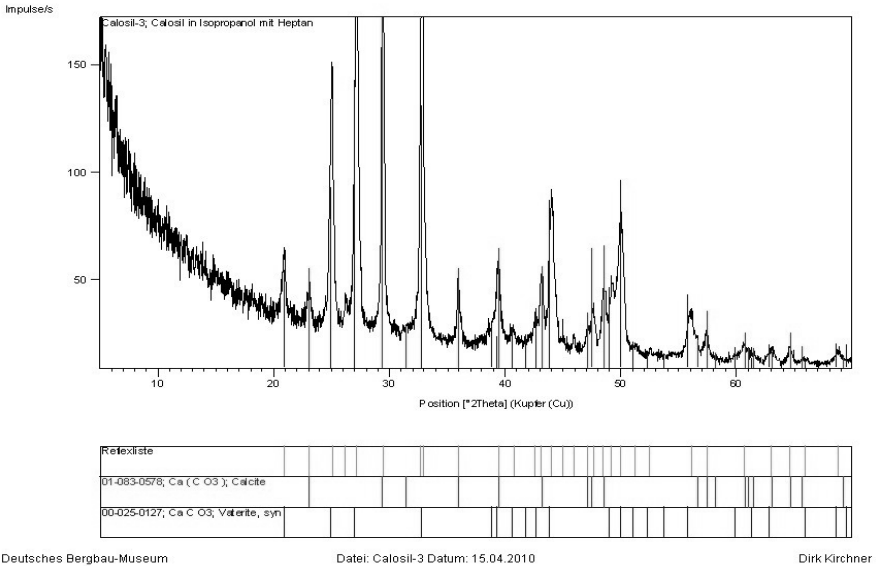

Fig. 1 XRD-pattern of nano-lime after carbonation showing the presence of calcite and vaterite (measurements: D. Kirchner, Deutsches Bergbau Museum Bochum).

2.2 Injection grouts

Highly concentrated, paste-like suspensions of nano-lime were prepared using the paste-like CaLoSiL. This is a special material containing nano-lime in concentrations up to 350 g/L. The average particle size is a little higher than for the standard materials but is still in the nano-meter range (fig. 2). CaLoSiL was used in combination with natural fillers.

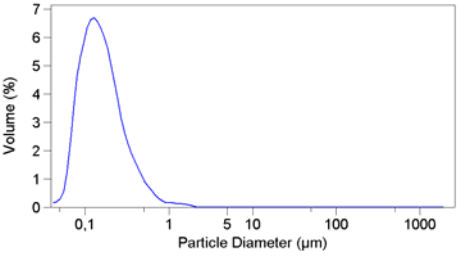

Fig. 2 Particle size distribution of CaLoSiL nano-lime

The injection grouts are characterised by a good stability in combination with a high flowability. After hardening, porous masses are formed which demonstrate a high capillarity. All masses are hydrophilic and are able to act as capillary-active,

zone-bridging mortar surfaces, mortar structures and masonry. Another important property is the good adhesion to historic mortar components. The injection grouts are able to adhere to single mortar pieces. Selected physio-chemical properties are shown in Table 1. Typical compositions are given in Table 2.

Table 1 Selected physio-chemical properties of injection grout number 1

Properties	
water absorption (wt.% H_20)	23.2
porosity (vol.%)	36.2
capillary suction up to 5 cm [min.]	225
coefficient of water absorption kg/($m^2h^{1/2}$)	4.0
Compressive strength [N/mm^2] after 14 days	2.1
Compressive strength after 24 h water [N/mm^2]	1.8
Compressive strength [N/mm^2] after 30 days (temp.20°C, 60% rel. humidity)	4.3
Bending strength [N/mm^2]	1.1
Dynamic E-Modulus [N/mm^2]	4100
Adhesive tensile bending strength [N/mm^2] after 30 days	0.1
Shrinkage [%]	0.4
Hygric expansion [mm]	0.01
Freeze-thaw cyclic test, weight loss [%] after 25 cycles	20
Crystallization test, weight loss [%] after 10 cycles	42

Table 2 Examples of injection grouts based on CaLoSiL nano-lime as a binder

Grout number:	Composition	Mass ratio Binder : aggregates	Stability after storage at 50 °C for one week
1	10g CaLoSiL - paste 20g limestone powder, mpd[1)]: 0.8 µm 20g limestone powder, mpd:1.7 µm 10g limestone powder, mpd:2.4 µm 14g water 0.598g Lopon 890 (0.8%)	1:5	Stable
2	10g CaLoSiL -paste 25g limestone powder, mpd: 0.8 µm 10g limestone powder, mpd: 1.7 µm 15g limestone powder, mpd: 2.4 µm 15g water 0.58 g Lopon 890 (0.8%) 1% meta-kaolinite	1:5	Stable

3	10g CaLoSiL- paste 20g limestone powder, mpd:0.8 µm 10g limestone powder, mpd:1.7 µm 15g limestone powder, mpd:2.4 µm 13.75g water 0.55 g Lopon 890 (0.8%) 1% meta-kaolinite (0.69g)	1:4.5	Stable

[1)] mpd: mean particle diameter

2.3 Repair mortars

The use of a paste-like nano-lime as a binder allows the creation of materials with variable properties. Changing the ratios between the components and directed selection of the fillers and their particle size distribution allows the adjustment physio-chemical properties of the mortars to the historic materials. A typical recipe is described in Table 3. Characteristic data are given in Table 4. The high capillarity and water suction capacity are typical properties. Water uptake and release takes place rapidly and the mortars can take the role of a protection layer. The mechanical properties of the repair mortars developed are sufficient to protect the historic materials. The amount of water in the mortar, due to the use of ethanolic suspensions of nano-lime as a binder, is low and can be varied on demand.

The colour as well as the surface texture of the mortars can be adjusted by the addition of pigments and it is possible to imitate weathered and discoloured mortar surfaces.

Table 3 Repair mortar

Composition	Amount (g)
marl powder (0-250µm)	1000
CaLoSiL-paste	300
mixture of ethanol and water 1:1 Vol.	as necessary
meta-kaolinite	3% of the whole mass
lime paint umber and ochre	as necessary

Table 4 Properties of the developed repair mortar (the data are the result of duplicated measurements)

Parameter	
Density [g/ cm^3]	1.89
Specific surface [m^2/g]	2.9
Water absorption [wt.% H_20]	16

Porosity [vol.%]	24-29
Capillary suction up to 5 cm [min.]	20
Coefficient of water absorption in kg/($m^2h^{1/2}$)	4.85
Compressive strength [N/mm^2] after 21 days	3
Dynamic E-Modulus [N/mm^2]	4000
Bending strength [N/mm^2]	0.23
Shrinkage [%]	0.2
Hygric expansion [mm]	0.04
Thermal expansion (10^{-6}/K) [Δ_T x(10^{-6}l/ K)]	11.2
Freeze-thaw cyclic test, weight loss [%] after 25 cycles	20
Crystallisation test, weight loss [%] after 10 cycles	60

3 Application examples

3.1 Conservation of the facade of the rectory St. Peter in Aachen

The gable of the rectory of St. Peter in Aachen-Orsbach (1764) (fig. 3) was built of marl stones. Pointing was carried out using a mortar consisting of lime and extremely fine marl. During a previous restoration, some stones were replaced and the facade was partially re-pointed with cement based mortars which has contributed to the destruction of the remaining original materials (fig. 4). Conservation work performed in 2009 was based on the following steps: At first the mortar was structurally consolidated with CaLoSiL E-25 (fig. 5); after which flakes and shells were adhered to the surface by an injection mass based on a CaLoSiL paste. In the final conservation step, voids were filled with a mortar containing CaLoSiL paste as the binder.

Fig. 3 Rectory of St. Peter in Aachen - gable before the conservation

Fig. 4 St. Peter's in Aachen-Orsbach - original mortar underneath the flaking cement mortar

Fig. 5 St. Peter in Aachen-Orsbach, - residues of mortar were stabilised using injection masses

Fig. 6 Artificial samples of mortars developed using CaLoSiL paste for the conservation of mortar

3.2 Conservation of wall paintings in Mersch (Luxemburg)

The conservation of the wall paintings in Mersch was realised in several stages. First, unstable mortar underneath the paintings was stabilised through the injection of the nano-lime CaLoSiL E-25 (fig. 7); defects were then filled with a nano-lime-based repair mortar. Following this, voids, fissures and cracks were filled with an injection grout based on a CaLoSiL paste (fig. 8) and coloured lime was applied in the final retouching. Thus, the conservation was achieved with lime based materials which were fully compatible to each other.

Fig. 7 Consolidation and stabilisation of the plaster (fresco) with CaLoSiL E-25

Fig. 8 Filling of cracks with the developed injection grout

4 Conclusions

Nano-lime can be used as a pre-consolidant as well as a binder in injection grouts and repair mortars. Thus, a conservation concept can be realised in which

fully compatible materials are used in all stages. The advantages of this concept include the reversibility of the product as well as its great flexibility in respect to the physio-mechanical and aesthetic properties required.

5 Acknowledgement

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IV.36

High Fired Gypsum Mortar for Screeds, Terrazzo and Masonry Repair on Historic Monuments. Production, Properties and Sample Applications

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Abstract This study presents the production, the composition and the resulting properties of a gypsum mortar for restoration work. It is manufactured in the tradition of the medieval gypsum materials used for masonry construction and sculptures. Application possibilities of the mortars will be discussed on the example of the historical city hall of Lüneburg and the New Museum building in Berlin, ranging from static strengthening of gothic brick masonry to ornamental floor screeds (terrazzo).

1 Introduction

Gypsum has served as a building material in Europe for a long time. As far back as the Roman Empire gypsum has been used as a joint mortar, masonry mortar or as interior and exterior plaster in the vicinity of natural gypsum deposits. Besides its use as building material a great number of sculptures, reliefs, and ornamental screeds were created using gypsum in medieval times. In many studies the binder of the historic gypsum mortars has been identified as high fired gypsum [1-7]. It was particularly valued because of its hardness and resistance to weathering in both outdoor and indoor conditions and differed in its material properties significantly from today's gypsum materials.

Because of the application of modern hydraulic building materials knowledge of techniques for the production of gypsum mortars became less important in modern times and has therefore vanished.

However, as shown by a wide range of investigations, artificial as well as natural hydraulic components of repair mortars frequently lead to the formation of expansive minerals when in contact with historic gypsum mortars [8]. This has caused dramatic damage to historic objects leading to the loss of whole buildings.

In order to repair and restore historical buildings and ornaments in which gypsum mortars have been used, it is necessary to apply mortars that are not only adjusted to the visual appearance of the historical mortar but also possess compatible material and chemical properties.

Most gypsum mortars available on the building materials market proved not to be stable against environmental influences and are therefore not appropriate. However, there is a need for a durable repair material for restoration projects of historic monuments containing gypsum. At the suggestion of the preservation authorities a small enterprise at Hundisburg in Saxony-Anhalt has started to manufacture gypsum mortars according to traditional production procedures.

2 The Production

The knowledge of the historical firing technique has been reclaimed in the scope of the EU-LEADER project from 2005-2007. The involved test laboratories identified the influence of raw materials, firing conditions, mixing techniques, and after treatment, on the resulting gypsum mortars [9-11].

2.1 Raw material and firing process

For the production, two gypsum raw materials are currently used - one from the Zechstein period deposit in the Harz region (named *A3*) and one from the Keuper period deposit in Franconia (named *Keuper*).

The material from these quarries consists almost entirely of gypsum dihydrate. In addition minor constituents (mineral impurities) may be present:

A3: calcite (Fig.1), celestine ($SrSO_4$), anhydrite, Mg/Si-phases
Keuper: dolomite, dolomitic marl, celestine ($SrSO_4$), quartz, feldspar

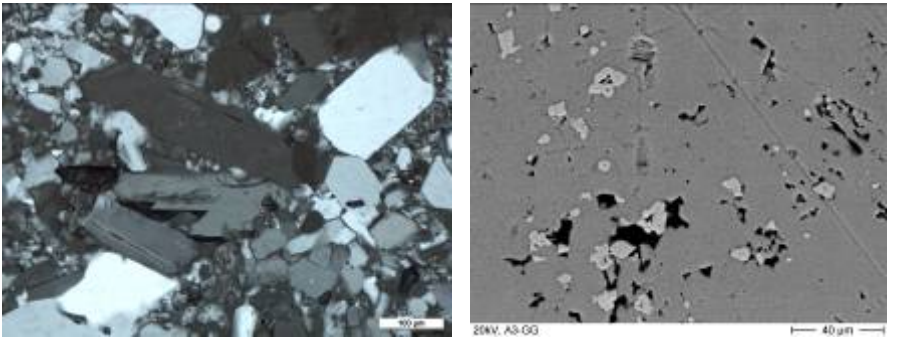

Fig. 1 Left: Typical micro fabric of gypsum raw material A3. Dihydrate in different grain sizes [Thin sections in transmitted light, x-pol.]; Right: Calcite impurities (bright grains) surrounded by dihydrate [SEM-BSE image on thin section]

In the past kilns of various types were used for firing gypsum raw material to produce mortars [1, 4]. The material described in the present article is fired in a kiln showing a square ground plan, a replication following one of the historical prototypes. The kiln is fired using wood and consists of a bigger chamber for the gypsum stones and a combustion chamber - separated from each other by a grate.

Care is taken to minimize contaminated deposit horizons as raw material. After crushing and separating by size, the gypsum stones are stacked by hand (Fig. 2). The bigger stones (20-25 cm diameter) are located in the lower part of the chamber, and the smaller ones (5-10 cm diameter) are located on the top. A sufficient space between the stones has to be kept for the removal of the flue gases. Tree trunks are placed vertically between the stones for the same purpose.

The firing time is 12-13 hours. Monitoring is done by measuring the firing temperature in the middle of the kiln (Fig. 3). Stacking and a continuous firing procedure are essential for the properties of the resulting material.

Fig. 2 Left: Crushing the bigger stones of the gypsum raw material; Right: Filling gypsum stones into the kiln above the combustion chamber. Tree trunks are placed vertically between the stones to obtain additional channels for removal of the exhaust gases.

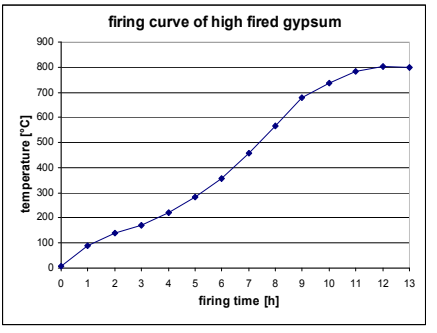

Fig. 3 Left: View at the combustion chamber of the kiln during firing. The gypsum stones (located behind the brick wall) are separated form the combustion chamber by a grate; Right: Typical firing curve of high fired gypsum

2.2 Phase content of the fired gypsum

This firing technique results in a mixture of varying degrees of calcined gypsum. The larger gypsum pieces are frequently well burnt in the outer areas, while unprocessed material can still be found in the nucleus. The combination of different mineral phases causes the relatively high initial strength and the typical dense micro fabric of the hardened mortar [1-6].

The mineralogical composition of the calcined gypsum is determined not only by the particular firing conditions but also by the geologically related minor constituents. XRD analysis and microscopic investigations show the following changes of the mineral content in the firing process:

- Gypsum (CaSO4 .2H2O) is almost completely dehydrated to anhydrite (CaSO4).
- Different types of anhydrite arise; microscopically two morphologies can be distinguished (Fig. 4, left).
  - I. Compact to fibrous or strip-shaped anhydrite (called thermal anhydrite)
  - II. Granular anhydrite, sometimes showing holes and melting marks (rounded edges, Fig. 4, right).
- With increasing firing temperature the proportion of granular anhydrite rises.
- Activation of Ca from dolomitic limestone or dolomitic marl particles.
- Loss of calcium leads to the formation of Mg-phases (probably brucite, Fig. 5).
- Calcite grains do not show any changes.
- Oxidation of Fe-containing minerals, leads to the typical brownish colour of these mineral grains.
- Non stoichiometric anhydrite or CaO thermally formed from gypsum, as indications for sulphur loss during firing at very high temperatures have not been observed.

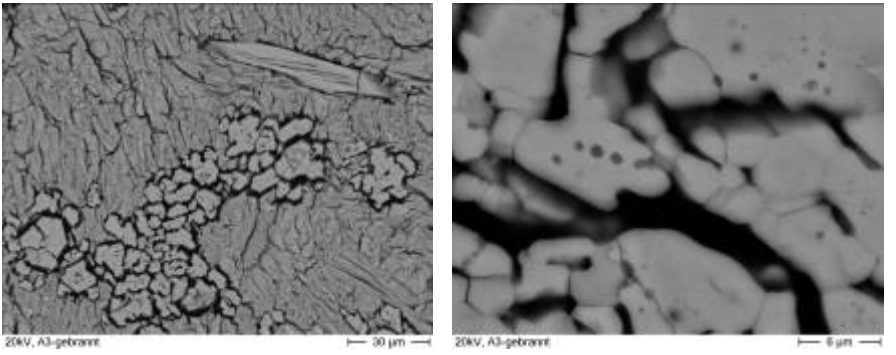

Fig. 4 Left: Different types of anhydrite. Compact to stripe-shaped anhydrite matrix including granular anhydrite grains showing holes; Right: Detail of a granular anhydrite grain, showing holes and rounded edges [SEM-BSE-images on thin sections]

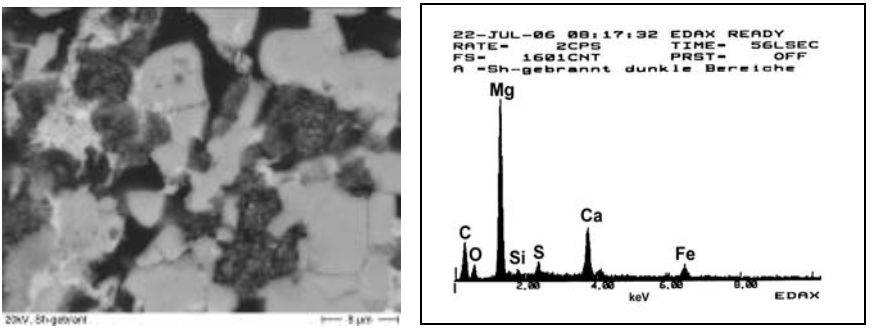

Fig. 5 Left: Thermal changed marl impurities (dark grey areas), surrounded by granular anhydrite [SEM-BSE-images on thin sections]; Right: EDX-spectrum of the marl impurities in the left image. The Ca:Mg ratio indicates the loss of calcium due to firing [EDX-analysis]

3 Properties of high fired gypsum mortar

The high firing temperature, the resulting phase content and the coarse grinding (0 - 4 mm) lead to favourable processing properties.

Contrary to other gypsum building materials mortar that has been manufactured by high fired gypsum achieves considerable strength and good durability over a hardening period of several weeks and is suitable for outdoor applications.

3.1 Hardened mortar properties

Through the contact with water a binder matrix of well-linked dihydrate crystals is formed (Fig. 6), including bigger grains of the firing product. Crystal

shape and size are different from those obtained by producing gypsum mortars from a hemi-hydrate (Fig. 7).

The microscopic studies show that the fibrous or strip-shaped anhydrite preferably dissolves and crystallizes as dihydrate. The granular anhydrite remains unchanged. Even a treatment with additional water, which simulates a regular moisture input under weathering conditions, does not lead to a hydration of this type of anhydrite. It follows that this anhydrite is considered insoluble.

On the grains of the firing product the reactive part of the anhydrite will dissolve, sometimes resulting in cavities. The typical fibrous strip-crystal forms of anhydrite are kept pseudomorph in the conversion of dihydrate (Fig. 8); at the same time dense sintering rims along the borders of the firing product grains may form.

In particular, the microscopic examinations enable the origin of structure characteristics typical for historic gypsum mortars to be traced.

The aforementioned water treatment of the hardened mortar under laboratory conditions leads to the increased hydration of the remaining available reactive anhydrite, thereby contributing to the growth of the existing larger dihydrate crystals. The effect of after treatment on the material characteristics can be summarized as follows:

- An increase in the gross density
- Reduction of the true density
- Reduction of the porosity and water absorption
- An increase in the strength and the dynamic modulus of elasticity

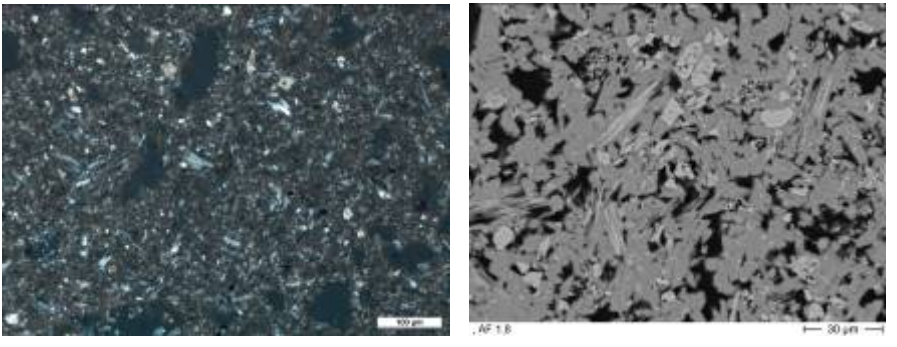

Fig. 6 Left: Typical micro fabric of the hardened mortar [Thin sections in transmitted light, x-pol.]; Right: The matrix is formed by well-linked dihydrate crystals. Some anhydrite crystals (bright grains) and the capillary pore spaces (black) are visible [SEM-BSE-images on thin sections]

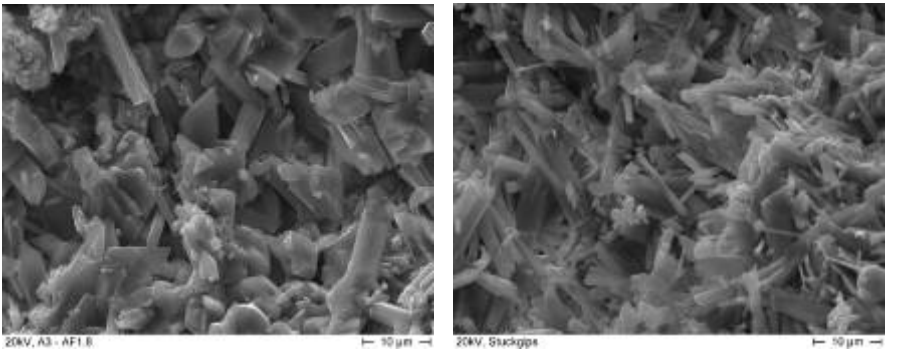

Fig. 7 Left: High fired gypsum; Right: Gypsum mortar from hemi-hydrate. Comparing the images, taken under the same imaging conditions (sample preparation, magnification, SEM-detector) it becomes clear that high fired gypsum shows larger and better linked crystals leading to a high strength and good durability [both: SEM-SE-images on fractured surfaces]

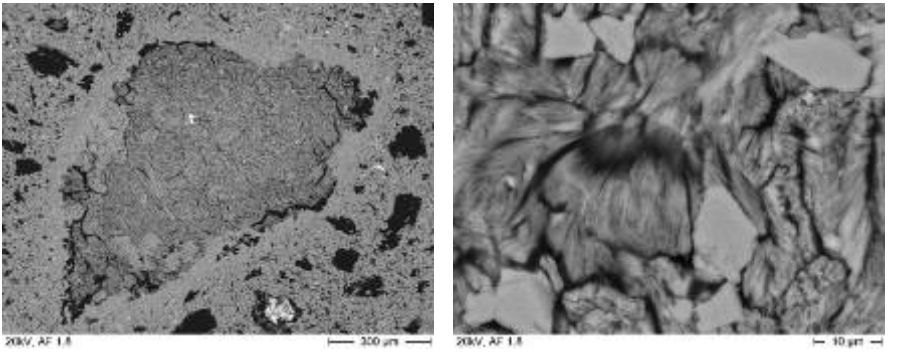

Fig. 8 Left: firing product grain with dense sintering rim along the border; Right: Detail from the center of the grain in the left image. Dihydrate pseudo morph to fibrous anhydrite, bright grains are granular anhydrite [both images: SEM-BSE-images on thin sections]

The relevant properties of the mortars manufactured from the raw materials A3 and Keuper are compared in Table 1.

Table 1 Properties of high fired gypsum mortars manufactured at ZIEGELEI Technisches Denkmal Hundisburg e.V., Saxonia-Anhalt, Germany. Analysis: Bremen Institute for Materials Testing (MPA)
Storing conditions before testing: 2 days 20°C / 95% RH.; 26 days 20°C / 65% RH

	A3	Keuper
Fresh mortar properties		
Water/gypsum ratio	0.30	0.31 – 0.32
Flow table test	146 mm	145 mm
Beginning of setting [1)]	80 min	68 – 105 min
End of setting [1)]	1.455 min	313 – 325 min
pH-value	11.3	11.1 – 11.2
Hardened mortar properties (28 d)		
Gross Density [kg/dm^3]	1.71	1.69 – 1.74
Water absorption [M-%]	12.2	9.9 – 11.9
Open porosity [Vol.-%]	20.8	17.3 – 20.2
pH-value [3)]	10.8	n.d.
Dynamic E-Modul [kN/mm^2] [2)]	8.3	12.2
Flexural strength [N/mm^2]	4.2	4.6 – 4.9
Compressive strength [N/mm^2]	17.8	19.7 – 22.3
Expansion / Shrinkage [mm/m]	n.d.	-0.20 – 0.30

[1)] determined by DIN 1168-2, chapter 2.5.2.2 respectivly 2.5.2.5, footnote 1

[2)] taken from Richter [10]

[3)] high pH values probably caused by the fired impurities dolomite and marl

4 Sample applications

In recent years high fired gypsum has been been successfully used in the following traditional applications:

- - Screed and Terrazzo
- - Mortar for constructing masonry
- - Plaster
- - Stucco

Typical examples for the use of high fired gypsum in restoration work are shown in Fig. 9. The floor of the church in Eschenbergen was reconstructed based on historical findings. The white areas between the ceramic tiles are renewed screed made of high fired gypsum. On the steeple of a church in Wernigerode consolidation of joint mortars and plasters has been done; again, in accordance with the historical findings high fired gypsum was used. At the church of Kehmstedt the outer walls have been plastered using this material.

Fig. 9 Left: Floor in the church of Eschenbergen. The white areas are screed, made of high fired gysum (photo: Rothe); Middle: Church tower in Wernigerode (photo: Srocke); Right: Church in Kehmstadt. The renewed plaster and joints consist of high fired gypsum (photo: Srocke)

4.1 City Hall Lüneburg

The medieval city hall of Lüneburg was built using gypsum as a masonry mortar (Fig. 10). For structural reasons, in the basement of the building several supporting pillars had to be rebuilt [12]. Preliminary studies have shown that a moderate humidity and salt stress in the pillars allowed the use of gypsum mortar [13]. With a view of the compressive strength required, high fired gypsum was chosen not only because it matched the historical material but because it ensured an optimum material compatibility. Due the relevance of static, it was necessary to ensure that the gypsum mortar, even in contact with moisture, achieved the strength required by regulations. [13]. Table 2 shows that proof of this could be provided successfully; even in water-saturated conditions and after 7 days stored underwater, the high fired gypsum mortar maintained more than 50% of its strength (Fig. 11). Gypsum mortars based on hemi-hydrate show a much greater loss in strength under these conditions.

Fig. 10 Pillars in the basement of the city hall Lüneburg. Left: Situation before start of repair work. The masonry consists of brick and gypsum mortar. The pillars are safeguarded by steel profiles; Right; Pillars in final state, rebuilt using high fired gypsum mortar

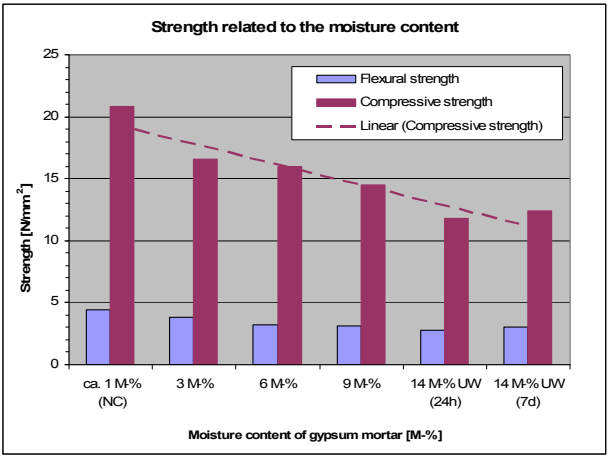

Fig. 11 Strength of high fired gypsum mortar related to moisture content of the mortar.

Table 2 Requirements and test results of high fired gypsum mortar in water-saturated conditions. Analysis: Bremen Institute for Materials Testing (MPA)

	Requirement by standards [1)]	Test result	Assessment
Compressive strength [N/mm^2]	≥ 5	11.8 ± 1.0	passed
Compressive strength in joint [N/mm^2]	≥ 5 (method II)	16.6 ± 2.2	passed
Bond shear strength [N/mm^2]	≥ 0.2	0.4 ± 0.2	passed

[1)] standards: DIN 1053-1; DIN EN 998-2; DIN V 18580; DIN V 20000-412

4.2 New Museum Berlin

The building of the new museum in Berlin was heavily damaged by the effects of WWII. Since the 1990s, extensive restoration work has been carried out [14]. The splendid terrazzo floors were reconstructed according to historical findings using high fired gypsum from Hundisburg (Fig. 12). For the very elaborate production of the floors in the New Museum, pigments and crushed stone were added as decorative elements, and the floor surface was ground in several steps, polished and sealed.

Fig. 12 New Museum in Berlin: Overview and detail of the terrazzo floors made using high fired gypsum as a binder material (photos: Kaiser)

5 Conclusions

The high fired gypsum produced in the building material factory TECHNISCHES DENKMAL HUNDISBURG e.V. is a material comparable to historic gypsum, in regards to the raw materials, firing process, grinding technology and properties. The raw materials are natural gypsum rocks that are processed with the typical variation in their composition. It is ensured that minimum contaminated deposit horizons are used and that production and application are free of chemical additives.

The mortar is characterised by a sufficient long processing time, high strength, and an optimal microstructure. According to the historical findings the material can be modified by the addition of pigments and coloured sands or stones.

Various surface treatments such as compaction by beating, grinding, polishing and smoothing to a shine are possible. The high fired gypsum can be used in all traditional applications of gypsum mortar.

The material has been extensively studied scientifically in recent years and is subjected to regular production control.

6 Acknowledgements

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IV.37

Design of Conservation Mortars for the Restoration of Piraeus Stone at the Monuments of the Acropolis of Athens

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Abstract Stone from Piraeus was used during the 7th and 6th centuries BC as the main building material for all parts of the monuments of the Acropolis of Athens. The stone is a limestone with different variations which can be outlined as dolomitic, fossilferous, marly and sandstone. During the restoration of the monuments, many architectural elements made of the stone were found in fragments which have been subsequently identified. The issue was to design a conservation mortar to reestablish the monolithic property of the architectural elements. The methodology that was developed included the measurement of the mechanical and physical properties of the stone in order to set the requirements for a bonding mortar. A number of different mortar compositions were designed and prepared. The raw materials selected were lime, hydraulic lime, metakaolin and Portland cement. The mortars were applied to bond stone specimens and the effectiveness of the bond between the stone and the mortar was evaluated. The selected mortar has compatibility to the stone characteristics.

1 Introduction

Stone from Piraeus is considered to have been used in great measure during ancient times to build the city of Athens. Several kinds of stone were employed for the construction of the Athenian Acropolis buildings during the Archaic period, but Piraeus stone was the main building material. Later on, in the Classical and Hellenistic periods, this stone still remained in use but to a smaller degree and mainly as a secondary material. From the Classic period the use of marble in the upper parts of the buildings superseded entirely the use of Piraeus stone which was restricted to the construction of foundations [1]. Two terms were used during that time to indicate the stones coming from the area of Piraeus: *Aktites stone*

which describes a hard dolomitic limestone which was the most commonly found, and *Mounichea stone* which refers to the soft, marly stones of the area. In cases where the stone was used in the visible, superstructure of the buildings, the hard, durable limestone was almost always preferred. On the contrary, the soft, marly stone was selected to be used for the substructure and the foundations of the buildings [2].

During the restoration works of the monuments of the Acropolis, conducted in the last decades, several fragments of architectural members made of Piraeus stone were found scattered in the archaeological site. These fragments were reassembled and the issue of re-establishing the monolithic properties of the architectural elements was raised. This was achieved by designing a bonding mortar for the stone which, as the restored elements will remain in situ and be onexhibition to the public, will be in respect to the traditional aesthetic quality of the site.

This paper presents the methodology that was developed to approach the problem, the experimental procedure that was conducted in order to test several raw materials which were used to produce mortar samples and finally the evaluation of the results obtained in order to propose and apply the most appropriate mortar composition.

2 Experimental

2.1 Methodology, requirements and evaluation criteria

The methodology developed is based on current knowledge of the laboratory procedures followed in similar studies. The petrographic characteristics of the stone, as well as its physical and mechanical properties, were studied in order to acquire as much information as possible about the material. To do so, stone samples from the monuments were collected. The requirements that the bonding mortar should fulfil were based on the results obtained.

The basic requirements of mortars applied in cultural heritage conservation depend on multiple conditions and several characteristics. An essential prerequisite for these mortars is that they should not cause any further damage to the stone after their application. The bond which is created between the stone and the mortar should not be stronger than the stones. If stress is applied on the bonded architectural member, then failure should occur in the bonding mortar or at the interface between the mortar and the stone rather than in the stone itself. Furthermore, the bond between mortar and stone must withstand humidity alterations, and frost or chemical attack. Mortar and stone should have similar physical and chemical characteristics, introducing as minimal a discontinuity as possible. In this case, compatibility with the stone from the physical, mechanical, chemical and aesthetic points of view should be strived for [3, 4]. Finally the

constituent materials of the mortar should be certified for their quality and technical characteristics [5].

Once the requirements were set, the constituent materials of the mortars were selected, their mixing proportions were studied and subsequently mortar specimens with different compositions were prepared using standard methods. Then, the physical and mechanical characteristics of the mortars were measured and compared to those of the stone. Four mortars were initially selected to bond specially cut stone specimens. Finally, the effectiveness of the bond between the stone and the mortar was evaluated. The evaluation was based on two fundamental criteria: the mechanical strength of the bond should not exceed the strength of the stone and the mortar applied should be physically and chemically compatible to the stone. The experimental procedure concluded with the final proposal for the use of the most suitable bonding mortar.

2.2 Characteristics of the stone

In our previous work [1], selected samples of the Piraeus stone were analysed and the mineralogical and physical characteristics were identified. Briefly, the results indicate that Piraeus stone could be recognised as either a; *dolomitic limestone*, which is hard, compact, whitish to creamy-coloured, with a low to medium porosity, a small grain size and good values of mechanical strength (apart from calcite and dolomite, very small quantities of fine-grained quartz and leaflets of sericite were identified); *fossiliferous limestone*, yellowish to light grey-coloured, rich in macrofossils and microfossils, with a high porosity and mostly low values of mechanical strength; *a marly limestone/dolomitic limestone* with an oolitic texture, brownish or yellowish to light grey-colour with a low to medium porosity and low values of mechanical strength (the calcitic oolites are connected with little cementing material; numerous grains of clastic quartz can be found within the dolomitic matrix); or a *sandstone* which is fine to coarse-grained, yellowish, brownish to light grey with a high porosity and low mechanical strength.

2.3 Materials

The materials used in preparing the mortars were: air lime, natural hydraulic lime (3.5z), white Portland cement, and metakaolin which is a pozzolanic material. No aggregate was used in the preparation of the mortars to minimise the thickness of the bond. The materials were mixed in different proportions taking into account the issue of compatibility and the development of sufficient mechanical properties.

2.4 Sample preparation

The preparation of the samples included both the preparation of the stone specimens as well as the production of mortar specimens to be tested. Nine mortar compositions were designed and three 4x4x16cm specimens were prepared for each composition, according to EN 196-1:1995 [6], (Table 1). The amount of water used in the mortars was calculated according to EN 1015-3:1999 [7]. The specimens were cured for 28 days in a storage chamber. The temperature was kept at 20±2°C throughout the curing period. Relative humidity was kept at 90±5% for the first 7 days and at 65±5% for the remaining 21 days, according to EN 1015-11:1999 [8]. After curing, the physical and mechanical properties of the mortar specimens were measured.

Table 1 Mortar compositions (% w/w)

Mortar	Air lime	Metakaolin	White cement	Hydraulic lime	Water
L0	50	40	10	-	100
L1	24	56	20	-	90
L2	20	45	35	-	82.5
L3	25	75	-	-	95
L4	-	-	100	-	45
L5	-	-	-	100	57
L6	25	25	50	-	75
L7	15	15	70	-	65
L8	30	70	-	-	90

The stone samples collected from the monuments were cut into specimens of 4x4x4cm to measure the compressive strength and into 4x4x8cm specimens to bond them with the selected mortars and finally 4x4x16 cm bonded stone specimens to test the efficiency of the bond. The bond behaviour of the mortar mixes was evaluated using the two-stone specimen test method [9]. The stone faces were pre-conditioned by mechanical reworking and wetting. The mortar was applied on one face and then the stone specimens were joined by placing them vertically one on top of the other. The joint was kept moist with a damp cotton gauze and a polyethylene sheet. The specimens were then placed in a storage chamber for 28 days, according to the conditions described in EN 1015-11:1999 [8].

2.5 Physical and mechanical properties of the stone and mortars

In order to further study the properties of the stone as well as to characterise the properties of the mortars, their physical and mechanical properties were measured. Water absorption was determined according to EN 13755:2002 [10]. Capillary

water absorption measurements were performed according to EN 1015-18:1995 [11] and EN 1925:1999 [12]. Bulk density and open porosity tests were performed by total saturation with water under vacuum and hydrostatic weight according to EN 1936:1999 [13]. For the mortars, shrinkage deformation was tested according to DIN 52615 [14]. Finally the mechanical properties of the stone, the mortar and the bonded stone specimens were characterised by measuring the uniaxial compressive strength and the flexural strength according to EN 196-1:1995 [6], EN 1015-11:1999 [8] and EN 12372:2006 [15].

3 Results and discussion

3.1 Physical and mechanical properties of the stone

In Table 2 the physical and mechanical properties of the stone are summarised. The results indicate the use of both the hard dolomitic limestone, with a low porosity and water absorption capacity and high values of compressive strength (Ere-d, Acr-1), and the sandstone, with higher values of physical properties and low strength.

Table 2 Physical and mechanical properties of the stone

Stone samples	Water absorption capacity (%)	Capillary rise coefficient ($g/m^2/s^{-½}$)	Porosity (%)	Compressive strength (MPa)	Flexural strength (MPa)
Ere-d	5.62	1.61	12.7	42.7	7.11
Ere-a	18.3	0.67	28.5	13.0	7.08
Acr-1	8.66	0.47	17.9	63.9	9.68
Acr-2	14.7	1.22	24.6	8.64	-
Acr-a	6.10	0.15	12.7	19.7	11.9

3.2 Physical and mechanical properties of the mortars

In Table 3 the physical and mechanical properties of the mortars are presented. The compositions designed gave a variety of results. At this point, the properties measured were correlated with the corresponding properties of the stone in order to select the mortar compositions that fulfil the requirements set [16].

Table 3 Physical and mechanical properties of the mortars

Mortar	Water absorption capacity (%)	Capillary rise coefficient ($g/m^2/s^{-½}$)	Porosity (%)	Shrinkage (%)	Compressive strength (MPa)	Flexural strength (MPa)
L0	43.3	0.28	42.5	0.50	7.90	1.00
L1	42.3	0.17	44.1	1.25	11.7	0.79
L2	40.9	0.24	44.3	0.62	17.9	1.05
L3	37.7	0.32	41.0	0.75	9.86	1.73
L4	21.3	0.16	34.7	0.50	22.0	2.31
L5	44.6	0.50	51.0	0.90	4.35	0.88
L6	30.2	0.15	39.4	0.25	28.5	1.00
L7	40.3	0.17	48.6	0.25	22.2	1.16
L8	39.2	0.31	39.7	0.28	11.1	0.70

3.3 Selection of the bonding mortar

Four mortar compositions were selected to be tested as bonding mortars: L0, L2, L3 and L6. Their properties meet the general requirements set and the specific criteria described. The selection was based on the relation between the mechanical properties of the stones and the mortars. These four compositions gave the highest values of flexural strength by using less than 50% (w/w) cement, a fact which is important as far as compatibility issues are concerned. Colour was not important since the bond is often covered with a layer of coloured plaster to match the colouring of the stone. Stronger mortar compositions L2 and L6 were tested with the higher strength dolomitic stone (Acr-1, Ere-d) and weaker compositions L0 and L3 with the weaker marly stones and sandstones (Acr-a, Ere-a).

Three stone-mortar specimens were built for each mortar composition and each stone type. In total 24 specimens were built. After the mortar was cured, the specimens were tested for flexural bond strength. The results, presented in Table 4, indicate that mortar compositions L2 and L6 gave adequate tensile bond strengths ranging from 1.00 to 4.74 MPa . The mean value of the flexural strength is 2.42 MPa for mortar L2 and 2.36 MPa for mortar L6.

Taking into account the experimental results, both L2 and L6 compositions have similar flexural strengths which are equal or higher than 1 MPa. Furthermore, the highest flexural strength of the bond (4.74 MPa) is lower that the corresponding lower value measured for the stones (7.08 MPa). L2 and L6 also gave increased values of flexural strength in the stone-mortar specimens when compared to the corresponding values measured for the mortar specimens (compare Table 4 and Table 3). In addition, the faces of the stone specimens were examined macroscopically and microscopically in order to observe the fracture area. In all of the specimens, fracture occurred at the bond and not at the stone,

leaving the faces of the stone intact. In most of the cases failure occurred within the mortar.

Table 4 Flexural bond strength between stone and mortar

Mortar	Stone type	Flexural bond strength (MPa)
L0	Acr-a, Ere-a	0.38 – 0.62
L2	Acr-1, Ere-d	1.00 – 3.65
L3	Acr-a, Ere-a	failed
L6	Acr-1, Ere-d	1.14 – 4.74

Although both compositions presented adequate physical and mechanical properties, L2 was selected as the bonding mortar since the quantity of cement used is minimal, producing in this way a mortar more compatible to the ancient material.

