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The Vitruvian legacy: mortars and binders before and after the Roman world

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A brief history of the nature, use and technology of binders in ancient constructions and buildings is outlined, including the apparent chronological discontinuities related to technological developments. The skilled and clever use of mineral resources is at the base of the technical achievements related to architectural activities, from simple adobe to high-performance modern concrete. It is argued that among pre-industrial binders the Roman pozzolanic mortars were highly optimized materials, skillfully prepared and very durable. Their innovative use in architecture is one of the keys of the successful expansion of the Roman Empire. The role of mineralogy and mineral reactions is emphasized in terms of: (1) the preparation and manufacturing of the binding materials; (2) the hardening process and the development of the physical properties of the binder; and (3) the archaeometric reconstruction of the ancient materials.

1. Historical survey

Living in a sheltered place, permanently or temporarily, is a fundamental need of humans. Nevertheless, the use of natural materials to build shelter is not exclusive to humans: termite mounds, bird nests, beaver dams, and beehives are perfect examples of efficient architectural skills on the part of animals. According to Mike Ashby "the difference lies in the *competence* demonstrated by man in his extraordinary ability to expand and adapt that competence and development" (Ashby, 2013, p. 11). After dwelling in natural caves and an extensive period of preparation of temporary structures made of organic materials (skin, wood, leaf, *etc*.), the development of long-lasting architecture in human prehistory was based necessarily on the clever use of natural rocks and/or man-made binders (Wright, 2005).

1.1. In the beginning it was clay ...

The use of clay-rich mud to plaster huts and floors is the most direct use of natural minerals to solidify surfaces and make them impermeable (Wright, 1983; Staubach, 2013). This follows from the physical properties of clay minerals (Brown and Brindley, 1980; Bailey, 1988) which exhibit a small particle size and a marked flat morphology derived from the layered crystal structure. Clays in excess water form colloidal

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suspensions, and the settled fractions possess ideal plastic properties, so that readily formable materials can be obtained easily by soaking dry clay minerals.

Clays (and loess in China) have been used since Neolithic times to plaster walls (inside and outside), to consolidate and smooth rough floors and eventually reshape them repeatedly after use, to waterproof roofs made of organic material, and eventually as a mortar between stones and, finally, mudbricks. There is ample evidence of this architectural use of clays in the Middle East starting from the 10th millennium BC (see for example Schmandt-Besserat, 1977). In its simplest form, with no use of pyrotechnology, a masonry wall can be composed of sun-dried bricks (adobe) bound by a moist layer of mud that, on drying, makes the wall a solid mass of dry clay (Artioli and Secco, 2016). In other cases earth-based structures are formed by direct application and shaping of the constructions: these techniques are variously referred to as cob, if they have a load-bearing role, or wattle and daub if the earth has an infilling role (Friesem *et al.*, 2017). In some cases the clay slabs or blocks can be cut directly out of clay or muddy soil if they are naturally consolidated by organic material (turf, sod) or other pedogenetic processes (Huisman and Milek, 2017). The man-made clay bricks and the clay mortars regularly contain a substantial organic (straw, dung) or inorganic component (gravel, pebbles) in order to avoid cracking upon drying; a technology developed before or in parallel with pottery making. The past use of unfired or sun-baked clay products is often difficult to assess in the archaeological record, because they are subject to rapid degradation mainly by wind erosion, water and salts (Friesem *et al.*, 2017). Only in rather arid climates are ancient occurrences still recognizable (Figs. 1, 2), in most cases as structures embedded in mounds (tells) formed by layers of sequential human activity.

The earliest evidence of the use of sun-dried bricks is reported from the Pre-Pottery Neolithic layers in Jericho, Israel (9th millennium BC: Kenyon, 1981), in Nemrik, Iraq (Kozlowski and Kempisty, 1990) and in Ganj Darreh, Iran (Vatandoust *et al.*, 2011) at least from the 8th millennium BC. Evidence of the use of mudbricks in the Indus Valley (Harappa, Mohenjo-Daro) started at about the same time (end of the 8th millennium BC: Khan and Lemmen, 2013). Jericho stands as a special site combining the early systematic evidence of the use of mud-brick buildings alongside the earliest example of a Cyclopean structure, a massive round tower ~10 m in diameter and standing to almost the same height; though the significance of such massive construction is still debated (Kenyon, 1981; Bar-Yosef, 1986). There is ample use of mud-brick structures in the site of Çatalhöyük (7500–6000 BC: Hodder, 2006, 2012) and a number of other Anatolian sites, together with painted mud plaster covering internal and external structures, for both practical and symbolic purposes (Figs 3, 4). Interestingly, although there is evidence that the Çatalhöyük people could have used pyrotechnologically produced lime plaster, there is no firm evidence of it being employed. The wall surfaces as well as the interior floors of the structures at Çatalhöyük were carefully plastered and frequently re-plastered in time, but were coated in earthen plasters, which were supplemented by a thinner coat of local white marly clay (Kopelson, 1996; Arkun, 2003). The first Mesopotamian building in brick on a monumental scale occurred in the

Figure 1. The massive body of the Deffufa ('mud-brick building' in Nubian) of Kerma, Nubia. It was built entirely of sun-dried bricks and was the reference structure of the classic Kush civilization (2000–1500 BC).

Figure 2. Mud-brick qubba in the cemetery from the Islamic period near Dongola, Sudan. Qubbas are domed mausoleums which contain the grave of a saint or some important personage.

Figure 3. Sun-dried mud bricks with clay mortar in a Neolithic wall at Çatalhöyük, Turkey.

Figure 4. An internal wall of a living quarter in Çatalhöyük showing wall plastering and decorations.

Tell Halaf period (5th millenium BC: Oates, 1990; Robson, 1996). Rectangular mould-based bricks were introduced in Mesopotamia at least from the 4^{th} or 3^{rd} millennium BC (Tell Braq, Syria: Oates, 1990; Halaf, Syria: Davidson and McKerrell, 1976), rapidly becoming decorated or inscribed.

The tradition of using earthen architecture based on a mixture of clay, water and straw is still largely present in many rural areas of the world (Figs 5, 6), the splendid multi-story Al Mihdar Mosque of Tarim, Yemen and the Mosque of Djenne, Mali being two amazing examples of earthen architectural achievements. The technological basis of modern earth constructions is very similar to that inferred from the prehistoric record (Oates, 1990). It is worth mentioning that several trends of contemporary architecture (earth architecture, sustainable architecture, bioarchitecture, *etc*.) actively propose the modern use of clays or consolidated clays as natural materials in buildings (Minke, 2012). Furthermore, in the field of modern and ancient earthen architecture there are many unresolved issues concerning earthen conservation, capacity building and dissemination of information for appropriate conservation interventions on historic buildings, settlements and archaeological sites composed of earthen materials (Avrami *et al*., 2008; Fratini *et al*., 2011). The Getty Conservation Institute (GCI) through its Earthen Architecture Initiative (EAI: www.getty.edu/conservation/our_projects/field_projects/earthen/overview.html), a long-term legacy of the past Terra project, is at the forefront of active research and education on the theme.

Figure 5. Modern production of sun-dried bricks in Sudan.

Figure 6. Mud-brick walls in Sardinian houses. Traditional earthen architecture is preserved alongside to modern concrete building.

1.2. And then fire came ...

The Sumerian, Babylonian, Assyrian and Hittite civilizations used sun-dried clay tablets widely for cuneiform inscriptions, which was the written system for most of the languages of the Mesopotamian region (Walker, 1987). Large archives of tablets are available starting from about the 4th millennium BC and they present a number of conservation problems because they are fragile and salt-loaded (Organ, 1961). Only a very small number of them were originally fired, often accidentally during destructive conflagrations, and these are the most stable ones. Paradoxically, high temperature helps their preservation, so that modern electrical heating up to 740ºC seems to be one of the best conservation treatments to stabilize these materials (Thickett *et al.*, 2002). By firing clay tablets at high temperature, conservators are now applying the long-known pyrotechnological process which has been the basis of production of clay figurines since Upper Palaeolithic times (see the Venus of Dolní Věštonice, Vandiver *et al.*, 1989), the making of early fired ceramics in Eastern Asia since at least ~15000 y BC (Kuzmin, 2006; Wu *et al.*, 2012; Gibbs, 2015), and the shift from sun-dried to fired bricks in Mesopotamia around the 3rd millennium BC. It is the very same firing process transforming plastic clays into stable structural products (Artioli, 2010; Heimann *et al.*, 2010; Staubach, 2013): during firing the clay minerals are dehydroxylated progressively and reactive oxides are formed, yielding glass and a variety of high-temperature crystal phases, depending on the starting clay composition and the time-temperature path followed. High temperatures and long firing times imply more complete reactions, better crystallization and highly sintered micro-structures (Cultrone *et al.*, 2004). Technically, fired bricks are ~15% denser than corresponding mudbricks of the same size, and about five times more resistant to compression. They are also lighter than natural limestone but possess almost doubled values of the compressive strength of many common carbonate stones. Bricks represent an almost ideal unit material for masonry.

Fired bricks bearing inscriptions (Fig. 7) have been found in most Middle Eastern excavations, including Babylonia (Oppenheim, 1965), Nimrud (Oates, 1961) and Nippur (McCown, 1952). The buildings in many of the Mesopotamian tells are made of mixed construction materials: mainly mudbricks, but also fired bricks and stones. In fact "...once bricks had been developed, it became general practice to build the mass of a building in sun-dried bricks, whilst facing the lower courses and paving the floors with kiln-fired bricks. In a country short of wood for fuel, baked bricks were a luxury, commonly used only where necessary to protect the unfired from erosion by wind or water." (Moorey, 1999). The large prevalence of mudbricks may prove that "burnt bricks were not as fundamental to Mesopotamian civilization as was fine stone dressing to Pharaonic civilization" (Wright, 2005, p. 110). The culmination of burnt brick construction in Mesopotamia was during Neo-Babylonian times (see the famous Ishtar Gate and Processional Way at Babylon, which also represent a great example of glaze

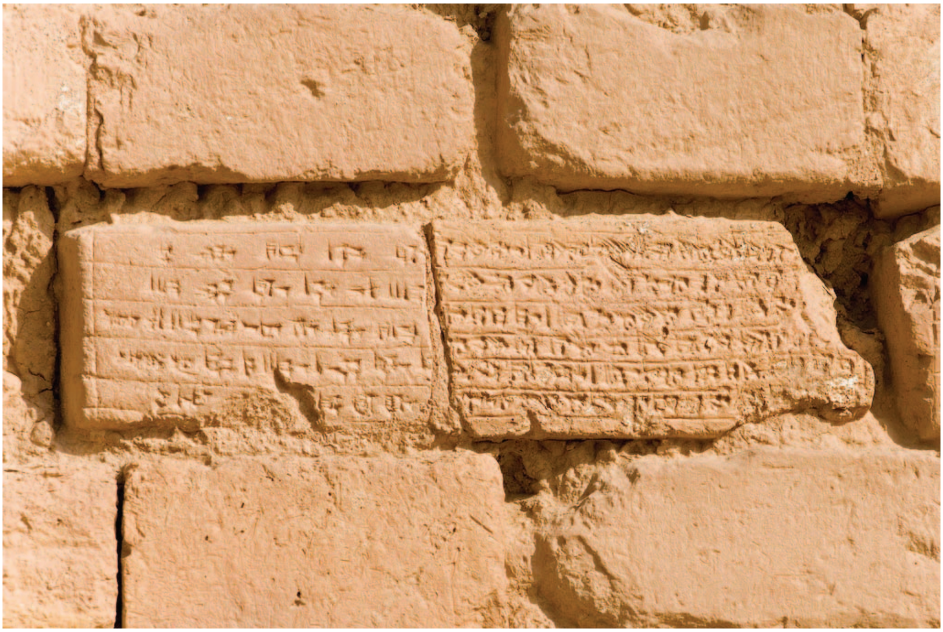

Figure. 7. Inscribed bricks in the wall of Chogha Zanbil, the great Elamite zigurrath in Iran, some 30 km south-east of Susa.

decoration of bricks). A Mesopotamian-type evolution of building techniques is present also in the Indus Valley, where the transition from mudbricks to fired bricks appears in the Kot-Dijan period (2800–2600 BC) and burnt bricks become common in the mature Harappan stage (2600–2450 BC; Kenoyer, 1991; Khan and Lemmen, 2013), used mostly with simple clay mortar (Mackay, 1938). There are no other known examples of structural use of fired bricks elsewhere in the world until the first half of the 1st millennium BC, whereas already in the 2nd millennium BC there is ample evidence of the use of terra-cottas for roofing tiles and temple decorations in Greece and later in Etruria. Roofing tiles were also introduced in China during the Shang Dinasty (1700–1027 BC, Sui Pheng, 2001).

