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Composite materials in ancient structures

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Abstract

Mortars and concretes employed in ancient structures concern composite materials which have exhibited excellent durability through time. They were used as lining materials in cisterns, wells, aqueducts, shafts and duct drains, as supporting materials for pavements and mosaics, as plasters on external and internal walls, as supporting materials for frescoes and as joint mortars on masonry structures. They were comprised of various binding materials (or mix of them) and natural or artificial aggregates, along with natural or artificial pozzolanic additions, primarily of volcanic origin, that improved their performance and prolonged their longevity. Moreover, various types of organic substances were employed to increase plasticity and regulate setting rates, while fibrous materials were commonly used to obtain greater strengths or to avoid cracks due to the shrinkage during setting. The comprehension of the production procedures employed and of the physico-chemical and mechanical characteristics of such composite materials can be achieved by integrating properly the results of various analyses. Data obtained from tests performed on a large number of historic composites sampled from ancient structures in the Mediterranean Basin permitted the identification of physico-chemical and mechanical characteristics of the most typical mortars encountered in ancient structures.

Keywords: Historic mortars; Lime; Hydraulic lime; Pozzolana; Thermal analysis; Microstructure; Strength

1. Historical background

Mud seems to be the first binding material employed to fabricate mortars in ancient building, which is in use till now in some areas all over the world. In ancient Egypt mud mortars were used to joint mud bricks, while for the joining of carved stone blocks gypsum was preferred. The gypsum mortars placed in between the carefully squared stone blocks were not actually used as joints, but mainly as lubricant agent in order to accurately arrange stone blocks on the structure. Materials such as clays and mud earth mixed with chopped straw or cane were used in ancient times for the preparation of mortars in the Middle East and up to now they are considered to be typical traditional mortars. At least since 3000 BC, asphalt mortars were employed to joint bricks and they remained in use for a long period of time. In later constructions built at Babilonia, at Nabucodonosor period, asphaltic mixtures were replaced by slaked lime, in which clay, asphalts, ashes and other materials were usually added. It seems that the practice of limestone calcination was known even since 2450 BC at ancient Mesopotamia, while at Khafaje the ruins of a furnace, used for lime production, were found [1]. Moreover, the use of gypsum mortars at the Middle East lasted over 4000 years. It is considered that mortars technology was diffused to the Greeks and after to the Romans from the Middle East area [1,2].

Among others, Romans mainly developed the extensive use of mortars and concrete for building purposes. Concrete, "opus caementitium", is commonly supposed to be a Roman procedure [2,3]. The use of mortars and plasters in Greek building, as mentioned and in detail described by Vitruvius, indicates that the concrete probably was known in the pre-Roman periods [4]. Studies of the cistern of Kameiros–Rhodes (500 BC), where pozzolanic concrete is covering the walls of the cisterns, are confirming this statement [3].

The advantageous addition to lime mixtures of what is now called pozzolanic material (due to the improvement of their hydraulicity) was discovered by observations and firstly appeared in areas where natural pozzolana existed [2]. Before the Romans, the Greeks

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used Santorine earth in building. Pozzolanic mortars found in old structures on the island of Delos, near the island of Thera, dated back to the 2nd century BC. In the Roman period the technique of adding pozzolanic materials to lime based mortars and concretes was spread all over the empire [5].

The ancient treatises, among which Vitruvius is the most important, describe the use of crushed bricks in lime mortars. These materials were indicated by several names, such as *opus testaceum*, which seems to be the most significant [5,6]. Romans spread their use throughout their empire in Europe, northern Africa and West Asia (Turkey). These materials were employed for several purposes. Dust bricks were mainly used for rendering and for the upper layers of floors, but crushed bricks with large grain size were recommended not only for masonry walls, arches and foundations, where high humidity or water were present, but also to improve the performance of mortars and conglomerates in normal conditions [5,6].

During the latest time of the Roman Empire, the use of crushed bricks in the joints of load-bearing walls became more frequent, while the thickness of the horizontal joints was gradually increased from 10–15 mm up to 60–70 mm. This was continued during the Byzantine period until the joints reached a thickness of 70 mm in Hagia Sophia, Istanbul [7]. The use of crushed bricks lasted for the duration of the imperial times and seems to be less dealt with during the medieval times [6].

