Archaeological and Anthropological Sciences (2021) 13: 144
https://doi.org/10.1007/s12520-021-01404-2

REVIEW

Mortars and plasters—how to characterise hydraulic mortars

Anna Arizzi[1] · Giuseppe Cultrone[1]

Received: 25 January 2021 / Accepted: 30 June 2021

Abstract

Mortars are heterogeneous building materials whose raw materials, manufacturing processes and application conditions have evolved continuously throughout history. The fact that apparently small changes in the components or dosages of mortars can affect their overall performance in the masonry makes the study of historic mortars a complex task that needs to be tackled via a multidisciplinary approach, with the support of complementary analytical techniques from the field of chemistry, mineralogy, physics and engineering, among others. This review is intended to be a useful tool for researchers working in the field of archaeology and/or cultural heritage conservation, as it offers a complete overview of the most widely accepted analytical techniques and physical-mechanical tests used in the characterisation of historic mortars and plasters. Although the methods described here are common to both air-hardening and hydraulic mortars, we focus above all on the latter, paying special attention to aspects relating to the chemical, mineralogical and petrographic investigation of the calcium silicate and aluminate hydrated phases that may indicate the use of one or other hydraulic binder in historic mortars, all this taking into account and discussing the practical aspects, drawbacks and limitations of each technique. European standards for the study of mortars are also addressed in this paper.

Keywords Hydraulic binders · Hydrated calcium silicates and aluminates · Analytical techniques · Chemical-mineralogical characteristics · Physical properties

Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments.

The first group of contributions explains how mortars have been made and used through the ages (this paper, Ergenç et al. 2021, Lancaster 2021, Vitti 2021). An insight into their production, transport and on-site organisation is further provided by DeLaine (2021). Furthermore, several issues concerning the sampling, degradation and conservation of mortars and plasters are addressed from practical and technical standpoints (Gliozzo et al. 2021, La Russa and Ruffolo 2021; Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Medieval (Murat 2021) wall paintings clarify the archaeological and historical/cultural framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red, yellow and brown ochres (Mastrotheodoros et al. forthcoming), Cu-based greens and blues (Švarcová et al. 2021), As-based yellows and reds (Gliozzo and Burgio 2021), Pb-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021), Hg-based red and white (Gliozzo 2021) and organic pigments (Aceto 2021). An overview of the use of inks, pigments and dyes in manuscripts, their scientific examination and analysis protocol (Burgio 2021) as well as an overview of glass-based pigments

---

This article is part of the Topical Collection on *Mortars, plasters and pigments: Research questions and answers*

✉ Anna Arizzi
arizzina@ugr.es

Giuseppe Cultrone
cultrone@ugr.es

[1] Department of Mineralogy and Petrology, Faculty of Sciences, University of Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain

(Cavallo and Riccardi forthcoming) are also presented. Furthermore, two papers on cosmetic (Pérez-Arantegui 2021) and bioactive (antibacterial) pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

Introduction

Definition of hydraulic mortars and plasters

Mortars are artificial building materials composed of (1) one or more inorganic *binders*, whose main function is to join loose grains together by means of different chemical transformations in their mass; (2) one or more *aggregates* (or *sands*), which are added to confer volume stability on the mortar mass during drying and enhance the mechanical resistance of the hardened mortar; (3) and water, which is needed to mix all the mortar components into a viscous paste. In addition to these three basic components, other secondary components called *additives* and *admixtures* are frequently added to mortars to improve specific characteristics or properties, or to introduce new ones (EN 16572 2015).