It is puzzling to note that everywhere in the world the process of mudbrick firing for architectural purposes occurred several thousand years later than the use of pyrotechnology to fire lime and ceramics in the same regions. The production of fired bricks of course required large fuel resources and substantial manpower (Potts, 2014). In any case the bricks were used to produce more flexible architecture and more stable masonry, even if the brick units were not strengthened with binder. In Mesopotamia a mixture of gypsum and clay was mostly used as mortar, apparently following an interesting regional pattern (see fig. 14 of Kingery *et al.*, 1988), although the lack of scientific analyses and the use of ambiguous terminology for materials makes many of the early archaeological reports rather unreliable (Moorey, 1999, p. 330). Note that some of the Mesopotamian buildings encompass the early known water-treatment structures (Sanizadeh, 2008): in several of them some degree of waterproofing was obtained by use of fired bricks and tar plastering. In Mesopotamia the first use of bitumen (or a mixture of gypsum and bitumen) as mortar in masonry is recorded (Moorey, 1999; Sauvage, 2011), as also reported by historical sources (Herodotus 1, 179, 1–4): "Further, I must relate where the earth was used as it was dug from the moat and how the wall was constructed. As they dug the moat, they made bricks of the earth which was carried out of the place they dug, and when they had moulded bricks enough, they baked them in ovens; then using hot bitumen for cement and interposing layers of wattled reeds at every thirtieth course of bricks, they built first the border of the moat and then the wall itself in the same fashion. ... There is another city, called Is, eight days' journey from Babylon, where there is a little river, also named Is, a tributary of the Euphrates river; from the source of this river Is, many lumps of bitumen rise with the water; and from there the bitumen was brought for the wall of Babylon." The latter phrase of Herodotus indicates how common the tar material was in the area.

2. Classification of inorganic binders: their chemistry and mineralogy

Before delving into the details of binder developments through prehistory and history, it is necessary to summarize the nature and properties of the materials. Because of the ample literature available (Barnes and Bensted, 2002; Hewlett, 2003; Artioli, 2010), only a brief introduction will be given.

To avoid confusion, we will define the terms used for the binding materials following the physical condition and context of use (Hobbs and Siddall, 2011). 'Cement' is a powder material providing internal cohesion derived from some sort of chemical reaction, mostly with water; 'concrete' is a composite made by a binder and large-sized (inert) aggregate material; 'mortar' is a composite made by a binder and small-sized aggregate material, mostly used as structural binder between masonry units (bricks, stones); 'plaster' is any mortar or binder material used for wall and floor covering, mainly for smoothing, waterproofing, or preparation for paintings and decorations.

Cements based on Portland-type clinkers, mortars (pastes and plasters prepared with fine aggregates) and other inorganic binders form an important class of construction material: they are all supplied as powders and when mixed with water they form a fluid mass (paste) that can be shaped, moulded, added to other components or attached to the surface of other materials. The paste then hardens spontaneously under normal environmental conditions. Binding materials are used in buildings with the aim of (1) making structural elements for constructions; (2) increasing the resistance of the construction by linking the structural and architectural elements; (3) increasing waterproofing and protecting masonry surfaces from environmental degradation; and (4) preparing substrates for artwork and decorative purposes.

Excluding the tar products mentioned above and binders and adhesives based on polymeric compounds, virtually all binders used in antiquity were based on carbonates (calcite, dolomite), sulfates (gypsum) or alumino-silicates (cements). Table 1 provides an overall classification of inorganic binders based on their chemical nature and the main reaction process when mixed with water. The important concept is that in all cases the pyrotechnological production process yields a reactive material that transforms into a more stable product during setting and hardening. The major differences between the different binder types are: (1) the nature of the starting material that determines the chemical reaction pathway; and (2) the temperature of the firing process that controls the quality and reactivity of the starting binder.

Furthermore, a fundamental difference concerning the nature of the reaction processes of lime-saturated binders is whether they involve simple absorption of CO_2 from the gas phase to produce carbonates (aerial carbonation), or whether they also involve more complex processes of dissolution of alumino-silicate phases and precipitation of hydrated calcium-aluminium-silicate phases ('pozzolanic' reactions). The former are known as aerial binders, because they set in contact with the atmosphere. The latter are called hydraulic binders, because they may harden even under water.

In practical terms, if the binder is used as produced from the kiln with adequate grinding, then the binder/water mixture is called 'paste', *i.e.* the whole volume of the mixture comprises reactive phases and it will convert finally into a material composed entirely of the recrystallized reaction products. Therefore, if a lime paste undergoes complete aerial carbonation it will end up as a material composed totally of fine calcite crystals. A magnesian lime paste will yield a material composed of calcium carbonate and magnesium carbonate. The re-hydration of a bassanite paste will produce a plaster

Table 1. Main types of inorganic binders, their nature and reaction processes.

Type of binder		Starting material	Appx. *T* of firing (ºC)	Reactive material product	Reaction process
Binders based on carbonate	Lime plaster	limestone	800−1000	Quicklime (CaO) Slaked lime ($Ca(OH)_2$)	aerial carbonation
	Hydraulic Lime plaster	limestone		Slaked lime + pozzolan	pozzolanic reaction
	Natural Hydraulic Lime plaster	limestone + clays/volcanic glass		Natural hydraulic lime	hydration reaction
	Magnesian plaster	dolomite		Slaked magnesia-lime ($Ca(OH)_2$) ($Mg(OH)_2$)	aerial carbonation
Binders based on gypsum	Gypsum plaster (Plaster of Paris)	gypsum	250−300	Bassanite $CaSO_4 \cdot 0.5H_2O$	hydration
Binders based on Portland clinker	Portland clinker (cement)	limestone + clays/marls	1400−1450	Clinker phases (alite C3S, belite C2S, Ca-aluminate C3A)	cement hydration

composed totally of gypsum. Finally the complete hydration of a clinker should yield a material composed largely of Ca-Si-hydrates (C-S-H) and calcite (from the carbonation of excess portlandite). As may be suspected, it is the recrystallization of the reaction products in the matrix and the entanglement of the crystals of the newly formed phases that confers mechanical resistance to the mature binder. The microstructure (*i.e.* the size, shape and orientation of the crystal phases) of the binder thus fundamentally controls the physical and engineering properties of the material.

In practice, the reaction normally goes to completion for gypsum and lime plasters; the reactions of these processes are kinetically quite fast at ambient conditions. However, it is often found that the kinetics of magnesian plasters are much slower, so that reaction products (MgO and $Mg(OH)_2$) are commonly present quite some time after the application. In the case of Portland cement, the hydration reaction barely goes to completion, so that a substantial part of the starting phases is invariably present with the reaction products even a long time after the mixture has been prepared.

Pure binder pastes are used rarely. It is much more common to mix part of the binder with a nominally unreactive phase (the so-called inert phase, or aggregate) such as quartz, in order to reduce volume changes during hardening and thus limit shrinkage effects. The role of the aggregate is to reduce macro-cracking during drying of the binder/water mixture, to increase the bulk modulus of the composite, and to increase the overall volume of the binder. If the aggregate is added with particle size in the sand range (generally referred to a standard with grain size in the range 0.6–0.8 mm), then the binder/aggregate/water mixture is called ‘mortar’. Depending on the mineral nature of the binder, we may have lime mortars, natural hydraulic lime mortars, magnesian lime mortars, gypsum mortars, or clinker mortars. Lime mortars and gypsum mortars are the materials mostly found in the archaeological and historical record. They are still much used for small-volume applications such as decorations, panels, wall plastering and repointing.

In the case of Portland clinker, which is used as the main material in large-scale applications, there is need of large-volume aggregates in the size range of coarse sand or pebbles. The cement/large aggregate/water mixture is called ‘concrete’. In most cases the various size fractions of the aggregates from fine to coarse are planned carefully through gradation models (following Bolomey, Fuller, Graf or Rissel curves; Day, 2003; Collepardi *et al.*, 2007) in order to produce an optimal volume packing of the particles in the mix. The planning of the optimal quantities and sizes of cement, aggregate and water is defined ‘concrete mix design’.

3. The composition and properties of ancient mortars

3.1. Lime-based binders, technology and development

The first artificial binders used by mankind are the limestone- and gypsum-based plasters used widely in the Near and Middle East in the 7th and 8th millennia BC (Frierman, 1971; Gourdin and Kingery, 1975; Kingery *et al.*, 1988). The technological basis of plaster material is very simple: the reactive compound (quicklime in the case of lime plasters) is obtained by burning limestone at the appropriate temperature (Table 1). Then the heated block is ground to a fine powder and slaked with water to form a slurry (at high water/solid ratio) or a paste (at low water/solid ratio) composed of portlandite (calcium hydroxide, $Ca(OH)_2$). In Roman times long aging of the slaked slurry in excess water was a priority with respect to the modern attitude of using the ground powder and mixing it with water into a paste at the time of application. The effect of aging on the properties of the lime putty has been investigated thoroughly (Rodriguez-Navarro *et al.*, 1998; Cazalla *et al.*, 2000), as the issue is relevant for the preparation of restoration lime mortars (Ruiz-Agudo and Rodriguez-Navarro, 2009).

The reactions involved in the production and use of lime are:

$$CaCO_3\text{(calcite)} + \text{heat} \rightarrow CaO\text{(lime)} + CO_2\text{(carbon dioxide) [production of quicklime]}$$

$$CaO\text{(lime)} + H_2O\text{(water)} \rightarrow Ca(OH)_2\text{(Portlandite)} + \text{heat [quick hydration]}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \text{ [long term carbonation]}$$

The temperature needed to produce CaO should be ~850ºC (Rodriguez-Navarro *et al.*, 2009), though the decomposition reaction of the carbonate can also proceed at slightly lower temperatures (780–800ºC) in reducing conditions. Operational temperatures of lime-kilns are in the range 920–1000ºC in order to speed up the decarbonation reaction. Excessive temperatures are avoided because they produce unreactive'dead-burned' lime. The production of lime therefore is a very energy-intensive process and it requires a substantial amount of biomass fuel. It has been estimated that the ratio of fuel biomass/quicklime is in the range 2–5 (Kingery *et al.*, 1992; Hauptmann and Yalcin, 2001), so that about 4–8 tons of wood would be required to produce the quicklime necessary for one house. Considering the diffusion of lime plaster resulting from the excavations in the Levant, the production of lime could have had a serious impact on the environment (Rollefson and Kohler-Rollefson, 1992; Redman, 1999). Similar claims were raised for the Mayan Lowlands (Wernecke, 2008).

Traditionally, the burning of carbonates (limestones, dolomites, travertine, marbles, but also shells and corals) is performed in lime-kilns, which are massive furnaces sometimes several metres high, charged from above with decimetre- to metre-sized blocks of limestone, and then fired for days by adding wood or charcoal to the combustion chamber at the base (Oates, 1998; Williams, 2004). Several ancient lime-kilns have been excavated from Roman (Dix, 1982; Coulson and Wilkie, 1986), to Late Classic Maya (Abrams and Freter, 1996), to more recent times (Williams, 2004). A detailed description of lime burning operations in Roman times was supplied by Marcus Porcius Cato (Cato the Elder: *On Agriculture*, XXXVIII).