In the Middle Ages, it is known that certain impure limestones from specific quarries were used to produce limes, which had to be slaked on use because they hardened fast and set under water [8].

The renaissance treatises seem to propose again the lesson learned from Vitruvius related to the choice and preparation of raw materials, with slight divergences regarding the compositional ratios of the mixtures and application techniques. The treatises refer also to the use of white lime obtained from the calcination of river pebbles and to the use of dark lime (hydraulic lime) obtained from the calcination of grey and dark limestones as substitutions of the pozzolans [9,10].

The illuministic and neoclassic literatures of the 18th century, always concerned about the construction techniques of the past times, proposed again the ancient technology [11].

During the 19th century, the time cement was discovered, the manuals still suggest the use of traditional materials, but only after going into the details and explaining to the professionals about their right use and composition [6,12]. Thanks to the researches developed from Vicat parameters and scientific instruments were defined for the classification of aerial and hydraulic limes in substitution to empiricist criteria used in the past [13,14].

2. Materials of ancient mortars and concretes

Mortars and concretes employed in ancient structures concern composite materials comprised of a binding material (or mixture of binders), of natural or artificial aggregates or mix of them and pozzolanic additions (natural or artificial), in order to ameliorate lime-based mortars and prolong their longevity [15]. Sometimes, in order to improve rheological and mechanical characteristics, some organic additives and vegetable and animal materials as reinforcement were used [16].

Masons had to rely on experimentation or information past on orally to understand and learn the properties of the employed materials and the effects they could have produce when added to a mortar. Occasionally, literature might be available [17]. Literature refers to the use of mortars as isolating lining materials in cisterns, wells, aqueducts, shafts and duct drains, as supporting materials for pavements and mosaics, as plasters on external and internal walls and as supporting materials for frescoes, as well as joint mortars on masonry structures [1,2,5]. The ancient builders did not have at their disposal advanced materials for the manufacture of mortars and concretes. Being unable to invest in the strength capacity of the materials, they invested in craftsmanship. Excellence of quality of work, from the selection of raw materials to the mixing, bedding or molding, compacting or maintaining, was applied to their mortars and concretes [2,4].

For the preparation of mortars and concretes various materials were employed; gypsum lime were used for rendering since ancient times, but in structural mortars and concretes lime use dominated, possibly because of problems created by gypsum. Builders had a good empirical knowledge of limes of different origins, such as aerial limes from high purity limestones and hydraulic limes from marly limestones. Raw materials were burnt at about 900 °C and converted into quick lime, which was slaked with water. It seems that burning and slaking conditions played a significant role in the reactiveness of the lime, along with its long-lasting slaking in the pits [1,18,19].

The advantageous addition of natural or artificial pozzolanas to lime mixtures in order to obtain hydraulic mortars was well known, though they were certainly ignorant of the chemistry of inorganic materials. Natural pozzolanas, primarily of volcanic origin, either as coarse aggregate or finely powdered in the matrix, were used extensively for waterproofing renderings and pavements as wells as for the preparation of conglomerates. Artificial pozzolanas, such as ground fired bricks and tiles or ceramic shreds, were used whenever natural pozzolanic materials were not available and a mortar insoluble in water was needed [2,5–6,20–22].

Natural or artificial aggregates or mix of them were employed for the preparation of mortars and concretes.

Pit sand and see sand was used as fines. The hygroscopic properties of sea sand, as well as the risk of bleeding salts (efflorescence), were well known [2,4]. River gravel, crushed limestone and crushed bricks or tiles were used as rubble. The last made a lightweight concrete that provided an intelligent way to fit the large volume of old concretes without increasing their density. Pumice was sometimes used as an alternative. It appears that masons were aware of the aggregates gradation [3,6,20]. The proportion of lime to sand was adjusted to the sand quality. Maximum size of aggregates was selected according to the application purpose. This indicates good judgment in matching the characteristics of materials with the specific requirements of the construction [4].

The workability and consistence of mortars and concretes is remarkable. Since they were compacted by hand using simple tools, the fresh mixtures should had an adequate plasticity in order to be applied easily without being too fluid. To increase plasticity and regulate setting rates many types of organic substances were used; egg whites, blood, milk of figs, egg yolk, casein, animal glue, beer, vegetable juices, tannin, urine, etc [16,17].