If we exclude raw clays and gypsum, which are both among the most ancient binding materials used in the history of construction, binders, and therefore mortars, can generally be classified into two main groups:

1) *Air-hardening (or aerial) mortars*, which harden when exposed to air due to the reaction between $Ca(OH)_2$ (in *fat lime* or *calcitic lime*) or a mixture of $Ca(OH)_2$ and $Mg(OH)_2$ (in *lean lime* or *dolomitic/magnesian lime*) with atmospheric CO_2 to produce $CaCO_3$ or a mixture of different Ca and Mg carbonates, respectively (Lanas and Alvarez 2004) (i.e. *carbonation process*);
2) *Hydraulic mortars*, which can set under water. This group includes a large number of binder types, all of which are discussed in this review. The main differences between these binders lie in the chemical and mineralogical composition of their raw materials and the firing conditions applied during the manufacturing process. The fact that hydraulic mortars can set under water improves their mechanical performance and durability compared to air-hardening mortars. They are also ideal for use in hydraulic construction works and in masonries in contact with water (e.g. aqueducts, bridges, ditches, dykes, tanks, etc.) or exposed to high relative humidity conditions.

It is worth highlighting that the term *mortar* refers to an artificial mixture of the aforementioned components applied in masonry for various different final purposes (e.g. bedding, jointing, and bonding of masonry units, among others), whilst the word *plaster* refers to a mortar used to coat masonry surfaces (EN 16572 2015). Despite the fact that European standard EN 16572 (2015) specifies that plaster is an internal coating (as opposed to the external coating known as *render* or *rendering mortar*), in the literature, the term plaster is commonly used to refer to both types of coating, as well as to the coat applied to a surface to prepare it for painting (e.g. in murals).

Historic evolution of hydraulic mortars

The binders used throughout history in mortar production have varied depending on the moment in history and the geographic area (Varas et al. 2005; Elsen et al. 2012).

The first hydraulic mortars date back to the tenth century BC (Collepardi 1990), although the Greeks (since the eight century BC) were the first to use volcanic dust (*Santorin earth*) or crushed ceramics, mainly for the manufacture of plasters (Cowper 1927). From the third century BC onwards, the Romans improved both the production technology and the quality of hydraulic mortars, which they made by mixing air-hardening lime with crushed bricks (*cocciopesto*) (Megna et al. 2010), pumice powder (*pumex Pompeianus*), scoriae (Izzo et al. 2018) or pozzolana powder (*pulvis puteolana*[1]). The latter was a brownish volcanic earth from the city of Pozzuoli (Bay of Naples, Italy) with remarkable hydraulic features (Oleson et al. 2004), which was considered “an admirable material” by Seneca himself, as highlighted by Ordóñez Agulla (2017). *Cocciopesto* was mainly used for the manufacture of floors, plasters, tanks and aqueducts, when natural pozzolans were unavailable (Pecchioni et al. 2018). As many researchers have found, many different Roman buildings have survived for thousands of years thanks to the careful selection of raw materials and the manufacture of mortars with hydraulic features, which ensured their strength and durability (Borsoi et al. 2010; Frankeová et al. 2010; Jackson et al. 2010; Kramar et al. 2011).

The first discoveries about the hydraulic nature of mortars were made quite by chance by an 18th century civil engineer called John Smeaton. In 1756, Smeaton began to study how to improve the resistance of lime against the action of sea water, in order to manufacture a mortar that could join the stone blocks used in the construction of the Eddystone Lighthouse (Plymouth). The best results were achieved with limes produced from rocks with a considerable proportion of clayey material (Cowper 1927). Later, in 1796, James Parker patented his *Roman Cement* (so called because it was very similar to the Roman hydraulic mortar), which he had accidentally obtained by burning a marlstone from the Isle of Sheppey, i.e. a

---

[1] According to Vitruvius and Morgan (1960), *pulvis puteolana* was (from the Latin) “a kind of powdery sand which by its nature produces wonderful results. (…) This material, when mixed with lime and rubble, not only furnishes strength to other buildings, but also, when piers are built in the sea, they set under water, (…) and neither the waves nor the force of water can dissolve them”.

