

Characterization of binders employed in the manufacture of Venetian historical mortars

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Abstract

This research focuses on the characterization of historical mortars collected from a covered dockyard, called *tezzone* 105, erected in the Arsenal of Venice during the XVI century. The mortars date back to different building phases. A stratigraphical analysis of *tezzone* 105 has proposed a chronology of building interventions. The building phases recognized by the stratigraphical analysis belong to the original structure (XVI century) and to later interventions from XVI to XX century. Mortar samples are investigated by granulometric analysis, infrared spectroscopy (FT-IR), simultaneous thermal analysis (DSC/TG) and X-ray diffraction analysis (XRD) in order to identify the technology peculiar of each building phase. Mortar sampling was carried out on indoor masonry and foundation. Masonry mortars appeared to be characterized by the application of air-hardening binders, whereas foundation mortars were characterized by hydraulic binders. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Mortar; FT-IR spectroscopy; Simultaneous thermal analysis; X-ray diffraction; Air-hardening binder; Hydraulic binder

1. Research aims

This work reports research on historical mortars conducted in the framework of a multidisciplinary study concerning the Arsenal of Venice (Italy), CNR Project 'Target: Venezia'. At present, the necessity of restoration interventions on a covered dockyard, called *tezzone* 105, with materials which are compatible with the masonry structure, has required a detailed study on these materials. The mortars belong to different building phases recognized by the stratigraphical analysis. The aim is to supply additional scientific knowledge on mortar manufacture, in order to identify the building materials peculiar to the historical phases and applications. Moreover, this research offers useful parameters to evaluate the behaviour of these materials under the environmental conditions of the Venice Lagoon.

2. Introduction

The physical-chemical characterization of mortars used in ancient Venetian masonry has provided historical and technological information as regards their manufacture [1]. The use of air-hardening binders as lime and inert aggregate as sand is widespread. This sand was collected in some cases from the Venice lagoon and was previously washed. The employ of *cocciopesto* in the mixtures was another well-known feature in Byzantine and post-Byzantine buildings, and more generally in traditional ones. The *cocciopesto* mortars are composite materials, constituted by lime, ceramic fragments and/or ceramic powder, and other stone aggregates. The nature of these materials is hydraulic due to a chemical-physical interaction between calcium hydroxide and brick surface forming calcium silico-aluminate [2]. Moreover, the use of a mortar called *calce nigra* deriving from the Euganei hills, likely of hydraulic nature, has been previously mentioned [3].

The composition of historical mortars can hardly be determined owing both to the chemical transformations of the components during setting and hardening, and to the double function (binder and aggregate) often carried out by the same substance. Consequently, the reconstruction of the

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Table 1
Mortar samples collected from *tezzone* 105, Arsenal of Venice

Sample No.	Stratigraphical unit	Building phase	Age	Description
69M				
69A	69	I	1500	Mortar, indoor wall (E)
78	78	I	1500	Mortar, indoor wall (E)
79	79	I	1500	Mortar, indoor wall (E)
7	7	II	1500	Mortar, indoor wall (N)
231	231	II	1500	Mortar, indoor wall (S)
94	94	III	1800	Mortar, indoor wall (E)
269	269	III	1800	Mortar, indoor wall (S)
273	273	III	1800	Mortar, indoor wall (S)
229	229	IV	1800	Mortar, indoor wall (S)
240	240	IV	1800	Mortar, indoor wall (W)
105	105	V	1800	Mortar, indoor wall (E)
138	138	VII	1800	Plaster, indoor wall (E)
242	242	VIII	1900	Mortar, indoor wall (S)
C1	-	-	1500	Mortar, foundation (1.2 m depth)
C2	-	-	1500	Mortar, foundation (1.5 m depth)
C3	-	-	1500	Mortar, foundation (1.8 m depth)
C4	-	-	1500	Mortar, foundation (2.2 m depth)
C5	-	-	1500	Mortar, foundation (2.7 m depth)
C6	-	-	1500	Mortar, foundation (2.8 m depth)
C7	-	-	1500	Mortar, foundation (3.1 m depth)
C8	-	-	1500	Mortar, foundation (3.6 m depth)
C9	-	-	1500	Mortar, foundation (3.8 m depth)

original mixture composition can be attained only by combining and comparing the results of various complementary techniques of investigation [4,5].