As some mortars had very low strengths it was not uncommon to find fibrous plant materials or coarse animal hairs mixed in for greater strength or in order to avoid cracks, due to the shrinkage during their setting [7,17].

3. Physico-chemical and mechanical characteristics of ancient mortars and concretes

Historic composites concern "disturbed" systems, as in "service" for decades of centuries under severe mechanical and environmental loads. Therefore, the characterisation of such materials can be achieved by integrating properly the results of the various analyses, in order to understand the procedures employed to produce the final composites and their physico-chemical and mechanical characteristics [23].

Within this concept, data on historic composites arisen from a systematic research performed at a large number (approximately 400 samples) of ancient Greek, Hellenistic, Roman, Byzantine, post-Byzantine and later historic mortars and concretes sampled from Fortifications, Monasteries, Churches, Historical Buildings and masonry structures in the Mediterranean Basin [23–29]. The chemical characteristics of the mortars were determined by thermal analysis (DTA-TG), following an appropriate methodology, which proved to be an effective technique for the characterisation of the ancient mortars [23,24,26–29]. The determination of the microstructural and mechanical characteristics was performed by mercury intrusion porosimetry and fragment test method, respectively, due to the small quantity and irregular shape of mortars permitted to be sampled [23,25,28–34]. The ratio of binder to aggregates was determined after physical separation and sieving analysis of the composites [23,25–29].

Tables 1 and 2 report the data obtained from the tests performed, as mentioned above, permitting the identification of physico-chemical and mechanical characteristics of the most typical mortars encountered in ancient structures, which are described below.

3.1. Lime mortars

These types of mortars are the most commonly encountered in ancient structures. They present low percentages of physically bound water (adsorbed water usually <1% w/w), relatively low percentages of structurally bound water (chemically bound water <3% w/w) and high carbon dioxide content ($CO_2 > 32\%$ w/w). The ratio of CO_2 to structurally bound water, which inversely expresses the level of hydraulicity, is usually above 10, when aggregates are mainly calcareous, while when the silicoaluminate nature of the aggregates prevails the above ratio ranges between lower values (7.5–10), according to the structurally bound water of the aggregates fraction and the percentage of the binding material. These mortars exhibit a binder to aggregate ratio (per weight) which ranges between 1:4 and 1:1.

Table 1
Chemical characteristics of historic mortars as deriving from thermogravimetric analysis

Mortar type	Physically bound water (%)	Structurally bound water (%)	CO_2%	CO_2/structurally bound water
Lime mortars	<1	<3	>32	10[a], 7.5–10[b]
Lime mortars with unaltered portlandite	>1	4–12	18–34	1.5–9
Hydraulic lime Mortars	>1	3.5–6.5	24–34	4.5–9.5
Natural pozzolanic mortars	4.5–5	5–14	12–20	<3
Artificial pozzolanic mortars	1–4	3.5–8.5	22–29, 10–19[c]	3–6

[a] Aggregates of calcareous nature.
[b] Aggregates of silicoaluminate nature.
[c] Byzantine "concrete".

Table 2
Physico-mechanical characteristics of historic mortars

Mortar category	Cum. Volume (mm^3/g)	Bulk density (g/cm^3)	Pore radius average (μm)	Specific surface area (m^2/g)	Total porosity (%)	Tensile strength (MPa)	Binder to Aggregate ratio
Lime mortars	170–320	1.5–1.8	0.8–3.3	1.3–3.3	30–45	<0.35	1:4–1:1
Lime mortars with unaltered portlandite	105–241	1.8–1.9	0.03–6.5	1.67–10.63	20–43	0.06–0.7	1:1–1:2
Hydraulic lime mortars	90–230	1.7–2.1	0.1–3.5	2.5–13.5	18–40	0.35–0.55	1:4–1:1
Natural pozzolanic mortars	160–265	1.6–1.9	0.1–1.5	3–14	30–42	>0.60	1:4–1:5
Artificial pozzolanic mortars	170–280	1.5–1.9	0.1–0.8	3.5–9	30–40	>0.55	1:3

Their total porosity is higher than 30%, while their tensile strength does not exceed 0.35 MPa [23–26,28–32].