The fired blocks are then ground to obtain the fine powdered quicklime that is, however, rather unstable in normal humidity conditions and tends to hydrate quickly to portlandite. If the CaO powder is mixed with an exact (*i.e.* stoichiometric) amount of water (lime/water = 75.7/24.3 = 3.12 by weight) the product is a fine dry powder and the process is called 'dry hydration' because there is exactly the right amount of water required to produce portlandite. If the CaO powder is mixed with excess water then a smooth paste is obtained in a slurry form, and the process is referred to as 'lime slaking'. The portlandite paste (slaked lime or lime putty) can then be used as a binder and an architectural component (filler, adhesive, cracks sealer, floor consolidant, surface smoother, *etc.*) or as a raw material for modelling objects, vessels and even artwork. After the application the paste dehydrates slowly and reacts with atmospheric CO_2 producing a hard material composed of microcrystalline calcite. The kinetics of carbonation are slow (Van Balen, 2005) so that in recent samples the reaction is not complete and residual crystals of portlandite may be observed.

The quality of the binder depends on a variety of parameters, including the composition, porosity and impurity content of the fired limestone, the maximum temperature and the time–temperature path of the firing, and the conditions of slaking. The starting limestone should have a non-carbonate mineral content (usually silicates and clays) of <5–10 wt.%, and the carbonate should be pure calcium. If the carbonate contains flints or a substantial amount of clays, then some (alumino)-silicate reactive phases may form at high temperature, the material acquires hydraulic properties, and it is called natural hydraulic lime (NHL). This material will be discussed later. If the carbonate contains magnesium, derived from the presence of magnesian calcite ($Ca_{1-x}Mg_xCO_3$ with $x < 0.1$) or dolomite ($CaMg(CO_3)_2$), then the material is a magnesian- or dolomitic-lime (Table 1). The periclase (MgO) produced together with lime during firing has much slower rehydration kinetics with respect to CaO, so that in the magnesian putty both periclase and brucite ($Mg(OH)_2$) are present together with portlandite (Blauer-Bohm and Jagers, 1997).

During carbonation and hardening the microstructure of the slaked lime paste changes significantly (Leslie and Hughes, 2002; Arandigoyen *et al*., 2006). The identification of lime-derived calcite from an unconsolidated archaeological layer of ground calcite therefore is essentially based on the carbonate particles' dimensions (in the range 0.1–2.0 mm), its texture, and its mechanical properties (Kingery *et al*., 1988; Affonso and Freiberg, 2001; Karkanas, 2007). Optical microscopy (Fig. 8) is therefore a very useful tool to investigate the nature and texture of ancient lime mortars (Elsen, 2006; Pecchioni *et al*., 2014), although it may prove difficult to discriminate between fine-grained calcite of geological origin (chemically precipitated) and that derived from portlandite.

The presence and role of calcite nodules in the mortar (the so-called 'lime lumps') have been the subject of ample discussion, because of their importance in identifying ancient mortars (Hughes *et al*., 2001; Karkanas, 2007), in the quantitative determination of the original binder/aggregate proportions (Lindqvist and

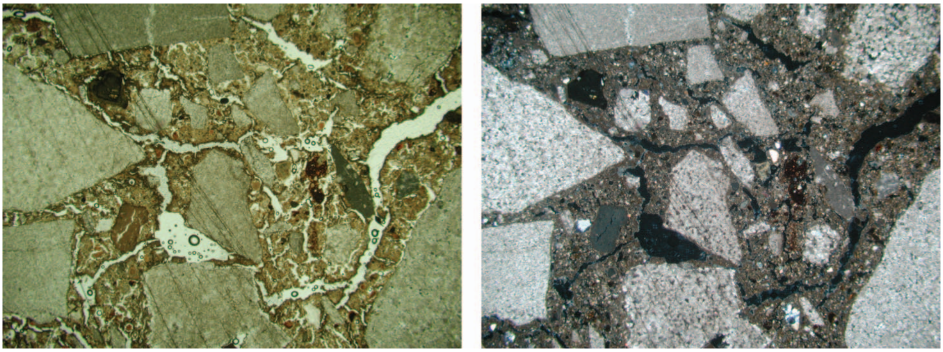

Figure 8. Optical micrograph of the thin section of a Medieval lime mortar from the Sachuidic castle, Friuli, Italy. The images in plane polarized light (a) and cross polarized light (b) show fragments of geological carbonate, lime lumps and the lime binder matrix.

Sandström, 2000; Elsen, 2004), and in the protocols sometimes employed for radiocarbon dating (Pesce *et al.*, 2012). In general, we may summarize that calcite nodules in the binder may have originated in one of three ways: as residues of unburned geological carbonate, as inhomogeneously slaked lime putty forming portlandite lumps that underwent late carbonation, or as reprecipitated late calcite. Failure to identify the proper nature of the lumps may lead to serious errors in the interpretation of the material and eventually in radiocarbon dating of the inappropriate fraction of the binder.

Very careful Fourier transform infrared spectroscopy (FTIR) work, based on the ratios of specific absorption peaks of calcite (specifically the ratio between in-plane and out-of-plane bending modes of the carbonate group), has been proposed as a technique to discriminate lime derived-calcite from natural calcite (Chu *et al.*, 2008; Regev *et al.*, 2010b). This discrimination may also be done using the luminescence properties of calcium carbonate (Machel *et al.*, 1991; El Ali *et al.*, 1993), as shown in the example of Fig. 9. Both methods rely on the different density and distribution of atomic defects in the calcite crystal structure. In principle the fractionation of carbon and oxygen stable isotopes during portlandite carbonation could also be used to test the nature of the carbonate phase (Ambers, 1987; van Strydonck *et al.*, 1989; Kosednar-Legenstein *et al.*, 2008). Once more, the issue is especially important when characterizing the carbonate fraction for radiocarbon dating of the mortar. In many cases the presence of ‘anthropogenic‘ (*i.e.* man-made) carbonate is identified through micromorphological features (Stoops *et al.*, 2017), or by textural elements such as clear smooth surfaces representing the floor used, sometimes with a finishing coating (Affonso and Freiberg, 2001; Shahack-Gross *et al.*, 2005; Karkanas, 2007; Karkanas and Goldberg, 2007).

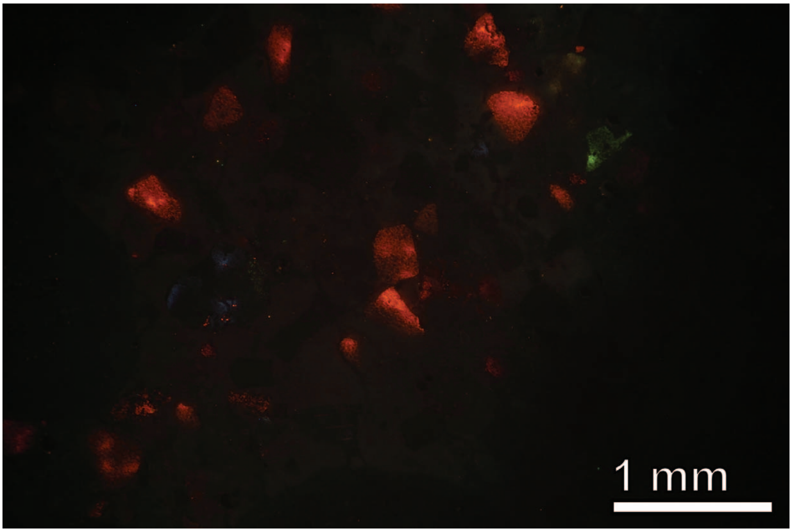

Figure 9. Cathodoluminescence image of a mortar showing sub-mm grains of geological carbonate embedded in the mortar binder.

The earliest well characterized example of quicklime production is the Hayonim Cave in Israel (Kingery *et al.*, 1988; Goldberg and Bar-Yosef, 1998), dated to the Natufian period at ~10.4–10.0 ky BC. Numerous other reports of lime-plaster in the Pre-Pottery Neolithic sites of the Levant (8.7–7.0 ky BC) were reviewed and characterized carefully by Kingery and co-workers (1988). They demonstrated beyond any doubt that there was a widespread use of pyrotechnologically produced lime-based plaster in the Near East coastal area from Palestine to Anatolia (Thuesen and Gwozdz, 1982; Garfinkel, 1987; Malinowski and Garfinkel, 1991; Poduska *et al.*, 2012). Especially striking are the plastered faces from ‘Ain Ghazal in Jordan, originally modelled on human skulls (Griffin *et al.*, 1998), and the exceptional sculptured head found in Jericho (fig. 10 of Kingery *et al.*, 1988; Goren *et al.*, 2001) and Yiftahel (Milevski *et al.*, 2008).

There are numerous interesting issues concerning the prehistoric development of lime-based binders in the Pre-Pottery Neolithic of the Levant. In the first place, as already mentioned, it is curious that limestone firing and production of reactive quicklime pre-dates ceramic pyrotechnology (Frierman, 1971), although this gap is now being partially revisited (Biton *et al.*, 2014). Further, the plasters in this early phase “do not comprise the rendering of the floor, they are the floor itself” (Wright, 2005, p. 157), *i.e.* they are made as durable surfaces supporting loads and meant to be cleaned. They also rapidly extended to walls for protection and decoration (Fig. 4). It is evident, however, that at least several thousand years separate this early burst in the use of lime binders from any structural use connected with fired bricks in the region. Actually, there seems to be a puzzling discontinuity between this widespread use of lime plaster in the 8th and 7th millennia BC in the Levant (especially in skull-plastering, figurine modelling and floor plastering), and the subsequent evidence of use of lime in architecture in the 2nd millennium BC.

The case of Lepenski Vir, a small Neolithic village on the banks of the Danube, stands as an isolated example apparently unconnected with the previous Levantine experience and the subsequent reprise of lime plaster in the Minoan world. In Lepenski Vir a large number of peculiar trapezoidal huts have been excavated, each with a thick floor of red-coloured limestone plaster (Srejović, 1972, 1981; Radovanović, 2000; one XRD analysis of a Lepenski Vir sample is reported by Thuesen and Gwozdz, 1982). The settlement has been radiocarbon dated to the Early Neolithic (6200–5400 BC), though there are claims of early Mesolithic occupation (Radovanović, 1996; Borić, 2002; Bonsall *et al.*, 2008). Despite the uncertainty in the early life-span of the village and nearby settlements (Vlasac, Padina and Hajdutka Vodenica), the question of interest to us is whether the lime pyrotechnology on the Danube has anything to do to the previous Levant experience, or rather is a stand-alone development of lime production. Carefully contextualized investigations are needed to clarify the problem. The report of the use of lime at Makri, Thrace and at the Drakaina Cave, Kefallonia, Ionian Islands in the 6th millennium BC (Karkanas, 2007; Karkanas and Stratouli, 2008; Karkanas and Efstratiou, 2009) may prove to be an interesting link between the Levant and the Serbian lime experiences.

After the Lepenski Vir case, there were some four thousand years of technological discontinuity, or maybe lack of archaeological information. Chronologically, the successive occurrences of lime mortars and lime plasters are in the Minoan world (2nd millennium BC), where lime-based materials were used extensively in Crete, Cyprus and elsewhere for wall decorations and cistern waterproofing (Shaw, 1973; Wright, 2005). Without dwelling on the details too much, extensive lime plastering in the walls has been found, mainly to cover rough wall surfaces and floors, leaving the smooth ashlar unplastered. Plasters covering wall surfaces have a fine lime finish or wash as they serve as support for the famous Palatial paintings (*i.e.* Knossos, Fig. 10) and decorations. They are always lime-based, even when the wall-building stones are rock gypsum (Cameron *et al.*, 1977; Zoppi *et al.*, 2012). We stress that no hard evidence is observed in this period of the use of lime mortar as a structural component (*i.e.* to strengthen the masonry or ashlar blocks): all the Minoan, Mycenean and the later Classical Greek ashlar is dry.