In the Arsenal of the Serenissima Republic a continuous sequence of constructions, interventions and adaptations of existing buildings to different uses is readable on architectural surfaces. *Tezzone* 105, a covered dockyard erected in the Arsenal during the XVI century, is an interesting building from both historical and technological points of view, especially as regards the comparison between construction materials employed in the original structure and in the following centuries.

In this study the characterization of a significant number of historical mortars, collected from *tezzone* 105, is performed on the total sample and on the finer particle size fraction ($< 63 \mu\text{m}$) which is mostly composed by the binder [6]. The typology of binders used in the mixtures is identified by means of simultaneous thermal analysis, infrared spectroscopy and X-ray diffraction analysis performed on the finer particle size fractions.

3. Materials and methods

3.1. Sampling

Stratigraphical analysis and survey of decay of *tezzone* 105, carried out by R. Parenti and E. Danzi respectively, had indicated the sites interesting for mortars sampling. As a matter of fact, macroscopic observation by stratigraphical analysis had revealed the presence of eight building phases and 276 stratigraphical units.

According to stratigraphical analysis, samples of mortar and plaster were collected from indoor masonry that dates back to the original structure and later interventions, from the XVI to the XX centuries. The samples were taken from the upper parts of the building in order to avoid phenomena caused by capillary rise.

A second sampling was carried out on the foundation by coring to a depth of 8 meters. In sequence order from the floor the foundation is composed of cobblestones (1 m thick), an Istria stone slab (15 cm thick), layered masonry (3 m thick) and wood. We had assumed that the foundation dates back to the original structure (XVI century).

Information about age, site and typology of mortars collected from indoor masonry and foundation of *tezzone* 105 is listed in Table 1.

3.2. Analytical techniques

Identification of mortar typologies had required the granulometric analysis of samples by mechanical sieving (ISO 565 series sieves, meshes of 500, 250, 125 and $63 \mu\text{m}$). The most significant granulometric fraction, for the aim of this research, is that of particle size $< 63 \mu\text{m}$ containing the binder; although a little amount of fine grain aggregate frequently is present in this fraction [7]. Afterwards, the finer particle size fractions ($< 63 \mu\text{m}$) were analyzed by infrared spectroscopy (FT-IR NICOLET NEXUS 670/870), X-ray diffraction (Philips PW 3020 X-ray θ - 2θ diffractometer) and simultaneous thermal analysis (DSC/TG performed by NETZSCH STA 409C).

The DSC/TG curves were obtained in the temperature range 20–1000 °C. The sample mass was varied between 30

and 40 mg. The dynamic experiments on DSC/TG were carried out in nitrogen atmosphere at a flow rate of 25 ml min^{-1} and an heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

For comparison purpose the coarser particle size fractions ($> 63 \text{ }\mu\text{m}$) were investigated following the same procedure.

4. Results and discussion

4.1. Infrared spectroscopy

Infrared spectroscopy was employed for a qualitative characterization of the mortar samples. The finer ($< 63 \text{ }\mu\text{m}$) and the coarser ($> 63 \text{ }\mu\text{m}$) particle size fractions were analyzed by FT-IR spectroscopy in order to determine the presence of calcite ($2520, 1795, 1440, 875, 850$ and 715 cm^{-1}), portlandite (3642 cm^{-1}), brucite ($3693, 1638, 1005$ and 963 cm^{-1}), quartz ($1165, 1090, 800, 780, 694, 520$ and 400 cm^{-1}), and K-feldspars ($1100\text{--}1070, 1035, 690$ and 670 cm^{-1}).