4 Conclusions

The results of this study demonstrate the particularities of designing a mortar that will bond stone fragments. The stone characteristics are very important in the development of the methodology. The bond which is achieved should not exceed the tensile strength of the stone. Where failure occurs, this should be in the mortar or at the interface of the mortar with the stone. Furthermore, the mortar should be compatible to the stone. In the present study, the aforementioned criteria were fundamental not only for the process of selecting the constituent materials of the mortars and designing different compositions to be tested, but for the final selection as well.

The stone of Piraeus present a variety of characteristics and properties that had to be considered. For this reason, different mortar compositions were designed and prepared that could cover the demands of a bonding mortar for the stone. The margin of the values obtained on the physical and mechanical properties of the mortars was wide. The requirements a bonding mortar should fulfil were already set and the selection was narrowed to four compositions from which one was proposed. The selected mortar composition is compatible to the stone properties. The developed bond is good but it does not exceed the strength of the stone. The study of the stone faces after failure of the bond, indicate that the fracture occurs either in the mortar or at the interface between the mortar and the stone without causing any damage to the stone. Furthermore, the constituent materials of the mortar are compatible to the stone and the use of cement is minimised.

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IV.38

Repair Mortars Studied for the Conservation of Temple G1 in Mỹ Sơn, Vietnam

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Abstract Since 2001 the authors have been involved with the archaeologists of the Fondazioni Lerici, Politecnico di Milano, in the preservation of some Hindu temples in Mỹ Sơn, Vietnam. The characterisation of the brick- masonry materials was carried out at the Politecnico di Milano. Especially interesting was the successful study of the natural resin used to bond externally the bricks in the masonry; this allowed the formulation of a new compatible resin to be used for the conservation project. In the masonry internal leaf, the joint material, based on clay, was substituted by a new hydrated lime and powdered bricks mortar. The results of the research presented here allowed the direct application of the new materials in the conservation project of G1, G3, and G5 of group G.

1 Introduction

When the contemporary principles and theories of conservation that have been developed mainly in the Western world are applied to Asian monuments, it is a difficult task to compromise with the position of the experts in that part of the world. Furthermore, when the monuments are at the state of ruin in archaeological sites it becomes more difficult to apply these principles. Conservation in countries that have suffered wars and consequent poverty is even more difficult, also due to lack of advanced techniques and materials.

The authors have been working since 2001 on the conservation of a group of buildings in Mỹ Sơn, Vietnam (called group G by H. Parmentier). The groups of temples in Mỹ Sơn were called by alphabetic letters from A to N by Parmentier, who discovered them in the jungle near DaNang at the end of the 19th cent. Conservation works on group G began in 2004, followed by the Politecnico di Milano, within the framework of a tripartite contract between Politecnico, Institute for Conservation in Hanoi, and UNESCO, supported by the Italian Ministry of Foreign Affairs. The group G was built, as all the others, in brick masonry with some peculiarities.

Principles were applied to the preservation of the buildings, especially for the use of new materials, mortars, resins, and bricks. The choice of the new materials was made according to some important criteria: (i) the possibility of finding local materials and production techniques, (ii) control of the parameters defining the quality and compatibility of the new materials, and (iii) execution of the works on site by non-specialized workers.

The climate in Mỹ Sơn, typical of the tropical areas, has deeply influenced the choice of the mortar to be used to consolidate the internal part of the wall, which was two- or three-leaf masonry; the original material between the pieces of bricks constituting the internal leaf was simply clay and brick powder. In the meantime, the external joints were found to be made with a resin coming from a local tree. Therefore, when the works on the G group started, an investigation was carried out in the Northern and Central part of Vietnam in order to find a hydraulic binder. On the basis of the experimental research based on chemical, physical, petrographical, and mechanical tests, different compositions - from hydrated to hydraulic lime-based mortars - were examined. Unfortunately no suitable hydraulic lime was found in Vietnam, so the only possibility was to prepare a mortar based on hydrated lime and brick powder, which testing indicated was the best fit due to the proven pozzolanicity of the brick powder.

The paper will describe the results of the experimental tests in laboratory and on-site, where some specimens were prepared following the special conditions of temperature and humidity of the site. The difficulties of preparing the brick powder following the imposed grain size distribution and of realizing on-site the mortar composition and the quality control with available rough tools will also be described.

The chosen mortar composition gave acceptable properties in the short- and long-term, and some samples from the site examined in thin section and at SEM after two years gave evidence that very good pozzolanic reactions had taken place. Even at visual inspection, the top joints exposed to humid and rainy climate is still showing compactness.

2 Description of the Mỹ Sơn Hindu temples

The archaeological area of Mỹ Sơn is situated in Central Vietnam, 30 km southwest from Da Nang; it is located in a valley surrounded by low mountains dominated by the Rang Meo mountain, and it is crossed by the Thu- Bôn river. The Mỹ Sơn area (Figs. 1, 2) is 15 ha wide and composed of several groups of buildings made with brick masonry, each organized around a main temple (*Kalan*). Mỹ Sơn is the most important holy place of the Champa kingdom. The Cham people built over seventy buildings here, from the 6th to the 14th cent AD, but now only thirty with at least 1 m in elevation are still recognizable. The site was rediscovered after centuries of abandonment in 1898 and studied at the beginning of the 20th cent. by French architect H. Parmentier, from the École Française d'Extrême Orient (EFEO) [1]. A Vietnamese-Polish expedition (lead

from 1982 until 1986 by K. Kwiatkowski and K. Hoang Dao) carried out restoration works on some group of buildings damaged during the war at the end of the sixties [2].

The buildings in Mỹ Sơn are made of fired bricks thinly joined by natural resin. The wall section is made of two leaves with small connections or three leaves, with brick rubble in the middle and faced externally with bricks (Fig. 3). The most peculiar characteristic of the brick masonry was the special construction technique which created a bond between bricks so tight they practically did not show real joints (Fig. 4). The special building technique protects the walls from the attack of the vegetation; where the thin joint is not damaged, there are only very low biological attacks [3].

Fig. 1 The archaeological area of Mỹ Sơn.

Fig. 2 Mỹ Sơn: view of the groups C and D of temples.

In order to realize a more tight physical bond, the technique of *rub-joining* was used during wall construction before applying the resin. Scratches can be seen on the horizontal and vertical surfaces of the bricks in contact with other bricks. The scratch can be clearly observed by a magnifier and even by naked eye (Fig. 5) [4].

Following some hypotheses that organic natural materials could have been used as binder between the bricks as in historic buildings in other parts of Vietnam and Southeast Asia, a careful study was carried out on materials sampled from the Mỹ Sơn masonry walls. Furthermore, it was decided for the safety and durability of the masonry in the future to use a new mortar based on hydrated lime and brick powder in the locally reconstructed parts and, when possible, to connect the three or two leaves.

Fig. 3 Section of the wall.

Fig. 4 The thin mortar joints masonry in prospect.

Fig. 5 Scratches due to the rub-joining procedure.

3 Characterisation of the existing materials

In order to carry out laboratory research on the masonry materials, samples were taken during several visits to the site, starting from 2000. The samples were collected from the groups A, D, E, and G, which was a group of interest for the Italian pilot project. At DIS, Politecnico di Milano, the authors carried out several tests on the sampled materials in order to detect the properties of: bricks, brick assemblages, and joint material.

3.1 Material sampling

Due to the difficulty of sampling without damaging the walls, the number of samples was rather small to be statistically representative of the materials used. Nevertheless the experimental research gave rather good results, as will be shown below. All the brick samples were taken from the material available on the ground (buildings A1, A13, B9, D4, and G1) or in the ruins (E4, E5, and E7) in order to avoid spoiling the standing parts of the buildings. In 2001, a special glue of vegetal origin, used for caulking of boats, was bought at the local market in Hoi An (RES1); in 2004 another resin coming from local trees (called Daù Raì) and sold as glue was bought close to the Mỹ Sơn site (RES2).

3.2 Chemical, physical, and mechanical tests on bricks, joints, and rubble filling

The analyses concerned the bricks and the binder in the external joints and in the inner leaf of the walls. Chemical analyses according to [5] were carried out on the sampled materials [6].

The results showed that the composition of all the sampled brick is the same, despite apparent visual differences, and that the composition of the bricks and of the so-called joint is the same, but also contains an organic resin. The presence of a very low CaO content in the joint (from 2.33 to 4.48%) showed that no lime was used in the external joints. Chemical analyses were also carried out on the material sampled from the internal leaf of the walls. They show that the composition of this material does not differ from that of the bricks [7].

Physical tests were performed on four to six small brick cubes (40 mm side) cut from the bricks; the tests were carried out according to the European standard (UNI EN 2001). The results show a certain in-homogeneity; nevertheless, some orientation values can be given as an average: (i) bulk density = 1,630 kg/m^3, (ii) I.R.S from 0.41 to 1.92 kg/m^2/min, (iii) water absorption coefficient = 160.09 g/cm^2×s$^{0.5}$, and (iv) water absorption by total immersion between 18.18 and 23.99%. Some XRD tests carried out on a specimen from A1 show that the bricks were fired at a temperature below 900°C, [7].

Compression tests were carried out on cubes (40 mm x 40 mm x 40 mm). Once

again, all of the values were very much scattered, between 8 and 14 N/mm^2. The modulus of elasticity E and the Poisson coefficient were also calculated, and the values are typical of a rather soft material [7].

4 The natural resin used for the external joints

The "Giulio Natta" Department of Chemistry, Materials and Industrial Chemistry of the Politecnico di Milano (G. Zerbi), and the Institute of Biology of the Faculty of Science of the University of Milan (F. Tomé) have performed the chemical characterization of the resin found in the joint [8]. The identification of the main components of the organic materials was carried out mostly by means of infrared spectroscopy with FT-interferometers. To help in the analysis, a few procedures of separation of the components have been followed, such as evaporation *in vacuo* and extraction with suitable solvents.

The idea behind these analyses was that the materials used in the building of the Mỹ Sơn temples should be fully related to what nature offers in the area and what people can manufacture locally from the resins of the trees that grow in the surrounding area. These trees belong to the species of the *dispterocarpaceae.*

The results of the analyses are as follows:

- 1) Identification of the chemical nature of sample of resin found in the area of Mỹ Sơn, RES1 (a special resin, liquid at room temperature, used for caulking boats) and RES2 (extracted as viscous fluid from a local tree called "Daù Rai"). The infrared spectrum of RES1 shows that Dammarenediol seems to have the highest relative concentration with respect to many other possible substances in much lower concentration. Difference spectroscopy provides the infrared spectrum of the volatile component of RES 1, which can be identified as alloaromadendrene. The two materials RES1 and RES2 are practically identical, thus indicating that the local people obtained the glue from local trees.
- 2) Analysis of the material scratched away from the joint (JRES1). Fig. 6 shows the great similarity of the organic component extracted from JRES1 with the solid residue of RES1. The spectrum shows, however, that some chemical modifications have occurred from RES1 to JRES1. It is likely that the resin taken from the brick originally could have been just the resin from the trees; self-oxidation processes that possibly occurred over the many years could justify the spectral changes observed.

In conclusion, the new resins have a similar composition to the old ones and can be used for joint repair.

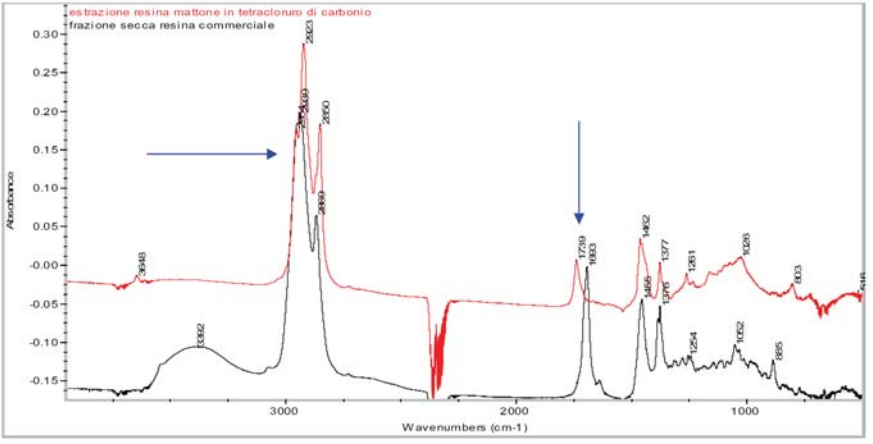

Fig. 6 Comparison of the FT-IR spectra of the material extracted with carbon tetrachloride from the brick (red) and the FT-IR spectrum of the solid residue of RES1

5 The repair mortar composition

It was decided to use a lime based mortar for the repair or reconstruction of the internal leaf of the walls; the resin could not be used because the internal joints between rubble bricks were rather thick and the original joints were simply filled by clay. This mortar should be a hydraulic one, but as said above, it was practically impossible to find a hydraulic lime in the Mỹ Sơn area. Therefore, it was decided to choose a mortar made with hydrated lime and brick powder and/or pebbles if it could be detected that the Mỹ Sơn bricks were pozzolanic. Tests were carried out on powdered bricks from the site. The bricks were ground very fine and the powder showed a positive behaviour at the pozzolanicity test carried out at the Politecnico di Milano (Fig. 7). The pozzolanicity test was performed according to the European Standard [9] used for cement, adapted to the special case. The bricks showed pozzolanicity after 30 days.

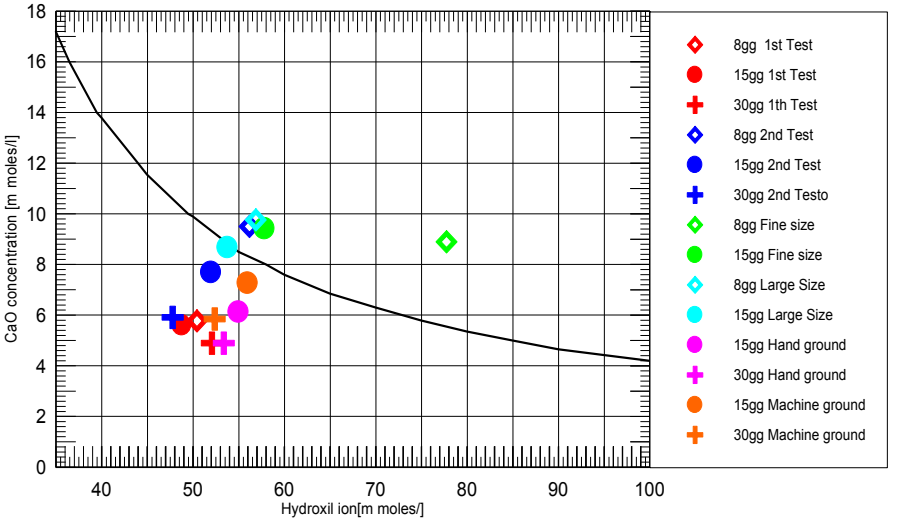

Fig. 7 Pozzolanicity tests on sampled bricks

In the meantime, the research of the lime was started in the area around Mỹ Sơn in order to minimize the price of transportation. Since it was impossible to find a lime from stones, as the existing quarries had been closed in order to avoid the continuous spoiling, only natural lime coming from the sea shells could be found. Lime samples from the nearby village of Lang Co, from the village of Kiem Lam, and from Hoi An were collected along with a putty lime from Ha Noi. The third lime from Hoi An was finally chosen after comparison by chemical and physical tests was carried out in Milan at DIS, Politecnico [10]. It was the best mortar available in the Mỹ Sơn area, and therefore it was chosen.

It was then decided to produce two types of mortars: (a) with fine aggregates for thin joints and (b) with coarser aggregates for thicker joints. The maximum diameter size varies according to the thickness of the joint from 2 to 16 mm (Figs. 8 and 9).

During the intervention, specimens were prepared on-site, cured at the site environment, and sent to Milan for testing (Fig. 9). Flexural and compressive tests were carried out in Milan according to the European Standard [11].

The results are given in Tab.1, where σ_f is the flexural strength and σ_c is the compressive strength. As seen in Tab.1, the mortars were tested at different ages of curing, but the number of days did not follow the same increase as is normally done in laboratory. This was due to the fact that some mortars were prepared on-site and tested in Milan whenever possible. Nevertheless both the scattering in the data and the values of the tensile strength were rather acceptable for a low strength hydraulic mortar.

The chosen mortar was first used for the repair of the two remains of the buildings G3 and G5, which only emerged from the ground from 50 to 100 cm, in order to check the compatibility of the new materials used in external and internal

joints. The works ended in 2005, and up to now they have shown a very good behaviour. In 2009 the works started on the most important building of group G, the Kalan G1.

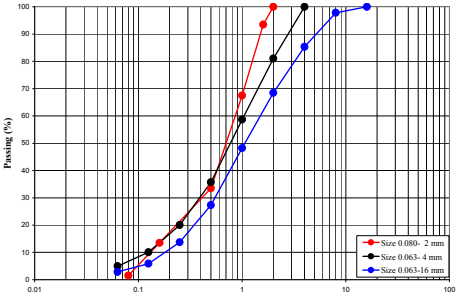

Fig. 8 Grain size distribution of aggregate for new mortars

Fig. 9 Specimens realized on site

Table 1 Flexural and compressive tests

Specimen	Age of curing	σ_f [N/mm^2]	σ_c [N/mm^2]	Age of curing	σ_f [N/mm^2]	σ_c [N/mm^2]
MT.04.1	90	0,79	2.15	480	1.25	4.77
MT.04.2	90	0,66	2.85	480	0.82	3.05
MT.04.3	270	1.37	4.40	270	1.37	4.40
MV.06.1	28	0.85	2.12	90		2.64
MI.06.1	28	0.96	3.19	90		2.35
MS.05.1	240	0.53	1.36	240	0.53	1.36
MS.05.2	160	0.67	1.40	160	0.67	1.40

The results found by the observation of new mortars in thin section and with the SEM-EDS were very interesting. Three specimens were observed, two sampled on-site from G3 (MS.05.1 and MS.05.2) and one in the laboratory at DIS-Politecnico (MS.06.1). The results of analysis of the thin sections of MS.05.1 on a polarised microscope are shown in Figs. 10 a and b. It can be easily seen that in all the sections, reaction borders between binder and brick pebbles are present, also showing a pozzolanic reaction which is still ongoing in MS.05.1. The SEM-EDS observations of MS.05.1 (Figs. 11 a, b, and c) show the presence of reaction borders composed of calcium and aluminium, calcium and silica, silica, and calcium and aluminium.

6 Conclusions

After the application of the new materials on G3 and G5 ended in 2005, the

observation of their durability and the optical tests on the sampled mortars some conclusions can be made: (i) the resin and mortar used in Mỹ Sơn show a good durability after five years, (ii) the optical observations of the new mortar made after two years show good pozzolanic reaction of the brick powder with the lime, and (iii) the new materials can be adopted in the conservation of the main kalan G1.

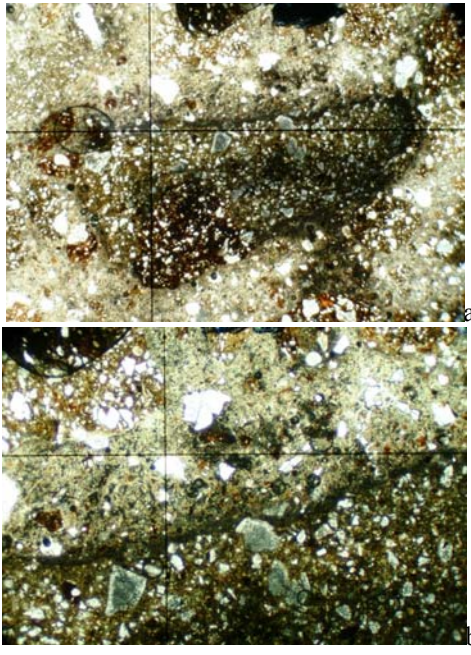

Fig. **10** Specimen MS.05.1: a) photomicrograph in transmitted light (3.5×); b) photomicrograph in transmitted light (10×)

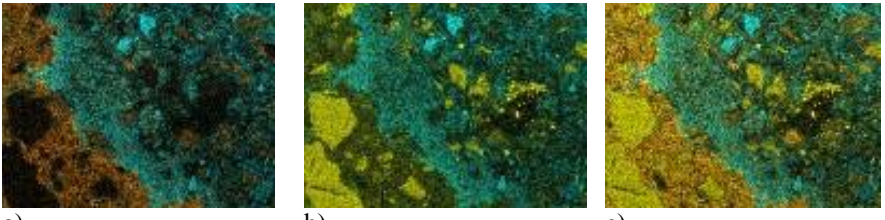

Fig. 11 Reaction borders composed: a) calcium and aluminium; b) calcium and silica; c) silica, calcium and aluminium

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IV.39

Two Siliceous Grouts for the Preservation of Stone

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Abstract The reattachment of spalling stone has been achieved by various means but traditional methods involving lime, Portland cement and synthetic adhesives all have defects that render them unsuitable for sandstone in the long term. Research into grouts fully compatible with siliceous rocks has led to the development of two materials composed entirely of silica. The first, developed in 1992 and refined for trial use in 1994, relies on the binding properties of ethyl silicate. The second, developed for application to water saturated volcanic tuff relies on the binding properties of lithium silicate.

1 Introduction

Two questions form when confronted with a crumbling stone monument. "Why has this stone crumbled and what was holding it together?" and "If ethyl silicate can strengthen stone, can it not form a cohesive grout?"

This paper explores these and several other questions that have led to the design of two grouts using ethyl silicate for one and the less discussed lithium silicate for the other. Both grouts have met their design objective and both have been applied to stone surfaces for varying periods. The ethyl silicate grout commenced development in 1992 and has been evaluated at regular intervals since. It has limitations in terms of very low tensile strength and cohesiveness. These limitations have been addressed in a recent investigation of lithium silicate.

2 The two binders

Liquid silicates have been available commercially since the first discovery of sodium silicate in the 19th century and have been used for stone repair [1, 2, 3]. Sodium and potassium silicates make very strong grouts but the release of free

ions as by products means that the grouts bloom quite dramatically as they release salt, making them unsuited to preservation use.

2.1 Ethyl silicate

Ethyl silicate was the first cation free liquid silicate to consolidate stone without forming salts. Ethyl silicate has been available commercially and applied to stone for several decades [4] and has been applied repeatedly to sandstone and other siliceous stones [5, 6, 7] with great success. Application to limestone [8]) and plasters [9] has also been widespread but the compatibility of ethyl silicate with calcium remains an issue [10, 11]. Ethyl silicate differs from the earlier water glass products in not being water miscible.

To overcome the brittleness of ethyl silicate based grout one supplier includes a modified version with urethane additives to impart flexibility in the cured product.

2.2 Lithium silicate

Lithium silicate is the most recent iteration of the water miscible silicates. It has the clear advantage of not releasing cations and has found application in the traditional use of water soluble silicates for the stabilization of concrete. Its high alkalinity (pH 10.8) is a desirable condition for reinforced concrete but presents some issues when used as a consolidant or grout on siliceous rocks. Lithium silicate has clear advantages when consolidating or grouting permanently wet rock (Fig. 1). The formula for lithium silicate is shown in Fig. 2.

As previously mentioned the traditional water soluble silicates produce high strength grouts and this is also true with lithium silicate to the extent that while it is weaker than its predecessors, a 20% dilution will result in a far more cohesive and durable grout than that possible with 100% ethyl silicate binder.

Fig. 1 Detail of a permanently water saturated ignimbrite wall containing carved canoes. The water flow and plant roots are causing delamination in many places.

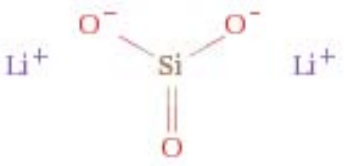

Fig. 2 The structure of lithium silicate

3 Design criteria

Design criteria, established at the beginning of the development in 1992 largely followed the recommendations of previous grout research. [12, 13, 14] including - setting time, shrinkage, tensile and compressive strength, water permeability, salt content, workability, pore distribution, and viscosity.

These design criteria were established largely for the reattachment of fresco plasters, generally within enclosed and protected locations. Additional design objectives were defined by the author to address issues relevant to the placement of grouts in outdoor conditions with direct exposure to the weather.

- 1. The grout should not promote biological growth.
- 2. The grout should contain only stable and compatible components
- 3. The colour must match its surroundings both in wet and dry conditions.
- 4. The material should be microscopically distinguishable from the natural stone.
- 5. The grout should be easily formulated on site.
- 6. The grout should be removable without threat to the original object.
- 7. The first treatment should not make subsequent treatments more difficult.
- 8. Tensile strength should be adequate to support the reattachment.

With so many competing design considerations not all can be met. Those adopted from the literature were critically reviewed to weight their relevance for the design grout and each assessed as an essential or desirable property.

Of the eleven published recommendations one major departure emerged relating to tensile strength limits. For a grout to function well as a reattachment mechanism tensile strength must match the forces of detachment, not those of the failed detaching material. Early trials using unmodified grout quickly broke bond after a year or two where the joint was longer than 30 cm or so. This was the case on a number of headstones on the Isle of the Dead, Tasmania, serving as a test site for the ethyl silicate based grouts and for which previous environmental and deterioration studies have been published [15, 16].

Following the failure patterns observed from the 1992 grout applications, a more detailed study of hydrothermal stress [17] has quantified the stresses imposed by wetting and drying compared to other mechanisms, and further shown that mineral grouts are unable to resist such forces.

Early experimental ethyl silicate grouts incorporated synthetic resins. It was found for example that the acrylic, Paraloid B72, could be dissolved directly into MEK thinned Wacker OH, producing a more cohesive grout. The issues of selective resin degradation, and greater bioactivity are overshadowed by the hydrothermal differential inherent in synthetic resins. The incorporation of non cross linking resins into the grout has been abandoned for these reasons. Instead the tensile strength requirements are fulfilled through the point application of thermosetting resins prior to grouting. Crack propagation theory indicates that the highest stresses are generated at the propagation point [18], the most difficult location to apply a grout to, even if it did possess sufficient tensile strength. The current grouting methodology allows for the application of epoxy resin to the propagation point where the detachment is considered large enough. It is well known that epoxy is vulnerable to UV degradation [19] and the system ensures that these resins are capped with grout.

The properties are all considered in relation to their significance and impact on other considerations. The authors own design considerations relate specifically to outdoor exposure, particularly wet to dry colour change. Synthetic repairs can be made indistinguishable in dry weather but become very obvious when the surroundings are wet while they remain impervious.

A greater consideration however is in the grout's nutrient supply. Calcium minerals provide the ideal nutrient for mosses and lichens. This is especially the case with gypsum transformed from calcite, where not only does it provide calcium and sulphur but also a conducive humectant environment.

4 Grout design considerations

The first feature of sandstones affecting their durability is particle size distribution and the second, mineral overgrowth or cementation. Each contributes to the packing arrangement that determines the durability of sandstone.

Particle packing has been approached theoretically by considering the void spaces in two arrangements.

Two theoretical models, referred to as cubic and tetragonal, consider the diminishing void spaces of particles initially packed one on top of the other, or where the upper particle falls into the recess of the two below. The order of particle sizes required to fill each diminishing void have been determined as ratios and calculations for each model determined in Table 1.

In each model chaos prevailed after 4 or 5 orders. It is clear from these ratios that the primary particle size constitutes the majority of the matrix and yet this requires addition of the second order onwards to achieve greater cohesiveness.

Table 1 Particle size ratios determined from theoretical models.

Order	Particle radius	Volume	Ratio	% Mass	% Pore volume
Cubic model					
1	10	4188	1	91	47.65
2	4.35	344	1	7.8	43.35
3	1.2	7.2	6	0.9	42.8
4	0.46	0.41	24	0.2	42.7
5	0.15	0.014	144	0.04	42.7
Tetragonal model					
1	10	4188	1	99.4	47.65
2	1.7	20.6	1	0.5	47.4
3	0.6	0.9	4	0.1	47.3
4	0.25	0.07	16	0.03	47.3

Particle ratios have been matched to sandstones of known particle distribution. Two points emerge from this theoretical consideration.

- 1. The second order and below is no more than 10% of the primary particle size.
- 2. Particles of all size orders need to be incorporated to ensure maximum grain contact. It is further assumed that particle size distribution should extend finer to ensure maximum connection between particles and ethyl silicate bridges.

To achieve the desired particle size distribution the size of all ingredients was considered. This brought in the need for colour control as well as ways to incorporate particles below 1 μm. Pigments seem the natural choice of colorant and provide fine particles to 1 μm while fumed silica offers nano-particles.

Initially the design aimed to include stable minerals only. This meant that all particle sizes could be achieved using silicate minerals or in the case of pigments, synthetic iron oxides. Physically and chemically unstable minerals such as clays and carbonates were particularly excluded from the formulation.

4.1 Ethyl silicate based grout

Early experiments with sands (50-1000 μm), quartz flour (3-300 μm), pigments (1-2 μm) and fumed silica (0.005-0.030 μm) failed to produce a cohesive grout. Pre-gelling the ethyl silicate with fumed silica provided a cohesive grout and for this further refinements were possible. The pigment was found to be the least satisfactory addition to the grout, leading to higher variation between wet and dry appearance and giving the least convincing stone like appearance in general.

To ensure stable components only silica based minerals were considered initially. Iron oxide pigments were considered stable. The addition of quartz flour

limited the colour range enormously and in particular required excessive pigment compensation. Later grouts relied on the use of pozzalanic additives, not for their reactive properties but simply as a suitable and stable colorant in a particle size range equal to that fulfilled by the quartz flour. To produce the typical colour range for most sandstones the ratio of quartz flour trass and pigment is adjusted.

The final list of ingredients, in decreasing radius, includes;

- Washed sands and other local relevant aggregates
- Quartz flour, Trass, oxide pigment, fumed silica gelled ethyl silicate.

The dry particles are pre-mixed to complete a whole project. The gel is introduced daily and no batch is used for more than a day, despite remaining workable for longer. Frequent batching is preferable. The application site is immediately pre-wet with ethyl silicate, but care must be taken not to over consolidate the surrounding stone, which may result in a darker appearance.

The grout has high thixotropy, which is utilized to work the grout to a more fluid state for application then quickly become a more rigid grout to set up once in place. Final working of the surface involves further compaction of the grout and finishing using a range of firm sponges and wooden implements as required.

This grout has performed well in situ since 1994 with the following limitations.

- 1. The ethyl silicate pre-consolidant limits application to dry conditions and prevents the use of aqueous treatments for several weeks after grouting.
- 2. The grout lacks tensile strength, as do all other approved mineral grouts, and thus requires the addition of thermoset spot adhesion to ensure the reattachment remains secured to the surface.
- 3. Ethyl silicate is a transport hazard and this can make getting the treatment to remote locations a logistical headache.
- 4. The hydrophobic cure period, as long as 8 weeks, limits the usefulness of an ethyl silicate based grout in situations where water flow through the object is an important consideration.

Fig. 3 Three ethyl silicate grouts attempting to match the stone above

4.2 Lithium silicate grout

Having developed the ethyl silicate grout over a number of years the incorporation of a lithium silicate binder has required far less investigation. Development was sparked by a need to consolidate and grout a permanently water saturated volcanic tuff cliff wall that could not endure the long hydrophobic cure of ethyl silicate (consideration 4 above). The danger with ethyl silicate was that water pressure would build behind the treated surface and exfoliate *en masse*.

Lithium silicate as supplied by PQ Corporation is 23% silicate dispersed in water. The pure product makes a very strong grout but somewhat weaker than grouts achieved with sodium silicate.

A few points of departure from the design requirements of ethyl silicate grouts are sufficient to describe the lithium silicate grout. The first of these is that the aqueous silicate does not gel with fumed silica. Early formulations showed that a grout can be formed without fumed silica but it has been retained for the particle distribution issues discussed previously.

Whereas ethyl silicate required an undiluted binder, lithium silicate can form a suitable grout with concentrations as low as 5% of supplied product (1.2% solids). This has slightly less compressive strength than the best ethyl silicate grout whereas 10% lithium silicate is stronger.

Initial consolidation of tuff and grout samples showed a distinct brown fringe. Lithium silicate has a pH of 10.8 and lowering this to 8.5 eliminated the staining issue. The exact pH at which staining ceases to appear has not been determined at this time but is considered important to reduce acetic acid buffer to a minimum.

The preparation of lithium silicate is easier than with ethyl silicate, largely through the formulation flexibility inherent in a better binding agent. There is no need to gel the binder and particle size distribution becomes less of an issue, but is maintained for the structural benefits evidenced in the ethyl silicate formulation.

Lithium silicate has been shown to be stable in up to 2% halite solutions but has bloomed quite heavily when applied to a precipitated salt spall crust in an experimental shelter at Uluru [20]. Lithium silicate is miscible with lime water and has potential as a binding adjunct for limestone and marble.

5 Evaluation of grouts

The formulation of the grouts has in itself met many of the requirements outlined in the design criteria above. Those that have not been addressed in the development include durability, strength, colour stability and biocidal equilibrium. The advantage of having the ethyl silicate in place for 16 years is that accelerated aging has become less important as a performance measure.

Colour stability has been shown to depend to a very large degree on achieving the colour with sand and quartz/trass fractions and being less reliant on pigments.

Replicating the mineral colorants in the stone has proven the best means of achieving wet to dry colour compatibility.

Biocidal equilibrium refers to the ability of the grout to support biota to the same growth habit as the surrounding rock. Regardless of how well a grout is matches an outdoor placement, its long term match is governed by how well it matches the biological balance with its surrounding surfaces in the long term.

The tensile strength of mineral grouts has been reported on in brief [17] indicating that none of them provides adequate tensile strength to support larger detachments. Compressive strength has not been evaluated *per se* however a system for evaluating abrasion resistance has been adapted using a rotating wire scraped across the extremely fragile tuff surface and equally applied to the grout.

After 16 years of constant monitoring there has been no sign of selective abrasion within the ethyl silicate grouts applied to the Isle of the Dead headstones and most failures and defects have developed within 1-3 years after application.

6 Conclusion

Two grouts have been developed for slightly different circumstances but both can be used for the capping of voids and, to a large extent, the complete reattachment of stone fragments. Fully detached fragments can be successfully reattached where this allows for pressing of the grouted fragment back into place. The likelihood of failure increases as the separation void becomes increasingly inaccessible. Completely enclosed voids cannot be effectively grouted with ethyl silicate grout and only moderately well with the lithium silicate variant. Resin additions are required to achieve adhesive reattachment.

The ethyl silicate grout has been in place for 16 years on the Isle of the Dead in Tasmania and in that time the headstones have been inspected at three year intervals. In that time no further losses have occurred through failure of grouts. New detachments appear to have developed and it is only through modification of hydrothermal stresses that a long term stabilization solution can be achieved.

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IV.40

Cement-Stabilized Earth Mortars for Application in Archaeological Sites and Prehistoric Monuments

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Abstract The present work deals with the microstructure, hydration and properties, mainly physico-mechanical and durability, of mortars for the repair and strengthening of prehistoric masonry. Mixtures composed of earth, Portland cement in limited quantities and calcareous sand are examined. The aim of the research is the development of cement-stabilized earth mortars with good durability properties and able to ensure effective repair and strengthening, which is required in earthquake-prone areas such as Greece.

1 Introduction

Earth-based binders were often used in the construction of prehistoric buildings in Greece, e.g. mainly as bedding mortars, floorings or plasters [1, 2]. Nowadays, it is systematically observed that long-term exposure of the uncovered monuments to environmental strains has resulted in loss of original material and the creation of voids. These defects need to be filled with a suitable and compatible mortar to ensure long-term durability and, in the case of constructions such as the tholos tombs, stability and structural safety. The need to design and use earth-based mortars is derived from the analysis of the original materials [3]. Indeed, it is felt that even if they are designed to be perfectly compatible in physicochemical and mechanical terms, the use of lime-based binders is not suitable, as it could give misleading information about the technology of the original fabric.

Earth mortars are, however, vulnerable to environmental conditions and require protection to ensure their durability. An alternative could be the design of stabilized-earth mortars [e.g. 4-6]. These are earth-based mortars in which a part of the binder is typically replaced by cement or lime. The work presented here

reports part of the results of a research carried out to develop stabilized-earth mortars for application on prehistoric monuments in Greece.

2 Experimental

2.1 Selection and characterization of materials & compositions

An earth binder industrially produced in the Attica region was selected for the mortar production. Its morphology and EDX spectrum are presented in Figure 1. The binder's chemical analysis, performed by X-ray fluorescence (Philips 1606), is shown in Table 1. In oxide form, it corresponds to 62.9% SiO_2, 11.21% Al_2O_3, 11.04% Fe_2O_3, and 4.75% CaO. The material mainly consists of albite and silica, as confirmed by X-ray diffraction [8]. Its pozzolanic activity was assessed by the Chappelle test [9] and showed 78% pozzolanicity. Its grain size distribution [8], performed following [7], showed that it is composed of fine-grain sand (2.9%), silt (79.8%), and clay (17.3%). The Atterberg limits are shown in Table 2.

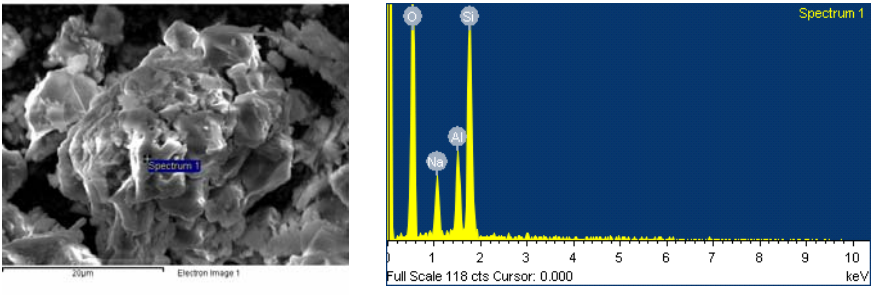

Fig. 1 SEM image (x3000) and EDX Spectrum of earth binder

Table 1 Chemical analysis of the earth binder

Elements	Concentration	Elements	Concentration
Si	29.2%	P	650ppm
Al	8.07%	Cr	330ppm
Fe	7.73%	Ni	300ppm
Ca	4.75%	Sr	250ppm
K	3.22%	Rb	240ppm
Mg	1.18%	Zn	210ppm
Na	0.911%	V	140ppm
Ti	0.585%	Cu	76ppm

Mn	0.166%	Cl	68ppm
S	0.118%	Zr	63ppm
Ba	780ppm	LOI	25.64%

Table 2 Atterberg Limits

Liquid Limit	LL	38.2%
Plasticity Limit	PL	22.2%
Plasticity Index	PI	16.0%

Two stabilized-earth mortar compositions were studied, with a binder to aggregate ratio equal to 1:1 by wt (Table 3). Calcareous sand of Attica was used as aggregate, whereas cement type CEM II 32.5N, in proportions of 12.5% and 25%wt, was added. The water content was defined on the basis of flow-table tests. A requirement for a 16-17 cm mortar expansion was set.

Table 3 Composition of the earth-based mortars

Composition	Clay-silt [%]	Cement [%]	Sand [%]
A	25	25	50
B	37.5	12.5	50

Mortar preparation took place with a standard Hobart-type mixer. The specimens were allowed to stay in the moulds in the wet chamber for 7 days before demoulding because of their slow strength increase. Then, they were carefully removed from the moulds and stored in a laboratory closet at 22°C and approximately 60-65% R.H. until the day of testing. Specimens destined for mechanical tests had dimensions of 40 mm x 40 mm x 160 mm, whereas those used for durability tests measured 25 mm x 25 mm x 285 mm, following ASTM C 490 [10]. The study of the mortars' hydration was done on fragments obtained after the mechanical tests. The fragments were immediately immersed once in acetone and twice in diethyl ether and allowed to dry under vacuum overnight in order to stop hydration. They were subsequently stored in air-tight vessels to avoid carbonation and hydration.

2.2 Experimental procedures

XRD (Siemens D5000 Diffractometer-Cu Ka, k = 1.5406 A˚) and TG-DTG (TGA/SDTA851e, Mettler Toledo) analyses were performed for the study of the mortars' hydration. The above study was completed with Scanning Electron Microscopy (Jeol6380LV Analyzer) coupled with EDX microanalysis in order to observe the morphology of the samples. A very important part of the study was the assessment of the mortars' hygric properties (not discussed here) and

durability. The mortars' hygric behaviour was studied through the determination of the water absorption and drying capacity of the mixtures at the age of 28 days. Durability was studied through constant immersion of the mortar specimen in deionized water and in sodium sulphate solution. At specific intervals, the specimens were removed from the water or the solution and their length and weight were measured. Then, the specimens were put back into water or the solution until the next measurement. The mortars were also subjected to cycles of wetting and drying. Moreover, mortar shrinkage under exposure in laboratory conditions (22°C and 60%R.H.) was monitored. To measure open porosity at a certain age, the specimens were first oven-dried at 60°C until constant weight. After having cooled, they were immersed in water until weight stabilisation. The saturated sample was then hung in a weight balance and immersed in water for volume determination.

3 Results and Discussion

3.1 Physico-mechanical properties

It is well-known that earth binders present important volume changes as a function of the environmental conditions. The length change of compositions A and B was measured as soon as the samples were removed from their moulds. Shrinkage of the mortars is observed until about one month (35 days), after which they seem to stabilize in the given laboratory conditions. The shrinkage values are quite limited: 2% and 3.5% for compositions A and B, respectively [8]. The evolution of the mechanical properties and open porosity is presented in Table 4.

As expected, the flexural and compressive strengths achieved by composition A are higher than those of composition B, due to the higher cement content. It is interesting to observe that an increase in both the compressive and flexural strengths of the mortars takes place until the age of 90 days. After this age, the compressive strength of both compositions seems to remain constant, whereas a small decrease of the flexural strength of composition B is observed. The open porosity of both compositions remains quite high: a value of approximately 29% was measured for composition A and 36% for composition B. However, some loss of material during testing cannot be excluded. In any case, the open porosity is sufficiently high, so as to be compatible with the majority of stone types used for the construction of prehistoric monuments in Greece.