A key development occurring in the Greek world is the consistent and systematic use of pozzolanic material (volcanic ash, *i.e.* 'Santorini earth', or crushed ceramics, *i.e.* 'cocciopesto') replacing inert aggregate in the mortar used for waterproofing cisterns and waterways in Bronze Age Crete and Cyprus (Maravelaki-Kalaitzaki *et al.*, 2003; Moropoulou *et al.*, 2005; Theodoridou *et al.*, 2013). The tradition continued in pre-Roman Rhodes (Koui and Ftikos, 1998). The later use in Laurion, Greece (4th century

Figure 10. The partially reconstructed Throne Room of King Minos in Knossos, Crete showing the ample use of lime plaster for wall decorations.

BC) of a very peculiar waterproofing layer obtained by mixing Pb-rich oxides (litharge) and Fe,Mn-rich ores with lime is also reported (Papadimitriou and Kordatos, 1993). This special occurrence is related to the mining and treatment of Pb-rich ores in the nearby mines, though it is difficult to define whether the layer investigated is a deposit developed as a byproduct of the ore processing or the conscious recycling of litharge slags during plaster manufacture.

As we will discuss, the reported occurrences bear two important consequences: (1) there is evidence of the appropriate use of hydraulic mortars and pozzolanic reactions in the Mediterranean area well before the Roman world; and (2) there is no firm evidence of the structural use of lime mortars in constructions (*i.e.* as a binder among masonry units) before the second half of the 1st millennium BC, except maybe the very early use of hot bitumen, discussed earlier, within the Mesopotamian context.

Outside the Mediterranean world, there is hardly any evidence for the use of lime plaster prior to the late 2nd millennium BC (Carran *et al.*, 2012).

No evidence is reported on the early use of plaster or mortar in the pueblo cultures of the US south west or in the South American Andean world, where the Inca's massive constructions of polygonal stones were assembled by smoothing the edges to make close contacts (Hyslop, 2014). Limited use of lime mortar, sometimes mixed with bitumen, has been reported at Machu Picchu (1450–1550 AD), though direct accounts and analyses are scarce (Prescott, 1847). In Central America the use of lime plaster is reported in Preclassical and Classical Central Mexico, and from the Classical Maya period (Hyman, 1970; Magaloni *et al.*, 1995; Abrams and Freter, 1996; Hansen *et al.*, 1997; Barba *et al.*, 2009). Some of the earlier examples are the plastered platforms at Cuello, Belize (1100–600 BC) and Nakbè, Guatemala (900–600 BC; Villaseor Alonso, 2009). In Mayan monuments the use of lime is structural, although spectacular use was made of lime as substrate to paintings and frieze decoration. Magnesian lime plasters were also extensively used (Villaseor and Price, 2008). An early use of pumices as lightweight aggregate in poured lime mortar is reported for the roof slab of Building Y in the El Tajin site, the sacred city of the Totonac people (850–1100 BC; Rivera-Villareal and Krayer, 1996).

Interestingly, there is ample evidence that in Mesoamerica the lime plaster was prepared by mixing different kinds of organic materials such as honey or juice extracted from a number of local plants such as cactus (nopal juice, *Opuntia ficus indica*; Littmann, 1957, 1960; Laws, 1962; Magaloni *et al.*, 1995). The type and extent of the effect of the organic molecules on the putty is still debated (Chandra *et al.*, 1998; Bensted, 1999; Rodriguez-Navarro *et al.*, 2017). On one hand there are claims that the organics destabilize portlandite chemically and release Ca ions, thus promoting pozzolanic reactions with impurity phases. On the other hand the physical effect of packing is emphasized, with the claim that the organics help the development of a more homogeneous microstructure, with smaller portlandite crystals, and ultimately a greater mechanical strength. The debate is open.

In China, there are accounts of the early use of lime during the Shang (1700–1027 BC) and the Zhou (1046–771 BC) Dynasties, the lime being mixed with sand and loess for wall facing and flooring. The palace site of Xianyang, Shaanxi province (350 BC) had the floors prepared with a mixture of lime, stone and pig's blood (Yang *et al.*, 2009) to give a dark red colour. The mortar formulation comprised lime, loess and sand; it became known as 'tabia' and became the regular material in use during the Eastern Tsin Dynasty (317–420 AD; Yang *et al.*, 2009). Lime-based mortars were used extensively in ancient architecture, with examples reported in the Qiantan River dam, Dutifulness Monument, Sticky Rice Bridge and others, completed mainly before the Ming (AD 1368−1644) and the Qing dynasties (AD 1644−1911; Huang, 2003; Yu and Chen, 2004; Zeng *et al.*, 2008). According to written sources (Song and KaiWu, 1982) lime-plaster production followed a traditional standard formula mixing lime and sticky rice solution up to 15−20 wt.%, and today the plaster is reported to be still in very good condition. Sticky rice is a type of rice grown in southeast and east Asia and it is composed mainly of amylopectin. Again, it seems that the organics influence the calcite dimensions and growth kinetics during carbonation (Zeng *et al.*, 2008). A variety of organic substances has been reported to have been used in traditional Chinese mortar recipes (Fang *et al.*, 2014; Zhang *et al.*, 2014; Zhao *et al.*, 2015), used both in masonry and in wooden buildings (Rao *et al.*, 2015).

The greater Indian region had a very early start with the use of mud and bitumen mortars (referred to as 'vajralepa' mortar; Kumar, 1984; Reza, 2008) related to the Indus valley civilizations, much as in Mesopotamia. The vajralepa bitumen was made of wood-tar and was used to waterproof walls and structures in bath houses (Sengupta, 1971; Kumar, 1984; Carran *et al.*, 2012). There is evidence of the early use of lime plaster in the ovens and pits of the houses in Kalibangan, Rajasthan, dated to the proto-Harappan period (3500–2500 BC; Sharma and Sharma, 2003), although it came into more common use since the last centuries of the 1st millennium BC. The pure lime binder was often obtained from 'kankar' (lime nodules) found abundantly among river gravel. Kankar contains ~70% calcite, 30% clay and a fraction of sand with other impurities, so that appropriate calcination of kankar may confer some hydraulic property to the mortar. Impure mortars with a variable sand/lime ratio are found in Buddhist settlements (Nagarjuna-Konda, 225–325 AD) and in the city of Kausambi, Uttar Pradesh (35–350 AD; Ghosh, 1989). A number of more recent buildings offer evidence of the widespread use of fired bricks and mortars, especially in mosques, temples (Thirumalini *et al.*, 2015), monuments (Singh *et al.*, 2014) and tombs (Gulzar *et al.*, 2013). The Great Stupa at Sanchi, Madhya Pradesh (Fig. 11) is the oldest stone building in India (3rd century BC) and one of the largest fired-brick domes in the world.

The Charminar in Hyderabad (1591–1593 AD) was built with granite stones and mortar (Singh, 1993). Lime plasters were also used extensively for decorations on temples and other monuments. The investigation of the decorations applied on rock at the carved Ellora caves (6–11 century AD; Fig. 12) surprisingly showed that many of the plasters contained a substantial amount of kemp hurd (*Cannabis sativa*), so that the decorations provide one of the first examples of kemp-reinforced plaster (Singh *et al.*, 2015). Furthermore, India offers a long tradition of organics mixed with lime allegedly to increase carbonation and durability: curd, jaggery, bel pulp (the fruit *Aegel*

Figure 11. The Great Stupa at Sanchi (3rd century BC) is the oldest stone building in India and one of the largest fired-brick domes (photo by Nagarjun Kandukuru, CC-BY-SA-2.0).

Figure 12. The Ellora caves show a spectacular labyrinth of rock carvings and paintings. Much of the artwork is plastered with one of the earliest examples of kemp-loaded lime of the 6th century AD.

marmelos), lentils, black gram and oil of margosa (Chandra and Aavik, 1983; Singh *et al.*, 1990).

The change in the paste properties resulting from the addition of organic compounds has long been known, (as mentioned briefly above) *e.g.* for traditional recipes for lime plasters in ancient Mesoamerica, China and India. Egyptians, Minoans and Romans modified the lime mortars with Arabic gum, animal glue, fig's milk, egg yolk and many other organic substances in an attempt to improve the mechanical or working properties (Sickels, 1981). In the *De Architectura* Vitruvius described explicitly the mixing of lime with oil (*calx ex oleo subacta*) to improve waterproofing. The practice was passed down to the Middle Ages and Renaissance, especially in the case of quality mortars for decoration and in applications exposed to weathering agents. A large variety of organic and proteic substances was apparently tested, with mixed results: cereal dough, animal blood, fermented wine, beer, milk derivatives including cheese, bee's wax, lard and many others.

3.2. Hydraulic mortars and pozzolans: the success of the 'Vitruvian' recipes

Mixing of lime plaster with partially or totally reacting aggregate marks the development from lime-based aerial mortar to hydraulic mortars. If the quartz aggregate of the mortar (formally inert) is replaced in part or fully with reactive Si,Al-rich material (generally defined 'pozzolanic material') then the highly alkaline environment created in the lime-saturated water induces the dissolution of the silicate or aluminosilicate phases and the subsequent precipitation of insoluble Si-rich hydrous phases (Hobbs and Siddall, 2011; Fig. 13).

The reactive pozzolanic material may be natural or synthetic silica glass, volcanic ash, radiolarite or diatomaceous earth, phytoliths, ceramics, clay, metallurgical slags, or any other reactive aluminosilicate compound. The materials employed in the past as pozzolanic additions in hydraulic lime mortars are also used today as supplementary cementitious materials (SCM) in the formulation of modern binders (Lothenbach *et al.*, 2011; Snellings *et al.*, 2012). Such materials can be represented in the lime–silica–

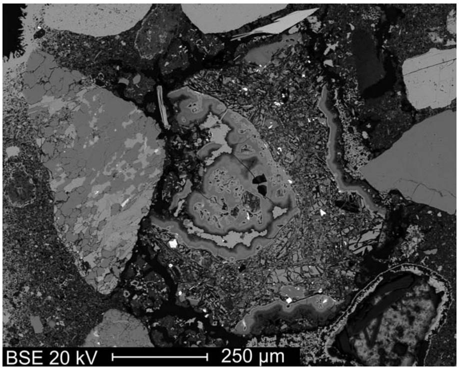

Figure 13. Reaction rim formed around a volcanic fragment in a lime matrix. The rim provides direct evidence of the pozzolanic reaction between the lime binder and the Si,Al-rich glass fragments inserted in the mix.

alumina (CaO–SiO_2–Al_2O_3) ternary diagram (Fig. 14). The reaction of lime with aluminosilicate phases is referred to as a 'pozzolanic reaction' or a 'hydraulic reaction'. When the presence of reactive aluminosilicate phases stimulates the pozzolanic reaction in the binder, then it is called a 'hydraulic' or 'pozzolanic' binder ('plaster', 'mortar') (Massazza, 1998). If natural volcanoclastic materials were not available, hydraulicity in the binder was often obtained by the use of crushed ceramics (pottery, bricks, tiles) together with traditional inert aggregates (Siddall, 2011). Fired ceramic is actually compositionally similar to volcanic materials, so the pozzolanic character of thermally activated clays and fired clay-based materials has been investigated thoroughly (Baronio and Binda, 1997; Böke *et al.*, 2006; Bakolas *et al.*, 2008; Zendri *et al.*, 2004; Fernandez *et al.*, 2011). The best ceramic-material yielding pozzolanic reaction is the very fine-grained kaolinite-rich pottery in which metakaolinite-type phases were formed by firing in the temperature range 600–900ºC (Bellotto *et al.*, 1995). The use of clay minerals in the production of the ceramics as well as firing at higher temperatures induces the formation of less reactive phases, such as mullite (Gualtieri *et al.*, 1995, Gualtieri and Bellotto, 1998), and thus reduced pozzolanic reactivity.