Indoor masonry mortars are characterized by a similar composition: calcite is the main component as regards both binder (the finer fraction) and aggregate (the coarser fraction), though it is present in larger amounts in the binder. The aggregate is composed by calcite and silicon containing compounds (quartz and potassium feldspars). Typical FT-IR spectra are shown in Fig. 1. Absortions characteristic of quartz and silicates appear also in binder spectra due to an inadequate mechanical separation of mortar fractions.

In comparison to indoor masonry mortars, samples collected from foundation reveal a different composition. In addition to a large absorption characteristic of calcite the binder fractions show the typical absorptions of calcium hydroxide (portlandite) and magnesium hydroxide (brucite), as reported in Fig. 2 and Table 2. The presence of portlandite could be connected both to a reduced carbonation of air-hardening lime and to the use of hydraulic lime. In natural hydraulic lime, a certain amount of free calcium oxide remains that will convert to free calcium hydroxide after slaking [8]. As concerns brucite its presence could be due to the use of air-hardening lime obtained from a partially dolomitic limestone, therefore to the hydration of magnesium oxide, or to the precipitation of magnesium ions contained in salt water. Foundation mortars were situated under the water level, thus the latter hypothesis is as likely as the first.

4.2. X-ray diffraction

A representative XRD diffractogram for indoor masonry mortars is shown in Fig. 3. The finer particle size fractions ($< 63 \text{ }\mu\text{m}$) are composed by calcite, dolomite, quartz, corrensite, halite, illite, mica and gypsum. The presence of halite and gypsum are connected to environmental and pollution actions, whereas dolomite, quartz, corrensite, illite

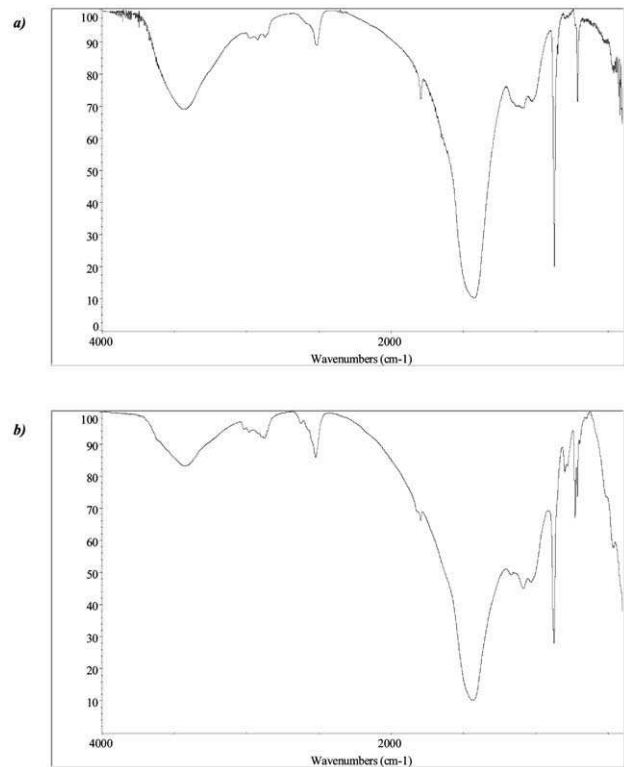


Fig. 1. FT-IR spectra of sample 229 (IV buiding phase, indoor wall): a) the finer particle size fraction ($< 63 \text{ }\mu\text{m}$); b) the coarser particle size fraction ($> 63 \text{ }\mu\text{m}$).