Table 4 Properties of compositions A and B

Age [days]	Flex.strength A [MPa]	Comp.strength A [MPa]	Open porosity [%]	Flex.strength B [MPa]	Comp.strength B [MPa]	Open porosity [%]
7	1.87	6.97	29.73	0.7	1.57	36.86
28	2.87	11.58	31.14	1.1	3.43	36.63
90	4.13	19.05	27.19	1.5	5.52	36.41
180	4.00	19.57	29.38	1.17	5.45	35.48

3.2 Microstructural study

In general, the hydrated products tobermorite 9Å, truscottite, and $Ca(OH)_2$, as well as $CaCO_3$ either as the main sand constituent or from a partial carbonation of the released $Ca(OH)_2$, were observed by XRD [8]. Calcium silicate hydrates are observed either in the pores or on the surface of clay grains. A satisfying pozzolanic reaction of clay grains has been observed, which leads to the formation of calcium silicate hydrates, especially in the case of B series (Fig. 2 and 3), even though less cement has been added (12.5 wt%) in comparison to composition A, meaning less $Ca(OH)_2$ was released. This is also concluded from the EDX spectra (Fig 2), where spectrum 1 corresponds to an unreacted large clay grain (rich in Si and Al) and spectrum 3 corresponds to a clay grain that has reacted with $Ca(OH)_2$, leading to calcium silicate hydrates with an approximate 1:1 Si/Ca ratio. At the age of 90 days, the pozzolanic reaction is achieved, as shown in Fig. 3.

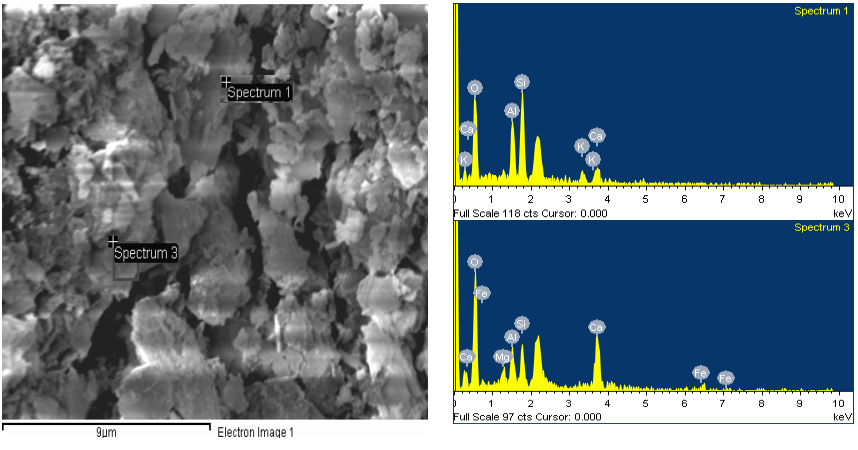

Fig. 2 SEM image (x6000) and EDX Spectrum of sample B28

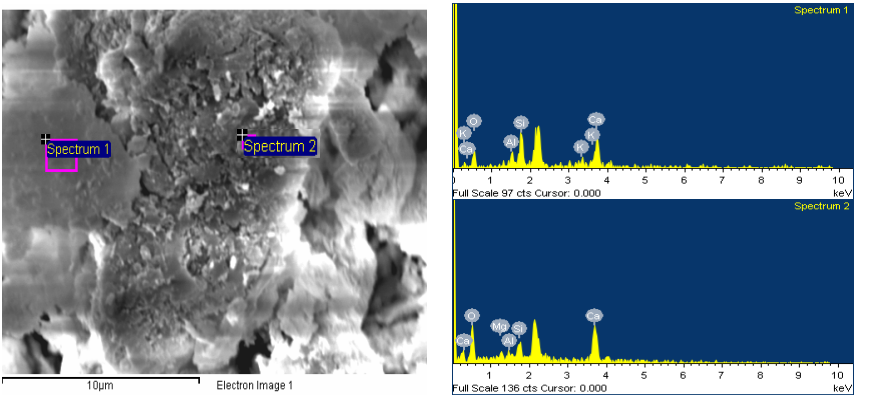

Fig. 3 SEM image (x6000) and EDX Spectrum of sample B90

3.3 TG-DTG study

The thermal profile of the samples studied, the weight loss of the various stages of thermal reaction at the ages of 28 and 90 days, and the first derivative of the above weight loss are presented in Fig. 4. In Table 5, the temperature changes of the various compounds are shown. An increase of tobermorite and $Ca(OH)_2$ production from 28 to 90 days is observed in samples of mortar composition A, due to their higher percentage of cement, in spite of some consumption of $Ca(OH)_2$ during the pozzolanic reaction with clay. In the samples of mortar composition B, the tobermorite increases from 28 to 90 days, while no $Ca(OH)_2$ can be observed, due to the small amount of cement added.

Table 5 SDTA peaks

Temperature Range (^oC)	Corresponding Compound
0-60	Sorbed moisture
60-140	Tobermorite 9Å, 11Å
140-200	Ettringite
490-510	$Ca(OH)_2$
780-900	$CaCO_3$ decomposition

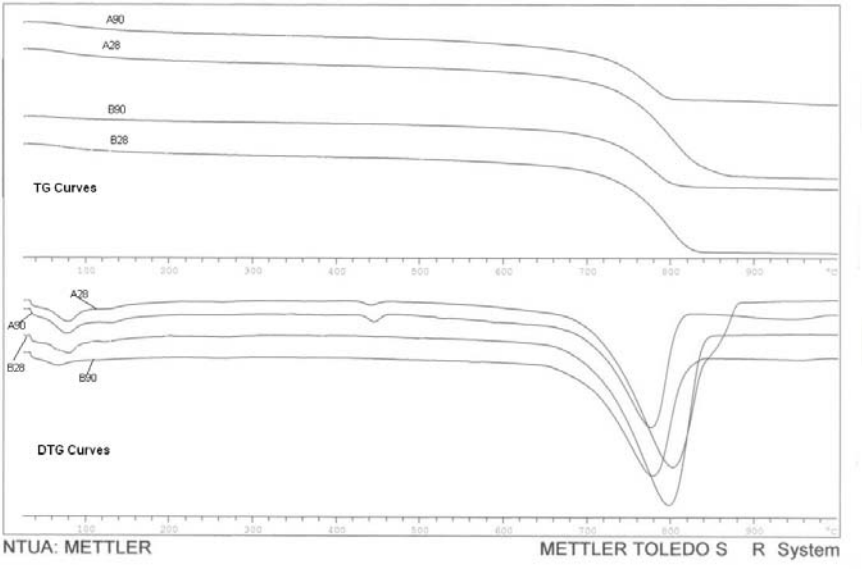

Fig.4 TG-DTG curves for the samples A28, A90, B28 and B90

3.4 Durability

The evolution of the length change of compositions A and B under various exposures is presented in Fig. 5. For the first 28 days, the specimens were cured as already described; therefore their length change reflects their drying shrinkage. At the age of 28 days, the specimens were subjected to the various tests.

When subjected to wetting and drying cycles, as well as when constantly immersed in deionised water, the two compositions exhibit a similar behaviour. Indeed, after an initial shrinkage attributable to the air-curing, the compositions exhibit a slight length increase as soon as they are put in the water. Very soon, the specimens' length is stabilized and remains practically constant. This exceptional stability should be attributed, at least partly, to the pozzolanic reaction that develops between the clay surface and the $Ca(OH)_2$ release during cement hydration. The presence of cement, however, creates the initial stable microstructure, inside which the other reactions can develop.

The evolution of the length change of the two compositions A and B, when constantly immersed in sulphate solution, is different. Composition B failed very quickly. On the contrary, composition A, with a higher cement content, exhibited a length increase and, despite the presence of small hairline cracks, it did not fail. It has to be noted that the acidity of the solution was quickly attenuated and a pH around 11 was restored. The solution was often renewed, nevertheless it still

became alkaline. Further research is required to check the mortar durability when the solution is constantly acid.

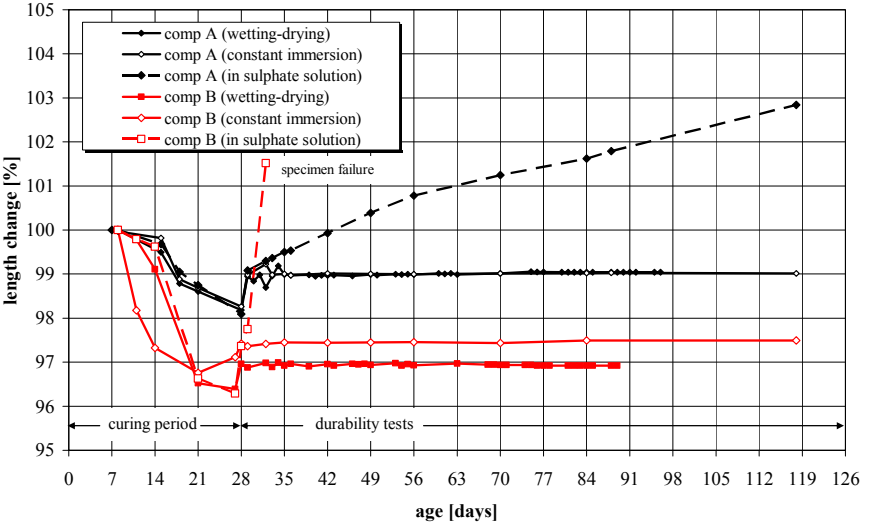

Fig. 5 Comparison of the behaviour of compositions A& B in cycles of wetting-drying and immersion in water and sulphate solution

4 Conclusions

The cement-stabilized earth mortars can develop a great variety of compressive and tensile strengths, some of which can satisfy historic masonry requirements, while open porosity values are compatible to most stonework. The study of the microstructure using Scanning Electron Microscopy, Thermogravimetric Analysis, and X-Ray Diffraction revealed the development of pozzolanic reactions between the binder and the $Ca(OH)_2$ that is released during the cement hydration process, which is a key-factor for durability. The studied compositions present limited shrinkage and very good durability in deionised water and wetting-drying cycles. A minimum cement content is required to improve the setting time and resistance against a mild sulphate attack.

5 Acknowledgments

The physico-mechanical tests were performed at the Hellenic Cement Research Centre Laboratory. Mrs Z.Tsimpouki, General Director, Dr V.Kaloidas, Technical Director and Mr C.Alafouzos, Engineer at HCRC, are gratefully acknowledged.

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Strengthening of Heritage Buildings by Means of Grout Injection - Problems and Solutions

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Abstract Many heritage buildings in Slovenia were built of stone or a mixture of stone and brick; until the 20th century the local stone represented the cheapest and most accessible building material. An efficient technique for improving the mechanical properties of the walls of such buildings is grout injection. Because of a lack of knowledge of the morphology and type of walls, incompatibility of existent and applied materials, errors during application, mistakes and even damage, may occur. For this reason, the methodology of work and the criteria to achieve a required quality should be defined. Based on the results of an extensive test campaign, chemical, physical and mechanical criteria for selecting optimal grout mixtures are given; the guidelines and research needed to assess the condition and type of walls that could be strengthened by means of grout injection and to ensure the quality of executed work, are also presented here.

1 Introduction

Historical buildings that were mainly built with lime-based mortars are frequently repaired and/or strengthened without previous research and analysis of structure and built-in materials. Such approach leads to inadequate repair procedures and usage of materials that are often not compatible with existing ones. Because of incompatibility of applied and existing materials, further deterioration or damage of structure and built materials may occur. That was the case in Slovenia in the period after World War II, as many historical buildings were repaired with cement mortars that were not compatible with existing ones in terms of chemical, physical, and mechanical properties.

Knowing that historical buildings in Slovenia and elsewhere were mainly built with lime-based mortars with or without additives, several compositions of

mortars (intended for various reparation techniques) and grouts (intended for strengthening stone or stone-brick walls containing voids) were designed. Hydrated lime and lime putty with additives such as ground granulated blast furnace slag (GGBS), volcanic tuff, and limestone powder were used. The presented tests were part of a wider test campaign and were meant to determine the basic compositions of mortars and injection grouts that will be improved in the continuation of the study.

2 Historical background

Regarding compatibility with existing materials in the walls of historical buildings, the use of lime-based materials is the most appropriate for the application of repair and/or strengthening procedures. Lime and hydraulic lime-based binders were used for centuries in the construction of various buildings. Although the Egyptians already knew how to produce lime, it was more widely used by Greeks and Romans. At first, lime mixed with water and sand was used for the preparation of air hardening mortar. Later it was found out that hydraulic properties can be obtained with the addition of volcanic ash. In the 1st century B.C., Marcus Vitruvius Pollio, a Roman architect and engineer, reported astonishing results when mixing lime and rubble with powder from the area around Mt. Vesuvius (natural pozzolana in the form of volcanic tuff), and the ability of such mixture to set under water [15]. Although the discovery of hydraulic mortar is ascribed to the Romans, the Phoenicians and the Israelis used hydraulic mortar for the protection of buildings exposed to water (aqueducts, piers, tanks) in the 10th century B.C. Drinking water reservoirs built in Jerusalem by King Solomon were built with hydraulic mortar obtained by mixing lime and crushed clay [3]. Characterisation of historical mortars in Slovenia, performed as part of archaeological post-excavation analyses, revealed that lime or lime with pozzolanic additives such as GGBS, volcanic tuff, and crushed brick were used when preparing such mortars [7].

3 Constitutive materials

In the test campaign, lime-based mortars and grouts with mineral additives were designed and subjected to testing in fresh and hardened state. Among available limes, hydrated lime in powdered state and lime putty were used. Lime putty was burned and slaked in the traditional way and was aged for more than 4 years, while the hydrated lime is an industrial product of the Slovenian company SIA. Limestone sand with a maximum grain size of 4 mm was used for the preparation of lime-based mortars. GGBS, volcanic tuff, and limestone powder were used as mineral additives. GGBS is a by-product of a steel plant in Trieste,

Italy. It was ground to obtain approximately the same grain size distribution as volcanic tuff, which was supplied by the Slovenian company Sanning. Limestone powder is ground limestone produced by the Slovenian company Calcit. Adequate fluidity of grouts was attained with help of naphtalensulphonate based-SP produced by the Slovenian company TKK Srpenica.

4 Test campaign

First, chemical and physical properties of constitutive materials were determined, then the materials were combined and the influence of different proportions of materials on the properties of mortars and grouts was analysed. In the continuation of the study, the proportion of a particular component was optimized in order to achieve better properties. In the case of grouts, hydrated lime and GGBS were combined to obtain “modern” or industrially produced materials, and lime putty and volcanic tuff were combined to obtain "traditional" materials. Limestone powder and naphtalensulphonate based-SP also were added to the grouts.

4.1 Chemical analysis, physical properties and pozzolanic activity of constitutive materials

4.1.1 Chemical composition

Chemical compositions of constitutive materials are presented in Table 1 and were determined according to SIST EN 196-2:2005 [9].

Table 1 Chemical composition of constitutive materials in % by mass

	SiO_2	Al_2O_3	Fe_2O_3	CaO	$CaCO_3$	MgO	$MgCO_3$	MnO	SO_3	CO_2	K_2O	Na_2O	l.o.i.
tuff	62.96	13.31	3.70	3.76	-	1.94	-	-	0.07	-	3.34	3.07	7.41
GGBS	38.10	9.80	1.10	38.50	-	9.50	-	0.60	2.30	-	-	-	-
limestone powder	0.07	0.17	0.05	-	97.60	-	1.72	-	-	-	-	-	-
hydrated lime	0.40	-	0.18	72.04	-	0.83	-	-	0.10	2.56	-	-	25.10
lime putty	-	-	-	85.99	-	11.51	-	-	0.04	1.46	-	-	-

4.1.2 Physical properties

Density and surface area of constitutive materials are given in Table 2 and were determined according to SIST EN 196-6:2010 [10].

Table 2 Physical properties of constitutive materials

	density (g/cm^3)	surface area (cm^2/g)
volcanic tuff	2.41	2910
BFS	2.85	2930
limestone powder	2.75	3300
hydrated lime	2.28	14920

4.1.3 Pozzolanic activity

Pozzolanic activity of volcanic tuff or GGBS was determined by strength characteristics of mortar prepared from hydrated lime, volcanic tuff or GGBS, standard sand, and water in ratio 1:2:9:1.8 by mass. The test was carried out according to former Yugoslav standard JUS B.C1.018 [5] that enabled us to evaluate the activity of both pozzolans when added to hydrated lime. Mortar was cast in a mould and hermetically closed in a metal box. For the first 24 hours the metal box was kept at a temperature of 20 ˚C, then for 5 days at a temperature of 55 ˚C and finally, until the age of 7 days, in the laboratory at a temperature of 20 ˚C. For each pozzolan, three specimens (a, b, c) were tested for flexural strength and six specimens for compressive strength. The results, given in Table 3, show that higher values were attained with GGBS.

Table 3 Flexural and compressive strength of mortar with volcanic tuff and GGBS at the age of 7 days

volcanic tuff	a	b	c	average
flexural strength (MPa)	1.5	1.6	1.6	**1.6**
compressive strength (MPa)	4.1/4.2	4.5/4.4	4.3/4.5	**4.3**
GGBS	a	b	c	average
flexural strength (MPa)	2.6	2.5	2.4	**2.5**
compressive strength (MPa)	5.1/5.2	5.2/5.2	4.9/5.0	**5.1**

4.2 Composition and properties of mortars

Lime putty and sand in volume proportion 1:3 were used for mortars. Mortar M1 was pure lime mortar and pozzolana was added to mortars M2-M5 (Table 4). The amount of added water was adjusted to obtain a flow value around 145 mm for mortar M1 and was the same for all compositions (M1-M5).

Table 4 Composition of lime-based mortars.

	Binder*	Sand*	Pozzolana**	
	(lime putty)	(0/4)	GGBS	volcanic tuff
M1	1	3	0	0
M2	1	3	10	0
M3	1	3	20	0
M3a	1	3	40	0
M4	1	3	0	10
M5	1	3	0	20

* volume proportion

** % by mass according to the share of dry binder in volume of lime putty

Density [12], flow value [10], water retentivity [8], and compressive strength [13] of mortars were determined. Obtained results are given in Table 5.

Table 5 Properties of lime-based mortars in fresh and hardened state

	Density (kg/m^3)	Flow value (mm)	Water retentivity (%)	Compressive strength* (MPa)
M1	2022	145	93.7	0.73
M2	2038	140	94.2	0.56
M3	2046	147	95.0	0.71
M3a	2046	139	97.2	-
M4	2032	137	93.8	0.53
M5	2038	130	95.1	0.65

* tested at the age of 28 days

Mortar M1 without pozzolanic additive and mortars M2, M3, and M3a with addition of GGBS have proven to have very good workability, while mortars M4 and M5 with addition of volcanic tuff were leaner and less workable. The latter fact was also confirmed by the flow value measurements. Flow value of mortars M1, M2, and M3 was between 140 and 147 mm, and it was between 130 and 137 mm for mortars M4 and M5. The lowest value of water retentivity was attained with mortar M1 (93.7%), and it increased when pozzolana was incorporated in the mortar (values between 93.8 and 97.2% for mortars M2-M5). The highest water retentivity was obtained with mortar M3a, i.e. 97.2%. As expected, compressive strengths were rather low, and they attained 0.73 MPa in M1. They were lower for mortars with the addition of 10% of pozzolana (0.56 MPa in M2 and 0.53 MPa in M4) and increased again for mortars with 20% of added pozzolana (0.71 MPa M3 and 0.65 MPa M5).

For the measurements of deformations due to shrinkage, the equipment developed by the research group at the Faculty of Civil and Geodetic Engineering [1] was used. Four moulds, 2 cm x 6 cm x 25 cm, and eight LVDT´s (two for each

specimen) with the accuracy of 10 μm were used. The main advantage of the equipment is that it enables the measurement of deformations due to shrinkage from the very beginning, i.e. from the moment when the filling of moulds with mortar is finished. It also offers a better estimation of actual (on-site) state compared to standard shrinkage test on prisms measuring 4 cm x 4 cm x 16 cm, considering former Yugoslav standard B.C8.029 [6]. According to that standard, lime-mortar specimens had to be left in moulds for at least three days to gain sufficiently high strength of the specimens, which should prevent failure of the specimens during demoulding.

As Fig. 4 shows, the main part of the deformation for both mortars M1 (11.5‰) and M3a (9.2‰) took place in the first three days of the test. This was also confirmed by Bosiljkov [2], who found that deformations due to shrinkage on pure lime mortar specimens from the age of three days onwards are expected to gain only up to around 0.02% in two months.

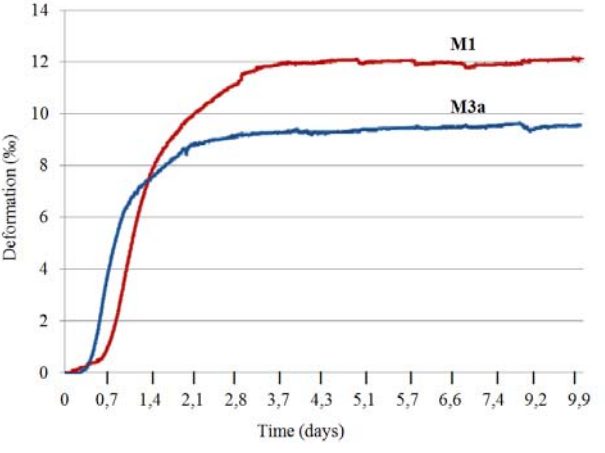

Fig. 1 Average deformations due to shrinkage of lime-based mortars M1 and M3a

4.3 Composition and properties of injection grouts

In the grouts, hydrated lime and GGBS were combined to obtain “modern” or industrially produced materials, while lime putty and volcanic tuff were combined to obtain "traditional" materials. Limestone powder, in the amount of 20 %, was added to the grouts G3, G4, G7, and G8. The fluidity tests with grouts containing lime putty (G5-G8) were begun without additional water. The addition of SP was optimized in the grouts containing hydrated lime and in the grouts containing lime putty. The influence of added SP was analysed on two mixtures, G1 (basic hydrated lime mixture) and G5 (basic lime putty mixture), by considering two criteria: adequate fluidity (around 20 s) and moderate bleeding (≤ 2.0%). The amount of added SP was optimized by gradually increasing its proportion from 0.5

to 2.5% by mass of binder and by simultaneously analysing its effect on fluidity and bleeding. After the comparison of the results, water/binder ratio (w/b) of 0.95 and the addition of 1.5% of SP were chosen for mixtures G1-G4 and w/b ratio of 0.95 and the addition of 1.0% of SP for mixtures G5-G8. Composition of injection grouts is given in Table 6.

Table 6 Composition of injection grouts in % by mass

	Binder		Filler	Pozzolana		SP	w/b
	Hydrated lime	Lime putty	Limestone powder	GGBS	tuff	(%)	ratio
G1	80	0	0	20	0	1.5	0.95
G2	60	0	0	40	0	1.5	0.70
G3	60	0	20	20	0	1.5	0.90
G4	40	0	20	40	0	1.5	0.65
G5	0	80	0	0	20	1.0	0.95
G6	0	60	0	0	40	1.0	0.71
G7	0	60	20	0	20	1.0	0.97
G8	0	40	20	0	40	1.0	0.68

Density [12], fluidity, volume change, and bleeding [4], and compressive and tensile strengths [14] of grouts were determined (Table 7).

Table 7 Properties of injection grouts in fresh and hardened state

	Density (kg/m3)	Fluidity* (s)	Volume change (%)	Bleeding (%)	Compressive strength (MPa)	Tensile strength (MPa)
G1	1400	16.2/15.6	4.7	2.6	0.8	-
G2	1510	20.3/18.2	3.9	3.2	1.9	-
G3	1460	16.6/16.1	4.3	2.8	1.1	-
G4	1560	17.4/17.0	2.4	1.6	3.6	-
G5	1435	12.6/13.9	11.1	1.3	2.5	0.9
G6	1516	17.6/18.1	6.2	0.8	2.8	0.9
G7	1488	13.1/13.3	9.6	1.0	2.8	0.8
G8	1616	11.8/12.0	5.3	1.6	2.9	1.1

*measured immediately after mixing and after 30 minutes

The most promising results were achieved with grouts G4 and G8, with the addition of 20% of limestone powder and 40% of pozzolana (GGBS and volcanic tuff, respectively). Relatively low fluidity values (17.4/17.0 s in G4 and 11.8/12.0 s in G8), moderate volume change (2.4% for G4 and 5.3 % for G8) and bleeding (1.6% for both grouts), as well as relatively high compressive strengths (3.6 MPa for G4 and 2.9 MPa in case of G8), were attained for these two mixtures. The

addition of GGBS seems to have a beneficial effect on volume change of grouts, as seen by the measured shrinkage deformations of mortar M3a containing GGBS.

5 Conclusion

The aim of the presented study was to design mortar and grout compositions for reparation and/or strengthening of historical buildings. Several compositions of mortars and grouts based on hydrated lime and mineral additives such as GGBS, volcanic tuff, and limestone powder were designed and subjected to testing. So far, the most promising results were achieved with lime putty mortar M1 without additives, lime putty mortars M3 and M3a with the addition of 20 and 40% of GGBS, respectively, and lime-based grouts G4 and G8 with the addition of 20% of limestone powder and 40% of pozzolana. The lowest value of volume change was attained with compositions containing 40% of GGBS (both mortars and grouts). The analyzed pozzolanic activity of the GGBS was greater compared to volcanic tuff. However, when applying GGBS in mortar or injection grouts compositions, one has to be aware of its limitations. Sulphates present in GGBS can, in some circumstances, be damaging for the old masonry to be treated [3]. In a continuation of this study, additional tests, such as "pull off," water absorption, and durability tests, will be performed in order to further evaluate and improve the properties of the proposed compositions. Furthermore, compositions based on natural hydraulic lime (NHL) with the same mineral additives as in the present research will be designed and subjected to testing.

6 Acknowledgement

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IV.42

Experimental Study of Hot Mixed Mortars in Comparison with Lime Putty and Hydrate Mortars

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Abstract Experimental work has been carried out in order to describe the influence of hot mixing on the properties of hardened mortars in comparison with mortars made of lime hydrate and lime putty. Lime from the same quarry and producer was used in the form of lime hydrate, lime putty and quicklime. Two types of quicklime were used varying in their calcination conditions and also their reactivity. Standard specimens 40 x 40 x 160 mm were cast and evaluated after curing. Mechanical (compressive and flexural strength) and physical properties (open porosity, bulk density and capillary absorption) were determined on the specimens of hardened mortars. Thin sections of the mortars were prepared and evaluated under polarising microscope in order to describe the structure of mortar including also the presence of binder related particles. The hot mixed mortars produced had comparable hardened properties with the lime putty and lime hydrate mortars. Due to the micro-cracks in the binding matrix the hot mixed mortars showed higher porosity and capillary absorption. The heterogeneity of the hot mixed mortars was a result of the preparation technology.

1 Introduction

Characterisation of historic mortars has recently become quite a common activity of workplaces specialising on historic buildings and materials. Many research laboratories are well equipped and existing publications about characterisation methods (e.g. RILEM [1]) provide examples which can be followed. Compositional, physical and even mechanical properties of historic mortars can be determined by established analytical procedures and tests. However, the interpretation and application of the results can be quite difficult. Results of characterization of historic mortars could contribute to design of repair

mortars and could also provide information about construction history and mortar production and preparation technologies. The latter point is quite important for a proper characterisation. Lack of knowledge about the production technologies and their effects on the hardened mortar properties and performance could lead to wrong conclusions from the characterisation of the historic mortars and misleading interpretations of results. Therefore, some basic research on the fresh and hardened properties of lime based mortars made using a variety of historic production technologies is needed.

When appropriate knowledge is lacking an analogy to modern lime based mortars or even cement based concrete is commonly assumed to be applicable, however this assumption may not always be correct. Historic mortars are specific because of their manner of lime burning and their technology of production. Historic limestone sources can currently be the same or similar.

A typical example of a historically widespread mortar preparation method, which is currently not well known, is hot mixing. Mortars prepared directly from quicklime, wet sand and water are called hot mixed mortars. This preparation of mortars has certain benefits as it allows a relatively fast mortar production on site, quicklime can be used soon after its production which minimises demands on storage of this reactive material, no storage of lime putty is needed and it is applicable for a variety of lime binder compositions. These points were considerably important for builders of historic buildings in the past. On the other hand, the mixing proportions are more difficult to control which leads to a high variability in the mortar produced. Moreover, the hot mixing also provides only limited control over the slaking process and thus historic hot mixed mortars often contain various binder related particles. Historic hot mixed mortars are typically rich in binder and can theoretically be distinguished from mortars made of lime putty or lime hydrate by employing light microscopy on thin sections [2], however more research is needed to identify their characteristic features. Similarly, the knowledge about the effects of hot mixing on the properties of hardened mortars is only limited [3].

Many researchers described the existence of binder related particles in historic mortars e.g. [4-6]. These binder-related particles are usually defined as particles of binder which contain no aggregate [7]. Elsen [8] in his review on microscopy of historic mortars distinguishes three types of the binder-related particles: under-burned fragments, over-burned fragments and lime lumps *sensu stricto*, and summarises the possible information which can be gained from their analysis: type of limestone and its composition (under-burned particles), maximum burning temperature (over-burned particles), the manner of mortar preparation (particles *sensu stricto*). Although several researchers have described historic hot mixed mortars containing lime particles, no general identification features exist for their characterisation in terms of the mortar technology production. Experimental production of replicas of historic mortars by traditional technologies can lead to a further distinction among them which could consequently be used for identification of their production technologies [9].

2 Experimental

The objective of the experimental work was an evaluation of the physical and mechanical properties of hardened non-hydraulic lime based mortars. It focused on the comparison of mortars prepared directly from quicklime by a hot mixing method with mortars prepared from lime putty and dry lime hydrate that were commonly used forms of binder. A series of three specimens per mix type were produced from lime hydrate, lime putty and two types of quicklime. Historic mortars are often rich in binder. Therefore, the specimens were prepared from two different binder / filler proportions representing the contemporarily recommended 1:3 and a more historic binder rich 1:0.9 mix proportion (by volume).

2.1 Materials and specimens

Mortar specimens 40 x 40 x 160 mm were prepared from lime (CL90) and quartz sand. The lime binder used was in three different forms, lime hydrate, lime putty and quicklime, and was from the same quarry and the same lime production factory. The overview of the used binders is presented in Table 1. The lime used contained over 95% calcium (according to the analysis of the producer). The quicklime used in the HB mix was more reactive when slaked with water than the one used in the HA mix. The filler was a standard masonry siliceous river sand with particles ranging between 0-4 mm and clay and dust content around 2.9%.

Table 1 Summary of the lime binders and their forms used in the experiment

Code	form of lime	additional information
HY	lime hydrate	Standard, commercially available lime hydrate CL90.
LP	lime putty	Commercially available 2 years old lime putty. The putty was produced by soaking and mixing lime hydrate CL90. Water content 32.6% (wt.)
HA	quick lime	quick lime $T_{max} = 73^{o}C$, $t_{max} = 33$ min
HB	quick lime	quick lime $T_{max} = 77^{o}C$, $t_{max} = 6.4$ min

Two mixing ratios 1:3 and 1:0.9 by volume were used based on lime hydrate to sand proportion. The gauging was carried out by weight calculated from the bulk densities of the lime hydrate and sand. The lime putty was dried out to estimate the amount of water it contained. The dry residue was assumed to be $Ca(OH)_2$ i.e. having the same molecular weight as the lime hydrate. Both quicklimes were assumed to be composed only of CaO (5% of the other compounds were neglected for the gauging purposes). The amount of the quicklime added proportionally corresponded (by molecular weight) to the same mass of $Ca(OH)_2$ gauged in the lime hydrate mix. Water was added to produce similar workability for lime hydrate and lime putty mortars. The workability was judged based on experience

and the mortar flow was evaluated on a flow table (to EN1015-3) where it reached values comparable to 150±5 mm. More water was needed in the hot mixes to provide water for slaking during the mixing and also to compensate for evaporation. The mortar was mixed in a standard laboratory mixer. The appropriate workability of hot mixed mortars was estimated by experience. Gauging and mixing procedures for the specimens are given in Table 2.

Table 2 Gauging and mixing procedure

Mix	Lime [g]	Sand [g]	Water [g]	L : S vol.	L: S wt.	Mixing details
HY	152	1465	250	1 : 3	1 : 9.6	Mixed for 5 minutes.
HYII	399	1100	380	1 : 0.9	1 : 2.8	Mixed for 5 minutes.
LP	226*	1465	180	n.m.	1 : 9.6+	Mixed for 5 minutes. Putty contained
LPII	592*	1100	190	n.m.	1 : 2.8+	Mixed for 5 minutes.
HA	115	1465	~ 700	n.m.	1 : 9.6+	Mixing with breaks, total time was 30 min. 400g of water was added initially; the rest was added several times in small amounts to compensate for the evaporation and at the end of mixing to adjust the workability.
HAII	302	1100	~ 700	n.m.	1 : 2.8+	
HB	115	1465	~ 700	n.m.	1 : 9.6+	
HBII	302	1100	~ 700	n.m.	1 : 2.8+	

+ L – lime, assuming by the weight of dry $Ca(OH)_2$; S – sand;

* additional water contained in putty 226g x 32.6% = 74g, 592g x 32.6% = 193g

Three prisms 40 x 40 x 160 mm were cast per mix type according to EN 1015-11 (Determination of flexural and compressive strength of hardened mortars) and stored at 20°C, 65% RH. The cast specimens in moulds were covered with a flat, saw cut sandstone block simulating the masonry suction and providing a sufficient weight which would keep the hot mixed mortars compacted inside the mould in case the slaking process would continue in the moulds for seven days. All specimens were exposed to accelerated curing conditions simulating 21 wetting and drying cycles for the last 70 days before their testing. Wetting was done by misting the specimens up to the point when the surface stopped absorbing water and started to be glossy. Non-hydraulic lime binders harden by carbonation, i.e. reaction of calcium hydroxide with carbon oxide [10] forming calcium carbonate. This reaction is a slow process and changes the porosity and pore structure of the binding matrix, mainly pores around 0.1 μm [11]. Carbonation speed depends on CO_2 concentration in the ambient air, pore structure and gas diffusion resistance of mortar (binding matrix), presence of moisture and temperature. Curing by the repetitive wetting and drying was selected as it is a dynamic process when variety of conditions favourable for carbonation can occur rather than keeping one stable condition in the laboratory.

Table 3 presents a depth of totally carbonated areas of mortars (identified by Phenolphthalein pH indicator) and the age of the specimens when tested. The carbonated depth divided by the age of specimens represents the carbonation rate

(speed) for a comparative purpose. It should be noted that the carbonation depth was only an indication of the totally carbonated zone, where pH is lower than 9.0, i.e. $CaCO_3$. The carbonation front was in fact deeper and the inner parts of the specimens were partially carbonated. This fact was confirmed by a thermal analysis which was carried out on the specimen made of lime putty. For the mortars LP and LPII the proportion of $CaCO_3$ of the total binder in the centre (pink, high pH) part is 48% and 10% respectively. The depth of carbonation and its speed was lower for the specimens richer in binder. The specimens HY were almost fully carbonated.

Table 3 Age of specimens and depth of carbonation at the time of testing

	HY	HYII	LP	LPII	HA	HAII	HB	HBII
Age [days]	202	101	195	160	160	77	139	98
Carbonation [mm]	17	6	10	3	8	3	8	4
Carb. rate [mm/day]	0.08	0.06	0.05	0.02	0.05	0.04	0.06	0.04

2.2 Testing methods

The flexural strength of the mortar specimens was determined by the three point bending test according to EN 1015-11. The compressive strength was determined according to the same standard on the halves of the specimens left after the bending test. Bulk density and open porosity of the hardened mortars were determined according to vacuum saturation method (EN 772-4 Determination of real and bulk density and of total and open porosity of natural stone masonry units). Capillary coefficient was determined according to EN 1015-18 (Determination of water absorption coefficient due to capillarity action of hardened mortar). The mortar structure was described on polished thin sections using a transmitted light polarising microscope.

3 Results

The hot mixed mortars were prepared from two types of quicklime and compared to the mortars made of standard lime putty and lime hydrate. Two effects were be observed in the test results; firstly, the influence of the form of binder and secondly, the influence of the amount of binder.

3.1 Strength

The mechanical performance of the mortars is summarised by the charts in Fig. 1. The highest compressive strength (1.4 to 1.6 MPa) was obtained for both

lime hydrate mixes and also for the 1:3 (vol.) hot mixed mortars. Both lime putty mortars had lower compressive strength around (0.8 MPa). The higher amount of binder (mixes 1:0.9 by vol.) caused lower compressive strength (apart from the lime hydrate mix). This reduction of strength in compression was very significant (half of the value) in the case of the hot mortar mixes and was probably connected not only with their increased porosity. The effect of the increased porosity connected to the increased amount of binder can be observed on the specimens HY and HYII in Fig. 2.

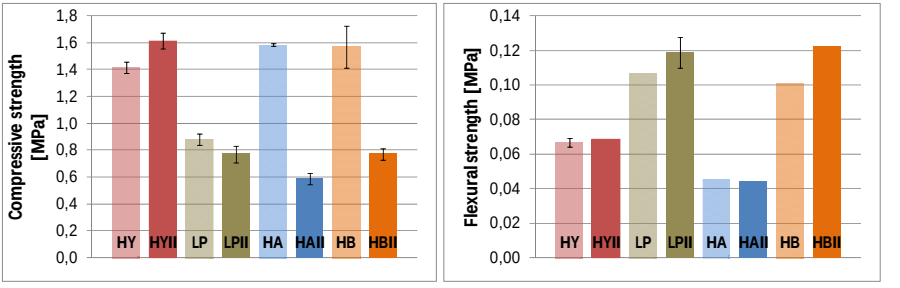

Fig. 1 Compressive and flexural strength of lime mortar specimens

The comparison of the influence of the different forms of binder shows that the lime hydrate binder produced mortars with a higher compressive strength than the lime putty mortar but in the case of the flexural strength it was the opposite.

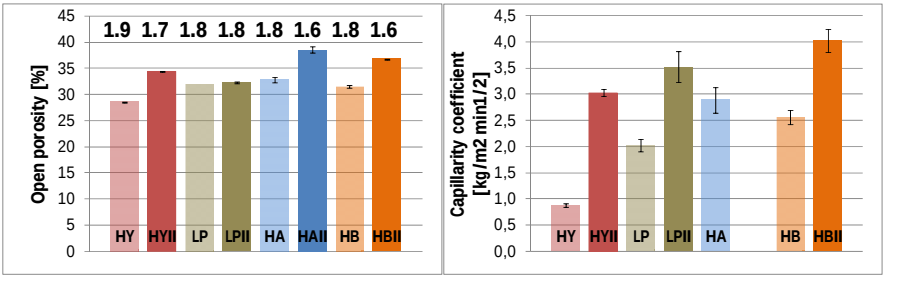

Fig. 2 Open porosity and coefficient of capillary absorption of lime mortar specimens. Bulk density of the specimens is given for comparison above the porosity values in g cm^{-3}.

The effect of the form of binder on the flexural strength was dual. In some cases (mainly LPII, HAII, HBII) a high shrinkage caused significant cracking and since the bending test is sensitive to imperfections like this, the specimens broke at significantly lower values. These measurements were disregarded and the error bars are not presented in such cases in the chart. For the specimens which were relatively sound it seems that the higher amount of the binder provided quite a good bond between individual sand grains, which was comparable if not better to

the 1:3 (vol.) mixes. Even though, there were some micro-cracks within the binding matrix observed by the microscopic analysis.

In cement and concrete technology, porosity and compressive strength correlates quite well [12]. Therefore, the open porosity of the specimens was determined along with the capillary absorption rate (see Fig. 2). The larger amount of the binder produced in all cases a higher open porosity (pores, voids, micro-cracks) and also quite clearly increased the capillary absorption rate. However, the correlation of the open porosity and compressive strength was not so clear in the case of the tested specimens. Specimens HYII, HAII and HBII had the highest open porosity. This was reflected by the relatively lower compressive strength of the HAII and HBII specimens. However, the comparison of open porosity and compressive strength of HY and HYII specimens shows that even as the porosity increased with the binder content the compressive strength also increased. The correlation of compressive strength and open porosity is, for non-hydraulic lime mortars, strongly affected by other factors which may be of the same magnitude [13, 14].

The structure of the specimens was described using polished thin sections under plane polarised light. The photomicrographs of the individual mortars are presented in Figs. 3 to 10. The higher amount of binder in the mortars is clearly visible in all four cases. The mortar specimens made of lime hydrate were well compacted without shrinkage micro-cracks or large voids. Occasionally rounded air voids were identified. The lime putty mortars (LP) showed a large number of irregular voids and the binding matrix was full of shrinkage micro-cracks, mainly in the mortar LPII where the areas of lime binder concentration between the filler grains were larger. The quality of the hot mixed mortars HA, AHII, HB and HBII was variable for all specimens. In some cases there was quite a large concentration of air voids (see Fig. 9). The hot mixed mortars with the higher amount of the binder (HAII and HBII) also contained a net of shrinkage micro-cracks in the binding matrix (Figs. 8 and 10). The hot mixed mortars also contained binder related particles (in the figures marked as LL). These binder related particles were considered to be produced by the method of slaking and mixing. When the quicklime was slaked separately it slaked well into lime putty and there were no larger particles left. Also the quicklime was from a commercial production which would suggest quite a high efficiency of calcination.

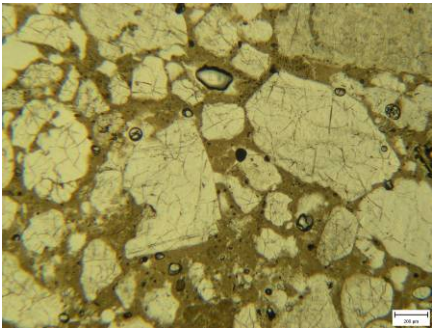

Fig. 3 HY (1:3) in PPL, scale bar 200 µm.

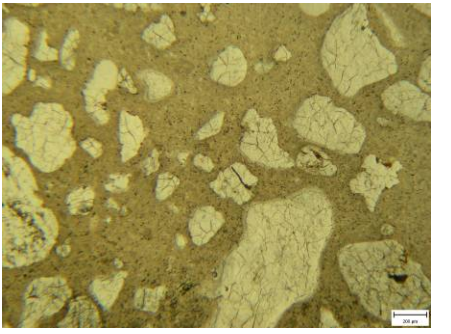

Fig. 4 HYII (1:0.9) in PPL, scale bar 200 µm.