limestone with a high content of clay rich in silica and alumina (Blatt and Tracy 1996; Hurst 2002). The reason why the mortars made with these binders show such high mechanical resistance was later investigated by a French engineer, Louis Vicat, who discovered that calcium silicates and aluminates were generated by burning a mixture of limestone and clays at high temperatures, and that these phases were responsible for the hydraulic features of the resulting binder. A decade later, in 1824, Joseph Aspdin patented the first *Portland cement*, whose colour when set reminded its inventor of the stone from the Isle of Portland in England. This binder was followed by many other modern (albeit lesser known) cements, such as *Magnesia cement* (also called *Sorel cement*, discovered by Stanislas Sorel in 1867, and mainly used in flooring mortars) and *Iron Hammer Scale cement*, mainly used in repointing mortars (Weber et al. 2012), among others (Edison 2010, Mertens et al. 2008). However, the chemistry of the first Portland cement, which was in fact a "*proto Portland cement*", was more similar to a hydraulic lime than to modern cement. The studies by Johnson (in 1845) on the sintering firing temperatures needed for the production of cement and the introduction of industrial rotary kilns (in 1890), which replaced the intermittent kilns that had been used until then, greatly improved the complex manufacturing process of Portland cement, which was initially quite expensive. Since then, the cement industry has been growing steadily and Portland cement has become the most widespread binding material in the world today, leading to the abandonment of traditional binders.

Types of hydraulic binders

After this brief review of the history of binding materials, we will now explore the main types of hydraulic binders likely to be found in ancient mortars.

- *Mix of air-hardening lime and pozzolans*: the traditional hydraulic binder was made by adding natural or artificial pozzolanic materials (such as admixtures or sands) to air-hardening lime. According to Alvarez et al. (2021), natural pozzolans are mainly the result of weathered lava that is worn down to fine grains, whilst artificial pozzolans are produced by the thermal activation of a raw material, such as clay.
- *Natural hydraulic lime*: lime manufactured from a carbonatic stone with a variable content of clay rich in silica and alumina, which is fired at temperatures of between 900 and 1250 °C. According to European regulation EN 459-1 (2011), its notation is NHL. The clay content in the raw material ranges from 5 to 25% (Cowper 1927; Pecchioni et al. 2018). Nowadays, natural hydraulic lime is considered one of the most suitable, most compatible binders for the production of restoration mortars with hydraulic features (Callebaut et al. 2001, Maravelaki-Kalaitzaki et al. 2005, Pacheco-Torgal et al. 2012, Gulotta et al. 2013, Grilo et al. 2014, Silva et al. 2014, Gulotta et al. 2015, Isebaert et al. 2016) as well as for the repair of large volumes of rammed-earth walls (Mileto et al. 2018).
- *Hydraulic lime*: prior to the First World War, hydraulic lime was manufactured by burning an artificial mixture of pure limestone and clay (Collepardi 1990). Nowadays, it is manufactured by mixing lime with other materials such as Portland cement, blast furnace slag, fly ash, limestone filler and other hydraulic and/or pozzolanic materials (EN 459-1 2011). According to European regulations, its notation is HL.
- *Formulated lime*: modern hydraulic binder consisting of mainly air-hardening or natural hydraulic lime with added hydraulic and/or pozzolanic materials (EN 459-1 2011). According to European regulations, its notation is FL. It may be identical to a hydraulic lime, the difference being that its main composition must be declared by the manufacturer.
- *Natural cement* (also called *Roman cement* or *Parker's cement*, Pecchioni et al. 2018): a nineteenth century hydraulic binder produced by the calcination of a naturally occurring argillaceous limestone at variable temperatures, always below the sintering temperature (which is over 1250 °C), before being ground to a fine powder. The clay content in the raw material can reach 45% (Holmes and Wingate 1997), which is why natural cements have a higher silica and alumina content than natural hydraulic lime. The properties of the product may vary greatly, depending on the rate and extent of heating (Cowper 1927). Indeed, quick-setting, slow-setting and half-slow setting natural cements may be obtained depending on the temperature reached in different parts of the kiln (1100–1400 °C, Mertens et al. 2008). *Quick-setting natural cement* was produced by grinding non-vitrified but completely decarbonated lumps. For its part, *slow-setting natural cement* resulted from the separation of the overburnt, vitrified lumps obtained in the parts of the kiln where the sintering temperature was reached (Callebaut et al. 2001).