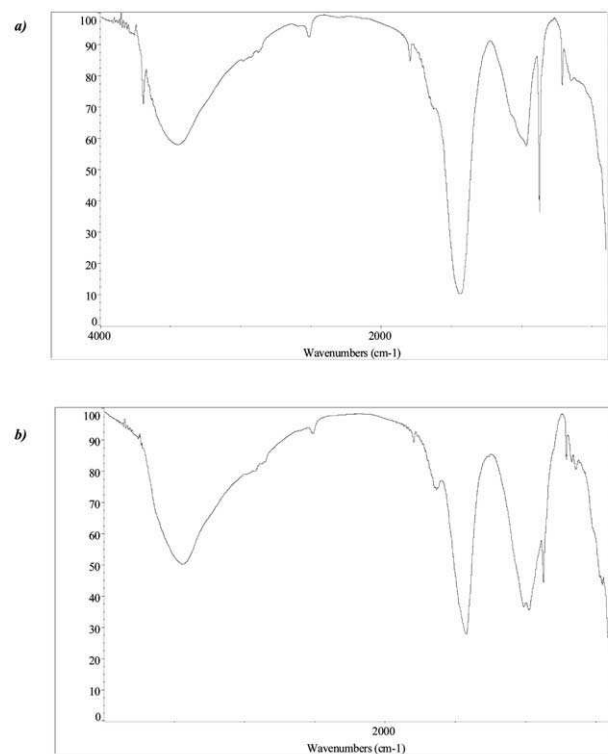


Fig. 2. FT-IR spectra of sample C7 (original structure, foundation): a) the finer particle size fraction ($< 63 \text{ }\mu\text{m}$); b) the coarser particle size fraction ($> 63 \text{ }\mu\text{m}$).

Table 2

Presence of portlandite and brucite revealed by FT-IR spectra of foundation mortars binder fractions

Sample No.	C1	C2	C3	C4	C5	C6	C7	C8	C9
Ca(OH) ₂					+	+		+	
Mg(OH) ₂	+	+		+	+		+	+	+

and mica are attributed to fine grains of aggregate passed through a 63 µm-size sieve. These results indicate the air-hardening nature of binders employed in the manufacture of indoor masonry mortars.

A comparison between XRD diffractograms of foundation binder fractions is reported in Fig. 4. The binder fractions are characterized by the presence of calcite, quartz, portlandite (sample C6) and ettringite (sample C3). Moreover, in all the samples analysed by XRD an unassigned line at about 11.35° was noticed. In order to assign the line two fractions of binder C6, characterized by the strongest line at about 11.35°, were treated separately with distilled water and diluted hydrochloric acid (3 mol l⁻¹). XRD diffractograms were collected on the treated samples (Fig. 5). These data show that the unknown compound has a solubility both in water and in hydrochloric acid comparable with that of calcite.

The identification of the compound corresponding to this line value is still not clear. Nevertheless, according to our opinion this line could correspond to the presence of an anionic clay as hydrocalumite (Ca₄Al₂CO₃(OH)₁₂·5H₂O), hydrotalcite (Mg₆Al₂CO₃(OH)₁₆·4H₂O) or sjogrenite (Mg₆Fe₂CO₃(OH)₁₆·4H₂O). Previous studies on formation of anionic clays [9,10] have reported that the addition of lime (and dolomite) to fly ash slurries produces the precipitation of hydrocalumite and hydrotalcite. The structures of both hydrocalumite and hydrotalcite are characterized by a stacked sequence of octahedral layers (portlandite or bru-

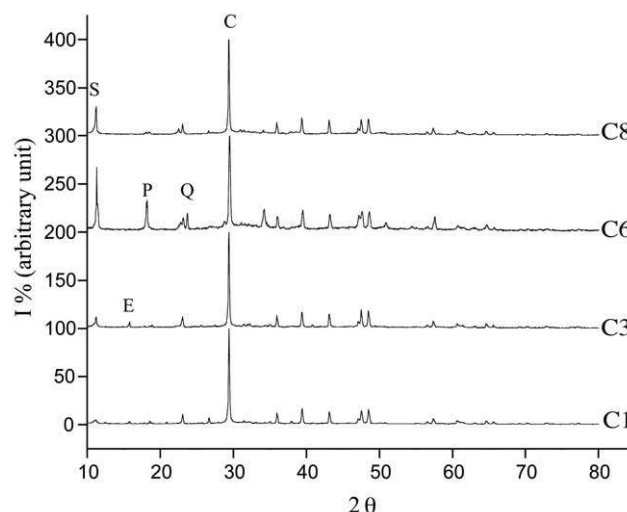


Fig. 4. XRD chart of finer particle size fraction (<63 mm) of mortar samples C1, C3, C6 and C8. Letters refer to principal diffraction lines of C, calcite; Q, quartz; S, sjogrenite, hydrotalcite of hydrocalumite; P, portlandite; E, ettringite.

cite) with interlayers of water molecules and CO₃²⁻ ions. Both minerals belong to a mineral class of double metal hydroxide known as anionic clays.