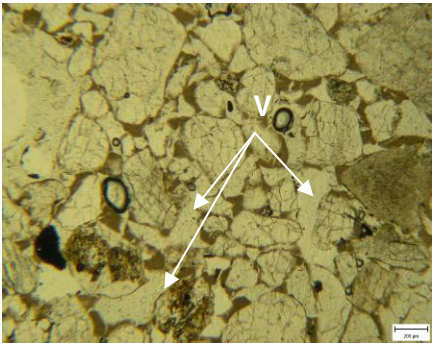

Fig. 5 LP (1:3) in PPL, scale bar 200 µm.
V – void, LL – binder related particle

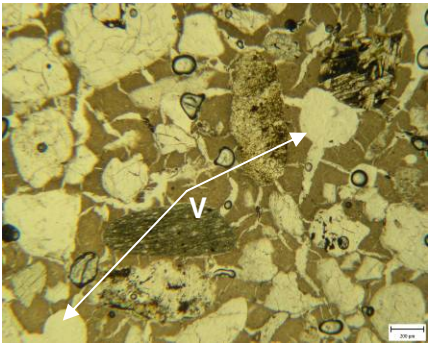

Fig. 6 LPII (1:0.9) in PPL, scale bar 200 µm.

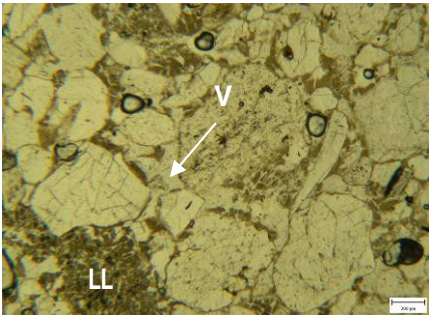

Fig. 7 HA (1:3) in PPL, scale bar 200 µm.

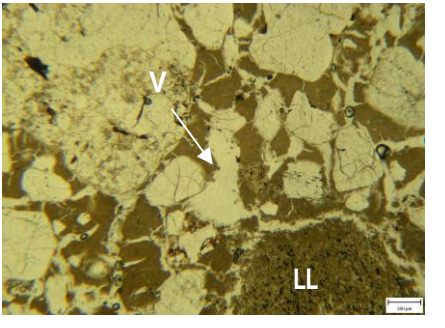

Fig. 8 HAII (1:0.9) in PPL, scale bar 200 µm.

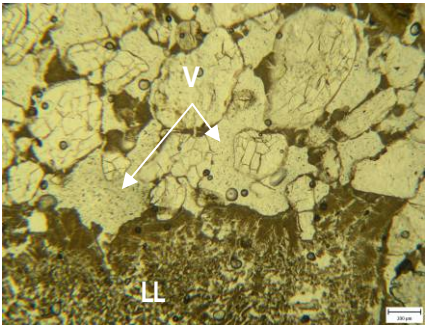

Fig. 9 HB (1:3) in PPL, scale bar 200 µm. V – void, LL – binder related particle

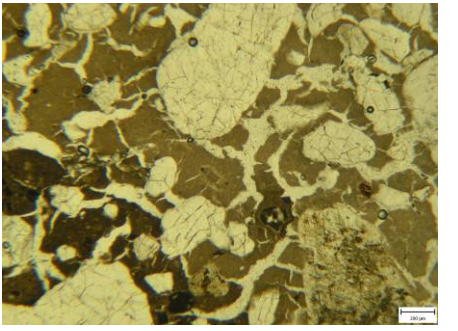

Fig.10 HBII (1:0.9) in PPL, scale bar 200 µm.

4 Discussion

The main point of the experimental work was the description of the hardened properties of the hot mixed mortars in comparison with the mortars made of lime hydrate and lime putty. All four types of mortars were made of non-hydraulic lime of the same origin and very similar composition. The results presented above show that the form of lime binder along with the way of preparation can significantly influence the hardened mortar properties.

The optical microscopy showed that consistent and well compacted specimens without any clear internal defects were produced only from the dry lime hydrate. The other specimens had some imperfections like larger voids, shrinkage cracks and micro-cracks in the binding matrix, uneven distribution of binder and in the case of hot mixed mortars also the presence of larger particles of binder. These imperfections influenced the hardened mortar properties and added to their heterogeneity. Some of these imperfections, like the presence of binder related particles, are characteristic features of the way of mortar preparation. However, the shrinkage cracks, micro-cracks and presence of larger voids indicate some technological deficiency during the preparation. Micro-cracks in the binding matrix, similar to those found in the putty and hot mixes, are not so often found in historic mortars which are even richer in binder. One possible explanation could be in the test set-up which may have not sufficiently simulated the moisture transport situation comparing to normal masonry when being build. Under normal conditions the water absorption by the adjacent bricks/stone may be much higher, resulting in much lower moisture content levels in the mortars during hardening.

Nevertheless, some interesting points resulting from the testing could be pointed out:

- The hot mixed mortars had in principle comparable hardened properties as lime hydrate and lime putty mortars. Although, there was no clear evidence of

continuation of slaking after casting (like popping out), there were differences in properties which suggested that the lime slaking process was not completely finished when the specimens were cast. This affected the heterogeneity of the specimens and thus also the results.

- The compressive strength of the hot mixed mortars was probably mostly affected by the internal integrity of the mortars. The larger amount of binder led to their significant reduction of strength in compression. Degree of carbonation, mixing proportions and amount of binder seemed to be less relevant, at least for the lime hydrate and lime putty mortars.
- The flexural strength was higher for the lime putty mortars. The higher amount of binder (1:0.9 vol.) have not affected significantly the flexural strength but it seems that if the binder is sound a higher binder proportion can even increase the flexural strength. All grains are well surrounded by the binder. Although the lime putty mortars had a comparatively lower compressive strength their flexural strength was one the highest. This was despite the fact that the higher amount of lime in the LPII mix caused the micro-cracks in the binding matrix.
- Binder related particles were found in the hot mixed mortars. They were unmixed, not well slaked lime lumps – sensu stricto. Their shape was rather irregular and the lumps did not contain any texture of the original limestone. Their presence was rather limited in comparison to some hot mixed mortars prepared from lime calcined by a traditional way at a low temperature (around 900°C) in a wood fired kiln [2]. The irregularity of their shape can be one of the recognisable features when there is a need to distinguish among the binder related particles and their connections to mortar production technology.
- The higher amount of lime binder slowed down the propagation of carbonation through mortar; i.e. there was more lime binder to carbonate per mm of depth. The higher amount of lime binder increased porosity and significantly increased the capillary absorption.
- Micro-cracks in the binding matrix identified by microscopy in the LPII, HAII and HBII were not found in the HYII mortar specimen. Even though the HYII specimen contained areas of binder larger than 0.2 x 0.2 mm, i.e. those which were typically cracked in the other mortars.

5 Conclusions

Hot mixed mortars are known to be produced in the past. The experimental study compared the hot mixed mortars with mortars prepared from more standard lime putty and lime hydrate binders. The hot mixing of quicklime with sand affected the properties of hardened mortar specimens on a comparable level to lime putty or lime hydrate. A large number of imperfections in the structure of the hot mixed mortars pointed out on the deficiency of the mixing and production technology. The main problem was the drying shrinkage which caused significant

cracks in all specimens apart from the lime hydrate mixture. The drying shrinkage was also probably the cause of small micro-cracks in the binding matrix. It was interesting to note, that the higher amount of the binder caused more micro-cracking but at the same time its effect on the flexural strength was not negative. Future studies on bonding properties of different limes to the aggregate grains could be interesting. Also the hardened characteristics of the hot mixed mortars should be better understood in order to improve our ability to characterise them. Hot mixed mortars will always be quite heterogeneous due to the nature of their production. However, analyses of historic mortars in the literature show that they used to be produced well compacted and without any significant micro-cracking of binding matrix. Further research could also help to re-develop this traditional technique for the purposes of cultural heritage repairs.

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IV.43

Conservation of Historic Renders and Plasters: From Lab to Site

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Abstract In an intervention on historic renders and plasters, the first step is to decide upon the strategy: repair or substitution, based on an evaluation of the cultural value of the render and of the building itself and on a careful diagnosis of the typology of defects, their density and reparability. New renders or repaired renders should fulfil the main functions they are required to, especially protection and aesthetic functions. In any case, compatible materials should always be used. Compatibility is needed for durability, not of the render, but of the wall as a whole, and also for preserving the testimonial and symbolic value of the building as well as its appearance. Compatibility is defined in relation with the substrate and the pre-existent mortars, therefore tests are to be carried out on the old materials and on possible solutions, to compare their characteristics and assist the selection of the best one. It is adequate to begin by non-destructive or slightly destructive in situ tests, because with them it is possible to collect useful information without destruction of the historic renders and in a quick way. Simple mechanical and physical tests can be carried out on the old mortars and a few chemical tests can also be performed nowadays, with the appropriate portable equipment. When more rigorous and complete tests are needed, some samples can be collected and tested in laboratory, using methods adapted to non-regular, possibly friable specimens. The characteristics of the mortars to use can be established with a basis on the set of results obtained, in order to fulfil both functionality and compatibility. However, sometimes it is not possible to get enough data concerning the old materials, especially concerning masonry, which is rather more difficult to test than mortars. For that situation, some general requirements have been established, based on previous work carried out on Portuguese masonry historic buildings, which can be used without risk of damaging pre-existent materials. The decision concerning materials to use, especially binder materials, should also take into account the climatic and environmental conditions. Then, appropriate application technique, workmanship and curing conditions are indispensable to achieve good results, from the aesthetic, physical and mechanical points of view; therefore it is important to know which conditions are available in the application phase.

1 Conservation strategy decision making

1.1 Strategy and factors

When facing an intervention on old renders, the first step – and probably the most important one - is deciding upon the strategy to implement. Two basic alternatives are possible:

- Preservation and repair with compatible materials
- Substitution by compatible new renders

Many factors should be taken into account, some of them of a subjective nature, others more technical and quantifiable:

1. Cultural value (for example combinations of historic value, artistic value, technical value and value associated with rarity).
2. State of conservation of the background and its capacity to be repaired (reparability).
3. State of conservation of the render: severity and intensity of anomalies and their reparability.
4. Compatibility of the render with its current (or foreseen) use and the environmental conditions.
5. Available workmanship.

Factor 1 dominates. However, most cases fall in the category of "medium cultural value". The technical team has essentially to deal with factors 2, 3 and 4, although an opinion on 1 and 5 is usually required. This decision requires a diagnosis and quantification of the wall's anomalies (both masonry and render), as well as an evaluation of the future actions on the rendered surface that are foreseen.

1.2 Diagnostics

In many cases of planning interventions on renders and plasters quite simple and quick investigations and observations are enough to establish a diagnosis [1]:

1. Observation by a trained person:
    1.1. Presence of moisture.
    1.2. Type of defects: fungus, black crusts, detachments, lack of cohesion, cracks and micro-cracks, brown stains of corrosion products.
    1.3. Density and localisation of defects.
2. Moisture measurements: localisation and intensity of moisture, map of moisture distribution (Fig. 1).
3. Mechanical and physical in-situ and laboratory tests (Figs. 2-4).

These actions allow important questions to be answered:

- Is moisture a problem? Observations 1.1, 1.2, 1.3 and action 2 should provide an answer. Where does the moisture come from? Actions 1.3 and 2 will help to discover it.
- Apart from moisture, what other causes of defects are there? 1.1, 1.2, 1.3, 2 and possibly 3 will furnish the appropriate information. Structural problems – deformation? Salty fog? Pollution? Corrosion of metallic elements (Fig. 5)? Wrong interventions with incompatible materials?
- Are there defects with a low degree of reparability (Fig. 6)? Detachment and lack of cohesion are usually the most difficult defects to repair [2-4]. Observations 1.2 and 1.3 will generally allow the identification of these types of anomalies and action 3 will permit some quantification.
- Are renders and plasters globally affected, in a significant degree? Namely, are they globally too weak and permeable? Action 3 will help to get this answer [5-7].

The results of these simple diagnostic actions and their careful interpretation should provide significant information including: the identification of the main causes of defects and the way to control them; the identification of the defects of masonry and the possibility of evaluating the need to remove the render or plaster locally or globally; the classification of the state of conservation of the render or plaster itself, considering the intensity of defects and their reparability classed as high, medium or low levels of degradation.

Fig. 1 Moisture measurements with a portable humidimeter

Fig. 2 Modulus of elasticity by ultra-sound measurements

Fig. 3 Water absorption by capillarity of irregular samples

Fig. 4 Compressive strength of irregular samples

Fig. 5 Corrosion of metallic elements may require partial removing of the plaster

Fig. 6 Repair of render detachment using grouts is a delicate, complex technique

1.3 Foreseen actions

Old buildings today can be subjected to different loads, due to change in use or diverse environmental conditions. It is necessary to verify if the current or future conditions of the building may suggest changes or enhancements to particular characteristics of renders and plasters. For example, for renders, higher pollution or traffic vibrations may now occur or for plasters, different uses such as museums, music or theatre rooms may require different physical characteristics.

1.4 Decision making

Based on the actions and observations mentioned above a decision about preservation and repair or substitution is possible. Table 1 gives an idea of the systematisation of decision processes for the case of “medium cultural value”.

Table 1 Support for intervention strategy decision making

Cultural value	State of conservation of the substrate	State of conservation of the render/plaster	Compati-bility with use and actions	Recommended strategy
Medium	Good	Good	Bad	Protect or reinforce the render/plaster in a compatible way (ex. silicate based painting)
	Good	Bad	Good	Repair and consolidation of the render/plaster
	Bad	Good	Good	Repair the substrate with techniques of low intrusivity; Keep the render/plaster filling lacunae and reintegrating aesthetically
	Bad	Bad	Good	Repair the substrate with techniques of low intrusivity; Partial substitution of render/plaster
	Bad	Good	Bad	Repair the substrate with techniques of low intrusivity; Reinforce the render/plaster in a compatible way
	Good	Bad	Bad	Analyse the viability of repair and consolidation of the render/plaster against partial substitution with compatible techniques and materials.
	Bad	Bad	Bad	Repair of the substrate and substitution of the render/plaster with compatible materials

2 Choice of materials

2.1 Fulfilment of main functions

The main functions of renders and plasters are:

- Protection of masonry (against external actions such as impact, abrasion, weather, pollution).

- Regularisation (making look smooth or consistent) of the walls.
- Finishing and decoration.

The repair or renewal of renders and plasters is intended to fulfil these main functions. They have no structural functions, but they have a significant role in the protection of structural old masonry and hence on its durability and general good performance. The mortars to use don't need high strength, but some resistance to friction and impact, some deformability to follow masonry displacements without cracking and some ability to delay rain water penetration and to allow the easy evaporation of water from inside old porous walls.

2.2 Compatibility

Renders and plasters are a part of the walls. Materials both for their repair and for their renewal should be compatible with the existing mortars and substrates [8-11].

This means essentially:

- there should be no production of new damage;
- they should be consistent with the overall appearance, now and after ageing.

How can repair and substitution materials be harmful to existing materials? Some properties of new mortars can produce damaging actions:

- The introduction of stress due to higher stiffness and different thermal dilation coefficients, producing differential deformations in relation to the old materials in contact. Shrinkage of the new mortar, thermal variations and deformations of the masonry will produce stresses at the interface between old and new materials, damaging the weakest material (Fig. 7). The stresses are higher when differences between characteristics are larger [12]. As the existent material should be preserved, it must not be the weakest.
- The reduction of the drying ability of the wall through the application of renders with lower capillarity and lower water vapour permeability than the existing ones may result in the retention of water inside the masonry and higher capillary rise on the wall. This could become a problem in historic buildings, especially when there is water coming from under the foundation level or when the masonry is water saturated due to roof deterioration. Any soluble salts present in the walls will be transported by capillary rise and spread into larger areas of the masonry. Eventually they will crystallise at the new drying surface, often the interface between masonry and render, producing damage of the masonry and detachment of the render (Fig. 8).
- Driving the water through older mortars or stones, due to lower capillarity compared to new materials. In fact, when more impermeable materials are used, the water transport through the capillary net is diverted to the most permeable old materials in contact, accelerating their degradation.

- Introduction of new salts due to the presence of cement or other constituents containing soluble salts [13].

How can new products affect appearance?

- Different texture or colour due to different aggregates, different binder nature or different pigments.
- Differential ageing due to the different nature of constituents (resins, organic pigments, etc).

A set of compatibility requirements can be established considering these issues. In Table 2 a correspondence is established between compatibility requirements and material characteristics.

2.3 Environmental considerations

The choice of materials is also limited by some environmental conditions: weather, the proximity of the sea and pollution. Rainy weather, salty fog and spray of salty water and high pollution are factors that may militate against the use of pure air lime mortars. In Portugal air lime mortars were used in the past in misty, salty environments [14, 15], but today it is difficult to guarantee appropriate conditions of application and curing, so some hydraulicity is advisable. In moderately dry climates (like the South of Portugal), away from the sea, air lime mortars can be a good solution, except when high levels of pollution exist and create the danger of damage by acid attack.

Table 2 Compatibility requirements and new mortars characteristics

Requirements		Rc and Rf	E	C	W vp	S	α	Materials (direct influence)
Main functions	Protection against impact and abrasion	M	M	-	-	L-M	-	-
	Protection against rain penetration	-	-	M	-	L	-	-
	Protection against pollution attack	-	-	M	-	L	-	Air lime ($Ca\ CO_3$) is vulnerable to acid rain and pollutant gases in general (SO_2, CO_2 and NO_2)
Compatibility	No introduction of stress	L	L	-	-	L	Similar to old mortars and substrate	No high proportion of cement
	No retention of water inside walls	-	-	M	H	-	-	No water repellents, no resins
	No driving water through old materials	-	-	Similar or higher than old mortars	H	-	-	No water repellents, no resins
	No introduction of new salts	-	-	-	-	-	-	No cement
	No affecting the appearance	-	Low	Similar or higher than old mortars	H	L	-	No cement, no resins Similar aggregates, similar binder Similar pigments
Global analysis		L-M	L-M	Medium – Similar to old mortars and/or substrates	H	L	Similar to old mortars and substrate	No cement, no resins, no water repellent, similar aggregates, similar binder, similar pigments

Rc – compressive strength; Rf – flexural strength; E – modulus of elasticity; Wvp – water vapour permeability; S – shrinkage; α – coefficient of thermal dilation; L – Low; M – Medium; H – High.

2.4 Site testing

Compatibility is defined in relation to the background and the existing mortars. Thus, it is important to determine the main characteristics of the masonry and the old renders, in order to design new mortars with similar characteristics. *In-situ* testing, especially using non-destructive methods, is a first approach to evaluate significant characteristics (Figs. 1, 2, 9 to 12). Generally they have to be used in a comparative basis, as there are currently no sufficient correlations with laboratory tests.

In Table 3 some simple tests, non-destructive or slightly destructive, are considered, and related (qualitatively) with performance.

Table 3 Relation of in situ tests with performance characteristics

	Moisture measurement	Pendular Schmidt hammer	Durometer	Ultrasound	Karsten tubes	Salt colorimetric stripes or salt kits
Mechanical Strength	-	X	X	X	-	-
Dynamic modulus of elasticity	-	X	-	X	-	-
Water permeability	-	-	-	-	X	-
Presence of salts on the surface	-	-	-	-	-	X

Fig. 7 Mechanical damage due to incompatible new render

Fig. 8 Damage due to reduction of water permeability of the walls

Fig. 9 Evaluation of water permeability with Karsten tubes

Fig. 10 Evaluation of Mechanical strength with Pendular Schmidt Hammer

Fig. 11 Evaluation of surface hardness with a durometer

Fig. 12 Identification of presence of some salts with colorimetric strips

It is also now possible to perform *in-situ* some mineralogical tests with portable equipment. One of the most used is X Ray Fluorescence, with portable equipment, permitting for example, the discrimination of the type of binder, or other compounds present, such as salts. The "Hercules Centre", of Évora University, in Portugal, makes this equipment available to the scientific community. X-ray diffraction with a portable apparatus is also possible.

For current situations *in-situ* tests may give enough information for decision making concerning materials.

2.5 Laboratory testing

More specific tests are carried out in the laboratory, whenever needed (Figs. 3, 4). Laboratory tests require the collection of samples, so in this sense they are always destructive. For this reason and also for economic and time constraints, they must be complementary to site testing and usually be limited to those that are unavoidable. Due to limitations of dimensions, shape and cohesiveness of plaster samples collected from buildings, not every laboratory technique can be used and

the number of possible tests is smaller than for laboratory produced specimens. In Table 4 the most useful groups of complementary laboratory tests are presented and related to characteristics and performance.

Table 4 Relation of laboratory tests with performance characteristics

Main laboratory tests on samples removed from site	Chemical mineralogical and microstructural characterisation [10, 16]	Compressive strength [17]	Capillary water absorption [18]	Porous structure by MIP [19]
Objective	Composition; microstructure; products of alteration	Protection from mechanical loads	Protection from water penetration and promotion of drying	Hygric behaviour, behaviour to salts and to ice

2.6 Requirements

The characteristics of the mortars to use can be established based on the sets of results obtained, in order to fulfil both functionality and compatibility, as summarised in Table 2. However, sometimes it is not possible to get enough data concerning the old materials, especially about masonry, which is rather more difficult to test than mortars. For that situation, some general requirements have been established, based on previous work carried out on Portuguese historic masonry buildings, which can be used without risk of damaging existing materials [10]. These requirements, summarised in Table 5, consider medium to low strength masonry of irregular stone, agglomerated with lime mortars, which are very common in old buildings in the south of Portugal.

Table 5 General requirements concerning some characteristics for rendering and plastering repair mortars for historic buildings

Type of render	Mechanical characteristics at 90 days (N/mm2)				Hygric behaviour at 90 days	
	Rf	Rc	E	A	Wvp Sd (m)	C ($kg/m^2.min^{1/2}$)
Exterior render	0.2 – 0.7	0.4 – 2.5	2000 - 5000	0.1 - 0.3 or cohesive rupture	< 0,08	< 1.5; > 1.0
Interior render	0.2 – 0.7	0.4 – 2.5	2000 - 5000	0.1 - 0.3 or cohesive rupture	< 0,10	-

Rf – flexural strength; Rc – compressive strength; E – modulus of elasticity; A – adhesive strength; Wvp – water vapour permeability; Sd – thickness of air with equivalent diffusion; S – shrinkage; α – coefficient of thermal dilation

2.7 Global analysis and decision making for repair and substitution solutions

A global analysis of all the data – observations, tests and available conditions – is then needed to choose a mortar for repair or substitution.

Table 6 Average range of characteristics of some types of mortars

Mix and volumetric proportion binder:aggregate	Range of values (indicative)			Basic application field (indicative)
	Compressive strength	Dynamic modulus of elasticity (by frequency of resonance)	Water capillary absorption coefficient	
Lime:sand (1:3)	0.2 – 0.8	2300 – 4100	1.1-1.6	Mild weather (not too humid nor very dry); non-aggressive conditions; interior surfaces (plasters)
Lime + pozzolan:sand (1:2 to 1:3)	0.5 – 2.3	2500-4500	1.3-2.3	Frequent presence of moisture, due to rainy weather or to capillary rising water (because the pozzolanic reaction needs moisture for long time)
Lime + some hydraulic lime:sand (1:2 to 1:3)	0.4-1.0	1600-5600	1.2-1.9	Variation between dry and humid weather
Hydraulic lime*:sand (1:2 to 1:3)	0.6-3.1	1100-7500	1.0-2.4	Variation between dry and humid weather and some aggressive conditions
Lime + some cement:sand (1:3)	0.9-5.1	3000-6500	1.0-2.0	Aggressive conditions: for example exposed to sea spray and high pollution

* use hydraulic lime free of salts and of low hydraulicity (NHL 3.5 or HL 3.5)

What are the choices for possible compositions of binder to use? The most compatible binders are: air lime, hydraulic lime free of salts and air lime plus pozzolans (either natural or artificial). Although cement should be avoided as a

single binder for the repair of historic lime mortars, lime-cement mixes can also be acceptable binders for that purpose, in some circumstances [20, 21].

The volumetric ratio 1:3 (binder:aggregate), or near this proportion, is currently adopted. This is the proportion that theoretically assures the highest compaction of the mortar, when the aggregate has a complete grain size distribution. It has also been verified in practice that contemporary renders with a higher proportion of binder have a strong tendency to crack, although there is much evidence of their successful use in the past.

The groups of mixes considered as possibly compatible, and their basic average range of characteristics, are compiled in Table 6. The range of results presented is based in previous work [20-24].

The characteristics of all these types of mixes may be adjusted and improved by manipulating the the aggregate type and grain size distribution, the type of lime, relative proportions when two binders are mixed, improving the method of application and the curing conditions and, possibly, using some additives or admixtures.

3 Application

After decisions about materials are made, it is important to guarantee the appropriate conditions of application, concerning technique, workmanship and curing.

For lime mortars, the application technique is particularly important: the exact quantity of mixing water (enough for good workability but not too much, for good compaction); long mixing; several thin coats; careful curing, avoiding quick drying and closing cracks when they occur during the early stage of application etc. [25, 26]. The application of air lime renders, or air lime and pozzolan renders, requires careful and rigorous workmanship. Current construction workers, not used to the application of this kind of mortars on large surfaces, will probably not achieve good results (appropriate physical and aesthetic characteristics), except if constant supervision is provided.

Appropriate curing is one of the main secrets of ensuring the success of lime renders. The carbonation of calcium hydroxide requires some humidity for the dissolution of the carbon dioxide but not too much, to allow its reaction with calcium hydroxide. This reaction is slow, so it is necessary to provide special conditions for several days, maybe some weeks. On the other hand, most of the mixing water of lime mortars is not used up in hydration reactions as happens in hydraulic binders, so it leaves the mortar, through evaporation or absorbtion by the substrate, causing high shrinkage. This can produce cracks, which must be closed while the mortar is still in a plastic state [22].

4 Examples

Some case studies of historic buildings' renders and plasters repaired with compatible mortars are represented in Figs. 13-16 [1, 6, 7, 14].

Fig. 13 Main LNEC building: repair with air lime mortar

Fig. 14 Inglesinhos Convent: substitution air lime render

Fig. 15 Sacramento church: repair and partial substitution of plasters using air lime plus hydraulic lime mortars and gypsum and air lime mixes

Fig. 16 S. Bruno Fortress: substitution air lime plus cement render

5 Conclusions

Decisions about conservation strategy and about the materials to use for the conservation of historic renders and plasters are based on several factors, both of a subjective and an objective nature. Tests play an important role, for an evaluation of the severity of anomalies and for an assessment of compatibility by a comparison of the characteristics of existing materials and proposed solutions. However, they are only a part of the methodology. They should come after a careful expert observation and they must be adequately interpreted. The type of

tests and their localisation are to be chosen in order to obtain the maximum information with the minimum intrusion and disruption to the original fabric, and without taking more time than is necessary to fulfil the objectives. Hence, in-situ tests must be used first followed by complementary laboratory tests. Previous results in similar buildings and materials must be taken into account. Functionality, compatibility and adaptation to the prevailing environment and foreseen actions must be considered. Considering all of these factors carefully, creates a new perspective that aims to ensure the improvement of the durability of the whole building, respecting its characteristics.

To plan adequate interventions on historic buildings is a complex task, requiring many skills; therefore a multidisciplinary team must be chosen to do it and given a reasonable amount of time.

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High-Temperature Gypsum Plaster: Investigations into Conservation and Restoration of Historic Gypsum Objects

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Abstract Applications of repair mortar mean that an additional heterogeneity is introduced to the system. Because of this the utilisation of identical material is a main objective of restoration. In consideration of this goal, high-temperature gypsum plaster has been tested in pure and modified varieties. According to the historical standard, high-temperature natural gypsum (Keuper (Triassic)) mixed with non-hydraulic lime and crushed gypsum stone to different ratios was used. The substantial interest is focused on the influence of the hydrated lime concerning physical and hydraulic aspects. Also the differences in the manufacturing method (e.g. duration of mixing) were taken into account. Investigations regarding thermal and hygric change in length, biaxial flexural strength and compressive strength, dynamic E-Modulus, water absorption, frost-thaw-change resistance were carried out. The aim of these investigations is to prove appropriate gypsum mortars for the exterior and the interior application respectively to initiate further research into conservation and restoration of gypsum.

1 Introduction

The application of gypsum for plaster, masonry, floor-mortar and also stucco became common in Middle Europe in the 10th-11th centuries. These mortars are very common when sites are located close to natural gypsum and anhydrite sources. Historic gypsum mortars are mainly high-temperature gypsum which is recognisable in its strength and the resistance to weathering. This can be applied for materials used from the Roman times to those used in the 18th century. The

focus of this paper is on high-temperature gypsum and appropriate repair materials. In this regard several questions are to be considered [1]:

- To what extent are changes in length (hygric/thermal) in the course of the hardening process occurring?
- Can the addition of lime influence length changes?
- What is the effect of a small amount of lime (2-5 M.-% (mass percent))?
- To what extent can hydration be increased by an addition of lime?
- Can the percentage of hydration/dehydrate be increased by a long mixing time?
- What effect can crushed gypsum have on the degree of hydration?
- What is the influence of the freeze-thaw resistance on the unmodified high-temperature gypsum and can it be optimised by the addition of lime?
- Can the E-Modulus be influenced by the addition of lime?

2 Damage characteristics

High solubility of gypsum determines the weathering and ageing of the mortars. Damage on plaster arises in the form of sanding, scaling, deformation and delamination from the background [2]. Cracks are another typical damage phenomena that especially occur on heavily used floors which are also prone to crumbling and a fragmentary loss [3]. In addition to these problems the plaster durability can be affected by poor materials or workmanship. So for instance a disproportion of gypsum and water will lead to an insufficient hydration and consequently, during subsequent contact with water, to an expansion because of subsequent hydration in the already hardened mortar structure. All this damage is the basis for the necessity of restorative works in form of fillings and plaster-modelling, whose optimised composition is the subject of this paper.

3 Repair materials

The existing conditions of the historic mortars determine the restorative material. Beside the chemical compatibility, the physical and hygric values must be checked and harmonised regarding the original material as far as possible. Concerning several parameters the material-identic complement is basically preferable. Previously applied materials were partially composed of a lime-base; but it is an often described phenomenon that application of lime on a gypsum surface is not compatible for long periods of time. A poor adhesion of the gypsum- and the lime-mortar could be observed in several cases.

3.1 Binder and additive calcium-sulphate

Binder material in the presented study is the high-temperature gypsum "Keuper" (in the following text abbr. "KG") (from Triassic deposits) produced by the Hundisburger Manufacture method. The natural gypsum was fired at about 900°C and crushed afterwards (0-4 mm). The pH-value is 11. The raw material comes from Sulzheim (Lower Franconia), Germany and is a sallow ochre to a reddish colour with ochre-brown inclusions.

The "Keuper" gypsum ("KG") features an anhydrite content of 95% (XRD-analysis). As additive crushed gypsum-stone, raw material of the binder "KG" was used (grain size 0-4 mm, coarse grains preponderate).

3.2 Binder lime

The hydrated lime CL 90 is from the factory Schraplau, Saxony-Anhalt, Germany. It contains 93.5% Calcium hydroxide.

3.3 Compositions

The lime fraction of the different compositions mainly imitates the majority of historic mortars that contain a maximum 8-12 M.% of lime. The addition of lime should reduce mass loss while maintaining the compressive strength and the optimisation of change in length. The addition of crushed gypsum stone is subjected to existing sample areas for further assessment of the Keuper-material as an exterior plaster. Beside the aforementioned parameter, the stimulating influence of calcium sulphate dihydrate in this form is to be analyzed. Among other things the composition "LZM", with a long mixing time, should be used to determine the hydration velocity. The following table (1) shows the used compositions.

Table 1 Composition of the mortars

	KG	Hydrated lime CL 90	Crushed gypsum KG
KG	100 M.-%	-	-
KG/WKH2	98 M.-%	2 M.-%	-
KG/WKH5	95 M.-%	5 M.-%	-
KG/WKH10	90 M.-%	10 M.-%	-
KG/ LZM	100 M.-%	-	-
KG/GB5	95 M.-%	-	5 M.-%

(KG - high temperature gypsum Keuper, WKH 2, 5 and 10 - hydrated lime in a content of 2%, 5%, 10 %, LZM – long mixing time, GB – crushed gypsum)

4 Methods

Various measuring techniques were applied to the compound of mortar and to the subsequent production of specimens to comprehensively ascertain the behaviour of the individual samples.

4.1 Specimens

Specimens with the dimensions 40 x 40 x 160 mm were prepared after DIN 13279-2 [4]. For every investigation method 5-6 specimens were made available. The preparation and subsequent storage of the specimens was carried out over a minimum of 75 days until the first test (ambient temperature 21±2°C and 65±5% relative humidity).

4.2 Tests

The following tests were applied:

- 1.) Determination of the heat of reaction using calorimetry to determine the reaction rate and the end of reaction.
- 2.) Volume changes during initial hydration (first 48h) using the shrinkage cone measurement.
- 3.) Volume changes during long term hydration was measured after DIN 13454-2 [5] after 2-5 days, 22-27 days and 75 days respectively
- 4.) Thermal dilatation was measured after 76 days on the prismatic specimens with integrated cones - length change during an increase of temperature from 20 to 50°C.
- 5.) Hygric dilatation was determined after a "specimen age" of 77 to 115 days according to DIN 13454-2 [5]. Following the application of repeated stress the dilation behaviour was tested by taking 4 measurements.
- 6.) Water absorption was determined according to DIN 52103, in the context with the 24h-water-storage of the hygric dilatation test.
- 7.) Determination of the degree of hydration (90-days-specimens) was by dry burning at 350°C. The further progression was calculated from the mass increase that was determined during the water absorption.
- 8.) Compressive strength after 102 days according to DIN EN 196-1 [6] following the biaxial flexural strength measurement on specimen halves.
- 9.) Ultrasonic velocity was determined for stressed and unstressed specimens after 90 days dry-storage.
- 10.) Freeze-thaw-change resistance was determined after 88 days according to [7] by calculating the mass loss in consequence of 50 freeze-thaw-changes.

5 Results

The following results are related to the question 'To what extent can the modification of high-temperature natural gypsum "KG" combined with hydrated lime and crushed gypsum stone during mixing, influence the physical and hydraulic aspects of the material.'

- *Development of the initial heat of reaction*

As expected an addition of 2% lime tends to result in a slight retardation of hydration, which is more evident with 10% lime. The increase of the heat of reaction could be observed only after 36 h. On the contrary the addition of 5% crushed gypsum shows no influence on the initial hardening velocity due to the slow solubility of the coarse dihydrate and/or the small quantity.

- *Swelling and shrinking during the initial hardening process*

(Samples were kept dry and measured with the shrinkage cone)

An addition of 5% crushed gypsum leads to a clear increase of swelling after 2 days. A 2% and 10% lime addition lead to a reduced swelling, independent of the amount. Dry-stored specimens used for investigations of the thermal and hygric dilatation were measured with a caliper 2 days after manufacture: The unmodified composition shows 2 mm/m shrinkage. The higher the lime content the higher the shrinkage (2% lime = 4 mm/m and 5% lime = 7 mm/m). The long mixing time of the unmodified KG resulted in a decreased distension of 0.2 mm/m.

The different values determined by the shrinkage cone and calipers are probably caused by different climate conditions during the storage. The material in the shrinkage cone is completely sealed whereas specimens made in steel moulds are stored open-top. Using lime as additional component this kind of storage must be assessed as inappropriate. This fact obscures the consideration to the relevance of climate conditions during the hardening process.

- *Swelling and shrinking during long-term hydration*

The measurements were carried out after 2, 25 and 75 days. Intermediate length changes are also possible. Referring to the unmodified material KG lime-modifications (2-5% lime) show an increase in swelling 2 days after stripping which is probably caused by the delayed hydration. The low values in conjunction with an addition of 10% lime reflect most likely an already superposed swelling and shrinking. In consequence of a higher water demand in the following a more intensive shrinking could be observed. Regarding KG, modification with 2% lime can be assessed as favourable because the initial shrinking is only slightly increasing. The low values of the LZM of only 0.1 mm/m after 77 days were considered very promising. Initially, the addition of crushed gypsum leads to a higher swelling and then subsequently to a positive reduction of the swelling.

- *Thermal dilatation*

As expected, the thermal linear coefficient of expansion is quite high. A reducing effect could be observed using 5% lime. A considerable decrease of the thermal dilatation of 16% (referring to KG) was caused by 10% lime. The addition of crushed gypsum leads to an increased expansion coefficient (119%).

- *Hygric dilatation*

The first 24-hour-water-storage leads to a dilatation of all varieties between 0.24-0.34 mm/m. A dependence on the lime content could not be observed. Lower values (0.24-0.26 mm/m) were caused by the LZM and the addition of crushed gypsum. But these values still exceed the requirements for joint mortar of 0.15 mm/m [8] and 0.2 mm/m (DIN 13454-2 [5]). The remaining expansion of all compositions after the fist cycle (water-storage / drying) is 0.15 mm/m which results mainly from the swelling during the delayed hydration. At the end of the 4 cycles for the lime-modified mortars a shrinking was observed. Thus, after the 3rd. cycle the initial value '0' was achieved. The unmodified material shows a higher swelling with every cycle. The long-time mixing has a positive influence on the length change. A reduction of 18-26% was achieved. But every water-storage cycle lead to a small increase in swelling. By adding crushed gypsum the dilatation values became reduced (10-26%).

- *Water absorption*

The increased water content in connection with a rising lime content results in a lower bulk density and higher values of water absorption. Referring to the unmodified samples an addition of 10% lime leads to a reduced sucking and a higher water absorption level. The admixture of 2% lime causes a decrease of water absorption and sucking. The LZM shows the lowest w-values. Referring to the unmodified material the water absorption of the crushed gypsum samples is clearly increased.

- *Degree of hydration*

After 90 days dry-storage the degree of hydration is comparatively low (33-39%) for all compositions. An increasing lime content is connected to an increase of the degree of hydration, but not in the expected dimension. However, after 4 water-storage cycles in the mixture with 10% lime, more than a half of the anhydrite was transformed into gypsum. Compared to the dry-stored unmodified variety (33%) this is a marked increase. The stimulating effect of the LZM is effective only at the beginning. After the water-storage cycles these compositions show the lowest increase. A stimulating effect of crushed gypsum was not detectable.

- *Strength and E-Modulus*

Increasing bulk density causes a higher strength, except for the LZM composition and those with crushed gypsum. For the LZM probably the hydration

degree causes higher strength values. For the crushed gypsum variety this is not the case. The strength is rather low (the values for compressive strength have a significant standard deviation, therefore, they are used with caution).

An increasing lime content is connected to a decreasing E-Modulus (2% lime = 11 kN/mm² and 10% lime 8.8 kN/mm²). The LZM has an E-Modulus of 13kN/mm² and the composition with crushed gypsum 9.8 kN/mm².

- *Ultrasonic velocity*

For unstressed samples rising lime content is related to decreasing velocities. After repeated stress (change between 24-hour water-storage and fast drying (40°C)) the values of lime-modified samples are increasing dependent on the lime content. The same stress results in a notable loosening of the structure (lower velocities). It appears that the addition of lime causes a higher weathering resistance.

- *Freeze-thaw-change resistance*

Former studies [9] state that historic gypsum mortars are very frost resistant; in the course of these investigations no cracks and flaking could be observed. The 50 freeze-thaw-changes are not enough to identify the characteristics of the different mixtures. In consideration of the macroscopic impression the compositions with 5 and 10% lime seem to be more durable.

6 Conclusion

With regard to the majority of properties of historic gypsum mortars, modifications of high-temperature gypsum with non-hydraulic lime appear promising. Only the addition of a small amount of lime has a significant effect on material characteristics. The addition of gypsum fragments has a rather negative influence. For all tested mixtures the high water absorption capacities measured are incompatible with the historic mortars. In the course of open exposure, an increasing compaction of the material and therefore a reduction of the water absorption are assumed and therefore, over the course of time, a harmonisation of the w-values of the historic and the repair mortars will occur. In terms of hygric dilatation for a large-scale external application, the addition of lime (2%-5%) is recommended. In areas with an exposure to sunlight, the addition of 5% or 10% lime is required in order to keep the thermal dilatation low. Within these limits, the higher the proportion of non-hydraulic lime, the higher the weathering resistance in the form of a favourable relation of compressive and biaxial-flexural strength combined with a higher elasticity.

With regard to the application of mixtures of high-temperature gypsum and non-hydraulic lime, several measures must be taken into account to avoid very fast drying and the formation of shrinking cracks. Also, a long ponding time is

advantageous. Changes in length caused by the hardening process or a hygric impact can be reduced by an increased mixing time which could be established for the unmodified high-temperature gypsum.

For masonry mortars an improved weathering resistance for areas which are subject to hygric stress can be achieved by a lime-addition of 5-10%. For minimally weathered masonry areas, additional lime is not necessarily required. Rather an object-specific adaptation of strength and E-Modulus are of an overriding interest. If there are high values needed, an unmodified, long ponded and mixed high-temperature gypsum can be recommended. In the case that higher elasticity and lower compressive strength is required, an addition of lime is recommendable. The higher the hygric stress, the higher the lime fraction should be to obtain a lesser expansive material with a higher weathering resistance.

In interiors, the applied high-temperature gypsum does not necessarily need an addition of lime to reduce the hygric and thermal dilatation. Nevertheless, in order to reduce all types of change in length and to increase the degree of hydration and consequently the strength, a long mixture time, a repeated mixing and a long ponding are recommended

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IV.45

Reducing Shrinkage Cracks in Roman Cement Renders

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Abstract Roman cements were key materials for the economic and easy manufacture of render (stucco) for the exterior of buildings during the nineteenth and early twentieth century. Fine surface cracks, caused by drying shrinkage, are a distinct characteristic of all Roman cement renders and architectural decorative details. Recently, Roman cements have been re-established in conservation practice. However, the formation of shrinkage cracking is one of the important barriers preventing broader acceptance of Roman cements as a cultural heritage material by the contemporary restoration and construction sector. This paper explores the mechanism of shrinkage cracking in Roman cement mortars by determining the drying shrinkage and the tensile properties of the mortars submitted to various curing and drying periods. Moisture content gradients in the mortar body on fast drying i.e. differential shrinkage between the surface and the centre of the element are considered. Optimum curing conditions minimising the damage processes are discussed.