One of the earliest instances of pyrotechnologically produced lime mortar mixed with volcanic ash occurs at Aşıklı Höyük, Turkey (Hauptmann and Yalcin, 2001). The pozzolanic reaction observed in the Pre-Pottery Neolithic B (PPNB) Aşıklı Höyük

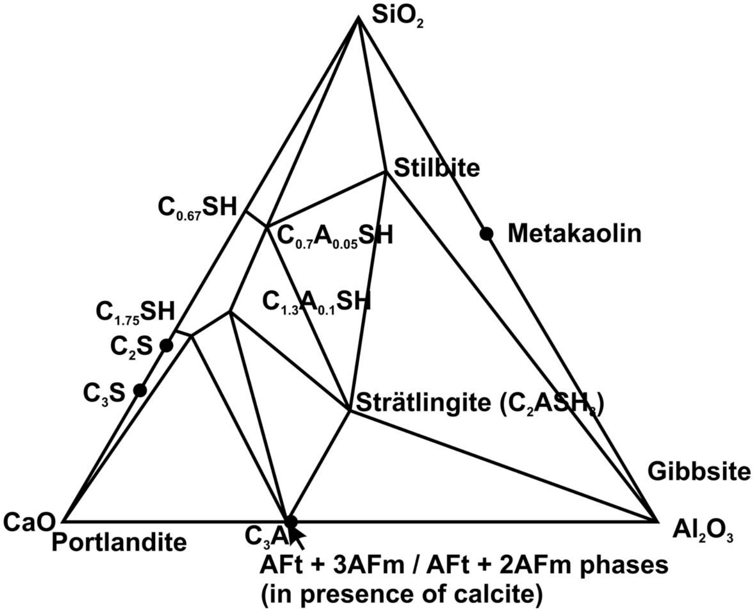

Figure 14. Simplified lime-silica-alumina diagram showing the clinker phases and some of the phases formed during cement hydration and pozzolanic reactions. Modified from Lothenbach *et al.* (2011).

plaster (8th millennium BC), however, is probably accidental and there is no evidence of systematic use of hydraulic materials in this early period. The possibility indeed exists that the silica phytoliths and other siliceous minerals derived from plant ashes could indeed have induced pozzolanic-type reactions in other cases of primitive plaster technology.

As discussed above, hydraulic binders based on pozzolanic reactions developed in the Greek and Aegean world in the 2nd millennium BC (Maravelaki-Kalaitzaki *et al.*, 2003; Moropoulou *et al.*, 2005; Theodoridou *et al.*, 2013). They became the technological basis for the highly successful binders used in later Roman architecture (Siddall, 2000). Between the Aegean tradition and the standardized adoption of the hydraulic mortar technology by Romans some thousand years later there is a fuzzy period of use and diffusion of these materials, possibly linked to cultural diffusion from the Eastern Mediterranean along the African coasts during the first Iron Age. Important clues to these pre-Roman developments are the hydraulic plasters of Tell es-Safi/Gath, Israel (Regev *et al.*, 2010a) and the carbon-containing mortars (ash mortars) used in Punic cisterns of Tunisia (Lancaster, 2012). It is again important to note that the hydraulic mortars in all these examples are limited to flooring and cistern plastering, mainly with a waterproofing function. Consistently, the analysis of the excavated structures and the mortars from a residential quarter in the Punic-Roman area of Palermo, dated firmly to before the final conquest of the city by the Romans during the First Punic War (254 BC), show only wall and floor plasters, with crushed pottery present in two of the samples investigated (Montana *et al.*, 2016).

The crucial evolution in the architectural use of hydraulic mortars occurred in a relatively short period in the first half of the 2nd century BC: the mortar is finally employed to strengthen masonry structures in both public and military buildings. It is the first fully recorded structural use of binders in architecture, in which the binder intimately links the units of the masonry and actively contributes to the mechanical strength of the composite structure. Marcus Porcius Cato (*De agri cultura liber*, dated approximately to 160 BC following the Oxford Classical Dictionary) described the systematic use of lime-based mortars as a binder in foundations, walls and complex architectural components of buildings (Greco, 2011). Following the critical chronological revision by Mogetta (2015), with which the present authors largely agree, the oldest known remaining example of concrete (*caementa*) in Rome is the *Porticus Metelli*, dated to ~130 BC. Most of the other concrete building traditionally dated to the late 3rd century or the early 2nd century BC (see table 2 in Mogetta, 2015) should be postdated to the last two decades of the 2nd century BC. Furthermore, there are recent indications that pozzolanic mortars were used to pour the foundations of fortification walls in wet areas far from Rome at very early periods (Aquileia: Bonetto *et al.*, 2016; Ravenna: Costa *et al.*, 2000). Apparently, Roman military engineers already knew that volcanic pozzolan performs better than crushed pottery in marshy or salt-water environments. If confirmed, such occurrences of pozzolanic reactions are even older than the examples in Rome, suggesting an early and rapid diffusion of the technology involving hydraulic reactions based on volcanoclastic material.

Three major innovations and/or technological optimization in the use of the binders were introduced rapidly and systematically at the beginning of the 2nd century BC or shortly thereafter (Lechtmann and Hobbs, 1987; Siddall, 2000; Adam, 2005; Hobbs and Siddall, 2011; Brandon *et al.*, 2014):

(1) The use of mortars to strengthen important architectural structures: for the first time binders are not limited to plastering and waterproofing.

(2) The systematic use of crushed ceramics (pottery, bricks, tiles) in terrestrial structures that required resistance to water. This technology, certainly derived from the Greek world, was carefully optimized in the so called *opus signinum*, widely used in cisterns, aqueducts, fountains and baths (Siddall, 2011).

(3) The exclusive use of highly pozzolanic volcanoclastic material in hydraulic mortars used to build structures in contact with sea water (Brandon *et al.*, 2014).

Not surprisingly, it was in late Republican times (2nd–1st centuries BC) that the architectural capabilities of Roman engineers, previously limited by the robust but cumbersome properties of ashlar (the Servian walls of the 6th century BC were still built in *opus quadratum*), started to produce efficient, solid and durable buildings rapidly complying with the formula later encoded by Marcus Vitruvius Pollio: "*Haec autem ita fieri debent, ut habeatur ratio firmitatis, utilitatis, venustatis*" (*De Architectura*, 1.3.2; 29–23 BC). As the only architectural book surviving from classical antiquity, the Vitruvian statements and prescriptions are considered the primary source of information concerning Roman and Greek building techniques. Vitruvius' *De Architectura* met with immense favour and reputation from the Renaissance to the end of the 19th century, becoming the conceptual reference for most Western architecture of the period. In his work, Vitruvius not only illustrated building techniques and architectural theories, but described at great length the nature and preparation of the materials, including mortars. As an example, Vitruvius in his Book II indicates clearly that the proportion of lime and sand must be increased if poor quality or marine sand is used as aggregate. His descriptions find neat experimental evidence in a number of recent investigations of Roman materials (Oleson *et al.*, 2006; Gotti *et al.*, 2008; Secco *et al.*, 2018), where Vitruvius' recipes for binder formulation and preparation found precise confirmation.

During the last part of Republican times, Roman engineers crucially improved the Aegean-derived technology of hydraulic binders by using slaked lime in a mixture with local high-alkali volcanic ash, first drawn from the banks of the river Tevere, and then from the volcanic sands found near Naples, at Pozzuoli; hence the name *pozzolan*, still in use today. Recent studies of the evolution of Roman mortars from Republican through Imperial times reveal specific changes in the composition and use of the mortar components. The mineral components of the ash outcrops within and around ancient Rome (especially the Pozzolane Rosse ignimbrite: Jackson *et al.*, 2007; Marra *et al.*, 2016) show that specific zeolite-rich tuffs with highly reactive properties were carefully selected from the very beginning in order to produce exceptionally hard and durable mortars. These important studies not only confirm the early chronology of

Roman mortars identified by macroscopic observations (Mogetta, 2015), but also confirm the incredibly detailed description of the materials that Vitruvius indicated as ideal for the preparation of quality mortars (black and red sands, or *harenae fossiciae*: *De Architectura* 2.4.1). Further, Vitruvius states that this pozzolanic material is the only one that is able to harden under water (*De Architectura* 2.6, hence the name 'hydraulic mortar'). The physicochemical and engineering characteristics of mortars used for the construction of Roman harbours have been investigated extensively in the frame of the ROMACONS project (Brandon *et al.*, 2005, 2014; Oleson *et al.*, 2006). Not only are the outstanding properties and durability confirmed, but the tuffs used in the mortars of the harbour of King Herod in Caesarea seem to have been transported all the way from the Bay of Naples. The Roman harbour builders knew very well that proper hardening of mortar at sea required good quality pozzolans, even at the cost of long-distance transportation.

The local occurrence of reactive volcanic sand (such as in Central Italy, or in the German Eifel area, known as Trass; Siddall, 2000), and the availability of recycled crushed pottery and bricks gave Roman engineers the appropriate technology to build flexible, innovative and durable architecture and ultimately set the basis for the efficient infrastructure of the Roman empire. In fact the Romans also developed the concept of lightweight robust structures by the use of innovative building techniques, such as the vaulting tubes, the use of appropriately shaped bricks, and the incorporation of lightweight pumiceous aggregates in the binder (Lancaster, 2005, 2015; Lancaster *et al.*, 2010, 2011. The arches of the Colosseum and the Pantheon dome are reported to have been made with such innovative materials and techniques (Lancaster, 2011).

Note that the word cement (*opus caementicium*) in ancient Roman times referred to the concrete masonry of monuments composed of cm-sized brick and tuff fragments (*caementa*) used as aggregates and which are bonded by hydraulic mortars with alkali-rich, calcium-alumino-silicate volcanic ash sands (Lechtman and Hobbs, 1987; Lamprecht, 1996). Only in recent times has the meaning changed to refer to modern clinker-based materials.

The ability of producing and using excellent mortars was lost slowly after the fall of the Roman Empire. The dome of the Hagia Sophia Basilica in Costantinople (532–537 AD) is probably the last great Roman building formed by the monolithic pouring of Roman pozzolanic mortar based on crushed ceramics (Livingston, 1970; Moropoulou *et al.*, 2002; Miriello *et al.*, 2017). Lime-based mortars continued to be used through the Middle Ages, though in many cases the mortars were of rather low quality, made of partially burned lime, sometimes mixed with charcoal and clays, and the lime putty was frequently unaged and poorly slaked. The careless preparation made them mostly porous and degradable (Furlan and Bissegger, 1975; Franzini *et al.*, 1999). Many of the Saxon, Norman and Longobardic materials are of this kind. The standardized production during the Roman Empire was thus followed by very local productions, mostly having only a small technological content, and it was only in specific and prestigious construction sites that high-quality binders were produced, as in the case of the Byzantine mosaics in Ravenna, or the Leaning Tower of Pisa (Franzini *et al.*, 2000).

In the latter case, the absence of volcanoclastic material and the presence of CSH products hints at the possible use of very reactive silica sources, such as diatomaceous earths. Most of the mortars used through the Middle Ages until the Renaissance to build cathedrals, fortresses and palaces are lime-based (Alvarez *et al.*, 2000; Franzini *et al.*, 2000; Pecchioni *et al.*, 2006). However, some binders show a limited hydraulicity (Moropoulou *et al.*, 2000; Elsen *et al.*, 2004) due to pozzolanic reactions. Although discontinuous, the tradition of making hydraulic mortars by the use of crushed ceramics persisted in several regions of the Roman Empire and beyond: it is called *cocciopesto* in Renaissance Italy, *horasan* in Turkey, *homra* in the Middle East, *surkhi* in India.

A peculiar kind of traditional material produced by clay activation is called *sarooj*. It was apparently used widely in ancient Persia and other areas around the Persian gulf, especially for cisterns and waterproof structures (Al-Rawas *et al.*, 1998, 2001). It is claimed that a number of ancient temples and buildings, such as the Elamite zigurrat at Chogha Zanbil, Iran (Fig. 7) were built partially using *sarooj*, although experimental evidence is scarce. The reported preparation of the material indicates that a mix of clays, dung and water was sun-dried into decimetre-sized blocks, which were then fire-heated for activation. The final product was ground and mixed with lime to produce the final binder (Masoumi *et al.*, 2015). *Sarooj* seems to be the earliest example in which thermal activation of clay was consciously and systematically employed to obtain hydraulic reactions.