Moreover, the amount of magnesium hydroxide (brucite) previously identified by FT-IR spectroscopy was not detected by XRD analysis, according to the opinion that not brucite but an anionic clay, or a mixture of both, is present in foundation mortars.

The presence of anionic clays would suggest that foundation mortars were produced by mixing lime with ashes or other aggregate of unknown composition giving some hydraulic characteristics to the mixtures.

A confirmation of the hydraulic nature of foundation mortars is the identification of ettringite

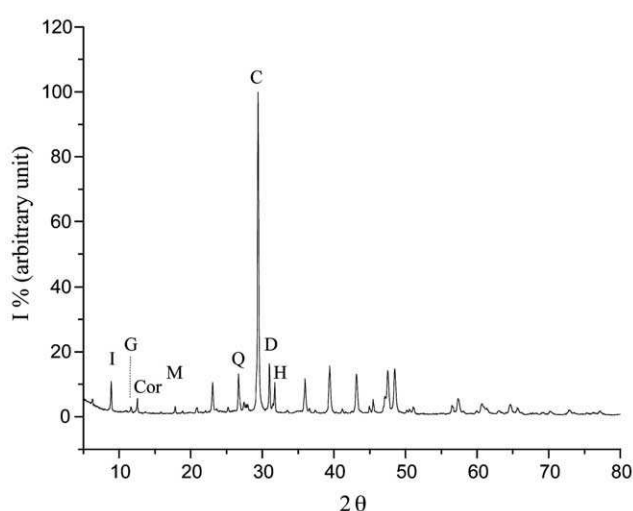


Fig. 3. XRD chart of finer particle size fraction (<63 mm) of mortar sample 269 (building phase III, indoor wall). Letters refer to principal diffraction lines of C, calcite; Q, quartz; D, dolomite; Cor, corrensite; H, halite; I, illite; M, mica; G, gypsum.

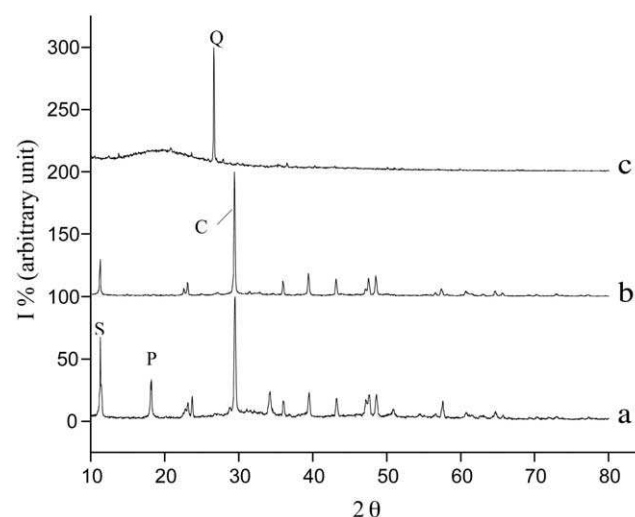


Fig. 5. XRD chart of finer particle size fraction (<63 mm) of mortar sample C6 before and after chemical treatment: a) untreated sample; b) washed with distilled water; c) washed with diluted hydrochloric acid (3 mol L⁻¹). Capital letters refer to principal diffraction lines of C, calcite; Q, quartz; S, sjogrenite, hydrotalcite of hydrocalumite; P, portlandite.