1 Historic usage of Roman cements

Highly hydraulic binders, known as natural or Roman cements, were key materials for the economic and easy manufacture of renders and cast architectural details for the exteriors of buildings during the nineteenth and early twentieth century [1, 2]. Roman cements were produced by burning naturally occurring deposits of calcium carbonate, rich in clay minerals, below their sintering temperatures and grinding burned stones to a required fineness. The materials offered a high speed of set, a beautiful texture, and warm ochre colour imitating those of natural stones, and they could withstand exterior conditions very effectively. The production and use of Roman cements declined in the first half of the twentieth century with the dominance of the newer Portland cement on the market and modern functional architecture, with its absence of ornament.

For a long time, conservation of the architecture of the late nineteenth and early twentieth century did not receive the same considerations as other periods, one of the principal reasons being lack of original historic binders that would closely match those of the original structure. Several recent research projects have extensively investigated historic renders based on Roman cements and have re-established this historic material and technology in conservation practice [1-8]. Also, the Vicat Company of Grenoble has continued to produce Prompt natural cement – a major historic natural cement used in France [9]. A detailed description of the history of Roman cements and of investigations of historic mortars may be found elsewhere in these Proceedings [10].

2 Roman cements – hydration, strength development, porosity

The hydration and strength development of Roman cements proceed according to a two-step mechanism [5]. Firstly, Roman cement pastes harden within a few minutes after the initial set. Six-hour compressive strength values up to 4 MPa are obtained. Secondly, after a varying dormant period, dependant on the source of Roman cement and calcination conditions, further strength development leads to high final strength values – after one year, compressive strengths exceeding 20 MPa were measured. The in-situ X-ray diffraction of the Roman cement pastes [6] revealed a correlation between the early strength development and the formation of crystalline calcium aluminum oxide carbonate (or carbonate hydroxide) hydrates (C-A-H). Optical and SEM microscopy of historic Roman cement mortars have shown that the formation of a dense microstructure, correlating with their final strength, is due to the hydration of dicalcium silicate – belite, yielding calcium silicate hydrates – the C-S-H gel [1, 10].

The two-step mechanism of the Roman cement hydration is reflected in a characteristic development of the pore structure [7]. At early ages, relatively open pore structure is produced by the quick growth of the C-A-H phases with the threshold pore diameter between 0.2-0.8 μm as determined by mercury intrusion porosimetry. The initial open structure remains unchanged during the dormant period of pastes, which can extend up to several weeks. Only then does the threshold pore width shift to smaller values concentrated around 0.02 μm, which is the result of filling larger pores by the formation of the C-S-H gel.

3 Shrinkage cracking of cement mortars

Fine surface cracks, forming an irregular network not related to building features, are a distinct characteristic of all Roman cement renders and architectural castings (Fig. 1). Usually they do not lead to damage. Only rarely can they widen

if the stucco is exposed to the severe impact of rain water, especially at the top of buildings (Fig. 2).

Fig. 1 Typical irregular network of fine shrinkage cracks characteristic of Roman cement stucco.

Fig. 2 Heavily eroded surface of a decorative element exposed to rain water; the shrinkage cracks are widened.

The fine cracking of historic Roman cement mortars was caused by their restrained shrinkage during the drying process. It is common to describe shrinkage values in microstrain, i.e. μm/m. Values of long-term concrete shrinkage are typically 200 and 800 μm/m, mortar shrinkage between 800 and 2000 μm/m, and cement paste shrinkage between 2000 and 6000 μm/m [11]. Shrinkage is primarily affected by the relative humidity in the environment of the drying mortar. Therefore, relationships between the two parameters need to be established by testing and then described by the mathematical formulae or models [12]. The total volume of aggregate in a mixture is another important factor affecting the shrinkage of mortar as only the cementitious matrix shrinks, whereas aggregate generally remains insensitive to drying. However, even the mortar shrinkage normalized to the cementitious matrix volume is considerably lower than that of the cement paste, as the aggregate grains act as rigid inclusions restraining the shrinkage of the matrix. Finally, an increase in the w/c ratio leads to an increase in the drying shrinkage because the additional water increases the porosity of the matrix.

Uniform, free drying shrinkage does not induce stress in the material. However, drying shrinkage in repair mortars is restrained by the existing substrate, which induces tension leading to irreversible stretching and eventual cracking. The level of restraint can be measured experimentally and expressed in terms of a restraint factor by which free shrinkage is modified for a specific configuration and surface conditions of the repaired substrate [13].

The repair mortar can also experience internal restraint as the moisture transport is not instantaneous and, with a reduction in relative humidity, the outer part of the repair will dry more quickly than the interior. The dry outer part will be restrained from the shrinkage, which will result in the outer shell going into

tension. The tensile stresses and microcracking due to non-uniform drying are known reasons for damage in dried concrete, prior to any mechanical loading [12].

The aim of the present research has been to study systematically the cracking of Roman cement pastes and mortars due to restrained drying shrinkage. Two fundamental properties of the materials are determined to assess the potential for cracking: drying shrinkage in response to a range of relative humidity levels in the environment, and relationships between tensile stress and strain, especially the critical levels of strain at which the materials fail mechanically. These properties must be known in sufficient detail for pastes and mortars at various curing times, as historic mortars have rarely been found to develop a dense fine-porous microstructure characteristic of the ideal conditions of long-term moist-curing [8]. The restricted hydration also can be expected in freshly prepared Roman cement repair mortars, which are exposed to dry real-world external environments. Furthermore, the pore structure of the repair materials can be influenced by a careful manipulation of the water-to-cement ratio of the mix and the curing regime, which opens a perspective of controlling their susceptibility to cracking to some extent.

4 Materials and methods

Roman cement burned from Folwark marl, Poland, was used to produce cement paste and standard mortar both at a water-to-cement ratio of 0.65. The characteristics of the original marl source, oxide and mineralogical compositions of the cement, as well as its strength development on hydration were described in detail earlier [5]. Standard sand from Kwarcmix, Poland, was used as aggregate (EN 196-1), and the aggregate-to-cement ratio was 3:1 by weight or 1.85:1 by volume.

The tested specimens were prismatic beams, 80 mm x 20 mm x 20 mm, cast in silicone moulds. The samples were demoulded immediately after setting and cured at room temperature over distilled water in a closed container, i.e. near 100% relative humidity until tested.

Shrinkage was measured at room temperature in a glass vessel with inductive displacement transducers from RDP Electronics Ltd, UK, with uncertainty of 1.25 μm. A relative humidity of 45% was maintained in the vessel using a saturated potassium carbonate salt solution. Faces of the tested specimens at which the sensors were positioned were provided with glass plates. A quartz beam was used as a reference specimen, which allowed correction for the thermal expansion of the mounting system induced by variations in temperature in the laboratory. Two specimens were measured for curing times of 28 and 90 days. As the repeatability of the results was excellent, the number of investigated samples was reduced to one for other curing times.

Tensile properties were determined using the Universal Testing Machine from Hegewald & Peschke, Germany. The specimens were fixed with epoxy resin into metal clamps in the machine as shown in Fig. 3 and subjected to tensile strain through ball joints to ensure a linear configuration of the test. The rate of the tensile loading was 10 μm/m/s. Four specimens were tested. Tensile strength was determined according to a historic test procedure using mortar briquettes in the shape of a number eight (Fig. 4) to be able to compare directly the results with the strength specifications for Roman cement mortars given in an Austrian standard of 1880, modified in 1890 [14,15]. Six specimens were tested, and the mean value of the tensile strength was calculated.

Fig. 3 Experimental set up for the measurement of the tensile properties.

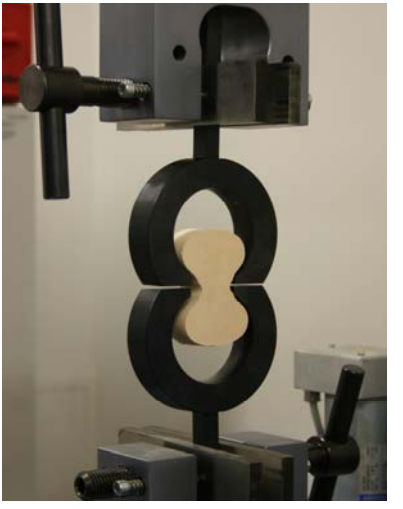

Fig. 4 Experimental set up for the measurement of the tensile strength.

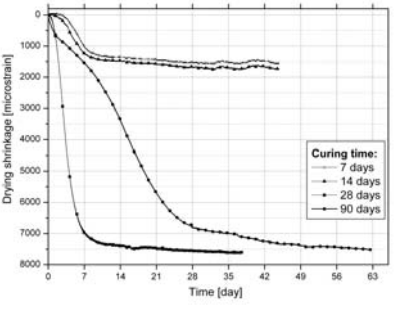

Fig. 5 Drying shrinkage of the cement pastes cured at various ages.

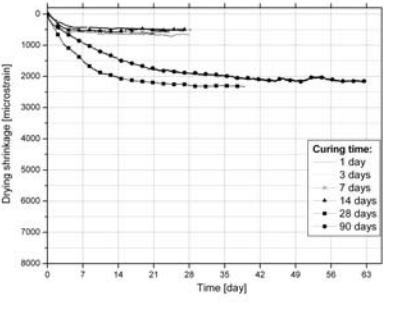

Fig. 6 Drying shrinkage of the mortars cured at various ages.

5 Drying shrinkage results

Figs. 5 and 6 show the evolution of shrinkage in the cement pastes and mortars as a function of time after a given curing time. By 65 days the shrinkage in all cases had levelled off.

There is a characteristic evolution of the shrinkage curves with the time of hydration. Young pastes and mortars, i.e. cured for less than 14 days, show much lower shrinkage than matured materials, the reduction factor being five for the pastes and four for the mortars. The observation can be correlated with the radical change in the pore structure, which occurs in the pastes with increasing curing time. As briefly discussed in part 2, a relatively open porosity structure is produced at an early age by the quick growth of the C–A–H phases in the pastes, with the threshold pore diameter of 0.8 μm determined by mercury intrusion porosimetry. Already after 14 days, the threshold pore size shifts to smaller values concentrated around 0.02 μm, which is the result of filling larger pores by the formation of the C–S–H gel. Because narrower pores lead to an increase in capillary suction, which is the primary cause of paste shrinkage, matured pastes will have higher shrinkage. As expected, the addition of aggregate considerably reduces the shrinkage, the asymptotic values for the matured pastes being 7500 μm/m when compared to just over 2000 μm/m for the mortars.

6 Tensile properties

Fig. 7 shows the tensile stress-strain relationships for wet mortars cured at four different ages. Fig. 8 compares the stress-strain relationships for wet pastes and mortars cured for 14 and 28 days.

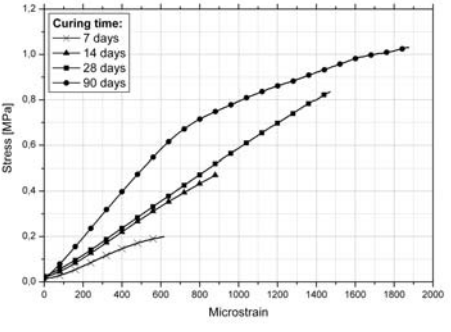

Fig. 7 Tensile stress-strain relationships of the mortars cured at various ages.

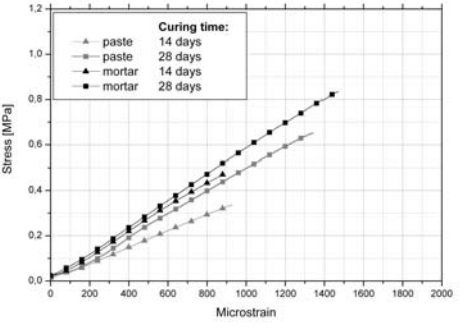

Fig. 8 Tensile stress-strain relationships of the cement pastes and mortars cured for 14 and 28 days.

The most important observation from the tensile testing is that breaking strain of the mortars considerably increases with the curing time, the range being from 600 μm/m at seven days, to almost 2000 μm/m at 90 days. Also the modulus of elasticity of the mortars, expressed by the ratio of stress to strain in the elastic region, increases with the curing time. Pastes have slightly lower modulus of elasticity than mortars, but their breaking strains do not differ significantly from those of the mortars.

The tensile strength determined using mortar briquettes was 0.4 and 1 MPa at seven and 28 days, respectively, which compares well with the specifications of the historic Austrian standard: ≥ 0.4 and ≥ 0.8 MPa at the same ages, respectively [14,15].

The results of the drying shrinkage analysis and the tensile strain testing clearly show that the high final shrinkage values for pastes dried at 45% relative humidity exceeds the breaking strain irrespective of the curing time, although the difference is particularly pronounced for the matured pastes. Therefore, pastes, and in consequence cement rich mortars, will be particularly susceptible to cracking on drying. The considerably reduced drying shrinkage in the mortars is comparable to the breaking strain in matured mortars and is even lower than the breaking strain in mortars at young ages. A competition between two opposite tendencies is observed: the young mortars show reduced shrinkage but their breaking strain is also reduced. The data obtained so far seem to indicate, however, that an optimum curing time of around 14 days produces mortars which should have the least susceptibility to cracking, as they have a low shrinkage that is also well below their breaking strain.

7 Conclusions

Roman cement pastes and mortars have been shown to exhibit strong variations in the drying shrinkage and tensile properties associated with different pore structures developed at various curing times. Young materials, with shorter curing times and a more open porous structure, show low drying shrinkage but at the same time low tensile failure strain. Mature materials, with longer curing times and a denser microstructure, show higher drying shrinkage but also higher tensile failure strain. Comparison of the shrinkage data and the tensile strain at failure has provided insight into the susceptibility of the mortars to cracking. It can be minimized by careful manipulation of the mortar compositions and curing conditions. A higher volume of aggregate in the mortar mix and a moderate curing time seem to produce optimum Roman cement mortars from the standpoint of reducing the risk of cracking. Further research will take into account creep strain, i.e. time-dependent increase in strain of the specimens under sustained tensile stress. The effect of cycles of re-wetting and drying of mortars on their cracking will be also investigated, as such cycles typically occur on the facades exposed to rainwater. Both areas of investigations will refine the presented analysis.

8 Acknowledgements

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IV.46

Correlation of Initial and Final Available Lime, and Free Water in Lime Putties to Carbonation Rate and Mechanical Characteristics of Lime Mortars

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Abstract In conservation practice it is usually observed that the capability of upgrading the characteristics of a lime through maturation appears to be limited due to a self-drying mechanism. Within the general framework of research on high calcium limes suitable for repair mortars, samples of fresh wet slaked lime putties were simply stored undisturbed in plastic bags and carefully monitored for two years. The present paper investigates how the differentiation of the available lime and free water during maturation is related to the carbonation rate and mechanical characteristics of repair lime mortars. TGA-DTA results in mortars indicate that the degree of conversion of calcium hydroxide into carbonate is more likely related to the dynamic available lime (influenced by maturation). The initial available lime (controlled by calcination) is the key factor-affecting mechanical characteristics, mainly the compressive strength.

1 Introduction

According to EN 459, the available (unbound) lime content, Ka, represents the amount of calcium oxides and calcium hydroxides that are available to enter into a desired chemical reaction in a particular process, and the free water content corresponds to the loss in mass when a sample is heated to 105°C (designated as w_F, expressed as a percentage by mass) [1].

The mechanisms by which water is rejected or retained in high calcium lime putties after slaking has initially been investigated [2], unraveling how traditional technology worked. It was suggested that putties have water in the form of free flowing or drained (or settled water w_s, according to EN 459-2, 5.9) and physically bound water (or free water w_F) [3, 4]. In the latter case, surface tension effects become dominant. Recent research monitored the extraction of water (free

flowing and physically bound) from calcium lime, natural hydraulic lime and Portland cement mortars placed on an adsorbent brick substrate. The importance of binder type on water retention controlling the flow of water into the brick was highlighted [5]. The result of the tests is that the virtue of the binder's water retentiveness is progressively documented [3, 5].

Historically, slaking was carried out in absorbent soil pits -favoring dewatering and salt rejection followed by a prolonged maturation time, as it was known empirically that storage under water has positive effects on the performance of lime putties and lime mortars. However, in conservation practice it is usually observed that the capability of upgrading the characteristics of lime through maturation is limited due to a self-drying mechanism [2] i.e. a process which varies clearly, despite similar samples and storage means, leading to gradual loss of plasticity.

The maturation process changes the morphological and physical properties of lime [6], raises the available lime, Ka [2-4], and triggers better rheological properties e.g. improved viscosity and yield stress in the fresh state [7]. It was interpreted that lime's upgrading lasts as long as the balance of the repulsive and attractive forces of lime's nanoparticle dispersion is retained. If the particles have little or no repulsive force then some instability mechanism will somehow have an effect e.g. flocculation, aggregation, etc. [8]. The availability and the stability of the moisture (mainly as optimal free water w_F), necessary for the dissolution of both carbon dioxide and calcium hydrate in water, accelerates the carbonation rate in mortar and consequently minimizes the crucial required time for a mortar to obtain its chemical and mechanical stability [3, 4, 8, 9].

The present paper investigates how variation of the available lime Ka and free water w_F during maturation of high calcium lime putties is related to the carbonation rate and strength of lime mortars.

2 Materials and methods

Samples of fresh wet slaked high calcium lime putties of known origin and calcination parameters (laboratory prepared and available in the market) were put in plastic bags two weeks after slaking (Fig 1). They were then stored undisturbed (a common site practice) and carefully monitored for a period of over two years.

The methodology for testing the samples was kept as constant as possible, thus controlling the technological characteristics during maturation. Water was not added to the plastic bags. Easily measured physical and chemical characteristics were obtained initially and then at random times - mainly according to EN 459: 2001 "Building lime" - and graphs were drawn correlating parameters with time. The analytical figures have already been reported [3].

Identical lime mortars were manufactured in two phases (A and B), and their technological and mechanical characteristics were studied in the fresh and

hardened state. Standard EN 196-1 sand was used as aggregate with a constant binder/aggregate ratio of 1:2 by volume (or ~1:2.35 by weight) and minimum water demand, controlled by the flow table test.

Five representative high calcium lime samples were selected [2]: four lab manufactured limes calcined at ≤1000°C (M2, D5, B7, K8) and, for comparison, an industrially produced lime calcined at ≤1100°C (K9). M, D, B and K correspond to active limestone quarries.

2.1 Lime binder

2.1.1 Physical characteristics

Free flowing or drained water (or settled water w_s, according to EN 459-2, 5.9) After slaking, in a double-walled slaking vessel with a lid (EN 459-2, 5.9), the drained water (above the lime) at 24 hours was measured (fig. 2). However, it was observed that the samples' water rejection varied noticeably, thus the settled water was also measured on the 2nd, 3rd, 5th, 7th, 10th, 15th day and after 1 month.

Physically bound water (or free water w_F) In high calcium lime putties, w_F is the non-settled water that embraces the molecules of calcium hydroxide like a film and cannot be discarded as settled water or by any mechanical means, except by heating. Free water was measured initially and at random times over two years, according to EN 459-2, 5.11 (EN 459-1, Table 5; gives limits 45%≤ w_F ≤70%).

Consistency of lime putty (or binder water demand w/l^{binder}) Measurements of lime consistency were carried out using a modified Vicat apparatus (ASTM C110: plunger No. 52, diameter 19 mm, weight 32 g, optimum depth of penetration 10 mm). The initial position of the plunger was 100±1 mm. The additional water required for acceptable lime putty consistency was recorded as w/l^{binder}.

Bulk density of lime putty The bulk density of the consistent and homogeneous lime putties was measured in order to accurately estimate the binder/aggregate ratio by weight (BS 890:1972, bulk density <1.45g/cm^3).

Fig. 1 Lime putty samples

Fig. 2 Slaking vessel (EN 459-2, 5.9)

2.1.2 Chemical characteristics

Available lime content (Ka) was determined according to EN 459-2, 4.7.2 (a simple test comparable to the old 'rapid sugar test'). Ka was calculated in terms of percentage CaO by mass. The measurement of lime can be carried out in terms of CaO (in quicklime theoretical max. CaO is 100%) or of $Ca(OH)_2$ (in hydrated lime theoretical max. CaO is 75.69%), but the final assessment should be done in terms of CaO.

DTA-TG measurements of $Ca(OH)_2$ were performed for comparison.

2.2 Lime mortar

2.2.1 Fresh mortar

Mortar water demand (w/l^{mortar}). The more consistent the lime binder is and with the highest possible w_F value, the lower the w/b^{binder} required (binder consistency tested as previously) and therefore the lower the w/b^{mortar} needed (controlled according to DIN 81555 flow table test, so as to give an extension of 15±1 cm for workable mortars).

2.2.2 Hard mortar

Carbonation rate. There is no standard procedure for testing the rate of carbonation [10]. DTA-TG measurements of $Ca(OH)_2$ conversion were used in order to establish a relationship between the degree of carbonation and the mechanical characteristics of the mortar samples.

Mechanical characteristics: compressive (fc) and flexural (f_f) strength. Mortar specimens 40×40×160 cm were manufactured and then cured at a temperature of 20±1°C and 65% RH up to 180 days. Compressive strength was measured at 90 and 180 days by crushing half a prism, following the flexural test (40×40×80 cm).

3 Results and discussion

3.1 Lime binder

3.1.1 Physical characteristics

Free flowing or drained water (or settled water w_s, according to EN 459-2, 5.9**)** Graphs reveal that the rate of free dewatering follows a logarithmic equation y=aLn(x)+b. The constant b directly correlates to the amount of water settled out

at 24 hours, while there is strong indication that both constants (a and b) directly depend on the (known) previous productive phases [2]. However, a broad experimental database is indispensable in order to further document the suggestion. After one month, the rejection of water is almost complete; the majority of water had settled out in 15 days (commercially acceptable aging).

Free water (w_F). The tendency lines are represented by the equation $y=ax^2+bx+c$. It was observed that w_F changes over time, generally inversely correlating to Ka increase. Also, early w_F measurements of lime putties may inevitably include small amounts of water not drained out in cases where non-absorbent (unlike traditional technology) slaking vessels were used.

Binder water demand (w/l^{binder}) and relative bulk density. Generally, it was concluded that the majority of the laboratory prepared lime samples needed a period of 3 to 6 months to obtain optimum consistency (and bulk density). In contrast, industrially produced samples became consistent after 1 to 2 years.

3.1.2 Chemical characteristics

Available lime content (Ka). The tendency lines are also represented by the equation $y=ax^2+bx+c$. Constant c is directly correlated to the initial available lime. The content of Ka increases over time (an increase of up to 40% was measured) obtaining maximum values at 6 to12 months for laboratory limes (after which Ka decreases again); industrially produced lime needed more than 18 months to reach a maximum.

Differential thermal analysis (DTA-TG). This analysis (e.g. measurements of $Ca(OH)_2$ and $CaCO_3$) always gives higher values than Ka. A possible explanation is that this powerful method may include not readily available forms of lime as well. This therefore suggests that DTA-TG measurements should be considered comparatively and carefully in the assessment of building lime putties.

Table 1 Physical and chemical characteristics of lime putties after slaking (*initial*, 15days)

Lime putty	Water rejection $ws_{(24h)}$ ml	Free water w_F %	Consistency NO w/l^{binder}	Bulk density org/cm^3 if yes	Available lime Ka %	DTA-TG $Ca(OH)_2$ % /$CaCO_3$ %
M2	5.0	59.0	NO	1.26	56.3	90.5/ 6.5
D5	12.0	61.5	NO	1.30	65.4	85.4/ 9.0
B7	58.0	63.0	NO	1.27	70.0	87.3/10.3
K8	37.5	53.2	NO	1.36	76.8	91.7/ 3.5
K9	-	-	NO	1.44	-	-

The analytical figures are extracted from my previous analytical contribution [2, 3].
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3.2 Lime mortar

3.2.1 Fresh mortar

Optimal binder performance relies on its free water w_F content (with no need for added w/l^{binder}) for the predetermined consistency combined with the maximum Ka (combined criteria). Both w_F and w/l^{binder} are crucial in achieving the desirable binder's open microstructure that promotes $Ca(OH)_2$ conversion. The w/l^{mortar} required for the predetermined flow table extension in mortars is a less sensitive test, thus, it is imperative to attain putty's consistency before adding the aggregates.

Table 2 Physical and chemical characteristics of lime putties & relevant *fresh* mortars *(Phase A)*

Lime putty	Free water w_F %	Dynamic Ka % (month*)	Consistency binder w/l	Consistency mortar w/l	max Ka % (month*)
M2	49.7	70.0 (9m)	0.35	0.00	78.2 (24m)
D5	45.6	77.1 (7m)	0.00	0.15	77.4 (8m)
B7	59.0	71.9 (4.5m)	0.00	0.11	84.8 (24m)
K8	51.0	79.0 (4m)	0.26	0.00	79.7 (7.5m)
K9	-	- (20m)	NO	0.22	-

Table 3 Physical and chemical characteristics of lime putties & relevant *fresh* mortars *(Phase B)*

Lime putty	Free water w_F %	Dynamic Ka % (month*)	Consistency binder w/l	Bulk density binder g/cm^3	Consistency mortar w/l	max Ka % (month*)
M2	49.2	75.6 (16m)	0.23	1.29	0.17	78.2 (24m)
D5	53.3	70.0 (14m)	0.20	1.32	0.10	77.4 (8m)
B7	55.6	77.0 (13.5m)	0.07	1.28	0.07	84.8 (24m)
K8	41.7	77.4 (13.5m)	0.25	1.34	0.07	79.8 (7.5m)
K9	44.9	64.1 (27m)	0.00	1.45	0.13	-

* months of maturation of lime putties

3.2.2 Hard mortar

Eliminating technological differences by using comparable lime putties, allows more accurate conclusions to be drawn (fig. 3). It seems that both low w_s and high initial w_F encourage the available lime, Ka, to increase over time up to a limit. TGA-DTA measurements in lime putties can only be used comparatively. It

appears that the maturation process will directly influence the carbonation rate in mortar by producing a more or less steadily homogeneous microstructure.

The degree of conversion of calcium hydroxide into carbonate is more likely related to the dynamic K_a (influenced by maturation). Regarding mechanical strengths, it is apparent that they are not analogous to calcium hydroxide conversion into carbonate. Other factors also influence mechanical characteristics e.g. the limestone origin and its relative bulk density, the calcination and slaking maximum temperature (that may affect lime's relative bulk density) [2] or the well-developed morphology of the carbonate [8].

Table 4 Mechanical characteristics of *hard* mortars *(Phase A)*

Lime mortar	Compressive strength 3M* MPa	Flexural strength 3M* MPa	DTA-TG $Ca(OH)_2$ %	Compressive strength 6M* MPa	Flexural strength 6M* MPa	Ratio f_f/fc
M2	1.20	0.66	-	1.96	0.80	0.41
D5	0.90	0.50	-	1.24	0.60	0.48
B7	0.69	0.32	-	0.81	0.43	0.52
K8	1.04	0.56	-	-	-	-
K9	-	-	-	0.91	0.41	0.45

Table 5 Mechanical characteristics of *hard* mortars *(Phase B)*

Lime mortar	Compressive strength 3M* MPa	Flexural strength 3M* MPa	DTA-TG $Ca(OH)_2$ %	Compressive strength 6M* MPa	Flexural strength 6M* MPa	Ratio f_f/fc
M2	1.09	0.54	61.0	1.21	0.64	0.53
D5	0.96	0.46	57.7	0.88	0.48	0.55
B7	0.76	0.30	69.3	0.78	0.36	0.46
K8	1.04	0.36	48.6	1.06	0.37	0.34
K9	1.82	0.65	45.2	2.18	0.76	0.35

* M: age in months of the mortar specimens

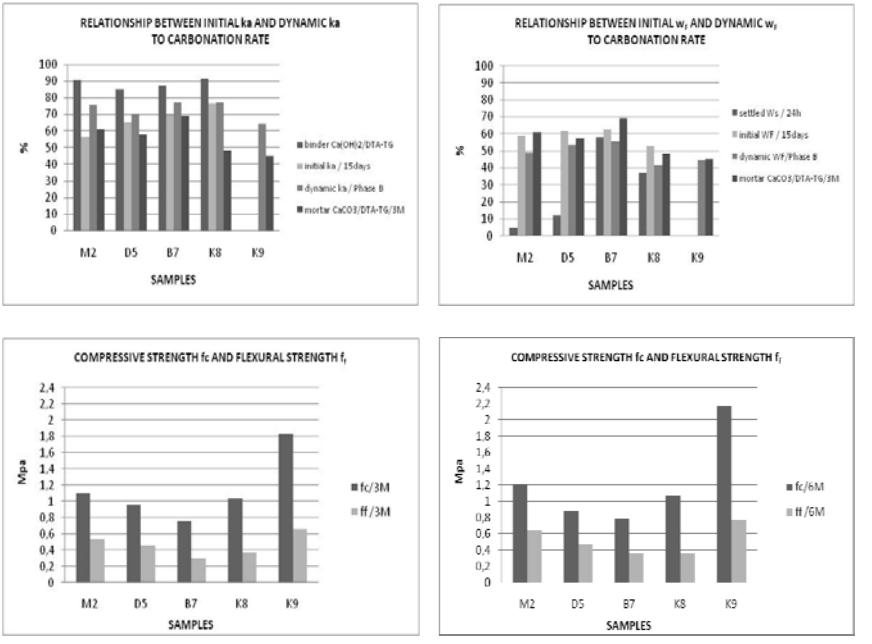

Fig. 3 Correlation of physical, chemical and mechanical characteristics (Phase B)

4 Conclusion

There is strong evidence that as long as the stability of lime's nanoparticle dispersion and the availability of moisture (predominately as stable w_F) – necessary for the dissolution of both carbon dioxide and calcium hydroxide in water - are ensured, carbonation rate accelerates. The resulting high water content in high calcium matured lime putties (calculating in total as w_F, w/b^{binder}, w/b^{mortar}) is responsible for the produced homogeneous and open microstructure and does not, as expected, reduce strength values since it promotes the diffusion of carbon dioxide. Furthermore, the obtained TGA-DTA results in mortars indicate that the degree of conversion of calcium hydroxide into carbonate is more likely related to the dynamic K_a (influenced by maturation). Respectively, limestone origin and the initial value of K_a (controlled by calcination) is the key factor affecting mechanical characteristics, mainly compressive strength f_c. Since flexural strength is a mechanical property very sensitive to internal micro cracking, the resulting high flexural to compressive strength ratio –compared to cement mortars- is due to maturation and ensures the minimization of micro-cracks and contributes to the durability of lime based mortars and their enhanced mechanical properties.

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IV.47

The Effect of Wet Slaked Lime Putty and Putty Prepared from Dry Hydrate on the Strength of Lime Mortars

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Abstract It is generally recognized that wet slaking endows the resulting hydrated lime with a colloidal rather than a crystallized character. It is also known empirically that the conversion of dry slaked (hydrated) limes into putties improves their physical characteristics. However, little scientific information can be drawn from the literature, on the effect that wet slaked lime putty and putty prepared from dry hydrate has on the strength of mortars. Two types of lime binder of the same origin, which were subjected to mild (lab research product) and intense (industrial product) calcinations, were studied. These were produced as a wet slaked binder matured for 2 months in both a non-absorbent plastic bin, and in an absorbent wooden bin (with and without sand) and a dry slaked lime converted into putty and soaked for 24h, used immediately after its conversion, or dry mixed directly with sand. Identical lime mortar mixes were then manufactured and studied. The results indicate that the maturation process mainly enhances flexural strength and also improves compressive strength by increasing the strength development rate. In contrast, dry slaked lime gives lower values for flexural strength.

1 Introduction

Advances in research in the field of nanoparticle colloidal dispersions demonstrate that the particle size distribution and the nanoscale morphology can be controlled to attain improved rheological properties. In this research frame, the slaking procedure indicates the potential to manipulate the character of the produced hydrated limes; i.e. wet slaking promotes the colloidal (sub micrometer to nanometer) dispersion of a lime more than the crystallised nature of the dry hydrated limes [1-3]. The implication of such a difference (colloidal versus crystallised) is related to the irreplaceable properties of the wet slaked limes e.g.

plasticity, workability, high water retentiveness, high sand carrying capacity and high reactivity [4]. In current conservation practice, however, the use of dry hydrated limes is increasingly recommended [5], classified and standardised [6]. This is because these limes harmonise better to the current construction market demands promising, consequently, their economical viability.

Furthermore, it is known empirically that the conversion of dry slaked air-hardening limes into putties also improves their physical characteristics [1, 2, 7]. According to recent research [8], putty deriving from a dry hydrate is susceptible to an aggregation of particles oriented in a particular direction; on the contrary, wet slaked lime putty grains remain randomly oriented generating, as a result, better plasticity and workability. The differences between wet slaked lime putty and the putty made from dry hydrate has been recently investigated scientifically [3, 9, 10]. However, to the best of the author's knowledge, there is no published information differentiating the effect that wet slaked lime putty and the putty made from dry hydrate has on strengths of lime based mortars. The question whether putty prepared from a dry hydrate finally achieves the incomparable qualities of wet slaked lime, should be further investigated.

Within the general framework of research on high calcium limes suitable for repair mortars [7], the present paper focuses on the impact of wet slaked lime putty vs. the putty prepared from dry hydrate, a research based on technological and mechanical characteristics of lime mortars.

2 Materials and methods

The selected methodology of research was based upon knowledge derived from the comparative study and evaluation of the traditional and current local practices in lime production and mortar manufacture (local state-of-the-art) vs. the international scientific literature and experience (global state-of-the-art) [7].

Two types of lime binder of the same origin were selected:

- A lime subjected to mild calcinations (lab research, max t≤1000°C). A wet slaked lime matured for two months with three empirical processes of aging.
- A lime subjected to intense calcination (industrial product, max t≤1200°C). It was slaked to produce a powdered hydrated lime.

For each sample, simple chemical and physical characteristics were taken into consideration, such as:

- a) Available lime content (Ka) according to EN 459-2, Part 2, 4.7.2 (limits exist only for dry forms).
- b) Physically bound water (or free water wF) according to EN 459-2, 5.11 (EN 459-1, Table 5; gives limits 45%≤ wF ≤70%).

- c) Consistency of lime putty (or water demand recorded as w/lbinder) according to ASTM C110 by using a modified Vicat apparatus (plunger No.52, diameter 19 mm, weight 32 g, optimum depth of penetration 10mm).

Identical lime mortars were, then, manufactured and their technological and mechanical characteristics were studied in the fresh and hardened state. Standard EN 196-1 sand was used as aggregate with a constant binder/aggregate ratio of 1:2 by volume (or ~1:2.35 by weight) and a minimum water demand (recorded as w/b^{mortar}), controlled by the flow table test (according to DIN 81555, so as to give extension 15±1cm for workable mortars) (fig. 2). Mortar specimens 40×40×160cm were then manufactured and cured at a temperature of 20±1°C and 65% RH up to 180 days. Compressive strength was measured at 90 days by crushing the half prism 40×40×80cm, following the flexural test.

2.1 Wet slaked lime putty

The wet slaked lime was matured in three different ways:

- 1) In a non-absorbent plastic bin for two months (code 50a)
- 2) In an absorbent wooden bin for two months (code 50b)
- 3) As (2), and then maturing with sand for 5 days (code 50c)

Table 1 Chemical and physical characteristics of lime putties and relevant fresh mortars (50, 2m*)

Lime putty	Available lime Ka %	Free water w_F %	Consistency w/l^{binder}	Consistency w/l^{mortar}	Total w/l
50a	-	-	0.00	0.05	0.05
50b	75.9	54.9	0.40	0.00	0.40
50c	75.9	54.9	0.40	0.00	0.40

* m: months of lime putties maturation

The first way corresponds to a common, current, market practice, where lime is packaged in non-absorbent plastic bags (15 days at the most, after slaking). It is characterised by a slow maturation process.

The second sample represents the traditional technology, where slaking and maturation often took place in absorbent soil pits. During its maturation, the soil sides and bottom function as thermal insulators allowing, in parallel, the soluble salts (sodium, potassium and chlorides) to be absorbed by the surrounding soil water in the form of free flowing water or drained water (or settled water w_s according to EN 459-2, 5.9) [6, 7, 11], while heavier particles (i.e. usually under burnt cores) settled on the bottom. The produced putty was as homogeneous as possible, with a minimal amount of soluble salts, thus decreasing the possibility of

efflorescence from mortars [1, 12]. This procedure was indispensable when the water used for slaking was not clear.
The third practice has been recorded both in local and global [1, 2, 7] current practices, as is considered to enhance both the mortar plasticity and sand carrying capacity. The two latter cases are characterised as 'forced' maturation processes.

2.2 Dry slaked lime

The dry slaked lime was treated in three different ways before mortar manufacture:

- 1) Converted into putty and soaked for 24h (code Ta)
- 2) Used immediately after its conversion (code Tb)
- 3) Dry mixed directly with sand (code Tc)

The first practice has been recorded both in local and global current practices, for improving mortar plasticity and workability in the fresh state [1, 7].

The second practice represents a transitional technology between traditional techniques of lime (putty) mortar preparation and modern dry mortar manufacturing knowledge.

The third way corresponds to common practice on today's sites (modern ready to mix or ready to use dry mortars), where dry hydrated lime is mixed directly with sand, adopting an approach similar to the production of cement mortars.

Table 2 Chemical and physical characteristics of lime putties and relevant fresh mortars (T)

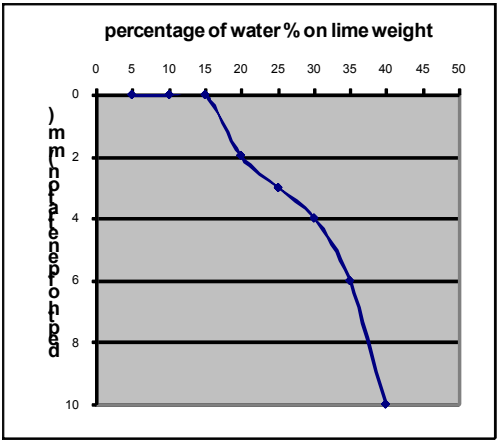
Lime putty	Available lime Ka %	Free water w_F %	Consistency w/l ^{binder}	Consistency w/l ^{mortar}	Total w/l
Ta (24h)	75.2	-	0.54	0.10	0.64
Tb (putty)	75.2	-	0.30	0.17	0.47
Tc (dry)	75.2	-	-	0.47	0.47

3 Results and discussion

As the samples are of the same origin, the available lime (a simple test comparable to the old 'rapid sugar test') and free water measurements do not vary. Also, the aggregate is not a variable as a standard sand was used. Differences exist in the binder water demand in order to obtain a standard consistency. Code 50a became consistent without adding any water, while 50b and 50c needed water up to 40% of the lime weight. It is recommended that in such tests the water should be added gradually (per 5% and 2 min stirring), as it was concluded that a larger

amount of water destroys consistency of lime (the plunger penetrates abruptly after 2 min stirring) (fig. 1). It is expected, though, that longer mixing periods will improve the cohesiveness of the binders.

Tables 3 and 4, present the physical characteristics of mortars and the results of the mechanical tests, based on the mean value of three measurements for flexural strength (fig. 3) and of six measurements for compressive strength.



Code 50b – 50c

w (%)	**depth** (mm)
5	0
10	0
15	0
20	2
25	3
30	4
35	6
40	10

Fig. 4 Correlation of depth of penetration (mm) to added water (%) after 2 min stirring

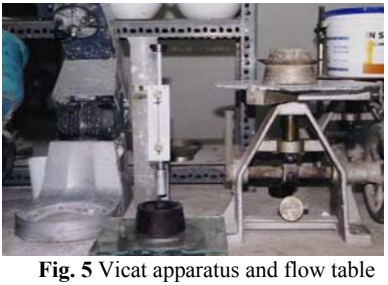


Fig. 5 Vicat apparatus and flow table

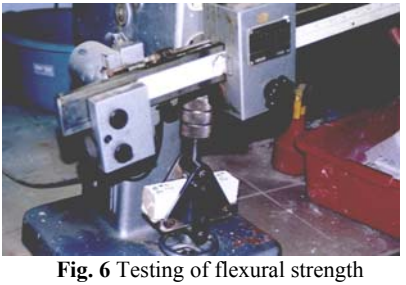


Fig. 6 Testing of flexural strength

Table 3 Physical and mechanical characteristics of wet slaked mortars after 3 months curing

Lime Mortar	ΔV %	Bulk density g/cm^3	Dynamic modulus Ed (GPa)	Flexural strength f_f (MPa)	Compressive strength fc (MPa)	Ratio f_f/fc	Indice fc/Ed
50a (2m)	-4.04	1.66	3.32	0.38	0.71	0.53	0.22
50b (2m)	-6.67	1.68	2.61	0.33	0.92	0.36	0.35
50c (2m)	-7.45	1.63	2.50	0.37	1.22	0.30	0.49

* m: months of lime putties maturation

Table 4 Physical and mechanical characteristics of dry slaked mortars after 3 months curing

Lime Mortar	ΔV %	Bulk density g/cm^3	Dynamic modulus Ed (GPa)	Flexural strength f_f (MPa)	Compressive strength fc (MPa)	Ratio f_f/fc	Indice fc/Ed
Ta (24h)	-5.84	1.66	2.83	0.30	0.68	0.44	0.24
Tb (putty)	-4.68	1.82	5.28	0.11	1.26	0.09	0.24
Tc (dry)	-4.01	1.87	5.45	0.11	1.10	0.10	0.20

The final water content in the fresh mortar should be calculated in total as w_F, w/b^{binder}, w/b^{mortar}. This total of high water regulates the porosity, strength development rate and ultimate strengths [4]. Also, it is responsible for the produced open microstructure and does not, as expected, reduce the strength values since it promotes the diffusion of carbon dioxide.