As will be discussed below, the technology based on thermally activated clays is regarded as one of the future solutions for the replacement of modern Portland-based clinker with more sustainable products (Scrivener and Favier, 2015). As a matter of fact, our understanding of the pozzolanic reactions that occurred in ancient hydraulic binders allows modern interpretation of their mechanical durability (Moropoulou *et al.*, 2000; Charola *et al.*, 2005), and has fundamental implications for the development and technological control of modern cement alternatives to Portland clinkers (Mahasenan *et al.*, 2003; Schneider *et al.*, 2011). On a technical note, the protocols of separation and characterization of the binder fractions for reliable radiocarbon dating of ancient mortars require adequate understanding of the phases present and their reaction history (Lindroos *et al.*, 2011; Addis *et al.*, 2016).

The presence and extent of pozzolanic reactions in ancient mortars is commonly assessed by:

1. measurement of the mechanical resistance to compression tests, which is substantially greater than those measured on traditional lime mortars,
2. calculation of empirical parameters derived from bulk-chemistry measurements (*i.e.* hydraulicity index, cementation index),
3. characterizing the nature and micro-textural features of the mineralogical phases present in the binder fraction of the composite, which are the result of pozzolanic reactions.

Testing the mechanical resistance is an indirect bulk measurement and leaves space for ambiguities in the interpretation of the mechanisms that lead to the development of the physical properties. The 'hydraulicity index' (HI = $SiO_2 + Al_2O_3/CaO$) or the 'cementation index' (CI = $2.8\ SiO_2 + 1.1\ Al_2O_3 + 0.7\ Fe_2O_3/CaO + 1.4\ MgO$) are generally proportional to the amount of Si,Al-rich species in the mortar (Elsen *et al.*, 2012), though the presence of aluminosilicate phases is not sufficient to indicate that the pozzolanic reaction did actually take place to a sufficient extent in the binder, as they can be inert or very slowly reacting.

On the other hand, a thorough mineralogical characterization of the phases and of the textures resulting from the lime–pozzolan interaction yields direct evidence of the pozzolanic reaction. Adequate characterization, therefore, requires identification of reaction products (by X-ray powder diffraction (XRPD), FTIR, Raman spectroscopy, or other micro-analytical techniques) and/or micro-imaging of the reaction textures, such as the reaction rims formed around the pozzolanic particles through dissolution-recrystallization processes (Fig. 13; see for example: Maravelaki-Kalaitzaki *et al.*, 2003; Diekamp *et al.*, 2012). The limiting factor of the pozzolanic reaction rate in general is the dissolution kinetics of silicate phases. The issue is fundamental when assessing the reactivity of materials to be used as supplementary cementitious materials (SCM) in modern binder formulations (Malhotra and Mehta, 1996; Lothenbach *et al.*, 2011; Snellings *et al.*, 2012).

The hydrous phases formed by the pozzolanic reaction have a variable composition depending on the chemistry of the system (Fig. 14). They range from pure C-S-H phases in the lime-silica join (tobermoritic Ca,Si-hydrates; Richardson, 1999, 2004) to more complicated C-A-S-H phases as the Al activity increases (Hong and Glasser, 2002, L'Hôpital *et al.*, 2015, 2016). Zeolite-like phases are favoured in complex N-K-C-A-S-H environments, and their formation is reported to be enhanced by interaction with sea water (Jackson *et al.*, 2012, 2013, 2017). It is the interaction between sea water and the volcanic tuff that yielded tobermorite and zeolitic phases and produced the extremely hard and durable binders of Roman harbours.

3.3. Natural hydraulic lime (NHL) mortars

A particular type of hydraulic binder was developed in Europe in the 18th and 19th centuries by firing impure limestones containing clays in lime kilns; they are called natural hydraulic limes (NHL) or "Roman cements" (Weber *et al.*, 2012). In these natural hydraulic binders the reactive phases are not added as aggregate, but formed in the kiln through the reaction of the clays and the quicklime. They can be considered the precursors of modern Portland clinker. NHL were very popular for building construction and façade decoration in Central Europe in the 19th century (Callebaut *et al.*, 2000, 2001). They were, and are still, used extensively for restoration of historical buildings (Maravelaki-Kalaitzaki *et al.*, 2005; Gosselin *et al.*, 2009; Bras and Henriques, 2012) because of their good mechanical properties and compatibility with ancient materials.

A very early instance of production and use of NHL in the 14th century AD was identified during the investigation of the mortars and slags of the Gothic Obřany Castle, Moravia (Kropáč and Dolníček, 2013): the interpretation is that the lime binder incorporated high-temperature phases derived from the kiln lining and local metallurgical activities. Slags from ore processing were also observed in the mortars of the medieval archaeological complex at Montieri, Tuscany, Italy (Chiarelli *et al.*, 2015), which is located in an area of intense exploitation of argentiferous ores.

Both pozzolan-added mortars and NHL were used in the Czech Republic to build 14th century bridges, such as Charles Bridge in Prague and the Gothic bridge in Roudnice (Frankeová *et al.*, 2012). The slightly hydraulic character of the Narni bridge, in Central Italy (3rd century AD) is thought to be derived from the accidental firing of impure limestones, containing cherts (Cantisani *et al.*, 2002; Frankeová *et al.*, 2012). In extreme cases, the burning in lime kilns of chert-containing limestones in the presence of alkali lowering the melting point of silica yields the production of amazingly coloured silica glasses, which were found at the base of the furnace after firing (Artioli *et al.*, 2009).

Vitruvius recommended the use of very white and pure limestone for the production of lime in classical times. It appears that whenever the Vitruvian recipes were abandoned or not followed closely, the accidental use of impure limestones with various amounts of silica or aluminosilicate phases randomly produced binders with very variable degrees of hydraulicity. Sometimes the fine-grained size of the original material and the heterogeneity of the microtexture makes it very difficult to assess the degree of hydraulicity and/or deduce unambiguously the complex dynamic of the production process (Riccardi *et al.*, 2007).

The emerging picture is one of unstandardized binders and largely uncontrolled production processes from late antiquity until approximately the 18th century AD, when systematic experiments were carried out to produce optimized materials.

4. The development of modern cement materials and the hydration process

A significant change from traditional lime mortars was made by John Smeaton in England in 1756, when he was involved in the reconstruction of the Eddystone lighthouse (Blezard, 2003). As the story goes, he was driven by the need to develop a masonry construction durable in a marine environment and thus built using a binding lime mortar that did not dissolve in seawater. Among several attempts, he also departed from the Vitruvian recommendations of using pure white limestone. Using clay-rich carbonates of marly composition he obtained better hydraulic properties than lime. As discussed above, this class of materials may be defined as natural hydraulic limes and can be considered intermediate between slaked lime and modern Portland cement. Eventually the material that Smeaton selected for the lighthouse was a mortar prepared with equal proportions of local argillaceous limestones (blue Liassic limestones) and pozzolan from Civitavecchia, Italy, the closest stuff he could access resembling the ancient Roman material. Slightly improved mixtures of this kind were in use until the introduction of Portland cement.

In the first half of the 19th century the search for optimal hydraulic binders was pursued actively in several countries (Bentur, 2002; Blezard, 2003). In England

Smeaton was testing alternative formulations of hydraulic mortars, and J. Parker introduced and patented a so-called "Roman cement" (Patent by James Parker, of Northfleet, Kent, England, No. 2120, 1796), defined as a "cement or tarras to be used in aquatic and other buildings and stucco work". It was made by calcination of nodules of argillaceous limestone (known as septariae) and it produced a quick-setting cement. In France, Louis Vicat's experiments (Vicat, 1818) led to the preparation of hydraulic lime by calcination of a mixture of high-grade quicklime (produced by the chalk of the Upper Cretaceous carbonatic formation of the Paris Basin) and clay (Vicat, 1828). His formulation, called the "twice-kilned" process, met with considerable success and led his son Joseph Vicat to establish the well known Vicat Cement company. This is considered by many to be the predecessor of Portland cement.

A lot of patents were issued around the same time establishing plants in southern England, including the London area. The most famous one is that related to the three-stage process of Joseph Aspdin (patented in 1824), who named his product 'Portland cement', because, at that time, the Portland limestone had a reputation among builders for quality and durability, and he wanted to capture the similitude between his cement and Britain's favoured quarried stone. Portland cement was marketed as an improvement in the production of artificial stone. In one of the several plants established by Aspdin or his son, the temperatures were running high enough to produce partial or complete vitrification and crystallize alite, as shown by the retrospective analysis of the type of clinker material from Aspdin's kiln (Blezard, 2003). The 'clinker' is the reactive product formed by cooling from the high-temperature processing (1450ºC) of the limestone and clay mixture within the kiln. The temperature is such that partial fusion occurs and the reacted molten material forms nodules that are partly crystalline and partly vitrified, the whole material being highly reactive with water. The four major phases making up the clinker are reported in Table 2, though the real situation is made more complicated by the existence of several polymorphs for each phase, and by compositional deviation from stoichiometry (Taylor, 1997). The basic chemical composition of Portland cement is shown in Fig. 14, where it is evident

Table 2. Main phase components of ordinary Portland clinkers.

Common phase name	Mineral name	Composition	Cement notation	Appx. wt %
Alite (tricalcium silicate)	hatrurite	Ca_3SiO_5	C3S	50–70
Belite (dicalcium silicate)	larnite	Ca_2SiO_4	C2S	15–30
Aluminate (tricalcium aluminate)	–	$Ca_3Al_2O_6$	C3A	5–10
Ferrite (tetracalcium aluminoferrite)	brownmillerite	$Ca_2(Al,Fe)_2O_5$	C4AF	5–15

that the composition of the two major phases (alite and belite) lies on the $CaO-SiO_2$ join as a result of the lime–silica reaction. The hydration products, composed mainly of calcium silica hydrates (C-S-H) and portlandite also lie in the same portion of the diagram.

Following Blezard (2003), the historical evolution of clinkers after the illustrated pioneering experiments moved from *proto*-Portland materials (*i.e.* Aspdin's original patent), which shows limited interaction between CaO and SiO_2 because of the limited temperature in the kiln, to *meso*-Portland materials, which are very heterogeneous materials showing some silica–lime interaction and containing mostly belite and some alite, and finally to *normal*-Portland cements as we know them today. The main characteristics of modern Portland clinkers are derived mostly from the use of rotary kilns in place of the traditional shaft kilns, a technical development that also allows continuous production in place of the batch process. The carefully-controlled initial formulation of calcareous and argillaceous components, together with the use of the rotary kiln that determines a long permanence at high temperature and continuous mixing, helps to: (1) minimize the amount of unreacted lime; (2) maximize the alite/belite ratio; and (3) obtain the appropriate crystal size of the mineral components, commonly in the range 10–40 μm. Modern clinkers contain about 60–65 wt.% of C3S, and <2 wt.% of unreacted free lime. The standard reaction properties of modern Portland clinker are essentially due to a high alite/belite ratio and to a careful control of the grinding of the clinker into a fine powder.

The very reactive Portland cement powder is mixed with water to produce a final hardened material through a series of complex reactions, the so-called 'hydration process', involving dissolution of the crystal phases, surface reactions, gel formation, precipitation of new phases and textural changes (Taylor, 1997; Gartner *et al.*, 2002; Bullard *et al.*, 2011). The different crystal phases present in the clinker have very different reactivities, C3A having the highest and C2S the lowest. In fact C3A is so reactive exothermally in water that it can cause unwanted rapid setting of the paste (flash set), with consequent loss of workability. Therefore calcium sulfate (commonly gypsum) is usually added to the clinker in the amount of ~4–8 wt.% as a set-controlling agent, because the sulfate ion retards the dissolution of the clinker phases, and promotes the formation of ettringite. The finely powdered mixture of clinker and gypsum is marketed as standard Portland cement (also called OPC = ordinary Portland cement), which is then mixed with water in the ratio water/cement >0.38, *i.e.* the least amount of water necessary for complete hydration of the cement phases. As in ancient binders (Table 1), when an aggregate material is added to the paste we have mortar (fine aggregate, such as sand with grain size <1 mm) or concrete (fine and coarse aggregate, such as coarse sands or gravel). They can both be considered to be cement composites, with the aggregate having the role of reducing the formation of fractures during the shrinkage that accompanies the hydration and hardening; for the same reason temper is added to pottery clays before firing. The aggregate may be composed of any type of loose or ground rock, and it is assumed not to react with the cement paste (hence it is referred to inappropriately as the 'inert' component), though this is not necessarily the case.