  Natural cement is now mainly used as a rendering material, although in the nineteenth century, it was extensively used for pointing, i.e. filling the outer part of a masonry joint with a mortar, especially in restoration and repair work (EN 16572 2015) and as a decorative material (Pecchioni et al. 2018).
- *Portland cement*: modern hydraulic binder manufactured by burning a mixture of limestone and clay-containing materials at temperatures of up to 1450 °C, so obtaining a clinker that is ground to fine powder and then mixed with gypsum (up to 3%, Eckel 1922) to delay the setting time (EN 16572 2015).

- *White cement*: among the many types of Portland cement with special characteristics (Sánchez de Rojas et al. 1993), white Portland cement stands out for its high degree of whiteness[2], obtained thanks to the absence of Fe compounds in the raw materials, and enhanced with the addition of TiO_2 (Pecchioni et al. 2018). White cement is sometimes mixed with air-hardening lime to make "ready-to-mix" repair mortars. When the white cement content is less than 5%, the manufacturer is not obliged to declare its presence in the binder (e.g. in the case of a *formulated lime*, Middendorf et al. 2010; EN459-1 2011). This means that the presence of modern cement in mortars that are intended for use in the restoration of historic buildings may go totally unnoticed. This can have negative consequences on the durability of the historic masonry repaired with these mortars, due to the chemical and physical-mechanical incompatibility between Portland cement and traditional building materials (Collepardi 1990 and 1999, Moriconi et al. 1994).

According to Collepardi (1990), all buildings built before the advent of Portland cement can be defined as "historic". This definition is based on the fact that the vast majority of historic hydraulic mortars were made with either (i) a mix of air-hardening lime and pozzolanic materials, (ii) natural hydraulic limes, or (iii) natural cements (Hughes et al. 2010). By contrast, if Portland cement (in any of its various types) is present in a historic building, this must be due to its use as a hydraulic binder in mortars for restoration work (Collepardi 1990).

Hydraulic phases and hydrated products

As commented earlier, the main reason for the hydraulic nature of the binders described above is the presence in the raw materials of a variable amount of reactive silica (SiO_2) and alumina (Al_2O_3) that react with lime (CaO) to form different calcium silicates and aluminates (Table 1). During the setting of these phases in the presence of water, various amorphous and crystalline hydrated phases of calcium silicates and aluminates are formed (Richardson 2008; Cizer 2009; Frankeová and Koudelková 2020) (Table 1).

In the cement industry, calcium silicates and aluminates are generally referred to as C_2S (*bi-calcium silicate*), C_3S (*tri-calcium silicate*), C_3A (*tri-calcium aluminate*), C_2AS (*gehlenite*) and C_4AF (*tetra-calcium Fe aluminate*), among others, whilst the hydrated phases are generally referred to as *CSH* (*calcium silicate hydrates*) and *CAH* (*calcium aluminate hydrates*), in which C = CaO, A = Al_2O_3, H = H_2O and S = SiO_2 (Collepardi 1990).

The identification of the different phases is crucial in order to be able to correctly identify the binder used in a historic hydraulic mortar. According to the literature, it is sometimes possible to distinguish between traditional hydraulic binders and modern Portland cement, based on the following:

- *Belite* (C_2S, Table 1) is formed at temperatures of around 1200 °C, as there is a lower ratio of CaO to SiO_2 at this temperature. This is why C_2S is the most common phase in natural hydraulic lime (Allen et al. 2003, Alvarez et al. 2021). It may be present in quick natural cements in small quantities (Mertens et al. 2008) and always in α-form (i.e. C_2S with high hydration velocity), whilst in Portland cement, it only appears in β-form (i.e. C_2S with low hydration velocity) (Pecchioni et al. 2018).
- *Alite* (C_3S, Table 1) is the predominant phase in slow-setting natural cements and Portland cement, as higher temperatures increase the proportion of CaO that binds to SiO_2 (Mertens et al. 2008). NHLs may contain small amounts of C_3S due to the existence of high temperature points (known as "hot spots") in the kiln (Callebaut et al. 2001).
- *Gehlenite* (C_2AS, Table 1) is found above all in natural hydraulic lime as it occurs at temperatures below 1200 °C (Callebaut et al. 2001; Frankeová and Koudelková 2020; Alvarez et al. 2021).
- C_3A and C_4AF are the main aluminates formed in Portland cement as a result of the reaction between alumina and lime in the presence of Fe. The mix of these two aluminates is known in the cement industry as *celite* (Table 1). In natural hydraulic limes, they are present in very low amounts or not at all (Alvarez et al. 2021).
- *Portlandite* (CH, calcium hydroxide, Table 1) is present in natural hydraulic lime and results from the slaking of free lime. It is not found in cements, as all the CaO is combined in calcium silicates and aluminates, so preventing slaking from taking place (Mertens et al. 2008). In cementitious mortars, calcium hydroxide is formed as a by-product of the hydration of the calcium silicates (Zhang et al. 2018).
- *Calcium silicate hydrates* (CSH, Table 1) in both amorphous and crystalline forms (*jennite*, *tobermorite* and *plombierite*, Table 1) are the main hydration products formed in hydraulic mortars. CSH are formed, firstly, by the hydration of calcium silicates present in hydraulic limes and cements, and secondly, by the reaction of the silica and alumina

---

[2] The EN 80305 2012 establishes a lightness value of L* ≥ 85 for white cements.

Table 1 Main mineral phases and chemical compounds in traditional and modern hydraulic binders (before and after hydration): notation (according to cement industry terminology, Collepardi 1990), chemical formula, and mineral or compound name

Notation	Chemical formula	Mineral name
C_2S	Ca_2SiO_4	*Belite*/Larnite
C_3S	Ca_3SiO_5	*Alite*
C_3A	$Ca_3Al_2O_6$	*Celite*
C_4AF	$Ca_4Al_2F\ e_2O_{10}$	
C_2AS	$Ca_2Al(AlSi)O_7$	Gehlenite
C_3S_3	$Ca_3Si_2O_7$	Kilchoanite/Rankinite
CS	$CaSiO_3$	Wollastonite
C	CaO	Lime
CH	$Ca(OH)_2$	Portlandite
$C_5S_2\hat{C}$	$Ca_5(SiO_4)_2(CO_3)$	Spurrite
CSH	$CaO\text{-}SiO_2\text{-}H_2O$	Calcium silicate hydrates
$C_9S_6H_{11}$	$Ca_9Si_6O_{18}(OH)_6 \cdot 8(H_2O)$	Jennite
$C_5S_6H_5$	$Ca_5Si_6O_{16}(OH)_2 \cdot 4(H_2O)$	Tobermorite (or 11Å-Tobermorite)
$C_5S_6H_8$	$Ca_5Si_6O_{16}(OH)_2 \cdot 7(H_2O)$	Plombierite (or 14Å-Tobermorite)
C_3AH_6	$Ca_3Al_2(OH)_{12}$	Hydrogarnet
$C_3AS_{3\text{-}x}H_{2x}$	$Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ *with* $1.5 < x < 3$	Katoite/Hydrogrossular
C_2ASH_8	$Ca_2Al(AlSi)O_7 \cdot 8(H_2O)$	Stratlingite/Hydrated Gehlenite
$C_6A\hat{S}\ _3H_{32}$	$Ca_6Al(SO_4)_3(OH)_{12} \cdot 26(H_2O)$	Ettringite
$C_3S\hat{S}\hat{C}H_{15}$	$Ca_3Si(CO_3)(SO_4)(OH)_6 \cdot 12(H_2O)$	Thaumasite
$C_4(A,F)X_2 \cdot y(H_2O)$	$Ca_2Al(OH)_6[Cl_{1-x}(OH)_x] \cdot 3(H_2O)$ *with* $0 < x < 1$	Hydrocalumite
CAH	$CaO\text{-}Al_2O_3\text{-}H_2O$	Calcium aluminate hydrates
$\alpha_1 - C_4AH_{19}$	$Ca_4Al_2O_7 \cdot 19(H_2O)$	
$\alpha_2 - C_4AH_{19}$	$Ca_4Al_2O_7 \cdot 19(H_2O)$	
C_4AH_{13}	$Ca_4Al_2O_7 \cdot 13(H_2O)$	
C_4AH_{11}	$Ca_4Al_2O_7 \cdot 11(H_2O)$	
$C_4A\hat{C}_{0.5}H_{12}$	$Ca_4Al_2O_7(CO_2)_{0.5} \cdot 12(H_2O)$	Monocarbon aluminate
$C_4A\hat{C}H_{11}$	$Ca_4Al_2O_6(CO_2) \cdot 11(H_2O)$	Hemicarbon aluminate
$C_4A\hat{S}H_{12}$	$Ca_4Al_2O_7(SO_3) \cdot 12(H_2O)$	Monosulphoaluminate