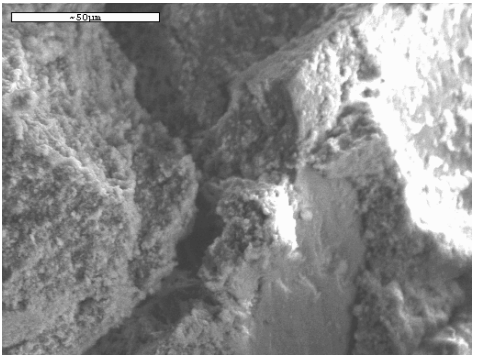
Samples 50a (due to a slow maturation process and the consequent high consistency), Tb and Tc (due to their denser microstructure and higher bulk density) have better volume stability. This fact implies that empirical knowledge, i.e. forced maturation processes or practices aiming to improve binders' plasticity and consistency in the fresh state does not necessarily improve all the physical characteristics of the hardened state of the mortars.

According to the mortar flexural strength results f_f, it is apparent that the implementation of any kind of maturation practice (slow or forced) has a positive effect on flexural strength. Higher values were obtained through the slow maturation process.

Samples 50c and Tb exhibit higher compressive strength, fc, for different reasons; the former relies on the obtained open microstructure that supports rapid and efficient carbonation, while the latter on its dense microstructure. This is affirmed because the degree of conversion of calcium hydroxide into carbonate is the predominant, but not the unique factor controlling the strength of the binder. Superior binder mechanical characteristics are also attributed to the morphology of the carbonate e.g. well-developed crystalline structures and crystal habits promoted by CO_2 gas pressure, exposure time or degree of compaction [4, 7, 13, 14, 15]. It seems that internal cracking (fig. 4) (high flexural strength prohibits rapid cracking development) does not directly affect the compressive strength test but only the fracture mechanism (fig. 5).

The most crucial observation is the low f_f/fc ratio of mortar samples Tb and Tc, which are comparable to those of modern cement mortars. All the other samples – in which the lime was subjected to some kind of maturation process present a high ratio of f_f/fc, a fact that suggests elastic-plastic behaviour. This performance corresponds inversely to their dynamic modulus of elasticity; high for Tb and Tc and low for the rest of the samples. Finally, the potential indices of mechanical behaviour fc/Ed reveal that wet slaking and matured samples tend to give higher

ratios, a suggestion that was demonstrated within the general framework of research on high calcium limes.



fc =1.10 MPa
f_f =0.11 MPa
Ed= 5.45 GPa
f_f/fc =0.10
fc/Ed =0.20

Fig. 7 Tc, dense mortar microstructure and internal cracking in the lime matrix

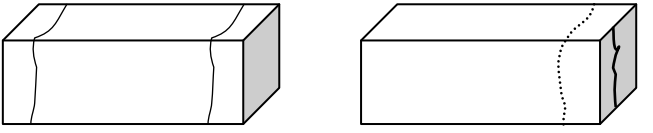


Fig. 8 Fracture mechanisms in the compressive test: plastic on left, (codes 50) and brittle on the right (codes T)

4 Conclusions

The results indicate that the lime maturation process not only enhances the flexural strength of mortar, but also improves the compressive strength though indirectly, by promoting the strength development rate. Higher flexural strengths were obtained through a slow maturation process. In contrast, dry slaked lime gives much lower values of flexural strength.

There is evidence that a higher compressive strength may be attributed to either to an open homogeneous microstructure and/or to a dense microstructure. An open microstructure is due to a high water content in lime mortars (mainly w_F or w/b^{binder}) that supports rapid, efficient and extensive carbonation and also promotes a well-developed morphology of the carbonate; it suggests a more elastic-plastic behaviour, where internal cracking is restrained by the higher flexural strength. A dense microstructure is due to a high degree of compaction

and/or to a high bulk density of the binder; it implies a brittle behaviour, concurrent with the rapid development of internal cracking.

Samples that have been subjected to some kind of maturation process acquire a higher total water content, open microstructure and a higher ratio of f_f/fc, which finally confers a better elastic-plastic mechanical behaviour on the mortar.

5 Acknowledgments

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IV.48

Historic and Modern Injection Grouts Used in Poland for Wall Painting Conservation

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Abstract Despite of over forty years of research on over the world, the ideal grout for re-adhesion of delaminated wall paintings has not been invented. Along with the industry development, traditional and already historic additives such as casein have been replaced by synthetic resins. Additionally old type recipes created by practicing conservators have been forgotten and squeezed out by commercial, ready to use, injection grouts. Due to the ease of application process those grouts were quickly accepted by conservators, sometimes without running a detailed analysis of their effect on specific historic object. The aim of this article is a revision of historic and modern injection grouts prepared and used by conservators for re-adhesion of wall paintings based on lime. The authors would like to pay more attention on grouts used in Poland in years 1950 - 2010. The research will be more interesting due to geographic location and political and economic aspects. Poland is an example of a country that has been under influence of trends from East and West of Europe. Lack of appropriate resources on the market in the past resulted in motivation for many experiments.

1 Introduction

The process of gluing detached wall paintings is based on placing a series of injections of a specific gluing material under the surface of the plaster. The injection of an appropriate grout is used with extreme caution, because once applied, it is very difficult to remove. In practice the material affects the historical object irrevocably and can to a certain effect change its properties.

The history of wall painting conservation throughout the world illustrates the fact that the application of a wide variety of separate substances has been used in order to rescue detached and delaminated wall paintings from total destruction.

Among the most common materials used for grouting are those based on mineral binders (lime, cement, gypsum), organic binders (casein), or synthetic resins (acrylic, vinyl, epoxy resins, polyurethane) blended with a different addition or combination of fillers i.e.: sand, crushed brick or marble powder. This variety of materials has been applied to different types of paintings. In Poland there are paintings mainly based on lime mortar with sand and additives such as: cement, gypsum, crushed brick, wood, carbon, reed or hair. These substances are applied to brick, stone, or wood mixed with reed. Wood and reed as a basis for mortar has widely been used for antique wooden ceilings. Painted layers have been applied either on wet plasters in a technique of fresco or sgraffito, or on dry plasters, using lime, casein, egg tempera or even oil as a binder. Conservation records refer to the use of a mixed technique for painting on wet and dry plasters. In the case of the more modern paintings we often encounter binders based on synthetic resins or liquid silicates.

The wall paintings in Poland, similarly to those in other countries of Europe, may be located outside or inside secular or sacred rooms, as well as within areas of public buildings. The individual character of every painting is particularly valuable and this should be considered before taking decisions about any plans that concern conservation work; as should any information about previous conservation work carried out on a painting.

2 Historical overview of methods for the re-attachment of wall paintings

Years have passed since the combination of different injection grouts supplanted the use of mechanical adhesives applied to detached plasters. Such reinforcement can include anchors, bolts and even threads. Now, we can conclude that these materials affected the aesthetic clarity of the paintings, and that there were limitations to the scope of their use. However each method fulfilled its role and proved to be less invasive for the structure of the paintings than the more modern injection grouts.

The information below presents facts relating to the materials used in Poland for injection. Statistics of the materials used for gluing the wall paintings have been collected on the basis of the documentation of conservation work carried out since 1950 to the present, published studies, and oral communication between fellow restorers (Table 1). Documentary research is limited to the districts of Cracow, Warsaw and Torun. The selection of these cultural centres is closely linked to the highly regarded conservation training institutes of the Academy of Fine Art in Cracow and Warsaw and the Nicolaus Copernicus University in Torun. The statistics include paintings on mineral substrates (lime-sand mortar on brick walls or masonry) but do not consider wall paintings on wooden supports. The review includes paintings located inside and on the facades of churches and

public buildings. Although the duration of the project was limited and the complete documentation could not be obtained, the collected data is sufficient to show a trend.

Table 1 Materials used in Poland for re-adhesion of wall paintings between years 1950- 2010.

Injection Grout	Number of used materials during years:					
	1950-60	1961-70	1971-80	1981-90	1991-2000	2001-2010
Lime-sand mortar	0	0	0	0	0	1
Lime-sand mortar + white cement + acrylic emulsion + chalk	0	0	0	0	1	0
Lime-sand mortar + Primal AC 33	0	0	1	0	0	1
Lime-sand mortar + polyvinyl acetate	0	0	2	0	0	0
Lime caseinate	1	1	1	0	0	0
Polyvinyl acetate (emulsion)	1	3	12	13	14	1
Polyvinyl acetate+ chalk	0	0	0	1	0	0
Polyvinyl acetate + chalk + marble powder	0	0	2	0	0	0
Osakryl KM	0	0	0	0	5	0
Vinavil NPC	0	0	0	0	1	2
Vinavil NPC + chalk + marble powder	0	0	0	0	0	1
Vinavil + Mowilith + chalk	0	0	0	0	0	1
Polivinyl alkohol	0	0	0	0	1	1
Polivinyl alcohol + silica powder + calcium carbonate + chalk	0	0	1	0	0	1
Primal AC 33	0	0	1	2	6	7
Primal AC 33 + chalk	0	0	1	0	0	0
Primal AC 33 + marble powder	0	0	0	0	0	1
Malta 6001	0	0	0	0	10	2
Ledan TB1	0	0	0	0	0	7
Rhoplex N560	0	0	0	0	1	1
Dispersed lime	0	0	0	0	0	1
Albaria Iniezione 100	0	0	0	0	0	1

The least amount of recorded documentation concerning the treatment of gluing the murals was found for the years 1951-1970 (Fig. 1). This was due to the

post war political and economic situation of Poland at the time when many cities including the capital were undergoing great periods of reconstruction. In Warsaw, most of the monuments along with many important murals were destroyed. The restoration of monuments and the creation of novel paintings took precedence over conservation projects. During this period, for example, decorations on the facades of most of the buildings in Warsaw's Old Town were created. In other cities, the conservation tasks were limited to those deemed most important. Much of the documentation from this period was not saved; the oldest documentation of the results is from the year 1952.

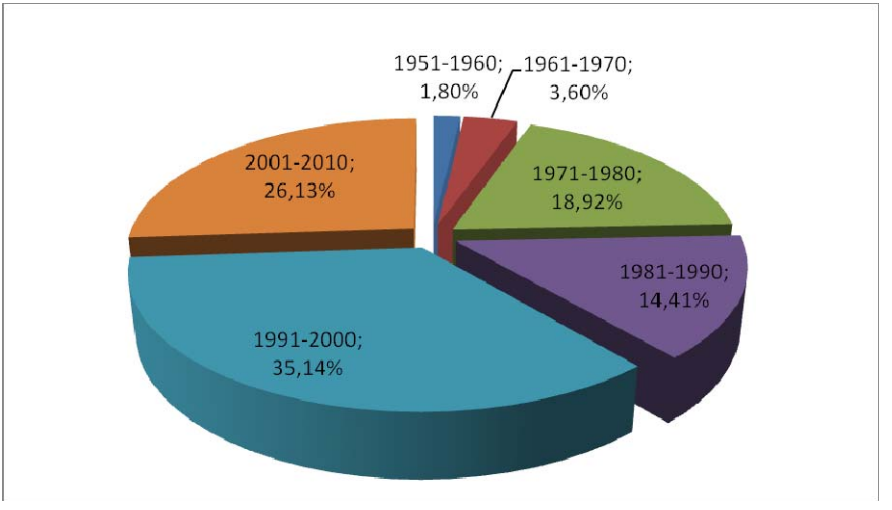

Fig. 1 Percentage of gluing tasks based on documentation of conservation works sorted by years.

2.1 Materials used during 1951-1960

Among the materials used for gluing the paintings during 1950-1960, cement and lime-sand mortar are said to have been applied to large detached areas and lime caseinate to the smaller areas. The biggest advantage of lime-sand mortar is its compatibility with the historical material. It was used rarely, probably due to the difficult injection process and its poor penetration. Lime caseinate was considered more preferably up to the 1970s. Casein binder was applied to provide re-adhesion of delaminated plaster or to fill voids between the plaster and brick support. It was also used to bond flaking paint layers to the plaster.

The preparation process requires experience and time, and even after the addition of antiseptic additives, the casein binder is required to be stored for a short time at low temperatures.

It was recognized from the early years that this compound had one major disadvantage; it requires a long binding time, e.g. 48 hours minimum, requiring the painting to be kept under pressure after injection. However the use of lime injection grouts did not cause stains at the paint layer; this was one of the greatest advantages of this substance.

2.2 Materials used in 1961-1990

In the 1960s synthetic resins appeared more progressively on the Polish market. This is evident from the data (table 1). Among the resins, polyvinyl acetate produced as Mowilith (Farbwerke Hoechst A.G), Afcolac (Ciba A.G) Vinavil NPC (Mantacatini - Edison) and Winacet (Zakłady Chemiczne Oświęcim) became popular, but polyvinyl alcohol and acrylic resins such as: Primal AC 33 (Bresciani), Rhoplex N560 (Rohm & Haas) and Osakryl KM (Zakłady Chemiczne Oświęcim) were also in use. Unfortunately, many documents lack detailed information as to the concentration and origin of each product, making it impossible to give a detailed description of the substances.

Extremely simple to prepare, ease of storage, and an effortless injection process earned many supporters among the practitioners of resin emulsions. The emulsions were used for consolidation and re-adhesion detached surfaces. Gluing effects were fast and in most cases did not require the application of pressure after injection.

Resins in aqueous dispersions were easily penetrating, had less coverage and were suitable for narrow slits, where the lime-based grouts with marble powder, chalk or casein and lime with sand, were difficult to access. Larger detached areas were treated with water dispersions of resins with the addition of chalk and powdered marble. The advantages of these, however, were soon verified. The commonly used polyvinyl acetate turned out to be useless or even harmful when applied to paintings on the exposed facades of buildings. The case of the conservation of the sgraffito facade at the castle in Krasiczyn demonstrates a direct cause of the emergence of secondary delamination and surface deformation after the application of polyvinyl acetate. It was noted that the destruction is linked to plastic membranes clearly pushing out and deforming the sgraffito surface. When injected, large quantities of plastic set in the structure of the plaster in the form of membranes of various sizes and thicknesses, these were located at different distances from the face, often in multilayer form [1]. The plastic membranes were also a cause of limited water vapour permeability. Usage of water emulsion resins for gluing resulted in their penetration of the layers of paint, which sometimes created a significant darkening effect of the glued part of the object.

2.3 Materials used in 1991-2010

After 1990 commercial mineral products appeared on the Polish market. On the basis of documentation and oral communication with conservators it can be concluded that the most common are Malta 6001 (Bresciani) and Ledan TB1 (Tecno Edile Toscana). Among the advantages is an alkaline pH similar to lime-sand mortar, and a resistance to microbial attack. In addition they have similar parameters to water vapour regarding permeability and absorption. But Ledan TB1 may cause stains due to a prolonged drying time. The much higher resistance to compression and tear of Ledan TB1 can cause damage when used for adhering detached plasters with a weak cohesion [2]. In practice Ledan TB1 penetrates detached areas very well and is easy to apply during the injection process. These facts are also confirmed by laboratory tests [3]. In dilution it is used to consolidate plaster.

After 2000, Albaria Iniezione 100 (MAC) came on to the market as did dispersed lime. Albaria Iniezione 100 binds rapidly; its suitability for use is about 30 minutes, which may be an advantage for rapid, necessary intervention. Drilling Resistance Measurement on replicas filled with Albaria Iniezione 100 [4] revealed that this grout has a significantly higher resistance to drilling in comparison to lime-sand mortar with a low ability to fill narrow slits. For the last several years, grouts from PLM series (CTS) have also been brought to the Polish market. The laboratory studies of PLM-A, PLM-AL, PLM-I [3] showed E-modulus and biaxial flexural strength values similar to the lime-sand mortar. The capabilities of these are much less penetrating than those of Ledan TB1. In the researched documentation, however, no record of their use in practice was found; these therefore have not been included in the research (Table 1).

3 Direction of future research

Before injecting the substance into an object one should closely examine the historical parameters of the plaster and take into account the individual characteristics of each of the known methods of gluing murals. Please also note that any restoration interference alters these parameters irreversibly and the quality of the work and the objects rate of survival for the future are reliant on the overseer of such projects. Ill conceived decisions or substandard interventions would contribute to a more rapid destruction of the ancient object. Despite many studies on injection grouts there are still many unresolved problems.

Compatibility of materials for the consolidation and injection of both disintegrated and delaminated plasters is a key issue. Are today's commercial injection grouts able to meet these requirements simultaneously? The lack of data regarding the effects of injection and the change of optical properties of painting

layers in the case of synthetic resin emulsion confirms that this is a problem worthy of attention.

Re-attachment of paintings on plaster and wooden supports, where historically materials of different characteristics (such as the lime-sand plaster, reed or straw and wood) have been assimilated is a problem that affects a number of monuments in Poland.

No accurate register of glued surfaces exists and because of this it is not possible to verify the effectiveness of various conservation treatments conducted over the previous years.

Lack of multi-annual monitoring of changes, the factors that have an influence on success or failure during the conservation process and information on whether and how long they satisfied the required needs combined with a lack of information on the impact after using different substances in the same building along with insufficient information about custom mixed grouts and their impact on the historic mortars in changing conditions, leads to a failure to determine a successful conservation strategy. Such a problem will become more apparent with the passing of the years and the increasing number of conservation interventions. Linked to this is another, larger problem - how to maintain objects already preserved?

These are just some of the dilemmas that are and will be a challenge for conservators and scientists in the future. This article is a brief summary of information on the injection grouts used in Poland and an introduction to planned future studies on the more detailed characteristics of the injection grouts for gluing murals. There is still a need for research into grouts with properties similar to the lime-sand mortars – as these are less harmful for the wall paintings.

4 Summary

The market for grout is constantly developing and improving. During the study period, injection grouts have evolved consistently. The components for improving the penetration depth, water permeability, resistance to a climatic conditions and microorganisms have transformed. Contemporary conservation has to deal with increasingly sophisticated tasks, as it concerns objects that have been repeatedly exposed to conservation treatment. At present the main problem for scientists and conservators is not only to strengthen a historic structure but to discern and react to the condition of objects influenced by previous conservators' interference. It is obvious that conservation has been influenced by different trends in the past, not always ideal for historic objects. It is a critical point for conservationists to consider the material that has been used by our ancestors in the past to be able to give the solution for the kind of problems we will have to deal with in the future during forthcoming conservation interventions.

5 Acknowledgements

The data gathered in Table 1 has been prepared based on information found in the documentation of the conservation works provided by the following institutions in Poland: Wojewódzki Urząd Ochrony Zabytków in Cracow, Torun and Warsaw, Biuro Miejskiego Konserwatora Zabytków in Torun, Akademia Sztuk Pięknych in Cracow, Uniwersytet Mikołaja Kopernika in Torun. The authors would like to thank these institutions for making their archives available.

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IV.49

Nano-Lime - a New Material for the Consolidation and Conservation of Historic Mortars

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Abstract The consolidation and conservation of historic mortars requires materials which are compatible with the components originally used. The application of nano-lime offers such a possibility. Lime nano-particles are stable when dispersed in different alcohols. The particles have sizes ranging between 50 and 250nm. Typical concentrations in such dispersions are between 5 and 50g/L. Ethanol, n-propanol and iso-propanol are used as solvents. Treatment of mortar with nano-lime results, after evaporation of the alcohol, in the formation of solid calcium hydroxide. This converts into $CaCO_3$ in a way similar to traditional lime mortars by reaction with atmospheric carbon dioxide. The solvent evaporates without leaving any unwanted residues. Another possibility to consolidate mortar is the combined treatment with esters of silicic acid. The calcium carbonate nano-particles formed after the nano-lime treatment catalyse the gel formation resulting in improved mechanical properties. This paper gives an overview of the typical properties of calcium hydroxide nano-sols and summarises a number of laboratory tests on them.

1 Introduction

Historic mortars and plasters are of manifold composition. Typical binders are lime, hydraulic lime and calcium sulphate. Deterioration by either erosion or weathering can result in damage of various kinds which can require different conservation and strengthening approaches. The main challenge is the consolidation of surfaces in which the particles comprising the mortar are no longer bound as well as the structural consolidation of loose zones, for example behind crusts and shells [1-2].

At present, esters of silicic acid are the most favourable material for the consolidation of mortars and plasters. Their application, however, is not without

problems. One aspect that has to be considered is the formation of hydrophobic surfaces after the application. Conversion back to hydrophilic surfaces requires days to weeks to occur and is dependent on the product used, its concentration and the climatic conditions [3].

The use of lime water as a consolidant has been discussed for many years, however, lime water contains not more than 1.6 g/L $Ca(OH)_2$ and the resulting consolidation effect is low. Additionally, large volumes of water are added to the treated areas which may result in new damage [4-5]. Barium hydroxide ($Ba(OH)_2$) has a much higher solubility (80 g/L) and reacts in a similar manner to $Ca(OH)_2$ with atmospheric carbon dioxide resulting in the formation of insoluble carbonates [6]. Deep penetration into mortar may be difficult to achieve due to its high reactivity with even traces of sulphate ions being spontaneously converted into $BaSO_4$. Alkali silicate solutions (water glass solutions), which form insoluble, amorphous silicates in contact with calcium or magnesium ions or silicic acid after mixing with acids, are strongly alkaline. The formation of silicic acid can also be caused by reactions with carbon dioxide. The penetration depth of water glass solutions is low. In addition, the formation of soluble salts is, along with the high alkalinity, the main disadvantage that prevents their use for the consolidation of mortar and stone [7].

One potential alternative for the consolidation and conservation of mortars and plasters is the use of suspensions of nano-sized lime particles, termed nano-lime. Products based on nano-lime are commercially available under the trade name "CaLoSiL" (producer: IBZ-Salzchemie GmbH & Co.KG, Germany). The letters behind the name indicate the used solvent; numbers associated with the product code give the total calcium hydroxide concentration in g/L. For example, E-25 means, 25 g/L calcium hydroxide dispersed in ethanol. This article will summarise typical properties of CaLoSiL and gives an overview about possible applications.

2 Experimental

The following methods and tests were used to characterise the properties of sols containing nano-lime:

- *Particle size distribution*: All measurements were performed using a Beckman Coulter Laser Diffraction Particle Size Analyser LS 13 320. Ethanol served as the solvent.
- *Density*: Conventional density determination by pycnometer was used.
- *Viscosity*: The viscosity was determined with the Brookfield DV-II viscometer at 25°C.
- *Zeta-potential*: The surface charge of the nano-lime particles in ethanol was determined by using the Field ESA system from PA Partikel-Analytik-Messgeräte GmbH.

The following tests were used to characterise the consolidation effect of calcium hydroxide nano-particles:

- *Consolidation of loose sea sand*: Plastic O-rings having a height of 1 cm were placed on a glass plate and filled with sea sand. Either CaLoSiL and / or the silicic acid ester were then introduced by applying them drop-wise onto the surface of the sand until the sand was fully saturated (Fig. 1).
- *Consolidation of mortar samples*: Mortar prisms with the dimensions 4 x 4 x 16 cm were prepared using sand and lime hydrate mixtures. Conventional concrete sand with a particle size < 2 mm served as the aggregate. The tests to characterise the achievable consolidation by nano-lime were carried out on prisms prepared using a volume ratio of sand to lime hydrate of 5:1. A volume ratio of 2.5:1 was selected for the tests of the combined treatment with nano-lime and silicic acid esters. All samples were stored for three months at atmospheric conditions and room temperature. The process of carbonation was followed by the periodic testing of samples that had been fractured by treatment with phenolphthalein. All treatments with esters of silicic acid were performed four weeks after the application of CaLoSiL. Funcosil 300 (producer: Remmers, Germany) and SILRES® BS-100 OH (producer: Wacker, Germany) were selected for the tests. Both the nano-lime suspension and the esters of silicic acid were applied as droplets onto the surface of the prisms until saturation was achieved. The consolidant uptake as well as the amount of calcium hydroxide / silicic acid ester precipitated was determined by the change in weight.

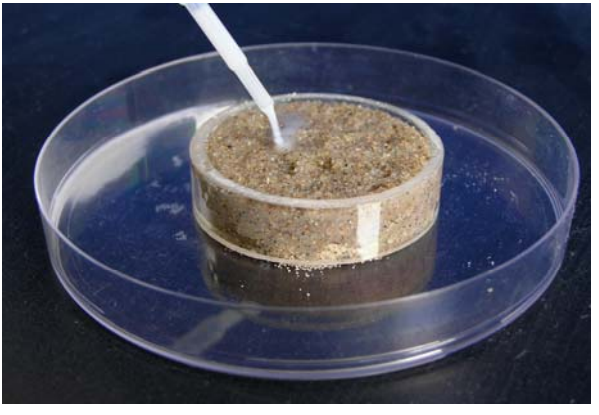

Fig. 1 Application of CaLoSiL onto the surface of an O-ring filled with sea sand

3 Results

3.1 Characteristics of nano-lime suspensions

Nano-lime suspensions are white to opal solutions containing stable dispersed calcium hydroxide nano-particles. A typical particle size distribution of nano-lime is given, in comparison to a conventional lime slurry, in Fig. 2. The extremely fine size of synthetic nano-lime results from its preparation, which is based on chemical synthesis. The particles are stable when suspended in ethanol, iso-propanol or n-propanol. Typical concentrations are in the range between 5 and 50 g/L.

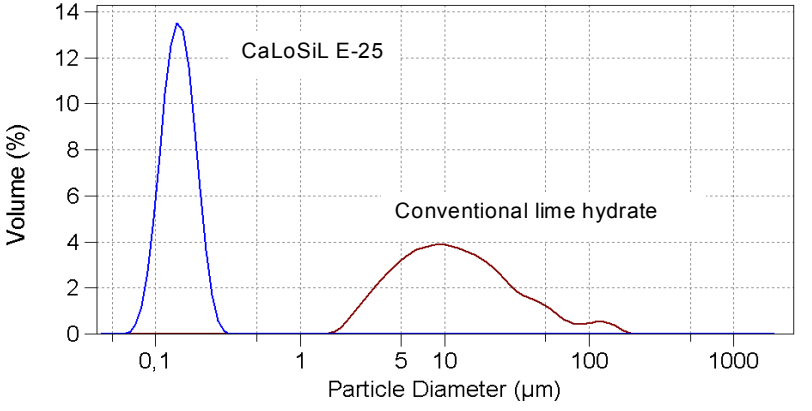

Fig. 2 Particle size distribution of nano-lime and conventional lime hydrate

Due to the small particle size stable sols are formed, meaning that the solids do not settle for a long time. Zeta-potential measurements have shown that calcium hydroxide particles have a positive surface charge in alcoholic solvents. The stability of the nano-lime suspensions is due to electrostatic repulsion. As long as these remain stable, the sols do not settle and a shelf life of between three and five months is possible.

Typical properties of different calcium hydroxide nano-sols are given in Figs. 3 and 4. As one would expect, the density (Fig. 3) of the sols increases with increasing solids content. The same is the case for the dynamic viscosity, whereas the absolute values remain low. This means, the flowing behaviour is only slightly impacted by the nano-particles.

After evaporation of the alcohol, nano-lime particles remain in treated materials. These react with atmospheric carbon dioxide in the same manner as conventional lime resulting in the formation of calcium carbonate.

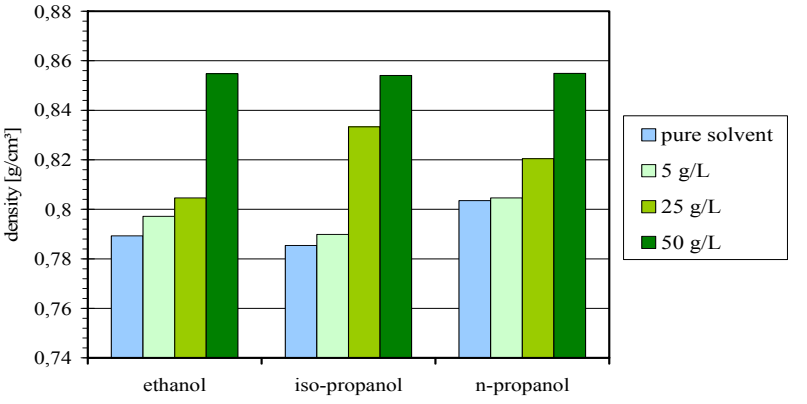

Fig. 3 Density of lime nano-sols depending on the concentration and the solvent

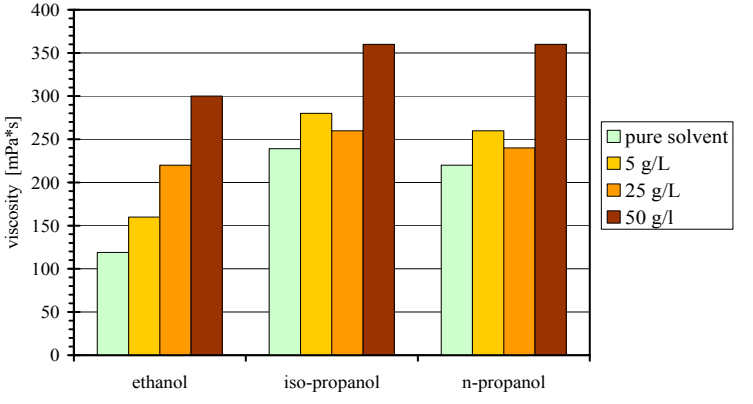

Fig. 4 Viscosity of lime nano-sols depending on the concentration and the solvent

3.2 Consolidation by carbonation

Due to the small particle sizes of the suspended lime the sols were able to fully penetrate the mortar samples. The change in compressive and bending strength as a result of the treatment with different types of CaLoSiL is summarised in Table 1. As expected, the consolidation effect increases with the increasing calcium hydroxide content of the sols, although the total relative increase in compressive and bending strength was low. However, this needs to be considered in respect to the total amount of binder brought by the sol into the prisms. The average absorption of the prisms was between 35 and 40 mL nano-lime sol. At a concentration of 25 g/L a total mass of calcium hydroxide of between 0.8 and 1.0 gram was introduced into the mortar samples following one treatment. It is clear

that such low amounts produce only a small increase both in compressive and bending strength.

Table 1 Mechanical properties of mortar prisms after the treatment with nano-lime sols.

Treatment process:	Compressive strength [N/mm²]	Bending strength [N/mm²]
Reference sample	1.1 ± 0.1	0.26 ± 0.05
Two treatments with CaLoSiL E-25	1.4 ± 0.05	0.54 ± 0.05
Two treatments with CaLoSiL E-25 and storage under elevated CO_2-atmosphere (1 vol.-% in air)	1.35 ± 0.05	0.52 ± 0.05
Two treatments with CaLoSiL IP-12.5	1.25 ± 0.1	0.55 ± 0.05

3.3 Consolidation by combined application of CaLoSiL and silicic acid esters

The use of calcium hydroxide offers the possibility of the alkaline hydrolysis of silicic acid esters. This reaction should be much faster than hydrolysis by moisture. The question is: Will the silicic acid gel formed by this reaction produce a consolidation effect? To test such a conservation strategy, sand treated with a first application of nano-lime suspensions (CaLoSiL), was then treated using different commercially available silicic acid ester-based products. The consolidation effect as well as the surface characteristics was assessed visually.

The treatment with CaLoSiL produced a first consolidation. Loose sand particles were bridged together and a solid, non powdering surface was formed. The penetration behaviour of all of the silicic acid esters tested was not disturbed by the pre-treatment with CaLoSiL. The sand was fully penetrated, both by Funcosil 300 and Wacker Silres BS-100 OH. As Fig. 5 shows, the loose sand particles were converted into a solid mass.

Fig. 5 Sea sand consolidated by CaLoSiL E-25 and the silicic acid ester Funcosil 300 from Remmers

SEM investigations have shown a morphology of the formed silicic acid similar to that achieved by conventional hydrolysis with moisture (Fig. 6). EDX-Analyses of the amorphous material between the sand particles have indicated that the calcium containing phases are fully incorporated into the silicic acid structure.

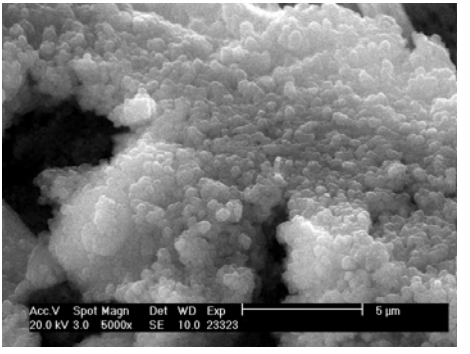

Fig. 6 SEM micrograph of sand particles fully covered by amorphous silicic acid resulting from the combined treatment with CaLoSiL E-25 and Funcosil 300.

Table 2 Mechanical properties of mortar prisms after treatment with nano-lime sols and esters of silicic acid (all data are the mean values of 3 different samples).

Test-No.	1. treatment	2. treatment	E-modulus untreated [kN/mm²]	E-modulus [kN/mm²]	Comp. strength [N/mm²]	Bending strength [N/mm²]
0	reference sample		7.98	-	4.3 ± 0.3	1.3 ± 0.1
1	CaLoSiL IP 12.5	CaLoSiL IP 12.5	7.13	8.54	3.6 ± 0.3	1.4 ± 0.1
2	CaLoSiL IP 12.5	Wacker BS OH 100	6.66	11.88	8.2 ± 0.15	1.9 ± 0.1
3	CaLoSiL IP 12.5	Funcosil 300	7.17	12.47	6.7 ± 0.4	2.7 ± 0.15
4	CaLoSiL E 25	CaLoSiL E 25	7.52	8.26	4.3 ± 0.4	1.2 ±0.1
5	CaLoSiL E 25	Wacker BS OH 100	7.61	11.81	8.8 ± 0.15	2.9 ± 0.3
6	CaLoSiL E 25	Funcosil 300	7.48	11.11	8.4 ± 0.3	2.7 ± 0.1
7	Funcosil 300	Funcosil 300	7.83	13.51	10.6 ± 0.15	2.6 ± 0.2

The lime – sand prisms used for the characterisation of the effect of a combined treatment with CaLoSiL and silicic acid esters were characterised by a compressive strength of 4.3 N/mm² and a bending strength of 1.3N/mm².

Two pre-treatments with either CaLoSiL E-25 or CaLoSiL IP-12.5 did not produce an increase in the compressive and bending strength (tests 1 and 4, Table. 2). In the mortar prisms treated initially with CaLoSiL E-25 followed by the application of Funcosil 300 and Silres BS-100-OH, respectively, a significant consolidation effect was observed. The increase in compressive and bending strength correlates very well with the dynamic elasticity modulus determined by ultrasonic measurements.

It is notable that the combined treatment with calcium hydroxide nano-sol and the esters of silicic acid produce strengths only slightly lower than those obtained by a double treatment with Funcosil 300 (test No. 7). It is considered likely that the calcium carbonate nano-particles formed after the nano-lime treatment catalysed gel formation resulting in improved mechanical properties. This is supported by the fact that the pre-treatment with the lower concentrated nano-lime (CaLoSiL IP-12.5) produced a lower compressive strength than when the 25 g/L $Ca(OH)_2$ containing CaLoSiL E-25 was employed.

4 Summary

Nano-lime suspensions containing up to 50 g/L colloidal calcium hydroxide stable dispersed in ethanol, n-propanol or iso-propanol offer new possibilities for the consolidation of historic mortars. Deep penetration into damaged zones is possible due to the small size of the lime particles. There are two possibilities to achieve consolidation: the carbonation by reaction with atmospheric carbon dioxide and the formation of colloidal silica obtained by the combined application of nano-lime suspensions and esters of the silicic acid. Apart from structural consolidation, nano-lime suspensions can be used to stabilise powdering and unstable surfaces.

5 Acknowledgements

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IV.50

Analysis and Testing Methodology of Mortars: a Case Study of the Báthory Castle in Şimleu Silvaniei, Romania

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Abstract A research programme was initiated within the laboratory of the Built Heritage Conservation Research and Design Centre, with the purpose of carrying out tests on mortars. This article is to outline our case study methodology for original mortars. We shall briefly present the work methodology developed in our laboratory, based on current standards and on international specialized literature. The methodology is illustrated by a case study. Old mortars from Báthory Castle were analysed through optical microscopy (OM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and wet chemical determinations. This analysis allowed us to gather precise data about the character of historic mortar.

1 Introduction

Worldwide, researchers in the field of historic structures are interested in better understanding historic technologies and in using suitable materials for conservation.

Therefore, various tests are made in order to determine composition, granularity of aggregates and binder/aggregate ratios. In Romania, technical standards referring to historic building conservation have not been clearly established yet. Hence, there is a great need for studies, for research related to the materials used in this area.

The methodology is illustrated in a case study. At the same time, the study completes the research, allowing researchers to obtain accurate pieces of information, which will be used for most of the historic buildings that require interventions.

The settlement from the mediaeval county of Crasna is first mentioned in 1251. In the second half of the 15th century, Nicholas II Báthory set his residence at Şimleu, and thus became the founder of the Şimleu branch of the family. Afterwards, his son, Stephen IV, started using the name of the property as part of his own name. There is evidence to show that there was already a curia (mansion) belonging to the family before 1508, which was replaced by the now-standing Castle. The town and the Castle were destroyed in 1660 by Tatar troops. The gate of the Castle was finished in 1592 and decorated with the coat of arms of the owners, Stephen Báthory and Susanna Bebek. The first inventory of the Renaissance complex, dating back to 1594, describes an exterior fortification and an inner mansion.

Due to the new function of defence, the Castle was subject to radical transformations. Documents on inventories and surveys from 1594, 1668, 1687, 1704, 1727 were preserved. After the fall of George II Rákóczi (1660), the Castle became a borderline fortification. The Castle was rehabilitated around 1727 and was used as armoury and food deposit by the Austrian troops. The walls of the edifice were fortified with Italian-type bastions. The Castle, in ruins starting with the beginning of the 18th century, was never rebuilt. Today, the remaining walls encompass a park, in which only two ruined cylindrical towers remind of the rectangular-shaped inner mansion, with four wings that enclosed an interior courtyard.

At the beginning of the 20th century, a public park is set up on the outskirt of the Castle, with alleys lined with green and flowering plants, while the remaining ruins of the gate and the two cylindrical towers are assembled and partially consolidated (Fig. 1) [1, 2].

Fig. 1 Overview of the Castle

2 Materials and Methods

2.1 About Materials

Load-bearing structures used in historic buildings are most frequently made of brick, stone or mixed brick-stone masonry. It has been observed by the authors that, in the case of the masonry load-bearing structure, mortar is usually the component that sustains the most severe damage along in years.

When implicated in the conservation process of historic buildings, architects and researchers are interested in finding a recipe as similar as possible to the original. In this process it is very important to make the new mortar compatible to the original one. Therefore, the first step to take is thorough analysis of the ancient mortar [3, 4].

Vitruvius noticed that there are differences in the composition of mortars, so he made an interesting observation in his memorable book on architecture: "The reason why lime makes a solid structure on being combined with water and sand seems to be this: that rocks, like all other bodies, are composed of the four elements. Those which contain a larger proportion of air are soft; of water, are tough from the moisture; of earth, hard; and of fire, more brittle" [5].

2.2 Sampling

Sampling and early visual analysis is a crucial stage of the practical, analytical procedure that is applied in all forms of historic mortar investigation. As it has been mentioned in several studies, this stage can influence the relevance of the performed analysis and therefore it should be pursued rigorously and cautiously. Sampling from culturally and architecturally important buildings is an invasive operation and therefore the number and the quantity of the samples must be kept at minimum [6].

For our case study we collected twelve samples from Báthory Castle.

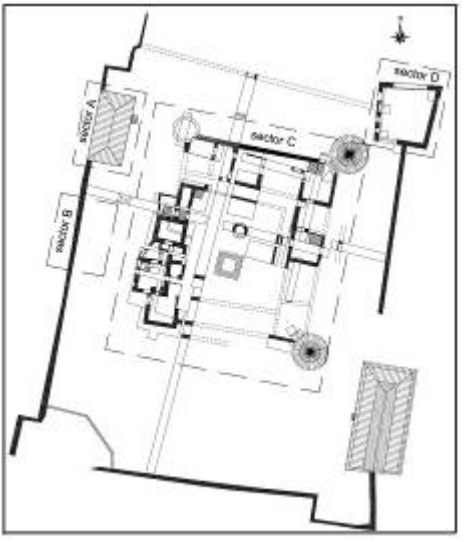

Fig. 2 Schematic layout of Castle ruins

Fig. 2 shows a schematic layout of the castle with sampling locations. Sampling was planned so as to cover the whole area.

Four samples of mortar were collected from the gate building (P1-P4 – sector A), one sample from the outer western wall (P5 – sector B), five samples from the inner walls (P6-P11 – sector C), and one from the north-east bastion (P12 – sector D) (Table 1). At the beginning of the ’90ies there had been some interventions in two of the towers, so we did not sample from these edifices, located in sector C.

Table 1 Characteristics of the mortars studied

Sample	Mortar type	Function of the structure containing the mortar	Localization
P1	Structural mortar	Gate building	sector A
P2	Structural mortar	Gate building	sector A
P3	Structural mortar	Gate building	sector A
P4	Structural mortar	Gate building	sector A
P5	Structural mortar	Outer western wall	sector B
P6	Structural mortar	Ruins of the castle	sector C
P7	Structural mortar	Ruins of the castle	sector C
P8	Structural mortar	Ruins of the castle	sector C
P9	Rendering	Ruins of the castle	sector C
P10	Rendering	Ruins of the castle	sector C
P11	Structural mortar	Ruins of the castle	sector C
P12	Structural mortar	Italian-type bastion	sector D

2.3 Applied Methods

2.3.1 Optical Microscopy

Mineralogical composition of aggregates can be analysed through optical microscopy. Our analyses were performed using a Nikon Eclipse E 200 microscope with polarized light. For the section and polished surfaces we used Canada balsam with refractive index of 1.539, in order to obtain information on types and sizes of aggregate and on binder [7, 8].

2.3.2 Chemical Analysis

Wet chemical analysis is a simple method for determining the main components of historic mortar: the binder, basically calcium carbonate soluble in hydrochloric acid, and the sand or aggregate. The analysis starts with gentle grinding of the mortar. Then, samples are moistened and treated with 14% hydrochloric acid to dissolve the binder. The filtration provides useful data on content of silicon dioxide (SiO_2), calcium oxide (CaO) and magnesium oxide (MgO). In order to determine grain size distribution, after the wet chemical analysis, part of the mortar under study was passed through a SR ISO 565 sieve [9].