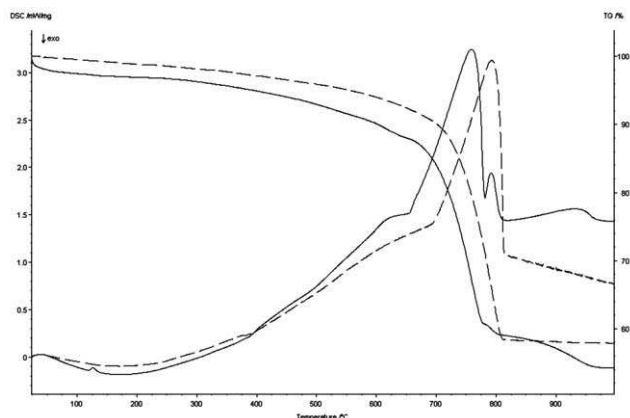


Fig. 6. DSC/TG plot of the finer particle size fraction of sample 78 (building phase I, indoor wall) before (straight line) and after (dotted line) washing in distilled water.

($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) in the finer particle size fraction of sample C3. The presence of ettringite is related to the reaction of gypsum with aluminates contained in hydraulic mortars [11].

4.3. Simultaneous thermal analysis

By means of differential scanning calorimetry (DSC/TG) we could identify and measure the amount of calcium carbonate (calcite), calcium sulfate dihydrate (gypsum), calcium hydroxide (portlandite) and magnesium hydroxide (brucite) contained in binder sieved fractions ($< 63 \mu\text{m}$).

In many cases, as shown in Fig. 6, the presence of soluble salts as sodium chloride (halite) gives rise to an unusual

course both in DSC and in TG curves from 600 to 1000 °C. Instead of a one-step decomposition of calcium carbonate thermal analysis shows a four-step decomposition (DSC peaks at 628.9, 758.8, 791.9, 933.3 °C). After removing sodium chloride and a little amount of gypsum the loss of carbon dioxide occurs, as usual, in one step (peak at 792.0 °C). The decrease of decomposition temperature of carbonates due to soluble salts has been previously reported [4,12]. Dimensions and defective crystal lattice of calcium carbonate formed during hardening and the presence of compounds favoring thermal decomposition are factors to be held in great consideration when reading DSC/TG curves.

The results obtained by DSC/TG analysis of the finer particle size fractions are shown in Table 3. The temperature ranges for the characterization of these materials have been proposed in previous studies [1,4,6]. In particular, the temperature ranges correspond to the weight loss due to adsorbed water ($< 120 \text{ °C}$), to the loss due to chemically bound water of hydrated salts ($120\text{--}200 \text{ °C}$), to the loss due to water bound to hydraulic compounds ($200\text{--}600 \text{ °C}$) and to the loss of carbon dioxide developed during the decomposition of carbonates ($> 600 \text{ °C}$). $\text{CO}_2/\text{H}_2\text{O}$ ratio (weight loss of carbonates $> 600 \text{ °C}$ /weight loss of hydraulic water in the $200\text{--}600 \text{ °C}$ temperature range) is a useful parameter to evaluate the hydraulic nature of the mixtures [6]. In Fig. 7 the values of hydraulic water content vs. the $\text{CO}_2/\text{H}_2\text{O}$ ratio referred to the binder fraction ($< 63 \mu\text{m}$) are reported.

The attention is focused on the comparison between indoor masonry mortars and foundation mortars with re

Table 3
DSC/TG analysis of the finer particle size fractions ($< 63 \mu\text{m}$), $\text{CO}_2/\text{H}_2\text{O}$ ratio, hydraulic water percent and weight percent of the particle size fraction $< 63 \mu\text{m}$ (binder fraction)