Upon mixing with water, the clinker phases react at different times to produce first a series of intermediate phases (the so-called AFt and AFm phases) such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$) or monosulfoaluminate ($Ca_4Al_2(SO_4)O_612H_2O$), and then the reaction proceeds to the final hydrous phases: portlandite and amorphous calcium silicate hydrate (C−S−H), which are the phases forming the interlocked gridwork of the material and producing high mechanical resistance. Figure 15 shows environmental scanning electron microscope (ESEM) evidence of the growth of ettringite and C−S−H at different times on the surface of the clinker grains. It is important to understand that it is the microstructure of the material, that is the final assemblage of crystalline and amorphous phases that governs the macroscopic and engineering properties of the material (Thomas *et al.*, 2011; Scrivener *et al.*, 2016). With time, portlandite will eventually convert into calcite through a carbonation reaction with atmospheric carbon dioxide, so that abundant calcite is found in old cements.

Reaction kinetics play a crucial role in determining the final microstructural properties. The completion of the hydration process may take days, months, or even years, depending on crystal size, defectivity and polymorphism of the phases, porosity of the paste, environmental conditions, *etc*. The system is so complex that reactions can be inhibited for a long time. It is often observed in old concrete that highly reactive species such as aluminates are still present years or decades after manufacturing (Secco *et al.*, 2014). Many of the practical problems in the modern cement industry derive from the lack of control of clinker composition, poor concrete design, or sloppy practice: even small changes may affect the hydration kinetics and determine substantial degradation of the engineering properties. Incidentally, the same problems, mostly due to human factors such as incompetence and fraud, were present and well recorded in Roman times (Oleson, 2011).

Strength development is related to the degree of hydration and to the speed of the process. In general, the slower the hydration kinetics, the higher the compressive strength developed. This is one of the differences observed between modern clinkers

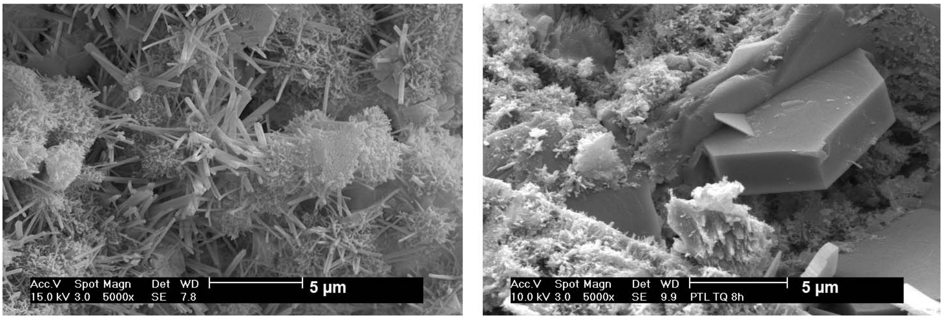

Figure 15. (a) Prismatic crystals of ettringite growing amidst C-S-H felt during the hydration of a Portland cement, and (b) well developed platy crystals of Portlandite. Images obtained by ESEM. (Courtesy of D. Salvioni, Mapei S.p.a.).

and those produced in the early part of the last century. Modern cement is required to develop high resistance to compression (>40 MPa) within a few days of emplacement, whereas early 1900s cements developed high strengths (in the range of 20–30 MPa) over much longer periods, because of the greater belite content. This has some consequences also in terms of durability. High-compression resistance combined with tensional resistance are, of course, obtained by steel reinforced concrete (SRC), which is a composite in which the concrete is poured and solidified around a metal skeleton. The French-Swiss architect, Le Corbusier, was one of the first to understand and exploit the properties of SRC in modern architecture. He had discovered the use of reinforced concrete very early in Paris from one of the pioneers of its use, architect Auguste Perret, and then employed it to realize his architectural vision (Fig. 16). He later wrote: "Reinforced concrete provided me with incredible resources, and variety, and a passionate plasticity in which by themselves my structures will be rhythm of a palace, and a Pompeiian tranquility" (Letter to Auguste Perret, 1915).

Figure 16. Reinforced concrete structures by Charles-Édouard Jeanneret (Le Corbusier): (a) The convent of Sainte Marie de La Tourette, France (1953–1960) (photo by Alexandre Norman, French Wikipedia, CC-BY-SA-3.0); (b) The palace of Assembly, Chandigarh, India (1952–1961) (photo by English Wikipedia, CC-BY-SA-2.0).

Nowadays only ~35% of the cements produced industrially for the global market are OPC, and most of the materials are special composite formulations (Odler, 2000; Chatterjee, 2002), where special components or SCM are added to enhance specific physicochemical or mechanical properties, such as resistance to alkali or sulfates, thermal resistance, or low-heat emission. The main added constituents are: (1) latent hydraulic components (granulated blast furnace slags, class C fly ash) that have self-cementing properties that need to be activated by OPC; (2) pozzolanic aluminosilicate components (class F fly ash, silica fume, metakaolin, pozzolan) that have no self-cementing properties and need to be activated by portlandite; and (3) non-reactive or poorly reactive components that modify the grindability of the clinker or the rheology of the paste.

Because of the low market cost of cement, the materials added to the clinker are large-volume but low-cost byproducts of other industrial activities. Therefore on one hand the production of cement represents a virtuous route to recycle large quantities of waste material (*e.g.* slags from the metallurgical industry, fly ash from coal plants); on the other hand the market for special cements will need alternative materials should the global changes in metal and energy production decrease the availability of SCM materials in the future.

One of the most important properties of modern cement pastes and concrete composites is fluidity: it ensures the possibility of transportation, pumping, levelling concrete to fit modern architectural requirements, and also proper consolidation by grouting. The rheological and working properties of the cement and concrete are so important that they are now controlled invariably by the use of chemical admixtures (water-soluble organic polymers) that allow good fluidity of the paste with a smaller water/cement ratio. The net result is also a lower porosity of the paste and a greater mechanical strength: ultra-high performance concrete and high-strength concrete are made this way, they can reach compression strengths in excess of 150 MPa. The modern generations of plasticizers, ensuring fluidity at low water content are called water-reducing admixtures (Chandra, 2002; Edmeades and Hewlett, 2003). Besides rheology, organic and inorganic additives are also used to control specific properties of the mortars and cements, such as air entrainment (for better resistance to freeze and thaw cycles), acceleration or retardation of the setting (to control the time of progressive increase in mechanical resistance; Cheung *et al.*, 2011) and even resistance to chemical attack. Virtually all modern concrete formulations include polymeric admixtures to optimize performances.

How do we investigate cement materials? At the industrial level, most quality controls are done by optical microscopy, X-ray fluorescence (XRF) and XRPD, with the quantitative phase analysis by XRPD offering a number of crucial advantages over bulk chemical analysis by XRF. Cement producers are among the most active users of advanced on-line testing protocols and instrumentation using automatic XRPD, including full-profile refinement of all clinker phases (Bellotto and Signes-Frehel, 1998; Manias *et al.*, 2000; De la Torre and Aranda, 2003; Bequette and Dhanjal, 2011; Snellings, 2016).

At the research level, the cement system is complex enough that one experimental technique alone is hardly sufficient to unveil the fine interplay between all chemical reactions acting simultaneously during hydration. Furthermore, the system is extremely sensitive to any environmental perturbation, especially dehydration, so that sample preparation without artefacts is a crucial part of any experiment. Virtually all experimental techniques have been employed to characterize and understand the behaviour and evolution of cement systems. In this chapter we will mention only some of the most recent developments providing a better insight into fundamental mechanisms of cement hydration processes. Time-resolved XRPD is one of the most powerful techniques for following the evolution of the cement/water system during hydration (Dalconi *et al.*, 2008; Hesse *et al.*, 2011; Valentini *et al.*, 2015). It allows appropriate quantification of the phases and evaluation of reaction kinetics (Fig. 17). If reaction enthalpies are sufficiently well known (Matschei *et al.*, 2007; Damidot *et al.*, 2011), then it is possible to back-calculate the measured curves from isothermal calorimetry and discriminate the underlying reactions (Hesse *et al.*, 2011; Jansen *et al.*, 2012; Valentini, 2013).

The use of synchrotron radiation, of course, allows access to much faster reaction times with respect to laboratory instruments (Merlini *et al.*, 2007, 2008; Snellings *et al.*, 2010), down to the millisecond timescale (Schlegel *et al.*, 2012). Synchrotrons offer the advantage of highly brilliant and coherent radiation, so that experimental techniques can be designed flexibly to suit complex samples (Aranda, 2016). Simultaneous and combined investigations are thus possible only at large scale-facilities. Concerning cements, ultra-high resolution imaging (Harutyunyan *et al.*, 2009; Monteiro *et al.*, 2011) and sub-micron computed tomography (Artioli *et al.*, 2010; Parisatto *et al.*, 2015) provide considerable advances in understanding the 3D evolution of the microstructure

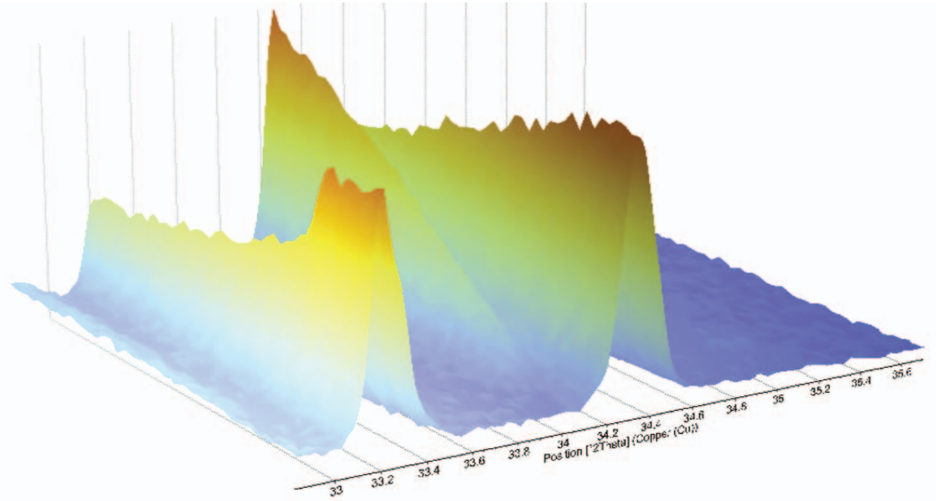

Figure 17. Time resolved XRPD patterns of a cement paste during the hydration process.

of the material in a totally non-invasive mode (Fig. 18). Furthermore, the innovative combination afforded by diffraction-enhanced tomographic imaging proved to be an extremely powerful tool for the investigation of complex materials (Voltolini *et al.*, 2013), and allowed, for the first time, direct imaging of nucleation processes (Artioli *et al.*, 2014a,b).

As a further link between the cement world and mineralogy, there is only one known natural occurrence of the calcium silicate phases (hatrurite, larnite) that are commonly produced in cement kilns. It is from a geological formation called the Hatrurim Formation, and it is exposed in various areas around the Dead Sea in Israel (Hatrurim Junction, near Arad), Palestine and Jordan (Maqarin). It is interpreted to occur as the result of pyrometamorphism of marls and limestones derived from gas or bitumen ignition in the underlying hydrocarbon-loaded formation (Burg *et al.*, 1991; Gilat, 1998; Sokol *et al.*, 2007). The natural combustion produced this unique rock formation of thermally metamorphosed 'cement zones' which are very close analogues of industrial cements. In the Hatrurim Formation the calcium silicate phases occur together with a number of exotic high-temperature mineral phases (shulamitite, bentorite, gazeevite, stracherite, zoharite, zuktamrurite, and others), most of them found only in this unique type locality.