Table adapted from Mertens (2009)

components present in pozzolanic materials with the calcium hydroxide produced when lime comes into contact with water (Zhang et al. 2018), as happens for example in lime-pozzolan mortars. However, the CSH formed in mortars with hydraulic binders, e.g. cement, are different from those formed in lime-pozzolan mortars in terms of both type and content (Alvarez et al. 2021).

- *Stratlingite* (C_2ASH_8, or *hydrated gehlenite*, Table 1) is formed in hydraulic binders and pozzolans with a high alumina content by the reaction between CSH and Al_2O_3. Together with CSH, *stratlingite* is expected to be found in historic hydraulic mortars made with air-hardening lime and pozzolanic materials.
- *Calcium carboaluminate* ($CA\hat{C}H$ or *monocarbon aluminate*, Table 1) and *hemicarbon aluminate* ($HCA\hat{C}H$, Table 1) are formed in the presence of aluminate phases from a pozzolanic material and a calcitic filler (Matschei et al. 2007a and b; Cizer 2009; Arizzi and Cultrone 2012). However, only $CA\hat{C}H$ is detectable in well hydrated pastes (Alvarez et al. 2021), and hence in historic hydraulic mortars.
- Hydrated calcium aluminate such as C_4AH_{13} (Table 1) is a metastable phase that only appears in the initial phase of the hydration reaction, due to its decomposition into *hydrogarnet* (C_3AH_6, Table 1) and *portlandite* (CH, Table 1) (Matschei et al. 2007a). Hydrogarnet is therefore the CAH phase that one would most expect to find in historic hydraulic mortars.
- In the presence of *gypsum* ($CaSO_4\ 2H_2O$), water and silicate and/or aluminate phases, *monosulphoaluminate* ($C_4A\hat{S}H_{12}$, Table 1) (Matschei et al. 2007a), *ettringite* and *thaumasite* ($C_3S\hat{S}\hat{C}H_{15}$, Collepardi 1999) can be detected. According to Van Balen et al. (1999), the presence of the latter salts together with C_4AF must be due to the presence of Portland cement.
- *Katoite* ($C_3AS_{3\text{-}x}H_{2x}$, Table 1) is associated with the presence of CH and stratlingite in lime-pozzolan mortars with

a low pozzolan content (Navrátilová and Rovnaníková 2016).

The archaeometric study of historic hydraulic mortars

General remarks

Research into historic mortars is a complex issue requiring a multidisciplinary approach (Middendorf et al. 2005a and b, Álvarez Galindo and Ontiveros Ortega 2006), using complementary analytical techniques above all from the fields of chemistry, geology and physics.