Sample	No.	Weight loss (wt. %) in each temperature range (°C)				$\text{CO}_2/\text{H}_2\text{O}$ ratio	Hydraulic water (wt. %)	Weight of the finer particle size fraction (wt. %)
		< 120	$120\text{--}200$	$200\text{--}600$	> 600			
69M, I	1.56	0.70	4.21	30.80	7.31	2.35	55.72	
69A, I	2.14	1.15	5.33	26.84	5.04	3.81	71.55	
78, I	1.33	0.10	4.89	36.11	7.38	3.48	71.18	
79, I	3.83	0.11	6.77	28.16	4.16	3.56	52.54	
7, II	0.61	1.02	2.64	10.56	4.00	2.37	89.97	
231, II	1.09	0.20	7.07	33.71	4.77	2.91	41.18	
94, III	3.77	0.22	7.10	27.06	3.81	5.41	76.18	
269, III	0.48	0.97	4.54	27.19	5.99	0.88	19.35	
273, III	0.69	0.43	4.50	28.98	6.44	1.16	25.76	
229, IV	0.52	0.99	3.12	31.34	10.04	0.57	18.18	
240, IV	0.43	0.75	4.89	19.07	3.90	1.57	32.22	
105, V	1.75	0.13	2.49	31.15	12.51	0.65	26.17	
138, VII	0.50	0.75	4.52	34.18	7.56	1.16	25.71	
242, VIII	1.73	0.35	7.78	22.90	2.94	2.07	26.67	
C1, F	2.37	2.54	9.09	19.85	2.18	5.78	63.60	
C2, F	2.32	2.53	9.29	21.90	2.36	8.77	94.44	
C3, F	3.02	2.82	11.11	18.82	1.69	10.28	92.51	
C4, F	3.11	2.94	10.39	22.05	2.12	9.96	95.86	
C5, F	2.79	2.98	9.52	22.24	2.34	8.84	92.84	
C6, F	2.70	3.55	8.09	21.88	2.70	7.74	95.70	
C7, F	2.90	2.47	10.45	20.87	2.00	8.93	85.43	
C8, F	3.06	3.24	11.08	19.39	1.75	8.93	80.63	
C9, F	2.07	1.69	9.97	25.74	2.58	8.47	85.00	

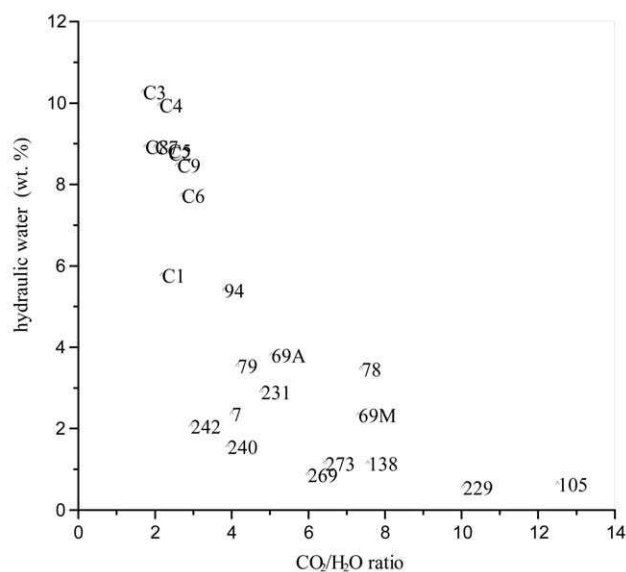


Fig. 7. Hydraulic water percent (calculated as product between the weight loss in 200–600 °C temperature range and the percent of binder fraction) vs. $\text{CO}_2/\text{H}_2\text{O}$ ratio (weight loss percent > 600 °C/weight loss percent between 200–600 °C) referred to the finer particle size fraction (< 63 μm).

gards to the amount of hydraulic water (calculated as product of weight loss in the 200–600 °C temperature range and finer particle size weight fraction) and the amount of carbonates ($\text{CO}_2/\text{H}_2\text{O}$ ratios) contained in the binder fraction (< 63 μm).