2.3.3 Thermal Analysis

Differential thermal analysis (DTA) can help particularly in determining calcium compounds present in the sample, but is can also indicate levels of calcium sulphate [10, 11, 12]. Quantitative analysis relies on thermal gravimetric thermograms, while differential thermal analysis provides valuable information for the qualitative identification of the compounds that suffer weight loss [13]. The analysis was performed using a Q-1500 type D thermal gravimetric analyzer. Analysis was carried out by raising temperature on samples between 20^{o}C - 900^{o}C at a heating rate of 10^{o}C per minute in atmospheric air.

2.3.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy observations were performed on a JEOL JSM-5510 LW scanning electron microscope coupled with an OXFORD INCA 300 energy dispersive X-ray spectrometer (EDX) to obtain information about the composition and the morphology of the historic mortar. Before the investigation, samples were coated with a 10 nm thin film of gold in a vacuum evaporation system [14, 15, 16].

3 Results and discussions

The application of optical microscopy, scanning electron microscopy and chemical methods allowed us to obtain more information about the character of the binder and the aggregate. Thermal analysis gives both qualitative and quantitative information about the binder used in the preparation of the old mortar. This is the reason why many scientists suggest corroborating the results of different instrumental and chemical techniques to back up information in mortar analysis.

Investigating the thin sections by optical microscopy observation showed that the aggregate contains fragments of various rocks and minerals. Microscopic study of the mortar has evidenced the following rock types: quartzite, gneiss, micaschists, sandstone, granite and sericite schists. Mineral fragments are represented by quartz, feldspar, biotite and muscovite. Binder matrix is formed by fine lime and may contain hydraulic additives or clayey materials.

Grain size distribution is an important analysis which permits the estimation of the binder/aggregate ratio. The results of the chemical investigation are summarised in Table 2. These results are mean values of three measurements for each sample. The average weight of a sample was 30 g. Additionally, we must note that for samples P8-P9-P10 – in sector C (layout), grains above 2 mm are almost completely missing. Furthermore, comparing the results of the analysis, we discovered interesting information regarding the extremely low rate of the binder for sample P5 – sector B. Table 2 shows pH values of mortars under analysis, ranging between 6.4-7.7, attesting a proper carbonation.

Thermal analysis generally showed values lower than 0.5% for magnesium oxide, which indicate that the dolomite is absent in the analysed samples and this fact was confirmed by the derivatograms. At the same time, the amount of silicon dioxide remains under 0.5%. The measurement also shows that the binder is mainly dominated by calcium oxide. The result of thermal analysis showed only one type of weight loss in the range of >550^{o}C, and this can be associated with the de-carbonation of calcium carbonate.

There is good concordance regarding the quantity of calcium oxide between the results of wet chemical analysis and thermal analysis.

Table 2 Results of chemical investigation

Sample	Binder / aggregate ratio	pH of the mortars	The mean values of the fraction size distribution (in mass %)			
			> 3.15 mm	1.00-3.15 mm	0.25-1.00 mm	< 0.25 mm
P1	1 : 2.17	7.2	15.43	14.52	60.15	9.90
P2	1 : 1.78	7.1	10.58	17.27	59.98	12.17
P3	1 : 1.27	6.7	6.29	14.90	52.20	26.60
P4	1 : 1.46	7.1	14.07	19.45	55.23	11.25
P5	1 : 6.68	7.7	28.26	26.56	29.84	15.34
P6	1 : 1.82	7.5	23.98	22.56	41.81	11.65
P7	1 : 2.30	6.4	26.54	21.12	43.84	8.50
P8	1 : 2.26	7.7	1.75	3.24	46.07	48.95
P9	1 : 2.06	7.3	0.86	2.63	61.98	34.54
P10	1 : 1.54	7.4	1.66	1.81	59.47	37.07
P11	1 : 3.50	7.4	27.14	22.82	40.24	9.80
P12	1 : 1.48	7.1	8.61	28.33	52.94	10.12

Three samples (P2 – gate building, P5 – outer western wall, P6 – ruins of the Castle) of mortar taken from the Báthory Castle were submitted for testing with SEM. Examining the images, we gather information on fragments of the aggregate, composition of the binder and pozzolanic additives, particularly with the help of EDX. This method helps to identify not only the main compounds of the binder such as calcium carbonate showed in Fig. 3, but also some other interesting compounds, like trass and diatomite crystals (Fig. 4).

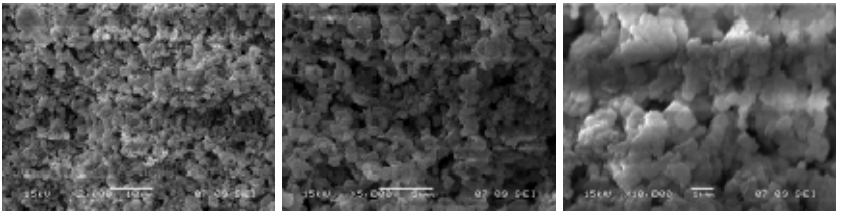

Fig. 3 Scanning electron microscopy – details of calcite crystals in sample P2

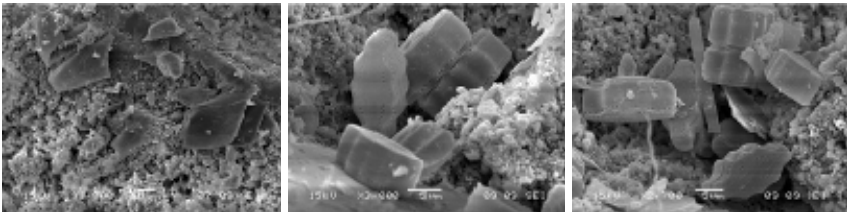

Fig. 4 Scanning electron microscopy – details of alumino-silicate crystals composed of silicon (Si), aluminium (Al), oxygen (O), potassium (K) and calcium (Ca) as mainly-detected elements (left); diatomite crystals (middle and right) in sample P5

4 Conclusions

We have investigated the mortar samples from the Báthory Castle by using different techniques. By confronting the results of the different analyses, we have drawn the following conclusions.

Based on the similar binder/aggregate ratio, most of the samples might belong to the same construction period. Sample P5 – sector B, because of its higher binder/aggregate ratio, could derive from a later intervention phase.

The higher strength of samples from sector C can be explained by the fact that these were preserved under the ground level, therefore freeze-thaw cycles and salt dissolution/crystallization processes have affected them less.

Aggregates contain a relatively high quantity of fraction under 0.063 mm. This might derive from the fact that sand had not been washed before use. This could be the possible source of the small size particles with hydraulic character revealed by some analyses.

5 Acknowledgements

The authors gratefully acknowledge Professors Zsuzsanna Józsa and Erika Csányi within the Department of Construction Materials and Engineering Geology at Budapest University of Technology and Economics for the thermal analysis; Professor Marcel Benea within the Department of Geology at Babeş-Bolyai University for the mineralogical study; and Lucian Barbu within the Electron Microscopy Centre at the Faculty of Biology and Geology from Babeş-Bolyai University for the SEM images.

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RILEM TC 203-RHM
Final Workshop

TC.01

The Role of Mortar in Masonry: an Introduction to Requirements for the Design of Repair Mortars

Members of RILEM TC 203-RHM

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Abstract The effective design of a mortar for repairing masonry depends on a clear understanding of its function within masonry. The functions of mortar materials in masonry are classified as bedding, pointing, grout, render, plaster and mortars for surface repairs. The requirements that each type of mortar must meet in service depend on its environmental exposure and its role in the structural integrity of the masonry element that it is found within. Technical requirements such as adhesion, strength, elasticity, water and vapour transmittance, drying behaviour, thermal dilatation, ability to deal with salt contamination and freeze-thaw cycling, and its aesthetic properties can be quantified. Different functions of mortar will be utilised in different repair interventions in masonry structures depending on these requirements. Mortar properties can be adjusted to meet technical requirements through the use of different binder and admixture types.

1 Introduction

Mortars have been integral to masonry construction for many thousands of years [1], and can be demonstrated to have originated in use independently in

many regions of the world, notably in central-south Africa, Central and Northern South America and present day India and China. The development of mortars in construction shows a pattern of functional evolution suggesting origins in small scale domestic settings as a surface coating. This evolved to use as a bedding or structurally integral material, linked to societal and technological development [2]. Significant developments in mortar technology took place in Europe during classical Greek and Roman times, in particular with the systematic use of pozzolanic admixtures to produce hydraulic mixtures for increased strength and where exposed to water, resulting in more specialised applications of mortars; lining cisterns and baths for example, (reviewed in [3]). Mortars mainly based on the use of lime are found worldwide, mainly in massive masonry structures for defensive residential and ceremonial buildings to small scale vernacular constructions. Technical developments following the renaissance and the 18-19thC industrial revolution, culminated in natural and artificial hydraulic binders that combined limestone with clay. In the early 19thC Portland Cement was patented and subsequently developed into the material we use today, associated with globalised industrialisation.

Historic masonry buildings require an understanding of their mortars, where present, for effective upkeep and positive intervention to ensure their future sustainability. The use of mortars in masonry can be generalised to a relatively limited number of functional uses. In this contribution we outline these functions, possible repair actions that affect the 'classification' of mortar types, and relate these at a first level, to technical requirements that each mortar must meet to function correctly, in relation to durability and environmental resistance. However, it is also very important that we remain aware of the requirement to design mortars that work towards the preservation of existing fabric. This can be at odds with the need to satisfy durability requirements, for example where a mortar is 'sacrificial', deliberately designed to erode more quickly than it's substrate. This contribution should be read alongside [4], which deals with the effect of mortar choice on the mechanical behaviour of masonry.

2 Definitions

Masonry is a composite comprising *units* (e.g. bricks, stone etc.) and *mortar* (i.e. binder, aggregate and additives, [5]). When combined, units and mortars form masonry *elements*: walls, floors, arches, piers, columns and domes [6] which combine to form a range of masonry structures [4]. The use that elements are put to determines the requirements for performance of both units and mortar. The morphology of the masonry structure is also important [4]. The function of mortar is integral to its role in a structure, and the structural function of the masonry itself will influence the requirements for a mortar.

3 Repair actions and mortar specifications

Table 1 contains a summary of possible repair actions and the classification of a repair mortar based on that repair action. To specify a repair mortar there needs to be an understanding of the *requirements* that it must satisfy. This means the performance characteristics of the mortar, constrained by several factors, including the environmental conditions in which the masonry is exposed and the properties of the substrate onto which it is applied. A mortar repair action can be classified by the function of the mortar, constrained by the typology of the masonry itself [4] and influenced by the choice of binder type.

Table 1 Possible repair actions and the classification of corresponding mortar

Repair action	Classification of Mortar
Replacement	repointing
	internal plaster repair
	external render repair
Rebuilding	masonry mortars for rebuilding
Surface repair and compensation	Surface repair, "plastic" repair
(Cosmetic / Modelling of masonry units/ sculptures)	compensation mortar
Consolidation of masonry	grouting
	deep or structural repointing
Replacements or additions to provide a specific function	salt-accommodating renders
	salt-absorbing poultices
	load-bearing coatings (e.g. shotcrete)
	fire-proof coatings
	thermal insulating renders
	deep repointing
Superficial protection	sacrificial coating
	protective layers (e.g. lime wash) *
	anti-graffiti *
	water repellents *

* not repair mortar mixes but treatments to mortars/renders and plasters which can significantly change their properties

4 The role of mortar in masonry

The role of mortar in masonry can be determined by a consideration of the types of structure and the elements that they are composed of, cross-referenced to

their specific mode of construction (Fig. 1). From this a general functional classification can be derived. The classification of a material must be approached systematically in a context of a full understanding of the typology of the masonry element where the mortar is found. The main functions of mortar can be categorised as:

- **bedding mortar** for setting units, adhesion, bearing load.
- **pointing mortar** sealing joints and for aesthetics.
- **exterior render** water penetration protection, aesthetic covering.
- **interior plaster** aesthetic covering, a substrate for decoration.
- **surface repair-** mortar used to replace and repair missing sections of masonry.
- **grout** – material filling of cavities in masonry to create monolithic behaviour.

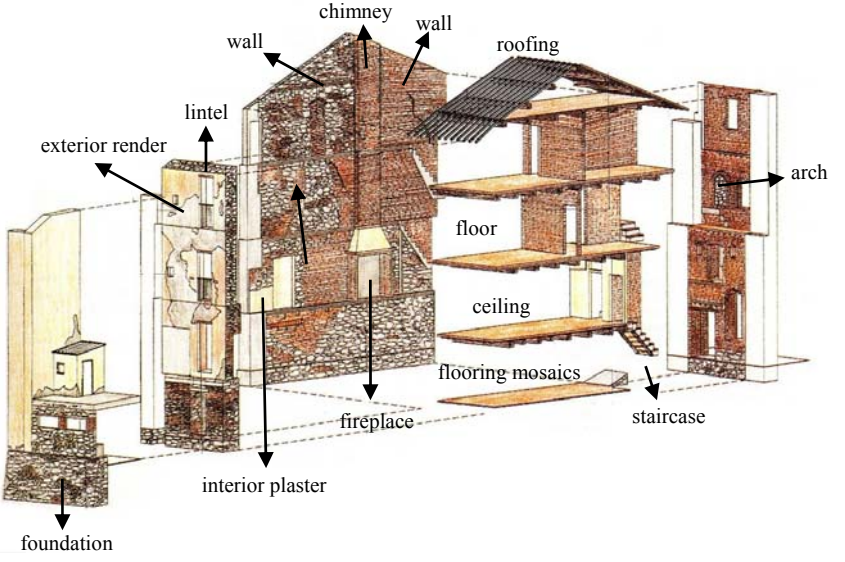

Fig. 1 Illustration of common elements of masonry buildings, structural features, surface coatings, and areas where mortar occurs. Each element and environment of occurrence presents specific demands on the requirements for mortar performance [7].

5 Technical requirements

The aim should always be to achieve the best compatibility between the substrate and the repair mortar with regard to hardened properties [8, 3, 9]. Compatibility requirements must be met to ensure durability, in combination with the structural and environmental resistance requirements, and considering the properties of the substrate. Table 2 (above) presents a ranking of the importance of functional requirements for the different mortar classifications outlined above, except for surface repair.

Table 2 Technical requirements versus classification of mortar. The rating scheme 0 = no importance to 3= very important

	Mortar Type Classification				
Technical Requirement	**Bedding**	**Pointing**	**Render**	**Grout**	**Plaster**
Adhesion (bond)	3	3	3	2	3
Strength (compressive, flexural, tensile)	2*	2*	1*	2*	1*
Deformability and elasticity (E modulus)	3	3	2	3	1
Weather protection					
Water penetration resistance	2	3	3	1	1
Freeze-thaw resistance	2	3	3	1	0
Thermal dilatation	1	1	3	1	3
Vapour transmission**	2	3	3	1	3
Wetting and drying behaviour	2	3	3	1	2
Aesthetic	1	3	3	0	3

* in relation to the substrate the strength and deformability values for mortar should be less than the masonry units.

The properties of mortars are fundamentally controlled by the binder that is used. This can be non-hydraulic lime (air lime, putty lime etc), hydraulic lime, pozzolan-lime hydraulic binders (where the pozzolan is considered to be part of the binder), calcium sulphate or clay-earth binder. We do not consider cement here as it is generally a non-authentic material for historic building conservation. Each has a variation of properties which in combination with different aggregates, additive and binders can be used in theory to provide a mortar with given properties within physical bounds. Table 3 considers the relative importance of physical properties related to achieving technical requirements presented in Table 2.

Table 3 Technical properties of mortar binder compositions. versus classification of mortar. This indicates how in principle mortar composition can be varied to meet requirements. The arrows indicate the direction of increase in values. The ***relative*** scale runs from 1 (low value) to 6 (high value).

	Binder type					
Technical Requirement	**Non-hydraulic lime**	**Hydraulic lime**	**Pozzolan lime**	**Calcium Silicate cements**	**Calcium Sulphate based**	**Clay Earth**
Adhesion	3	→	→	6	5	1
Strength (comp, flexural, tensile)	2	→	→	6	4	1
E-modulus	1	→	→	6	4	1
Water penetration resistance	3	→	→	6	2	1
Freeze-thaw resistance	2	→	→	6	1	1
Thermal dilatation	1	→	→	1	1	1
Vapour transmission	5	←	←	3	3	5
Aesthetic	Depends on specific requirements					

6 Conclusion

It is possible to identify the common functions to which mortar is put in masonry, and identify the general requirement which each function places on the mortar, in terms of physical and mechanical properties. Ultimately this understanding combined with a knowledge of the properties of different binders allows a choice to be made on the materials that will satisfy requirements and compatibility and authenticity constraints that operate in the conservation of historic masonry buildings.

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TC.02

Influence of Masonry Typology and Mortar Joints on the Mechanical Behaviour of Masonry Walls

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Abstract The aims of the paper are the following: to develop a consistent usable classification of historic masonry typologies, to outline general considerations about the mechanical behaviour of different masonry types, to outline the influence of mortar joints in masonry, and the consideration necessary when repairing and replacing mortar in different types of masonry (rebuilding, re-pointing, injecting grouts).

1 Introduction

When considering the mechanical and more generally the physical behaviour of masonry structures, it should be remembered that masonry is a non-homogeneous material, but also that there are many types of masonry. In fact the differences are not only due to the use of different materials according to the local sources (stones, bricks, earth, various types of mortars, etc.) but also by different construction technologies.

A definition of masonry as a composite material and of masonry elements has already been given [1]. Reference [1] also said that the structural performance of a masonry can be understood provided the following factors are known: (i) its

geometry; (ii) the characteristics of its structure (single or multiple leaf walls, connection between the leaves); (iii) the physical, chemical and mechanical characteristics of the components (brick, stone, mortar); (iv) the characteristics of masonry as a composite material [2].

The worst defect for a masonry wall is to show no monolithic behaviour in the vertical and lateral direction; this can happen for instance when the wall is made of small pebbles or of two external layers even well ordered but not mutually connected or containing a rubble infill. This causes the wall to become more brittle especially when external forces act in the horizontal direction. The same problem can happen under vertical loads if they act eccentrically [3].

It is also worth remarking that an apparently regular masonry surface texture often does not correspond to a regular morphology within the wall and vice versa (Fig. 1). This knowledge is not only important for modelling the mechanical behaviour of the walls, but also to make appropriate mortar choices when repairing, rebuilding or injecting damaged masonry.

Fig. 1 Apparent regularity of a wall and real morphology within the wall

For example, the main problems connected to grout injection can be summarised as follows: a) the lack of knowledge on the size distribution of voids in the wall, b) the difficulty of the grout to penetrate into thin cracks (2-3 mm), even if microfine binders are used; c) the presence in the wall, of fine and large size voids, which makes it difficult choosing the most suitable grain size for the grout (injecting large size voids with a fine grained mix can induce segregation); d) the segregation and shrinkage of the grout due to the high rate of absorption of the material to be consolidated; e) the difficulty of grout penetration, especially in the presence of silty or clayey materials; f) the need for sufficiently low injection pressure to avoid trapping air within the cracks and fine voids, or even wall disruption.

Multiple leaf walls can be made with very poor mortars and stones but have a very low percentage of voids (less than 4% voids is not injectable) and have internal filling with loose material, which is not injectable [4].

The technical improvements of the last years have allowed: (i) the development of new grouts with specific properties, such as a low salt content and ultra fine size aggregate, (ii) optimised injection methodology, such as the injection pressure

or the distance between the injectors, in accordance with the masonry characteristics.

Therefore, following the above discussion, it seems necessary to have at hand a classification of masonry types when dealing with the choice of mortar for repair.

2 Masonry classification

Modern and contemporary masonry made with solid bricks are usually classified according to the thickness of the section corresponding to a multiple of the brick header; the type of section is then very easily detected by its dimension.

Given the great number of existing cross sections and the great influence of the construction technique on masonry behaviour, a systematic study of the mechanical behaviour of stone and brick masonry should begin with an extensive investigation of the different geometry and building techniques which takes into account the different layers constituting the wall and the kind of constraints which may be present between the layers themselves. This systematic investigation of the morphology of masonry sections was started in the early nineties in Italy, by L. Binda and her collaborators [2, 4], to define guidelines for repair by grout injection, followed more recently by studies on mortars and grout for repair [5].

At the same time Giuffrè carried out in the early '90s [3] the first studies about the mechanical behaviour of stone masonry typologies based on visual inspection to recognise characteristics of the "rule of art" and, then, to a typology classification. The presence of some characteristic, such as connection elements called diatons, can be a discriminating parameter for the evaluation of the wall mechanical behaviour.

Other parameters can be: dimension of the elements, shape and workability of the stones, masonry texture, mortar quality, mortar quantity, presence of wedges, presence of horizontal courses, presence of leafs connections and diatons, characteristic of the section, homogeneity of the materials. Each masonry behaviour is then qualitatively evaluated.

In the following, the results of an investigation carried out by L. Binda and others are presented as a first attempt to classify brick and stone masonry sections.

Classification of brick masonry sections. Old and ancient brick masonry usually had very thick sections (600mm or more) with a much less homogeneous distribution of the bricks within the section; sometimes only the external leaf of the masonry was made with whole regular bricks, while, for economic reasons, the internal part was made with pieces of bricks and large mortar joints. The joint thickness was usually much lower than the brick thickness - a ratio 1-2/5. Nevertheless this was not the case with late Roman architecture and Byzantine construction where the mortar joints were much thicker. From a survey carried out in Milan (Roman walls) and in Ravenna (Byzantine walls), the following

classification could be made: a) solid walls with thin joints, b) solid walls with thick joints, c) solid walls with multiple leaves (leaves of different thickness)

Classification of stone masonry sections. In the case of stone masonry more different types were found, also with more subclasses than in the case of brick masonry. Four large classes can be distinguished, each one having subclasses as follows: a) one leaf solid wall, b) two leaves, c) three leaves, 4) dry stack wall

It must be said that this is not the only possible classification. Other descriptions of stone and brick masonry are given in other countries (UK, Greece, etc.).

3 Mechanical behaviour of different masonry typologies

No doubt that, due to the different technology of construction, masonry walls behave in different ways under vertical and horizontal loads. A description of these different behaviours for stone masonry is given by Giuffrè [6]. It is therefore clear that before deciding on the type of mortar or repair to be carried out on a damaged masonry wall the morphology of the wall section has to be known.

The investigation carried out by Binda et al. on masonry sections from different Italian regions not only takes into account the importance of collecting geometrical values, but also information on the presence of voids and defects. The investigation can be more easily conducted in areas where buildings were damaged by earthquake and have not yet been repaired. The survey of the wall sections defined some important parameters: (i) the percentage distribution of stones, mortar, voids which allows comparisons between the percentage of materials and voids; (ii) the ratio between the dimensions of the different layers, and the ratio between the dimension of each layer and the whole cross section; (iii) the dimension and distribution of voids in the cross section. These parameters, together with the chemical, physical and mechanical properties of the materials give a better description of the masonry and constitute a fundamental basis of any conservation intervention.

4 Influence of mortar joints on masonry mechanical behaviour

Masonry cannot be defined as “a material”, but as a composite. The variability of masonry types in historic buildings means an investigation should always be carried out before deciding on any restoration or repair, in order to define the masonry morphology with special attention to the wall section. The masonry components (mortar, brick/stone) have to be characterised from the chemical, physical and mechanical point of view. The joint thickness is one of the parameters with a large influence on masonry mechanical behaviour, as shown

experimentally with compression tests [7]. Thin joints can improve the strength of the masonry, but there is a lower limit in the case of lime and cement mortars, due to the aggregate size. The joints can be very thin, but only when the material for jointing is different from the mortar (e.g. glue). Thick mortar joints can reduce the strength of the masonry, but in the case of large aggregate size and good binder the strength can still be very good.

Fig. 2 presents, as an example, the results of an extensive investigation showing the dependency of masonry strength (ratio masonry/brick strength) on the thickness of mortar joints [7]. In conclusion, the dependency of the masonry strength on the joint thickness must be defined carefully and take into account the different classes of masonry. Every time a new case is found only an experimental investigation can give sufficient information to define the strength.. This also means that when repairing mortar joints with new mortars several parameters have to be taken into account.

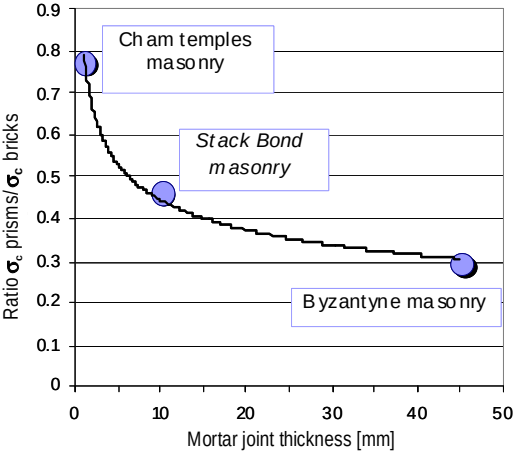

Fig. 2 Dependency of the ratio brick-masonry/brick compressive strength on the joint thickness

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TC.03

Repair Mortars for Historic Masonry. From Problem to Intervention: a decision process

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Abstract This article focuses on repair or replacement of mortars for historic buildings. With practical situations in mind, both the decision process and questions arising are dealt with in order to better define and illustrate technical requirements for mortars to be used for the repair or restoration (masonry mortars, plasters, renders). This article summarizes a document, meant to help professionals in their decisions on interventions, taking into account aspects ranging from the ethics of restoration to technical requirements.

1 Introduction

For those responsible for the execution of a restoration project, technical problems are only a part of the task that has to be dealt with. Redesign and re-use, i.e. the transformation of historic buildings, in order to meet present needs may be the main challenge for the architect. However, at the same time be aware that aspects like authenticity, conceptual, and functional requirements represent questions that have to be answered as well. In fact the architect, engineer or conservation specialist is going through a continuous process of decision-making during the realization of a restoration project.

Given the complexity of many restoration projects, it is considered important that all involved disciplines cooperate and arrive at well balanced decisions. Here a guideline is proposed that deals with these decisions in a logical way.

When dealing with the conservation of monuments and historic buildings, including replacement and restoration of historic mortars, decisions should be made from several points of view. Therefore a complete framework was proposed by RILEM TC 167- COM [1], ranging from the (more abstract) philosophical and authenticity questions to the (practical) mix design as a basis for the description of functional and technical requirements for repair mortars.

2 Assessment of the state of conservation

In the practical situation of a restoration, an assessment of the state of conservation of the building or construction concerned is the first and necessary step for defining the problem to be solved. This step also includes the decision on which investigations have to be performed.

After the assessment, major decisions have to be made[1]:

Theoretically, two directions could be followed for the intervention, i.e. for the choice of the repair mortar:

- a mortar based on authentic materials (that theoretically might be the most compatible[2] solution);
- a mortar that is inherently durable.

The historical assessment and the value assessment of the building should include past interventions. Their possible (historical) value should also be taken into consideration.

The assessment of the state of conservation (technical assessment), includes [2]:

- damage assessment
- exposure conditions
- description and identification of materials
- diagnosis

In addition several decisions are necessary:

- on the (technical) requirements for the mortar mix
- on suitable raw materials (salt content, pozzolanicity, reactivity, …)

[1] In what follows, reference will be made to the materials issues only. Structural issues or issues of morphological restoration are not considered here.

[2] Compatible is defined as: not causing any damage (in a broad sense, ranging from technical to aesthetical and historical) to the existing fabric and being as durable as possible under that condition

Table 1 Survey and interventions in historic buildings: steps to be taken

Assessment and documentation of heritage significance & state of conservation
Historical assessment
Technical assessment
Location, extent of different damaged building parts (show in plan of building)
Analysis and diagnosis of degradation phenomena o Analysis and diagnosis of damages (e. g. by NDT methods) o Assess properties existing mortar and masonry units (and masonry) o Monitoring of degradation and damage o Risk analysis related to environmental influences (earthquake, flood, storm, fire, …)
Compatible (and as durable as possible) intervention *and strengthening* o *Decide on concept: balance compatibility <=> durability* o *Quality assurance of intervention and risk assessment* o *Assess technical requirements / decide on composition / make trial mixes* o *Plan side measures*
Plan future maintenance activities and monitoring of the state of conservation

Finally, sound documentation of all decisions made is of utmost importance, not only for the particular structure, but also as a basis for future knowledge development.

3 Functional (design) issues, exposure and specific threats

Functional (or design) requirements are a set of qualitative imperatives that should be defined on the basis of the historical and technical assessment of the structure. They provide a rational basis for the choice of the raw materials and compositions to be used and the tests to be carried out. Requirements for a repair mortar are based upon its function inside the structure and its exposure or on specific threats it may be subjected to. Each of those issues provides a set of different requirements. The aim here is to describe how to arrive at the definition of those requirements in a concise way.

Function of a mortar

The main functional applications of a mortar can be categorised as: bedding, pointing, infill, render, plaster, and stone repair.

Exposure

Masonry, and therefore the mortar that is part of it, can be exposed to (environmental) conditions of varying severity, e.g. driving rain, freeze–thaw cycles or sea spray, or to a high permanent load and/or dynamic action, e.g. dead load, soil settlements, traffic or earthquakes.

Specific threats

A repair mortar, especially in historic masonry, may also be subjected to specific threats that should be dealt with, although the compatibility with the existing fabric should be given priority. These threats can derive from, for example, the presence of salts and/or rising damp, the presence of biological growth, use of frost sensitive materials, or human behaviour.

Damage can be classified according to its origin, i.e. chemical, physical or mechanical (Fig. 1).

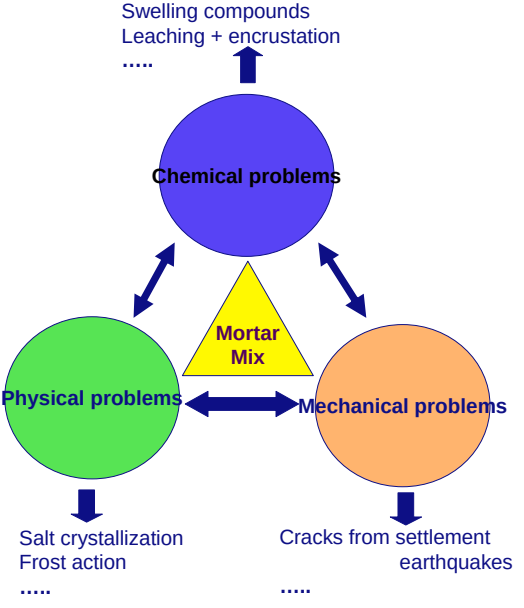

Fig. 1 Classification of specific problems

Set of simple recommendations for repair mortars

In general, the following aspects have to be taken into account:

- existing mortar and masonry
- surrounding materials and structure
- environment
- costs

The mortar should be made as workable and durable as possible (taking into account compatibility). The following aspects need a decision (keeping in mind the needed strength and stiffness):

- Binder and aggregate type
- Binder / aggregate ratio
- Additives
- Colour
- Porosity and pore size distribution
- Water absorption and drying behaviour

4 Frequently asked questions

Practical problems are described in terms of frequently asked questions, which are as much as possible answered in a general way. Both general questions and particular problems due to exposure or special threats are dealt with. This paper gives just one example of these questions. A description of the cause(s) of the problem is given, together with the possible mechanism that may have resulted in the observed damage. Then, a possible composition of the proposed repair mortar is given, and a description of how this mortar reduces the risk of new damage.

Which mortar composition is best to deal with sea salts?

The presence of sea salts in mortars may be the result of different events or conditions: direct contact in case of buildings constructed in seawater or subjected to flooding, deposit of sea salt in the form of aerosol on the surface; the salt may also be present due to the use of unwashed sand from the beach or even from the use of seawater in mortar preparation.

Damage to mortars (pointing, plaster or render) due to sea salts generally shows up as sanding or powdering or as a kind of pitting.

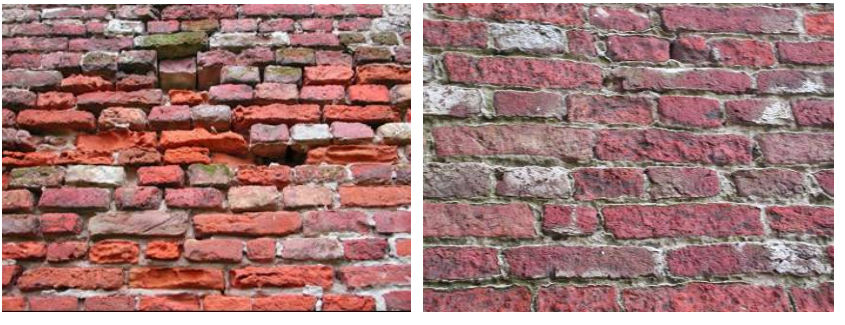

Fig. 2 Examples of the damaging effects of sea salts on respectively masonry and in lime mortar joints (pitting in the pointing mortar).

In lime pointing the damage (pitting) concentrates in the centre of the joints; re-pointing either with lime or cement mortars leads to the formation of voids at the brick (stone) mortar interface, where the salt present in the masonry units may quickly and in considerable amounts contaminate the mortar. In plasters or renders, pitting may occur, but also phenomena such as exfoliation and loss of adhesion between plaster and substrate.

The damage can be considered mainly the result of a physical process (cycles of crystallisation and dissolution); a chemical process (chemical transformation of calcite and sodium chloride into easily soluble calcium chloride), is considered less probable.

Traditionally lime-pozzolan-sand mortars were used under these conditions (for example 1:1:4 or 1:0.5:2.5 by volume).

Repair

For interventions, repair mortars in principle should be sacrificial, i.e. help protect the surrounding brick or stone from decay.

Lime-pozzolan-sand, lime-pozzolan-cement-sand, cement-pozzolan-sand, or hydraulic lime-sand can be used as repair mortars for masonry that was originally constructed with mortars on the basis of lime, lime-pozzolan or hydraulic lime. Examples of mortars used for renders can be found in [3]. In order to limit the risk of the repair mortar being too strong and stiff with respect to the strength of the brick or stone, and in order to create internal space for the salts, the use of an air entraining agent could be considered.

The addition of natural polymers (for example linseed oil; 2% of the binder weight) seems also to contribute to the mortar's resistance to the penetration of new sea salts [4].

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TC.04

Testing of Repair Mortars for Historic Masonry

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Abstract This paper summarizes the approach to test methods used for assessing repair mortars for historic masonry. It also discusses adaptations needed to the test methods when evaluating mortars with high lime content.

1 Introduction

Repair mortars are designed following the performance requirements that are specific to the repair and the reason for the repair. Appropriate tests, prior to and during the repair, are useful to assess whether the mortar will be able to meet the performance requirements. This paper highlights aspects of the chapter on test methods to be included in the forthcoming RILEM TC 203-RHM guide on repair mortars for historic masonry. Test methods will concentrate on repair mortars having binders derived from limestone (e.g. lime, hydraulic lime, natural cement, Portland cement). Tests on mortar components and existing mortars are largely covered in an earlier report and paper [1, 2].

Most of the tests are based on existing European and North American standards, and RILEM recommendations. The more commonly used (standard) tests methods will be presented. Although similar names may be applied to test methods in different standards it is important not to consider the data as interchangeable. There are frequently too many differences in the equipment and

the manner in which the test is completed to make a direct comparison. It would be necessary to complete round robin testing to assess the variations.

In addition to assessing performance requirements, testing can be used to ensure quality control of the repair mortar in both the laboratory and on-site. Quality control issues might include aggregate particle size distribution, consistency in materials such as solid content of lime putty, and consistency of the mortar during application. Thought needs to be given to test methods that result in useful but relatively quickly determined results for site use. For low strength, typically high lime content mortars, construction and curing procedures on site are more critical, and therefore need more careful monitoring than higher cement content mortars commonly associated with modern masonry construction.

Most of the tests for mortar properties involve testing the mortar only, and making correlations to its properties in the wall need to be considered carefully. For example, mortar cubes/prisms for compressive strength do not relate directly to the strength of the mortar in a wall; therefore they are most useful for quality control. In addition, the properties of a mortar tested at ages ranging from 28 days to one year need to be determined in order to understand the longer-term performance expected for the repair. High-lime mortars can take a long time to gain full strength, and furthermore properties such as porosity, strength and adhesion may change over time, through dissolution and re-precipitation of the binder.

The nature of mortar constituents also has an impact on the test method that is used. Many of the currently available standard test procedures are based on mortars containing a relatively high proportion of Portland cement in their binders. Adaptations may therefore be required for pure lime, lime-pozzolan and hydraulic lime mortars. Mortars with a binder having a high component of lime require curing conditions at a lower relative humidity than mortars with a binder containing a higher component of hydraulic binder.

Guidance in the forthcoming guidelines is given for use of the tests which are commonly available. The test methods are categorised according to the state of the mortar, i.e. plastic (fresh) and hardened and not according to the type of repair mortar (eg pointing, bedding, renders). Performance requirements for each repair mortar application should be initially determined and be used for determining the most relevant test methods. This is addressed in the chapters on performance requirements.

2 Testing of plastic (fresh) mortar

A workable mortar is a mortar acceptable to a mason for a specific purpose (e.g. bricklaying or rendering) in combination with a specific type of substrate. Workability is not a well-characterised physical quantity and cannot be defined by any single test method. It does not even have the same meaning for masons of

different regional experience or different practice (e.g. pointing, bedding, render). Nevertheless some aspects of it can be measured and are the subject of standardised tests. These include consistency, water retention, density, air content, workable life (board life), and initial bond to the substrate. The interplay of the binder type, aggregate particle size distribution and shape as well as the amount of water and possible additives all contribute to the characteristics of the mortar in the plastic state. Most standard tests for fresh mortar can be used without any modifications for mortars with a high lime content. However, different types of mortar binder do not require the same target value in these tests. For example: mortars with pure lime binders generally require a lower flow value than mortars containing a cement binder. This means that the results of the standard test methods are mainly used for comparative purposes. It is essential that workability be based on the judgment of masons. Thereafter, consistent workability for a particular mortar mix can be achieved by using the same binder and aggregate materials and ratios, and monitoring the consistency. An example of a simple test for consistency that can be used in the laboratory and on site is the cone penetration test [3]. The test is suitable for mortars with aggregates up to 3 or 4 mm in diameter. On site, it can be used to assess the uniformity between different batches of mortar from the mixer.

Workability is also related to the nature of the substrate: suction characteristics and geometrical aspects (e.g. size of masonry units, thickness of mortar layer). Usually a strongly absorbing substrate requires a mortar with a higher water retention or alternatively the substrate should be pre-wetted. Weather conditions during mortar application may also influence the requirements in a specific situation.

3 Testing of hardened mortar

Tests on hardened mortar, as with plastic mortar, are used to provide a framework for an estimation of the characteristics of the properties of the mortar once it is placed in the wall, or used for quality control of the mortar. The mortar may be prepared under laboratory conditions, or sampled and prepared at the site, but the final testing is commonly in the laboratory.

Regardless of mortar type the most typical tests include appearance (e.g. colour, efflorescence), physical properties (e.g. porosity, depth of carbonation), structural properties (e.g. flexural bond between mortar and masonry unit, compressive strength), deformation (e.g. elasticity, shrinkage), moisture properties (e.g. rate of water absorption, drying rate, vapour transmission), and durability (e.g. resistance to salts and freeze-thaw action). Test methods have been developed by different national standard bodies and most have been available for a long time. They are well characterized and generally well accepted.

Problematic, however, is the development of appropriate sample preparation and curing of pure lime and high lime (hydraulic lime) mortars. The mixing, moulding and curing procedures need to be different from those specified in most modern standards. High cement mortars achieve a significant proportion of their long-term characteristic properties after 28 days curing at 100% relative humidity. Under the same conditions lime in mortars does not carbonate.

4 Sample preparation and curing conditions for high lime mortars

Currently no common agreement among available test methods or research has emerged for the mixing, moulding, and curing procedures for high lime mortars. Mixing methods often are an adaptation of methods used for modern cement mortars. For pure lime mortars special pug-mill or mortar mill mixers are used on site to promote thorough mixing and effective kneading of the lime and aggregate. One adaptation for laboratory mixing is to extend the wetting and mixing time of the constituents [4]. Ensuring intimate contact of the binder to the aggregate is essential.

One of the largest challenges when preparing test samples of high lime mortars is that once moulded, they remain very fragile in the mould for days. Current standards specify leaving the mortar in the mould for at least 5 days [4, 5]. For pure lime mortars longer periods may be required. It has also been suggested to carry out demoulding in a series of steps in order to allow the diffusion of carbon dioxide gas inside the mortar specimen to allow hardening by the carbonation reaction to be started [6].

Curing procedures affect the mortar by altering the degree and the order of the hardening reactions which are principally hydration and carbonation; both occur in hydraulic lime and lime-pozzolan mortars. Pure lime mortars harden solely by carbonation which is best achieved by curing at a relative humidity in the range of 60 to 70% in contrast to the hydration reaction which requires 93 to 100%. A balance of moisture conditions needs to be achieved when the mortar binder contains both non-hydraulic and hydraulic components [7]. A longer initial damp curing time may therefore be needed before exposure to lower humidities. Full carbonation may take a year or more. Specimens stored outside to ensure adequate CO_2 and wetted at weekly intervals have been found to carbonate more quickly [8]. When testing mortar samples it will be helpful to measure the degree of carbonation after the test.

Examples of curing periods given in standards and research papers are 28, 60, 90 and 120 days, and 1 year. Curing conditions vary too. For example the European mortar standard [5] requires 7 days at 95 ±5% humidity and 21 days at 65±5%. In contrast, the new ASTM standard [4] requires 120 days at 70±5% for pure lime mortars, 120 days at 90±5% humidity for hydraulic lime mortars and

lime/cement mortars with lime ≥45% by volume, and 28 days at 100% humidity for hydraulic cement mortars (including lime/cement mortars with less than 45% lime). For high lime mortars a 28 day curing period in the European standard is very short, while the ASTM standard has a much longer curing period but it only allows carbonation to occur with pure lime mortars.

There is a need for clear guidelines derived from research for appropriate preparation and curing procedures. These guidelines may vary depending on the purpose of the mortar test (e.g. quality control, mortar characterisation).

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TC.05

Performance and Repair Requirements for Repointing Mortars

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Abstract A brief overview is given of performance requirements for repointing mortars for historic masonry.