The following information can be obtained when characterising a historic mortar:

- The nature of the mortar, i.e. whether it is air-hardening or hydraulic, the type and grading of the aggregates, the binder-to-aggregate (B/A) ratio and the presence of secondary components, among others;
- The manufacturing process, i.e. where the raw materials come from and how they were processed, for example during firing, slaking or mixing;
- The building techniques applied, in order to find out more about ancient and traditional methods of applying and curing mortars, and to recognise when subsequent interventions have been performed;
- And the state of conservation, in order to understand the decay processes suffered by the mortar and its resistance to alteration factors.

The decision as to which of these aspects to investigate will depend on the final purpose of the study, for example: (1) the conservation of a historic building or monument; (2) archaeological research; or (3) scientific research (Pecchioni et al. 2018). In all cases, however, the composition of the mortar and the amount of each component (binder, aggregate, additives and admixtures) must be determined.

This review presents the most generally accepted methodology for the study of historic hydraulic mortars, according to the literature and European regulations. The analytical techniques and methods usually applied in the characterisation of mortars are classified in this paper according to the basic principles (i.e. chemical, mineralogical and physical) on which they are based. The objectives, practical issues, drawbacks and limitations of each technique are also discussed.

This classification coincides with the recently published EN 17187 (2020) standard on the "Conservation of Cultural Heritage. Characterisation of mortars used in Cultural Heritage", which contains specific guidelines for the selection of the most appropriate methods to determine the chemical, mineralogical, textural, physical, and mechanical properties of mortars used in cultural heritage structures and objects[3].

This does not mean that all the analytical techniques have to be used. In some cases, they may not all be available or there may be insufficient amounts of sample. However, many of these techniques are complementary and an exhaustive knowledge of the historic mortar cannot be guaranteed if the tests are carried out alone (Pecchioni et al. 2018).

Mortar sampling

According to Hughes and Callebaut (2002), mortar sampling must be carried out properly and rigorously, despite the physical and other obstacles that may be encountered. The selected samples must be representative and must conform to the specifications (e.g. in terms of number, size, shape, location) of the analytical technique (EN 16085 2012). Given that the suitability of the samples will influence the quality and accuracy of the characterisation, it is crucial to have a clear plan regarding the methodology and objectives of the study before collecting the samples. One example is sample size. Samples must be big enough to guarantee the success of the analysis (Adriano et al. 2009), and the recommended weight is between 4 and 40 g (Chiari et al. 1996). Although smaller samples can be analysed, a large sample is preferable as this enables complementary or repeat analyses to be carried out if necessary.

In order to minimize errors and maximize confidence in the different analyses planned, a wide range of sampling procedures have been proposed in the literature on historic mortars and plasters (Chiari et al. 1996; Demelenne et al. 2010). They all coincide on the following recommendations:

1) Begin with a visual inspection and, when possible, a historic/artistic/archaeological study of the masonry/site/monument;
2) Make a photographic report before and after sampling;
3) Store and label each sample;
4) Make written notes on the location, state and general characteristics of the sample taken and regarding the reason for taking it.

Sampling methods and tools will be chosen on the basis of the following:

---

[3] It is worth highlighting that the EN 17187 standard recommends the application, in some cases, of methods that were initially intended for other types of building materials (mainly natural stone), but which are considered equally appropriate for the study of mortars. This is because of the heterogeneous features (e.g. mineralogy, porosity) of mortars, which make them similar to geological materials (although they are artificial) and explain why they are studied in a similar way (Artioli 2010), always bearing in mind the specific characteristics that make mortars different from any natural material (Pecchioni et al. 2018).

- The hardness of the mortar: strong mortars can be collected using a grinding wheel mounted on a portable drill, medium-hard mortars can be extracted by light blows with a hammer and chisel, and soft mortars can be sampled with a cutter (Chiari et al. 1996);
- State of conservation of the mortar: severely deteriorated mortars and plasters can show low cohesion and appear brittle during sampling. Special care must therefore be taken to collect a solid (non-powdered) fragment;
- The presence of different layers: the fact that a wall, for example, may have several layers of mortars and plasters with different macroscopic characteristics means that these layers must be selected as a whole, by extracting a core from the wall, so that each layer can be analysed separately in the laboratory (Chiari et al. 1996);
- The artistic value of the sampled area: if a sample must be taken from decorated (e.g. painted) plaster, this must be done with extreme care and always by an expert. In this case, a cutter can be used to collect a very small fragment of plaster (the minimum size to enable at least a microscopic study to be carried out).