Indoor masonry binders are characterized by different compositions and $\text{CO}_2/\text{H}_2\text{O}$ ratios. Except for samples 94, 240 and 242 the high values of $\text{CO}_2/\text{H}_2\text{O}$ ratios indicate the air-hardening nature of indoor masonry binders. The rela-

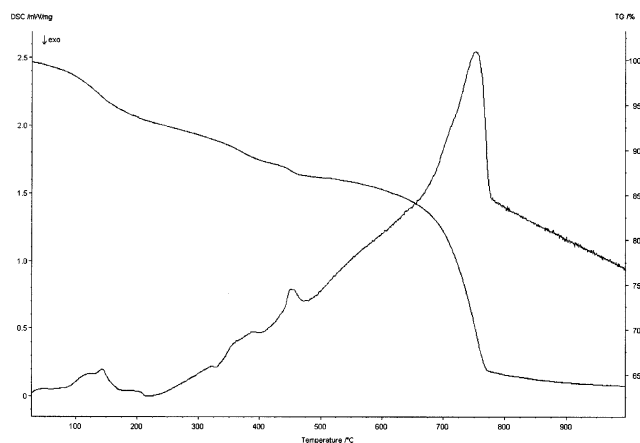


Fig. 8. DSC/TG plot of the finer particle size fraction of sample C6 (original structure, foundation).

tion between the historical construction phases and the analytical data can hardly be understood.

On the contrary, foundation binders show homogeneous contents of hydraulic water (5.78–10.28 %) and $\text{CO}_2/\text{H}_2\text{O}$ ratios (1.69–2.18) attesting similar original mixtures and conservation conditions. Table 4 illustrates the amounts of calcite, gypsum, portlandite and brucite evaluated by DSC/TG curves. Two weight losses were not clearly identified: the first in the 70–210 °C temperature range and the latter in the 330–420 °C temperature ranges (Fig. 8). As previously proposed, these weight losses could partially be related to the presence of an anionic clay. Nevertheless, the identification of this compound requires further confirmations.

Table 4

Compounds detected by DSC/TG analysis of the finer particle size fractions (< 63 μm)

Sample	No.	Amount (wt. %) of each compound				$\text{H}_2\text{O}_{\text{cryst}}$ % 70–210 °C	$\text{H}_2\text{O}_{\text{hydrox}}$ % 330–420 °C
		$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	CaCO_3		
69M, I	–	–	–	–	70.00	–	–
69A, I	–	–	–	–	61.00	–	–
78, I	1.91	–	–	–	82.07	–	–
79, I	6.07	–	–	–	64.00	–	–
7, II	–	–	–	–	24.00	–	–
231, II	6.49	–	–	–	76.61	–	–
94, III	6.35	2.84	–	–	61.50	–	–
269, III	–	–	–	–	61.80	–	–
273, III	–	–	–	–	65.86	–	–
229, IV	–	–	–	–	71.23	–	–
240, IV	–	–	–	–	43.34	–	–
105, V	1.41	–	–	–	70.80	–	–
138, VII	–	–	–	–	76.68	–	–
242, VIII	–	–	–	–	52.05	–	–
C1, F	–	–	–	–	45.11	4.42	3.14
C2, F	–	–	–	–	49.77	4.41	3.46
C3, F	–	–	–	–	42.77	5.04	3.18
C4, F	–	–	–	–	50.11	5.18	3.54
C5, F	–	–	4.28	–	50.55	5.05	3.19
C6, F	–	–	6.04	–	49.73	5.72	2.54
C7, F	–	–	–	–	47.43	4.65	3.81
C8, F	–	–	–	–	44.07	5.65	3.61
C9, F	–	–	–	–	58.50	3.24	3.98

5. Conclusion

The chemical characterization of mortars collected from the Arsenal of Venice (*tezona* 105) has provided useful knowledge as regards the ancient building materials. The results may be summarised as follows: **the indoor masonry mortars are mostly air-hardening and the foundation ones are hydraulic.** This difference of building materials is due to their respective use and condition.

Thanks to this characterisation, it will be possible, for instance, to prepare restoration mixture having characteristics compatible with the masonry structure, through a 'reverse engineering' process.

The individuation of the relations, in the analytic stage, among the several fields of research (history, stratigraphy, decay, chemical-physical analyses, static tests, etc.) allows advances to a possible consideration of the kinematics of decay, in order to estimate the level of danger for the conservation of the building, leading the planning of interventions as regards the real magnitude of the registered results, in order to select priorities of intervention and to quantify the conservation costs.

Acknowledgements

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