1 Introduction

This paper highlights aspects of the chapter on performance requirements for repointing mortars to be included in the forthcoming RILEM TC 203-RHM guide on repair mortars for historic masonry. Existing information on repointing is also available [e.g. 1-3].

Repointing is the (process of) filling of the outer part of an existing masonry mortar joint with a new mortar that may differ in composition from the existing bedding mortar. Repointing in historic masonry is usually carried out to replace deteriorated or damaged mortar in the outer part of masonry mortar joints. The depth of the pointing is usually 2 to 3 cm, but in special cases it may go up to 5 or 7 cm. For deeper repointing, structural assessment may be needed.

Repointing mortars for historic masonry are composed of a binder such as lime, an aggregate such as sand, and water which gives them initial plasticity. Additives or pigments may also be present.

Before repointing, the following initial preparatory work is recommended:

- A building condition assessment should include a thorough survey of the composition of the existing masonry and its condition (see paper 'Repair mortars for historic masonry. From problem to intervention: a decision process'). The cause of material deterioration should be determined and any repair work to reduce the risk of mortar deterioration should be addressed prior to repointing.
- An evaluation of the type and severity of climatic exposure for each element of each building elevation will assist with the selection of suitable mortar mixes, and point to any needed remedial work to minimize moisture loads on the masonry.
- Look for (traces of) original and other historical pointing. Its colour and form can be a guideline for selecting the new repointing material. The composition of the old mortar could serve as a reference for deciding on the composition of the new mortar unless other factors such as poor durability require a change in composition. The old mortar found should be documented by means of photos, and where needed, by analysis of its components [4].

Repointing just to improve the appearance is not recommended. Selective repointing of deteriorated areas under a long-term maintenance program is the best approach, unless difficulty of access makes it more effective to repoint the whole structure (e.g. the need for expensive scaffolding). Selective repointing is also the best choice for thin mortar joints where removal of the existing mortar is difficult and is very likely to damage the masonry units. The same may apply to hard pointing mortars. Even though the mortar may be inappropriate, removal may cause more damage to the existing masonry units than leaving it in place.

2 Design and construction issues

Requirements to consider for repointing mortars include:

Conservation issues

- *Historic authenticity/compatibility*
  - repair mortar to be compatible with the existing masonry units and mortar, and/or with the original mortar.
  - collect basic data about the mortar ingredients for both the existing mortar and the repair mortar.
  - where required for historic authenticity, the mortar ingredients should be matched to the original where possible. This may not be easy to do because the original ingredients may no longer be available, the original mortar may have insufficient durability, or the original ingredients may be difficult to determine. Chemical reactions with other materials in the mortar or the

environment, as well as deterioration processes, may significantly change the original composition over the years.

- *Try to have a repointing mortar which can be removed without damage to the masonry units in future repair (reversibility)*
  - mortar no stronger than needed for structural and durability requirements.

Aesthetic issues

- *Visual appearance*
  - assess colour (e.g. based on unweathered portion of existing mortar), texture and surface profile.
- *Not cause staining on the surface*
  - low risk of efflorescence or lime leaching (e.g. after repointing, avoid rapid drying, and provide temporary protection from rain).
  - no mortar staining on the masonry units resulting from the application of the mortar.

Moisture issues

- *Resist moisture ingress and do not restrict drying*
  - apply an appropriate finish (profile) to the mortar joint to encourage the shedding of water.
  - low risk of cracks developing. This means negligible shrinkage, compatible thermal and moisture expansion properties, adequate deformation under load (elastic modulus), and good bond with the masonry units.
  - have a properly cleaned out mortar joint, well filled during repointing and adequate bond to the masonry unit to hold the repointing mortar within the joint.
  - appropriate porosity to allow drying of the wall.

Service life

Service life not only depends on the mortar mix but also on how it is installed (workmanship) and cured, on the compatibility between the masonry unit and mortar, and on the severity of the environmental exposure, which in turn depends on weather, design, construction practice, operation, and maintenance.

- *Adequate service life of the pointing mortar (durable)*
  - Resistance to the expected environmental loads (e.g. freeze-thaw cycles, salts, wind erosion, acid rain, biological elements). For example, aggregate grading and air entrainment have an important influence on frost-resistance.

- *Repointing mortar will not have a negative effect on the durability of the existing masonry*.
  - repointing mortar should not cause stress concentrations in the wall.
  - mortar bond strength lower than the tensile strength of the masonry unit.
  - no damaging salts within the mortar.
  - promote drying; the mortar should have adequate moisture and soluble salt transfer properties.

- *Construction (execution) issues*
  'Successful performance of mortar repair work to historic masonry depends 50% on appropriate design and 50% on how well the work is executed on site' [5].
  - Repair mortars should be practical in application (e.g. workmanship, quality control, requirements for curing conditions).
  - Having a contractor experienced in the conservation of older masonry is a vital step in ensuring successful repointing.
  - Mixing procedures will vary depending on the mortar binder.
  - Supervision and quality control are important! Low-strength repair mortars, often used for older masonry, are less forgiving of errors.
  For example, inspect at each stage of the pointing
  (1) after the joints are raked out to make sure they are clean and square.
  (2) inspect after any back pointing is completed. The remaining part of the joint to be pointed must be clean for the final pointing.
  (3) inspect after the final pointing. Check that there are no voids left behind the pointing. A screwdriver inserted at random locations is one way of checking.
  (4) make sure curing is carried out properly (e.g. hydraulic lime and lime/pozzolan mortars should preferably be damp cured for a minimum of seven days).

- *Maintenance issues*

- For larger projects develop a maintenance guide documenting the evaluation of the masonry before the work started, the materials used for the work, and the installation practice. Recommendations on regular visual inspection for signs of deterioration should be provided, ideally in a checklist format.
- Ensure prompt repair of water shedding elements (e.g. gutters, downspouts).

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TC.06

Performance and Repair Requirements for Bedding Mortars

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Abstract A brief overview is given of performance requirements for bedding mortars for historic masonry.

1 Introduction

This paper highlights aspects of the chapter on performance requirements for bedding mortars to be included in the forthcoming RILEM TC 203-RHM guide on repair mortars for historic masonry. Existing information on bedding is also available [e.g. 1].

A bedding mortar provides an even bed and bonding for masonry units to ensure stability and an even transfer of load. The mortar also provides resistance to moisture and air penetration (weather-tight). It should also be durable. The bedding mortar may be exposed on the exterior surface or recessed for later pointing.

Bedding mortars for historic masonry are composed of a binder such as lime, an aggregate such as sand, and water which gives them initial plasticity. Additives or pigments may also be present.

There are five levels of restoration to consider: do nothing, stabilize, repair, restore, and/or replace [3]. Before deciding on any work, carry out a building condition assessment which should include a thorough survey of the composition of the existing masonry and its condition (see workshop paper 'Repair mortars for historic masonry. From problem to intervention: a decision process'). The cause of material deterioration should be determined and any repair work to reduce the risk of mortar deterioration should be addressed prior to repair. On bigger projects, it can be worthwhile to do a small initial project to obtain an idea of likely costs and unforeseen factors.

2 Design and construction issues

Performance requirements for mortars vary depending on the needs. They may also conflict with each other, and therefore the designer will have to decide on the priorities and make compromises. Furthermore there can be varying opinions on appropriate requirements. Requirements to consider for bedding mortars include:

Conservation issues

- *Historic authenticity/compatibility*
  - repair mortar to be compatible with the existing masonry units and mortar, and/or with the original mortar.
  - where required for historic authenticity, the mortar ingredients should be matched to the original where possible. This may not be easy to do because the original ingredients may no longer be available, the original mortar may have insufficient durability, or the original ingredients may be difficult to determine. Chemical reactions with other materials in the mortar or the environment, as well as deterioration processes, may significantly change the original composition over the years.
- *Able to remove the mortar without damage to the masonry units in future repair (reversibility)*
  - mortar should not be stronger than needed for the structural and durability requirements. This will reduce the chance of damage to the masonry units in future repairs. In the case of demolition, it may be possible to use the masonry units in other locations in the same structure or in other structures if the mortar is easy to remove.

Aesthetic issues

- *Visual appearance of the mortar if bedding mortar is carried to the face of the joint*.
  - assess colour, texture and surface profile (e.g. the particle grading and colour of the aggregate are factors of importance for the appearance).

- *Mortar should not cause staining on the surface*
  - low risk of efflorescence or lime leaching.
  - no mortar stains on the masonry units resulting from the application of the mortar.

Structural issues

- *Withstand imposed permanent and transient loads*
  - Gain strength sufficiently early to resist short-term applied loads.
  - Develop enough strength to resist permanent loads, and transient loads such as wind and earthquake. Pure lime (non-hydraulic) bedding mortars can take a long time to gain strength (fully carbonate). They need access to atmospheric carbon dioxide and a minimum humidity. Within thick masonry walls or damp walls it may take a very long time to fully carbonate if at all (especially walls with dense masonry units). Their use in such walls is therefore discouraged. A pozzolan or a small amount of cement should be added to ensure a more even and rapid gain in strength, or another possible alternative is an hydraulic lime mortar.
- *Withstand structural effects of short and long-term movements*
  - Assess loads induced by temperature and moisture movement (e.g. thermal movement in parapets can lead to cracks in mortar joints).
  - Assess effects due to shrinkage and creep.

Weather-tightness

- *Resist moisture ingress and airflow through the joint, and not restrict drying*
  The mortar should resist water penetration through the masonry. Most water infiltration through a masonry wall occurs at the interface of the mortar and the masonry unit, and voids in the mortar joints. Relatively little is transmitted through the mortar itself.
  - where exposed, the mortar joint should have an appropriate finish (profile) to encourage the shedding of water.
  - low risk of cracks developing. This means low shrinkage, compatible thermal and moisture expansion properties, adequate deformation under load (elastic modulus), and adequate bond with the masonry units.
  - mortar in the joints should have negligible voids, and full contact with the masonry units. Good mortar workability will increase the likelihood of full contact.
  - there should be good drying capability through the mortar joint should the masonry become wet. This is especially important in masonry with dense masonry units (the mortar will allow the masonry to 'breathe').

Service life

Service life not only depends on the mortar mix but also on how it is installed (workmanship) and cured, on the compatibility between the masonry unit and mortar, and on the severity of the environmental exposure, which in turn depends on weather, design, construction practice, operation, and maintenance.

- *Adequate service life of the mortar itself*
  - Resistance to expected environmental loads (e.g. freeze-thaw cycles, salts, wind erosion, acid rain & biological elements).
- *The risk of damage to the existing masonry not to be increased by the new repair mortar*
  - no damaging salts within the mortar.
  - mortar bond strength lower than the tensile strength of the masonry unit.
  - promote drying; the mortar should have adequate moisture and soluble salt transfer properties.

Construction (execution) to ensure good performance and service life.

In the elder days of art, builders wrought with greatest care each minute and unseen part; for the gods see everywhere [3]. This may not be an accurate reflection of past construction procedures, but it is something to aim for in the conservation of historic buildings.

- Use a contractor experienced in the conservation of older masonry.
- Repair mortars should be practical in application to encourage good workmanship.
  - Mortar should have a sufficient usable life before setting. Some mortars set very quickly (e.g. a natural cement mortar sets within half an hour).
  - Mortar holds together (cohesive) to reduce excessive flow and risk of staining masonry.
  - Spreads easily over the masonry unit, is plastic long enough after laying to allow placing of the next masonry unit, and stiffens rapidly enough so several courses can be laid without mortar squeezing out or deforming.
- Careful execution of the work including adequate curing conditions. The designer should talk to the masons and mortar mixer beforehand. Only one person should be assigned to mixing the mortar.
- Supervision and quality control are important! Low-strength repair mortars, often used for older masonry, are less forgiving of errors.

Maintenance is an important factor in service life.

- For larger projects develop a maintenance guide documenting the evaluation of the masonry before the work started, the materials used for the work, and the installation practice. Recommendations on regular visual inspection for signs of deterioration should be provided, ideally in a checklist format.
- Ensure prompt repair of water shedding elements (e.g. gutters, downspouts, flashings).

Performance requirements can be assessed with the help of tests (see the paper on testing of repair mortars for historic masonry):

- Performance of the mortar as part of the masonry is most important (e.g. flexural bond test). Performance of mortar specimens cast separately is useful for comparative testing and quality control.

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TC.07

Performance and Repair Requirements for Renders and Plasters

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Abstract This summary deals with repair or replacement of renders and plasters. Introducing design issues such as functional, technical, and performance requirements, and authenticity and compatibility, it eventually focuses on the aspects related to the choice of repair renders and plasters on salt laden substrates.

1 Introduction

Renders (exterior) and plasters (interior) constitute the protective and/or decorative skin of structures composed of stone, brick masonry or even adobe. They have been used continuously from prehistoric times to the present.

Renders and plasters show a wide variation in properties not only due to the method of application but also geographically and over time. The thickness of historical renders range from coats of considerable thickness to coats less than a centimetre in thickness [1]. The different layers generally show very good adhesion with the masonry substrate. Up to the 19th century most mortars were based on lime. The composition usually is comparable with modern non-hydraulic pure lime mortars but were sometimes sub-hydraulic to weakly hydraulic. An exception was mud mortars used in covering adobe. However, hydraulic

components such as pozzolans, brick dust, or other additions (gypsum, marble dust) were widely used for enhancing the protective role (impermeability) or for decorative purposes. After the 19th century cement gradually became one of the main constituents of renders and plasters; their use is covered in modern standards (e.g. EN, ASTM etc.). However, these standards do not cover the needs of repairing older historic structures.

2 Design issues

2.1 Functional requirements

Functional requirements derive from (i) the role or function of the mortar on the masonry element, and (ii) the role of the masonry element in the building. The requirements will differ depending on whether the mortar is applied on exterior surfaces (renders) or interior surfaces (plaster). Resistance to frost and rainwater penetration are clearly related to outdoor renders. Resistance to salts and mechanical actions may apply to both outdoor and indoor applications. If plaster is used as a base for artwork, further requirements may apply. The composition of mortar for the repair of renders/plasters should, through defined performance characteristics, be related to functional requirements.

2.2 Technical requirements based on performance

Introduction

Renders are used in exterior applications and *plasters* in interior applications, therefore their performance requirements may significantly differ. For renders (driving) rain, frost, and aerosols may be important threats to a long service life. At first sight for *plasters* a good surface hardness may be more important than frost resistance or its hygric characteristics. However, this may not be true if salts are present in combination with rising damp in an inner wall which may cause serious damage to a plaster.

For *renders* as well as *plasters* the boundary transition surface between masonry and mortar plays an important role on the bonding properties. Furthermore, the technique used for mortar application is a practical parameter that influences the bonding and depends on the technician's expertise.

Many practical aspects should also be considered, such as the proper consistency of the mortars that should be checked as well as premature setting; subsequently, measures should be taken in case of high temperature and low relative humidity; and finally the curing period and regime should be predetermined.

Performance requirements

General technical requirements for renders and plasters are:

- not to damage the existing substrate
- not be of higher strength than the existing old mortars
- be flexible enough for spreading and filling lacunae
- develop adhesion with the masonry
- low tendency to shrinkage
- resist as much as possible the local environmental conditions

Specific technical requirements for repair renders and plasters are:
(R): especially relevant to renders
(P): especially relevant to plasters

- moderate capillary water absorption (R)
- high drying (R)
- some degree of surface hardness
- low amounts of released salts
- good resistance to soluble salts
- good resistance to freeze-thaw cycles (R)
- colour and texture compatible with the objectives defined for the intervention

2.3 Historic authenticity & compatibility

Regular replacement of plaster and render has always been a normal maintenance activity. Deteriorated plasters are not only repaired for aesthetic reasons but more importantly for the protection and preservation of the underlying masonry wall. Render (and plaster) play a very important role in the protection of our cultural heritage.

Given the relevance of the medium and long-term performance of historic masonry in our built heritage, protection and preservation should be the first objective to be taken into account in the physical preservation of the existing materials and structures. This means that the repair mortar should contribute to this objective during its service life; moreover, it should be able to be removed without damage to the masonry once this functionality is lost. However, at the same time the repair mortar should also be as durable as possible, to avoid unnecessary maintenance.

Practice shows that protection requirements related to the masonry substrate may sometimes be contrary to those required for a durable repair material: avoidance of degradation of the substrate versus degradation of the repair material. An example in this respect is bond strength: a repair material with high durability often develops a strong bond with the existing materials. But high bond strength may cause substantial damage to the masonry substrate if the repair render has to be removed in future conservation work. From this it can be concluded that for the

selection a repair render-mortar different viewpoints must be considered, and consequently compromises are often unavoidable.

3 Repair render/plaster considering salt damage risks

3.1 Traditional mortars

This paper briefly considers the choice of mortars for salt laden substrates. Traditional renders and plasters were usually transporting systems: salts easily travel through the plaster to the surface. In simple constructions they were transported quickly through several layers of air lime mortars and lime paint. In important constructions (such as military and religious constructions) and where severe exposure to salts was foreseen, the mortars were prepared with binders, such as pozzolans or hydraulic lime, which conferred them some hydraulicity. In these cases they functioned as slow transporting systems [2].

In both cases they were multilayer systems with higher porosity and smaller pores in the external coats, thus salt crystallization occurred normally on the outer surface or at least in the outer layer. In these conditions frequent simple maintenance operations (in the outer layer) permitted good durability of the render system.

Plasters were not usually directly attacked by salts, as crystallisation took place at the outside face of the render. They were also multilayer systems, but the last layer was sometimes quite impermeable, for example ceramic glazed tiles or decorated plasters with water repellent additives.

The use of repair mortars that reproduce this functioning is a possible solution for repair, as it should work in the same way as the old ones provided there are no important changes concerning environmental conditions such as high pollution, climatic variations or internal conditioning [3].

3.2 Prefab mortars

Traditionally, renders and plasters have been made using locally available materials such as sand and binders (hydrated lime, hydraulic lime, pozzolanic binders, and more recently cement).

However, the application of traditional repair renders on salt containing substrates may lead to problems (bond, durability).

For some decades now, pre-fabricated renders/plasters have been developed to improve performance where salts are present. These industrially designed restoration plasters are often composed of various types of aggregates. Besides sand, lightweight aggregates such as pumice, perlite and vermiculite are used. The

binding agent is usually cement. Often additives are added to influence the salt-moisture flow in the mortar.
For the choice of an adequate prefab repair mortar see [4]. In [4] the choice of prefab repair mortars is related to the degree of risk, determined as a function of:

- the moisture load in the substrate; especially the number of wet-dry cycles or the number relative humidity cycles around an equilibrium RH of a salt (combination) present
- the porosity (mainly coarse pores) in the substrate
- the salt content in the substrate

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TC.08

Performance and Repair Requirements for Flooring Mortars

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Abstract Mortars have been widely used even in prehistoric periods in making pavements in open areas or floors inside dwellings. They are found as surface layers well-compacted and polished, as sub-bases on which stone or ceramic units has been applied (as well as the mortar between the units), and as multilayer substrates for floor mosaics. Repairing flooring mortars constitutes a great part of restoration projects of archaeological sites. In particular, the repair of mosaics attracts great interest since they could be considered as non-detachable work of art. This paper considers aspects of the performance requirements for repair mortars for mosaic substrates and joints in historic pavements and stairs.

1 Introduction

Flooring mortars may comprise the multilayer substrates of floor mosaics, sub-bases on which units such as stone or ceramic pavers have been applied (as well as filling the joints between the units), or even a finished or polished floor surface. Figures 1-6 show different floors found in archaeological sites and historic structures. Most of mortars are lime-based apart from those flooring mortars found in constructions dated from the period after industrial revolution which were often based on stronger hydraulic binders such as hydraulic lime, natural cement or

Portland cement. Flooring mortars which are applied on the ground are characterized by their high degree of compaction and high content of aggregates. This paper highlights aspects of the performance requirements for repair mortars for mosaic substrates and joints in historic pavements and stairs. This will form part of the chapter on flooring mortars in the forthcoming RILEM TC 203-RHM guide on repair mortars for historic masonry [1].

Fig. 1 Byzantine floor mosaic in the archaeological site of Filippoi, Greece (6th cent AD)

Fig. 2 Hellenistic substrate of a floor mosaic in Pella, Greece (4th cent BC)

Fig. 3 Hellenistic floor mosaic in Pella, Greece (4th cent BC)

Fig. 4 Floor mosaic of the Palace in Aiges, Greece (4th cent BC)

Fig. 5 Pavement in Urdiales fortress, Spain

Fig. 6 Floor paving subject to severe exposure. Note salt saturation from de-icing salts at the bottom of the columns (side entrance Parliament buildings, Ottawa, Canada)

The deterioration problems of floor mosaics and their repair have drawn the attention of many researchers [2-6]. This includes the conservation of tesserae

and consolidation of tesselatum [2] or damage of the thick stratified mortar substrate such as:

- Cracks due to ground movements.
- Loss of mortar layers or lacunae formation.
- Detachment of substrate mortar layers due to depression or bulging of the ground.
- Cavities due to intrusion of vegetation.
- Completion of missing parts of the mosaic substrate.

Most binders in flooring mortars are lime or lime and pozzolan, which are soft materials in comparison to cement based mortars.

In the floors of historic structures exposed to outdoors conditions (Figs. 5, 6), a common problem is the deterioration of the mortar in the joints between paving stones, due to air pollutants, frost action, de-icing salts, and marine environments where sea spray accelerates salt weathering mechanisms [7].

2 Functional requirements

Floor mortars should fulfil the following functional requirements:

- Compatibility so the authentic parts of the ancient mosaics or other floors are protected.
- Aesthetic harmonization with the old floor.
- Adequate mechanical strength and resistance to abrasion to serve as pavements.
- Resistance to leaching, freezing and de-icing salt attack.
- Low cracking tendency.
- Easy to remove and replace.

When repointing historic floors in cold climates, very often the compatibility issues are practised by pursuing the best match with the existing stone and a high resistance to salt and frost damage.

3 Pre-design issues

The input of a broad range of disciplines is strongly recommended (e.g. archaeologists, surveyors, geotechnical engineers, architects and material specialists). For example, several pre-mixed mortars are available for repair without sufficient documentation of their performance in practice. A material specialist could alternatively design a mortar mix for the particular project.

It is also advisable to choose an independent laboratory to undertake the monitoring and quality control during the restoration work.

3.1 Preparatory work: Repairing substrates for mosaics (Mediterranean conditions)

The following preparatory work is suggested:

- Document the authentic floor parts and record them on the ground plan. Make a representation of the ancient architectural design.
- Decide upon the conservation and protection of the authentic parts during the restoration work.
- Make a topographic plan of the field.
- Make a survey of the old floor, and map the damage and its severity. Collect information about previous earth movements, ground water level, ancient rivers, stratigraphy of the ground etc. as well as climatic conditions, soil characterization and other items.
- Study the ancient drainage system and save the existing parts.
- Describe the stratigraphy of the old floor mortar (Figs. 7, 8).
- Analyze systematically mortar samples from the old floor to find their characteristics and properties (Fig. 8).
- Do research to find local sources for raw materials.
- During excavations the sub-ground of the floor will be "disturbed", therefore measures should be taken for reconsolidation of the ground sub-base such as removal of plants and treatment of the soil for elimination of vegetation.

It must be pointed out that the compaction or modification of the soil base, on which the repair floor mortar will be spread, is of great importance for the service life. In addition, special care must be taken for the leveling of the finishing mortar layer in order to allow good water drainage.

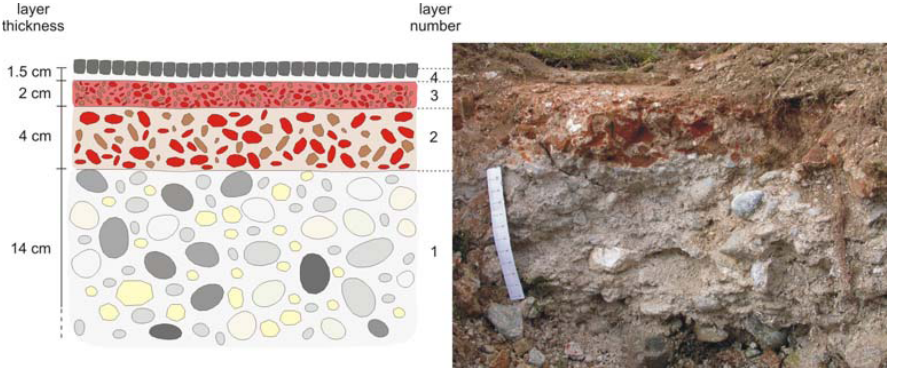

Fig. 7 Roman floor mosaic and stratigraphy of the substrate, ancient city of Dion, Greece (2nd cent AD) [8]

Fig. 8 Floor mosaic of the Palace of Aiges, Greece (4th cent BC)

3.2 Repointing historic pavements and stairs (cold weather conditions)

- For horizontal surfaces, drainage away from the adjacent walls should be ensured by having a minimum slope of 2%.
- It is important to understand how the components of the pavement (units and joint mortars) behave and interact.
- The severity of climatic conditions should be taken into account for the selection of a suitable mortar. Use of movement joints or sand joints is a possibility where needed. Expect cyclical maintenance every two or three years (Fig. 9).

Fig. 9 Condition of joint mortar in Spring (Canada)

4 Materials and performance requirements (Mediterranean conditions)

4.1 Repairing mosaic substrates

For repair mortars for floors, apply the general criteria of suitability mentioned in the RILEM TC 203-RHM document [1]. In the particular case of repair mortars for mosaic substrates, the aggregate's mineralogy and gradation should follow that of each layer of the existing floor. The binding system should be based on lime or lime-pozzolan as occurs in the old mortars. Admixtures free of sulphates may be used to improve workability. Mortar mixes for flooring must have low workability (about 11±1cm expansion measured by the flow table). In addition, it is essential to compact the mortar very well with a hand or mechanical tamper. Cold joints must be avoided and in large outdoor floors include shrinkage joints.

Colour, texture or design motifs of the finishing layers should aesthetically harmonize with the existing old floor. The appearance of soluble salts on the floor surface can be eliminated by controlling the salt and alkali content of all mortar ingredients.

Complete drainage is important for increasing the mortar's service life. Stagnating water on top of floors results in surface damage and scaling. It is important that water not to be retained within the mortar floor slab. In floors, water can infiltrate from the surface into ground and rise from the soil into the mortar. The use of a crushed stone layer at the bottom of mortar slab in contact with soil is an old and effective way to avoid damage from ground water.

Lime leaching from floor mortars could be eliminated by selecting binders in which lime will be sufficiently bound, such as lime + reactive pozzolan.

The design of the mortar mix for flooring includes strength requirements. The strength level should match as much as possible the strength of the old floor slab in addition to other performance requirements. Mortar strength has to be defined previously at the laboratory with sufficient tests in order to be reliable. Apart from compressive strength, bending strength may also be estimated by testing.

Lime-based mortars have a lower modulus of elasticity in comparison to cement-based mortars. This difference has to be considered in the selection of the binders. For comparing mortars, the modulus of elasticity may be evaluated by sonic equipment (dynamic modulus) or by stress-strain tests (static modulus of elasticity).

- Resistance to freeze-thaw cycles

These issues are discussed in more detail in the RILEM TC 203-RHM document [1]. The efficiency of air-entraining agents to improve resistance to frost is less in the case of flooring mortars which are fully compacted. Covering the mosaics in archaeological sites during winter with nylon sheet and sand seems to be effective in practice.

4.2 Repointing historic pavements and stairs (cold weather conditions)

Aggregates should fulfil the general suitability criteria about harmful impurities. Their colour should preferably match the existing mortar or the stone units. The size of aggregates should be selected according to the width of the joint.

Based on existing experience in North America, hydraulic lime and natural cement are not yet so reliable for these repair works, while mixes of lime and cement are more effective (with integral air entraining agent). Air entraining admixtures have been only used in restoration projects to improve resistance to frost attack. Pigments resistant to UV radiation are added after testing for optimum dosage.

The most crucial requirements for mortars used in repairing joints of pavements and stairs are those related to frost and salt damage (Fig. 10). To avoid such damage, the moisture content of the mortar must be kept low by taking care to have a proper slope on horizontal surfaces to avoid water stagnation. To eliminate efflorescence and salt crystallization within mortars, the salt content of all ingredients of the mortars and surrounding materials should be kept at low as possible.

Fig. 10 Salt damage on mortar, stones and concrete base of stairs. Partial dismantling (Canada)

5 Construction

Issues concerning the set-up and running of a worksite, site supervision, manipulation of the materials and sufficient mixing of ingredients are mentioned in more detail in the RILEM TC 203RHM document [1].

5.1 Repairing substrates of mosaics (Mediterranean conditions)

- Preparation of the ground sub-base

The floor mortar is in contact with the ground, and therefore directly affected by ground movement. Any differential deformation between surface layer and the ground sub-base could lead to cracking. In the case of large surfaces, permeable geomembranes are often used between the ground and the new floor mortar slab. Very often the old way of spreading a layer of crushed stone on the ground is also followed.

- Mortar mixing

Mixers of greater capacity and stronger than conventional ones are needed because of the high content in coarse aggregate. The bulk density of the mixture could be used as a measure of its homogeneity. Decide about proper moulds for taking fresh mortar samples for quality tests (mechanical strength and other properties).

The water demand for a desirable workability level has to be defined by trial mixes, and adjusted to weather conditions and the moisture content of the ingredients. The work plan has to be well scheduled since successive mortar layers will be applied and cold joints are unavoidable when the surface dries too quickly. In addition, because of the low water content in the mortar there is risk of rapid stiffening of the mix at high temperatures (e.g. >27°C). Measures have to be taken to protect the fresh mortar mix and the surface of the mortar layer.

In mortar mixtures with large size aggregate, the Vicat cone test method is not suitable to assess consistency. A simple cone slump test is preferred [1]. Special care must be taken with pigments to ensure a uniform distribution in the mix.

- Mortar application

It is important to keep the ground sub-base damp (but not wet) to avoid premature drying of the mortar mix. Decide upon the floor area to repair according to the status of the worksite (capacity of the mixer, personnel etc) and keep strictly to a work plan.

After placing the mortar, adequate compaction has to be provided (the method and degree of compaction to be decided beforehand using trial mixes). Work interruption is not acceptable or has to be programmed. The level of compaction can be checked periodically on site by taking cores.

In large floor areas, the cutting of joints must be decided beforehand as well as the method for finishing the surface. The joint spacing should be decided according to the mechanical strength of the mortar.

Temperature and wind conditions during application should be documented.

- Mortar curing and protection

Mortar slabs for flooring are very susceptible to shrinkage during the first 24-48 hours (depending on the mortar binder), as well as long-term drying shrinkage. The former can be reduced if proper curing is provided. The curing period should be extended in hot-dry weather. Experience from field-work showed that two weeks damp curing (provided by wet burlap covered with nylon sheets) is effective in the case of mortar binders with low hydraulicity (such as lime-pozzolans). Even with lime mortar, protection from drying is necessary.

The resistance to frost of moist lime-based mortars is low. The addition of air-entraining agents to flooring mortars which are spread and compacted is not very effective. Early frost damage is avoided by selecting the proper season for application. Even hardened floor mortars are covered with nylon sheets and a layer of sand during winter to avoid frost damage. This is considered part of the maintenance work.

- Quality control

Quality control tests include:

- Tests for suitability of the raw materials (binders, aggregates, additives). Aggregate gradation should meet the coarser gradation of the recommended ones in standards for concrete aggregate.
- Tests for fresh mortar.
- Tests for workability or consistency of the mortar.
- Air content of the mortar.
- Density of the fresh mortar (with and without compaction).
- Mortar samples must be moulded, cured and tested under a defined regime for testing compressive and bending strength. For mortar with large size aggregate, larger moulds may be needed depending on aggregate size (e.g. cubes 15x15x15cm and prisms 10x10x40cm).
- A curing regime must be defined depending on the type of mortar binder. For lime-pozzolan mortars longer curing periods are suggested.

5.2 Repointing historic pavements and stairs (cold weather conditions)

Adequate workability is very important for achieving good workmanship. Apart from testing the properties of a mortar for its suitability, trial applications on site are recommended.

Quality control tests should include control of mortar consistency, air content, setting time, bond of mortar to masonry units, checking for voids behind repointing, as well as mechanical characteristics by making test samples for each mortar batch. Simple tests such as Vicat cone test may be used to check the consistency of the mortar batches [9].

Fresh mortar joints should be protected from rain, wind and sun by keeping them damp for three to seven days to avoid shrinkage cracks or obscuring the natural colour of the mortar (Fig. 11). Mortar should also be protected against early freezing in cold weather.

A maintenance strategy after completion of repair work is of great importance. A technical description of the whole intervention should be delivered to the owner of the pavement/stairs with recommendations for regular visual inspections using a checklist.

Fig. 11 Curing with wet burlap and plastic for a minimum of three days

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TC.09

Performance and Repair Requirements for Surface Repairs

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Abstract This paper is a summary of a document prepared by RILEM TC 203-RHM on Repair mortars for historic masonry. It deals with requirements for the design of a repair mortar used for surface repairs of architectural surfaces. It considers design issues and requirements for mortar mixes which can be made at the construction site and it focuses on mortar mixes based on lime, lime-pozzolana and cement binding systems.

1 Introduction

Various terms are used, which have the same or very similar meaning to *surface repair* actions, such as application of *plastic repairs, surface fills, loss compensation mortars,* and *artificial stone mixtures*. All these methods have in common that a missing part of an original material is modelled by a new material which is pliable when applied and therefore can be adapted into various shapes and finished with required surface textures. All these repair actions are usually carried out on a small scale, with each particular case approached individually.

The individual approach to each case (modelling a material and/or an architectural detail) is the main difference from other repair actions when mortar is used.

Surface repair is a restoration treatment, where a new material and modern techniques are applied. The *General Approach and Conceptual Requirements* are set out by the Charter of Venice [1] as the following:

- no conjectural repairs
- efficiency of materials and techniques used for repair should be shown by scientific data and proved by experience
- replacement of missing parts must integrate harmoniously with the whole, but at the same time must be distinguishable from the original (no falsification of the artistic or historic evidence)

Mortar repairs used to replace deteriorated stone units have been in common use for some time and many historic stone buildings contain such repairs. Figs. 1 and 2 show an example of the application of surface repair.

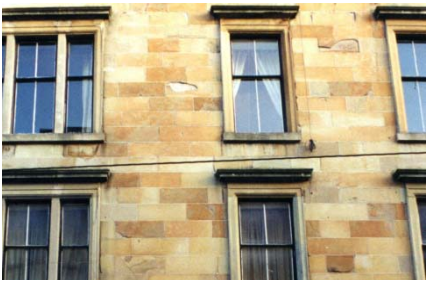

Fig. 1 Advanced deterioration of the 19th century sandstone ashlar masonry façade.

Fig. 2 Example of mortar application as a surface repair of deteriorated stone units.

The performance of surface repairs carried out in the past can, after some time of exposure, be evaluated. Fig. 3 demonstrates a repair which can be regarded as successful and Fig. 4 shows a surface repair which in a complex view is not performing satisfactorily any more. There exist also cases where the properties of the new mortar repair caused, along with the specific exposure conditions, accelerated deterioration of original material, which is not acceptable from a cultural heritage preservation point of view.

Fig. 3 Mortar was used to repair deteriorated stone parts and detailing of the main entrance portal of the cathedral in Évora.

Fig. 4 Surface repair of a stone masonry. The repaired surface is durable but stone continues to decay. Aesthetically it is not functioning very well and it could accelerate decay of the adjacent stone.

In order to prevent potential damage to the original material (stone) a compatibility concept has been previously introduced. The technical definition of material compatibility of repair mortars with the original material suggests that no damage should be allowed to the original material within the service life of the repair [2]. The specification of a repair mortar from the technical compatibility point of view is based on a comparison of the properties of the new mortar and the original material. A variety of important characteristics to be compared have been suggested in literature [3, 4] and the compatibility concept has been reviewed by Hughes and Valek [5]. The compatibility requirement is one of the main factors to be considered when a new repair mortar for historic masonry is designed.

It should be recognised that the surface repair technique is often more complex including also treatment of substrate, application of reinforcement and surface finishing techniques. It also has to be acknowledged that various commercial pre-mixed mortar products are available from local and international companies. The advantage of these products lies in their consistent composition and working properties. The disadvantage of these mixes is an uncertainty about the ingredients they contain. A thorough review of the materials and methods has been published by Griswold and Uricheck [6].

This document does not deal with these mixes as they have their own specifications, however, they should, in principle, comply with the functional and performance requirements set generally in this document and their compatibility with the substrate should be evaluated before their application.

2 Pre-design issues

First of all, it is important to decide, whether the use of mortar for repair is the optimal repair action. This decision should be based on a global repair strategy.

Decision factors (based on Ashurst [7]) when considering surface repairs are the following:

- Preservation of more original material than (stone) replacement
- Less disruption of fragile areas of original material
- Avoid removal of structural elements
- Sacrificial performance of mortar should be considered and designed
- Size of areas to be repaired has to be considered
- Visual appearance of mortar repair versus (stone) replacement
- Are there sufficient available skills and knowledge to carry out a high quality repair

3 Design issues

When *surface repair* is selected as the most suitable repair method then a set of requirements, which the repair action has to fulfil, should be considered. For an historic building, this should follow the general concept of a repair mortar design considering general values, and conceptual, functional and technical requirements [8].

3.1 Design of surface repair mortars – points to be considered

Materials

The use of individual mortar components depends on the type, colour and texture of the material to be reinstated. The final visual appearance imitating or matching the substrate is in many cases the paramount criterion. The selection of a binder (binding system) is a starting point of the mix design as it predetermines the physical and mechanical properties of the mortar mix as well as the capacity of the mix to be adapted to the appropriate form and appearance. Filler and additives can however significantly modify the properties of mortar. Standards (EN, ASTM, BS etc.) specifying individual components for mortars and concretes are available. They may not exactly apply to this specific type of application but should be referred to in general for characterisation of the individual components.

State of substrate and its treatment

Substrate is the material that is being reinstated, usually a part of a masonry unit within a masonry structure. Mortar used for surface repairs without reinforcement has to adhere to the substrate. In this case, the substrate must not be friable and the deteriorated parts have to be cut out. Good adhesion (bond) between the substrate and the repair mortar is commonly presented as one of the main measures of success of repair and its long term durability. However, the bond surface is also the zone, where two different materials have to perform

together (stresses from differential thermal expansion, water and water vapour transports etc). Having a bond strength higher than the tensile strength of the substrate is understood as being incompatible in the case of historic structures [4].

Preparation of repair area

The stone/brick should be chiselled back to sound material. A minimum depth of approx. 20mm for the repair is required and the edges should not feather out. For masonry units a rectangular shape with the edges parallel to the joints is recommended.

Reinforcement

A surface repair of thickness above approx. 50mm generally requires reinforcement. Stainless steel and/or non-ferrous metals should be used. Dowels and reinforcement rods should be set back from the mortar's surface, typically a minimum of 10mm or two bar diameters, in order not to be exposed when the mortar weathers.

Mortar mixing procedures and fresh mortar properties

A relatively small amount of water is added to obtain the consistency of damp sand. Basic principles of mortar mixing apply also for surface repair mortars.

Application procedures, curing and protection

Mortar is applied in well pressed and compacted layers around 20mm thick and usually no thicker than 30mm. The final layer is built beyond the surface of the original stone and after reaching initial set it is scraped away and tooled to obtain the required appearance. Curing and protection applies according to the common principles of masonry practice.

Number of layers

Deeper cavities are filled in several layers in order to reduce the shrinkage and improve the compaction of mortar. Thickness of a layer depends on the consistency of mortar and relates to the size of filler particles. Optimum thickness is around 10-15mm. It has been a common practice that a special thin layer of diluted mortar mixture is applied before the application of the mortar. The mortar is applied directly on the wet layer.

Finishing techniques and coatings

The appearance of the mortar is related to the approach adopted for the restoration. The colouring can be integral, through the whole mortar layer, which is usually recommended for long lasting repairs.

Quality control

The surface repair is typically carried out in small batches. Therefore it is possible to pay attention to precise gauging of mortar ingredients and to follow the

specific application procedures. Workmanship, experience and skills are the important factors for successful work. A small initial project with trial panels should be carried out for the proposed mortar mix and repair procedure. The colour and final surface finish has to be agreed in advance and the procedure should be adhered to.

Maintenance plans and consideration of long term durability

Long term performance of the repair should be considered during the design of the repair intervention. Recommendations for regular visual inspection for signs of deterioration should be provided.

3.2 Functional requirements

Aesthetic appearance

Appropriate colour, texture and final finishing.
No mortar staining resulting from the application.
Low risk of lime leaching.

Compatibility with the substrate – no damage to substrate as a condition

Similar vapour permeability (drying rate) to the substrate.
Similar thermal and moisture expansion properties to the substrate.
Mortar should be slightly softer/ sacrificial.
Adequate bond and interface allowing moisture and vapour transport (if needed reinforcement is applied).
Mortar should release the least possible amount of salts.

Adequate service life

Careful execution of the work including adequate curing conditions.
Low risk of cracks development. Low shrinkage.
Resistance to expected environmental loads. Ageing and weathering should not significantly change the colour and the texture.
Weathering and deterioration similar to the adjacent materials (e.g. stone).

Reversibility

Mortar no stronger than needed for durability requirements.
Adequate bond strength but no stronger than needed.

3.3 Possible failures

- Difficult to match the surface appearance and colour.
- Low durability of final finishing and colouring.
- Problems with incompatibility of original and new material.

- Low quality of work execution (it is a specialized repair requiring experience).
- Inappropriate bond.

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2nd Conference on Historic Mortars and RILEM TC 203-RHM Final Workshop HMC2010

Proceedings of the 2nd RILEM Conference

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An objective of the 2nd Historic Mortars Conference is to bring together scientists, technicians and professionals involved in research and studies of historic mortars to present and discuss advances in this topic. The main theme of the conference is the conservation of historic buildings and works of art, i.e. studying mortars with respect to repair. This is a unifying field where a truly interdisciplinary collaboration is needed and where contributions of archaeologist, architects, civil and structural engineers, geologists, material scientists, chemists, conservation scientists and art restorers interested in mortars should have their place. The special focus of the conference will be on the application of research and technical knowledge to conservation practice and vice versa in its reflection on such recommendations.

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