3.2. Lime mortars with unaltered portlandite

Mortars taken from structures many hundreds of years old, if injured, are found to consist of mainly calcium hydroxide, with the external portions having been converted to carbonate [22,35]. These mortars of aerated lime set with extreme slowness when not exposed directly to the air. In walls of medium thickness the final set can be figured in years, whereas in walls of very great thickness centuries may pass before the final set is acquired [35]. The process (carbonation) is slow under ordinary circumstances because the percentage of carbon dioxide in the atmosphere is low. In addition, diffusion beyond a thin surface of carbonated mortar deep into the masonry occurs at a very slow rate, if at all [35]. Moreover in areas with a high percentage of relative humidity content, the carbonation process is inhibited and unaltered portlandite crystals may occur [26].

The mortars of this category present >1% of physical bound water, 4–12% of structurally bound water (water bound to $Ca(OH)_2$) and CO_2 content that ranges between 18% and 34%. The CO_2 to structurally bound water ratio is 1.5–9. The binder to aggregates ratio ranges between 1:1 and 1:2. These mortars exhibit a wide range of total porosity (20–43%). Their tensile strength is higher than 0.60–0.70 MPa [23,25,26,29,31].

3.3. Hydraulic lime mortars

The binding material (hydraulic lime) derived from the burning process at low temperatures of marly limestones and the proper slaking of the obtained product. Obviously, the selection of the marly limestone was made empirically due to the good quality of the final product. These mortars consist of approximately 1% of physically bound water, with low percentages of structurally bound water (3.5–6.5%) and CO_2 content that ranges between 24% and 34%, when calcareous aggregates prevail or even lower when aggregates of silico-aluminate nature are in excess. CO_2 to structurally bound water ratio ranges between 4.5 and 9.5, depending on the hydraulicity degree of the lime and on the aggregates composition. Binder to aggregates ratio (per weight) ranges between 1:4 and 1:1. Their total porosity is higher than 30%, while their tensile strength ranges between 0.35 and 0.55 MPa [25,28–30].

3.4. Natural pozzolanic mortars

The mortars of this category present 4.5–5% of physical bound water, 5–14% of structurally bound water and CO_2 content that ranges between 12% and 20%. The CO_2 to structurally bound water ratio is lower than 3, which indicates mortars of high hydraulicity. The binder to aggregates ratio ranges between 1:4 and 1:5. These mortars exhibit the highest values of total porosity that may exceed 40%, with high percentage of pores with small diameter and high values of specific surface area. Their tensile strength is higher than 0.60 MPa [23–26,29–32].

3.5. Artificial pozzolanic mortars

Mortars of this category were mainly met at cisterns, aqueducts and duct drains as efficient waterproofing materials, with bricks in the form of ceramic fragments or ceramic powder to be the main characteristic of their structure. Hagia Sophia mortars are a common example of mortars of this category, which comprise of ceramic powder as pozzolanic additive and brick fragments in the matrix of the aggregates [5–7,21,23–25,27,34]. Due to the low bulk density of brick fragments, their presence led to the production of a lightweight concrete [6,7,34]. Their physical bound water ranges between 1% and 4%, their structurally bound water between 3.5% and 8.5% and their CO_2 content between 22% and 29%. However, in the case of Byzantine concrete the percentage of CO_2 ranges between 10% and 19%. CO_2 to structurally bound water ranges between 3 and 6 according to the pozzolanicity of the brick fragments and to the aggregates consistency. The binder to aggregate ratio (per weight) is approximately 1:3, while concrete with crushed brick exhibit values between 1:2 and 1:4. Their total porosity and all their microstructural characteristics depend significantly on the microstructure of the brick fragments and on their technological characteristics. They present tensile strength values higher than 0.55 MPa, while the corresponding values for concrete range between 0.5 and 1.2 MPa [23–27,29–32,34].

Figs. 1 and 2, derived from a number of historic samples representative of various structural periods and production techniques, aim to examine if there is any correlation between chemical characteristics of historic mortars deriving from thermal analysis (CO_2, structurally bound water) and mechanical tests (tensile strength) [23,25,30,31].

Fig. 1 presents CO_2 to structurally bound water (chemically bound water) ratio, which inversely expresses the hydraulic character of mortars, in relation to CO_2 (% weight loss). It is obvious that the inverse trend of hydraulicity of mortars is being augmented exponentially with CO_2.