The Maqarin site, located along the Yarmouk river near the Jordan–Syria border, has been investigated extensively because the subsequent interaction with groundwater caused the formation of hyperalkaline waters and C–S–H phases in the fractures of the HT-metamorphosed rocks. Such unique features were studied in detail in order to understand the long-term leaching and cation mobility in the only known natural analogue of a modern radioactive-waste repository. The investigation project was called The Maqarin Natural Analogue Project (Khoury *et al.*, 1992; Alexander and Smellie, 1998; Alexander and Blaser, 2002). This is another example showing the interplay of knowledge between natural and synthetic systems. This knowledge encompasses mineralogy, geology, hydrology, crystal chemistry, geochemistry and a number of other disciplines, and it is fundamental when tackling problems at a large or global scale.

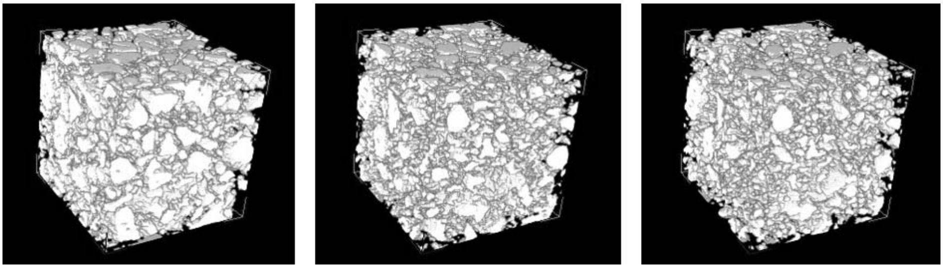

Figure 18. Virtual modelling of the microstructural evolution of cement can be compared directly to the experimental results obtained by computed micro-tomography (μ-CT).

4.1. Binders of the future

Modern cement formulations based on Portland clinkers are coming under serious criticism because of environmental issues. Cement is one of the industrial materials embodying the least amount of energy per unit volume, if compared, for example, with polymers, metals, and technical ceramics (Fig. 19). However, at present, modern society requires huge amounts of cement for infrastructures: the world production in 2016 was estimated at 4.2×10^9 tons/year (www.statista.com/statistics/219343/cement-production-worldwide/), higher than oil and gas, and second only to water. This is considered a problem because of the large emission of CO_2 during cement production (Worrell *et al.*, 2001; Barcelo *et al.*, 2014; Gartner and Hirao, 2015), estimated at ~1 ton of CO_2 emitted per ton of OPC. The emission of CO_2 derives from the fuel used in the kiln, grinding, transportation, but above all from the de-carbonation of limestone.

Increasing global concerns about sustainability and environmental compatibility (see the Intergovernmental Panel on Climate Change (IPCC) website: www.ipcc.ch/) stimulate active research towards more eco-friendly choices of materials (Ashby,

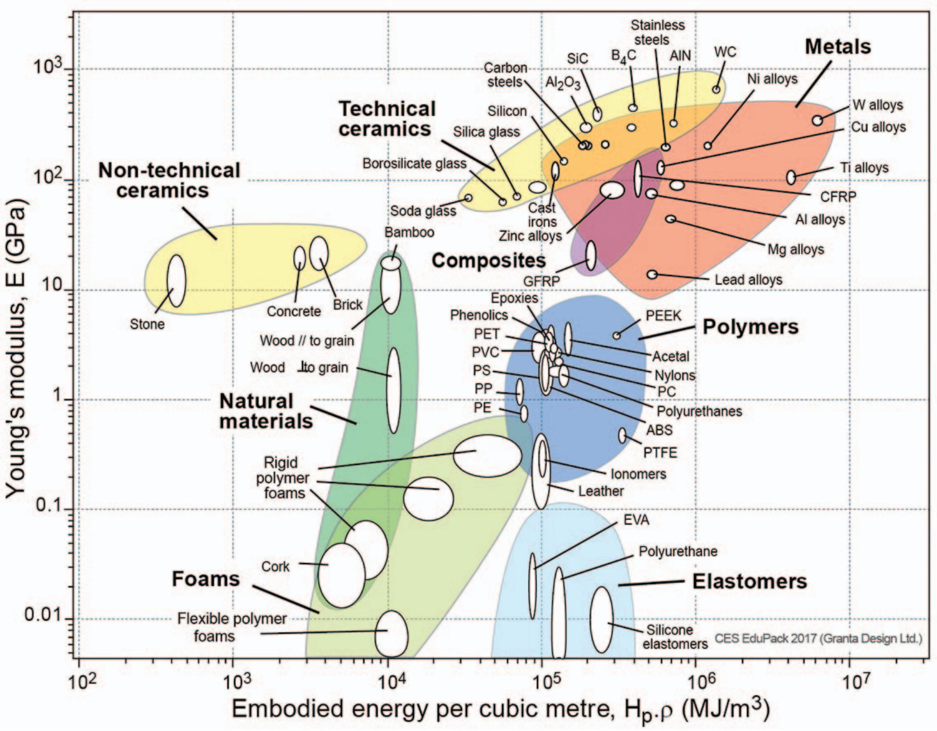

Figure 19. Young's Modulus *vs*. embodied energy per unit volume. (Chart created using CES EduPack, 2017, Granta Design Ltd. http://teachingresources.grantadesign.com/Charts-overview).

2013). The life-cycle assessment of building materials and methods is an active field of research, and concepts such as the 'transcendent quality' of building materials (Mora, 2007) and that of 'life-cycle thinking' (Buyle *et al.*, 2013) are finally entering the lexicon of construction planning. Comparative assessments of the life and energy cycles of traditional and alternative cements and mortars are on their way (Weil *et al.*, 2009; Chen *et al.*, 2010; Jiang *et al.*, 2014; Ouellet-Plamondon and Habert, 2015). Alkali-activated materials and fly-ash/slag-based geopolymers are being tested actively in the formulation of clinker-free binders (Shi *et al.*, 2006; Provis and Van Deventer, 2009, 2014; Pacheco-Torgal *et al.*, 2015). Thermally activated clays are also proposed to be a sustainable solution in the long time-span (Scrivener and Favier, 2015). It is accepted widely that the infrastructure and housing needs of modern society cannot avoid being dependent on cement-type materials (Schneider *et al.*, 2011), because the ratio between engineering properties and cost is more advantageous than for any other available material. Present trends and efforts are therefore clearly directed towards sustainability of construction materials (Liew *et al.*, 2017), which is the key word for future research and planning: despite the optimistic claims of the cement industry (Damtoft *et al.*, 2008) cement is certainly one of the materials in need of substantial improvement (Shi *et al.*, 2011; Flatt *et al.*, 2012; Kurtis, 2015).

5. Conservation of binders in architecture – Binders for conservation

Conservation of historical buildings and ancient architecture is a very intricate task. Sometimes the technical problems of conservation of the materials are not even the major difficulty: most of the problems are commonly connected with the management and decision-making of what to preserve and why. Economic, social, cultural and organizational constraints ought to be resolved before technical plans are developed (Aygen, 2013; Forsyth, 2007a. Are we sure we can distinguish the fuzzy boundaries of preservation, conservation, restoration, reconstruction, consolidation or stabilization? Following the indications of the ICOMOS Venice Charter (1964, International Charter for the Conservation and Restoration of Monuments and Sites, www.icomos.org/charters/venice_e.pdf), preservation involves the minimal repair and maintenance of remains in their existing state, possibly avoiding further degradation. Restoration involves the removal of subsequent additions in order to return to the pristine state of the building. In such a case archaeological and scientific support (dating the materials for example) are fundamental in understanding the different construction phases. Reconstruction also involves returning a building to an earlier state, but involves introducing new/old materials to complete or stabilize the structures. Therefore compatibility and reversibility are at stake, and the fundamental concept of authenticity should be pondered carefully (ICOMOS Nara Charter on Authenticity, 1994, www.icomos.org/charters/nara-e.pdf). Conservation may involve one or more of the previous interventions, as well as the adaptation of buildings to new uses. Present emphasis of engineering interventions is towards building retrofitting, *i.e.* adding new technology to old structures in order to comply with modern legislation or lifestyle standards, especially concerning seismic aspects (safety), energetics (environment) and comfort. The attitude to building preservation has shifted constantly in the past, and we can be sure that conservation philosophy (Earl and Saint, 2015) in the future will be different from that of today.

Leaving to managers and planners the general problems, which are clearly beyond the purpose of this review, there are two important points that should be kept in mind. The first one concerns the sustainability of any architectural or structural intervention: this includes a reasonable balance between resources and objectives, and then adequate planning aimed at monitoring the success and durability of the intervention. Monitoring and continuous maintenance are often neglected, mainly because of sheer costs, and this frequently jeopardizes, in the long run, the results of many technical interventions, even if they were carried out with state-of-the-art protocols. The second point concerns the planning of conservation at very early stages of the intervention plan, *i.e.* as soon as the building/site is earmarked for attention or, as in the case of archaeological excavations, even before the excavation has started. Present trends contemplate parallel planning of archaeological works and conservation (Agnew and Bridgland, 2006; Sullivan and Mackay, 2013; Pedelì and Pulga, 2013).

No matter what the intervention is going to be, materials are important. Prior to any preservation or conservation action, a considerable effort to identify the materials originally used and to assess the constructive techniques employed should be made, along with a careful analysis of compatibility with new materials and a critical evaluation of stability and permanence of restoration works to be undertaken. In conservation repair work, it is therefore imperative that an understanding of the structure and the materials be gained before specifying and undertaking any work (Forsyth, 2008). For ancient lime-based architectures this is particularly important, because the state of the structure depends on the materials employed, the quality of the application, the environmental conditions, the continuous or discontinuous use (abandonment) of the structure, *etc*.

The conservation process should encompass: (1) extensive diagnostics at various scales, including the characterization of materials; (2) modelling and structure analysis; (3) selection and testing of materials and architectural components; and (4) the intervention plan. The last should comply as much as possible with the guidelines of the ICOMOS Venice charter and the Nara document on authenticity.

Each structure must be treated as a specific case, involving a particular combination of material properties, architectural character and environmental parameters. Reaching a compromise between the structural intervention and the integrity/authenticity of the original structure is the most challenging task.

The choice of mortars and plasters to be used in conservation is important in relation to the three major factors governing the performance of historic fabric: porosity, flexibility and strength. Any change in these parameters will affect seriously the stability and durability of the structure. Therefore, the nature and properties of the materials employed must be controlled carefully in terms of compatibility with the existing materials (Van Balen *et al.*, 2005). If the intervention is extensive, reversibility

Figure 20. Brick masonry of an old factory converted to a modern building. The OPC cement used to repoint the joints is deleterious in terms of rigidity and salt leaching.

is hardly possible. Extensive work has been done to characterize and optimize repair mortars and grouts (*e.g*. Maurenbrecher, 2004; Faria *et al*., 2008; Schueremans *et al*., 2011). Compatibility between mortars and repaired stone materials has been addressed specifically (Isebaert *et al*., 2014). While in the past Portland cement has been used variously to strengthen historical structures, it is now widely accepted that the use of OPC or formulations using OPC are detrimental to ancient structures in terms of mechanical and chemical incompatibility. OPC has two major adverse effects. The first is that the mechanical behaviour in terms of compressive strength or Young's modulus is much greater than that of lime mortars, thus creating rigid insertions in the fabric and reducing flexibility. The second is that OPC contains sulfate ions that are inevitably leached into the structure and redeposited as salts, usually at the surface, causing well known effects of surface deterioration (detachments, spalling, efflorescence, *etc*.). Sulfate salts are also deleterious to bricks and stone units of masonry (Fig. 20). For these reasons OPC has been virtually banned from all interventions to pre-industrial age buildings and ancient lime-based architecture. From all evidence, historical lime and hydraulic mortars proved to be less performing but more durable than 20th century reinforced concrete. Actually, the restoration and preservation of last century historical buildings based on Portland concrete is turning to be a diffuse and urgent problem, particularly where it is exposed and subject to damage from reinforcement corrosion (Forsyth, 2007b; Macdonald, 2008).

Acknowledgments

Small parts of the text have been adapted from chapter 3.2 of Artioli (2010).

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