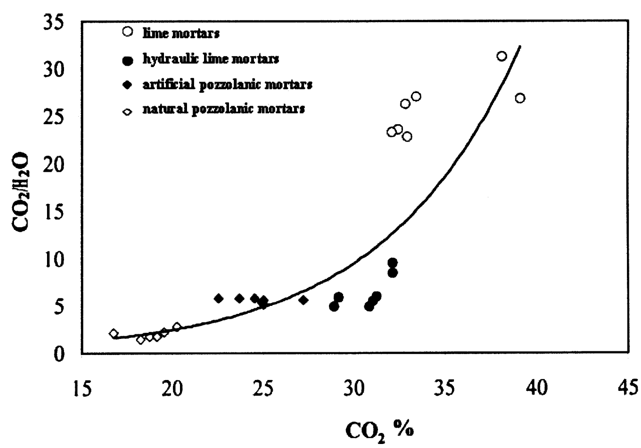

Fig. 1. CO_2 to structurally bound water ratio in relation to % CO_2.

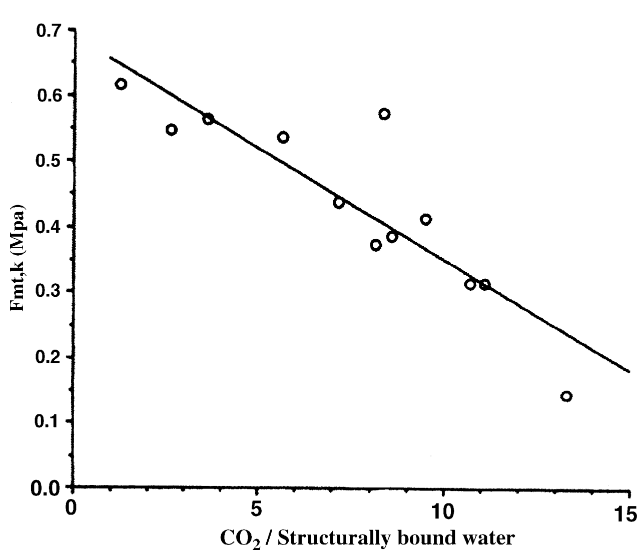

Fig. 2. Correlation between tensile strength (Fmt,k) and CO_2 to structurally bound water ratio.

The exponential correlation of CO_2 to structurally bound water ratio to CO_2 content indicates the non hydraulic, semi-hydraulic and the hydraulic character of the composites during setting, hardening and ageing of mortars. Hence, the grouping of mortars into well-distinguished "hydraulic levels" should be attempted in relation to the binding materials and to the natural or artificial pozzolanic additions.

Fig. 2 exhibits the linear correlation between mechanical properties (tensile strength-Fmt,k) and level of hydraulicity. An inverse proportionality between the CO_2 to structurally bound water ratio and the tensile strength is observed. Low values of CO_2 to structurally bound water ratio correspond to high values of Fmt,k. High values of CO_2 to structurally bound water ratio correspond to low values of Fmt,k. Intermediate values of CO_2 to structurally bound water ratio correspond to intermediate values of Fmt,k.

4. Conclusions

The ancient masons applied intuition and fantasy for the solution of their problems and, even more, a whole understanding of the role of all constituents that are an integral part of composites microstructure. They based on their intuitive knowledge and non scientific experience on the selected and applied materials. The ancients instinctively followed ways of ecology and economy. They did not waste valuable materials when materials of low value satisfied the requirements of the performance. They found ways to exploit to the maximum the potential of the available materials. They produced reactive lime and invented by empiricism criteria different types of pozzolanic materials and organic additives.

The physico-chemical and mechanical characteristics of the examined composites could be served in order to define specifications for restoration mortars with similar properties to the original composites employed in ancient structures. However, to assure the compliance of restoration mortars to these specifications a design process has to be adopted. This process should concern the nature and the quality of raw materials in use, the ratio of the binder/aggregates, the gradation of the aggregates along with the maximum grain size and the potential additives in order to ameliorate rheological and mechanical characteristics. Moreover, it has to take into consideration the purposes that the mortars have to serve in the masonry and their resistance and durability to the actual environmental loads.

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