Macroscopic study

Once the samples have been collected and prior to their manipulation, the macroscopic characteristics of the mortars must be studied using a stereoscopic microscope (EN17187 2020), in order to characterise the following:

- The aggregate (colour, approximate size and shape);
- The binder (colour);
- The texture (pores, fissures, etc.);
- The presence and thickness of layers and the adhesion between them;
- The degree of cohesion between the mortar components;
- The forms of deterioration (salts, microbial activity, among others);
- Any previous treatments;
- The presence of any other component (fibres, visible admixtures, pigments, etc.);
- The surface topography and roughness, as performed on building stone (Vázquez et al. 2016);
- The chromatic characteristics (the chromatic study will be detailed in Section 2.8.3).

When describing the types of damage typically affecting mortars, use of the terminology set out in the EN 16572 (2015) standard is recommended.

A recently developed technique that may be useful for the in-situ 3D macroscopic study of historic mortars is *Non-Intrusive Microscopy with High Resolution* (*N.I.M.H.R.* or *M.N.I.A.R*[4], Guerra-García 2015 and Guerra-García et al. 2019). By treating high-resolution microphotographs with chromatic analysis software, we can obtain valuable information about the features of the aggregate and the binder, the presence of organic and inorganic admixtures (such as fibres, hairs, plants, etc.), and the roughness of the mortar and its pathologies (Fig. 1).

Binder and aggregate separation

One of the first steps in historic mortar characterisation is to separate the binder from the aggregate, so as to be able to accurately determine the nature of the binder and the aggregate, and the B/A ratio. Separation can be undertaken by manual disaggregation or by wet chemical methods. Mechanical separation provides satisfactory results but it is a time-consuming procedure (Casadio et al. 2005) in comparison with chemical separation methods. The latter mainly involve attacking the binder with strong or dilute acids (e.g. HCl, salicylic acid) or with chelating agents (e.g. EDTA) and then treating the insoluble residue (Middendorf et al. 2005b).

According to Casadio et al. (2005), acid treatment with HCl drastically underestimates the aggregate content of mortars made with carbonatic aggregates (e.g. limestone, marble fragments, shells, etc.), which dissolve in the acidic solution. The HCl procedure cannot therefore be used on mortars made with carbonate aggregate. By contrast, treatment with salicylic acid can highly overestimate the aggregate content. A 0.05-M solution of EDTA (preferably the tetrasodium salt) is considered suitable for an approximate estimation of the B/A ratio, although it is still quite an aggressive procedure (the aggregate content is slightly underestimated).

There are various additional chemical separation procedures that can be used to determine the soluble silica (corresponding to the CSH phases), soluble Fe_2O_3 and soluble Al_2O_3 content in the binder fraction of historic hydraulic mortars (Middendorf et al. 2005b).

Separating the binder from the aggregate also allows us to determine the aggregate grading curve, a parameter that is especially interesting for conservation purposes. This procedure entails weighing and sieving the dry aggregate (with apertures of 0.063, 0.125, 0.250, 0.5, 1, 2, 4, 8, 16 mm, EN 933-1 1998) and then recording the weights of the fractions retained on each sieve. The results are represented in a cumulative semi-logarithmic diagram of the weight percentages passing through the sieves (Middendorf et al. 2005b).

Main limitations:

1) As mentioned above, acid dissolution cannot be used on mortars with a carbonate aggregate. In this case, mechanical separation or other conventional methods such as

---

[4] From the Spanish: *Microscopía No Intrusiva de Alta Resolución.*

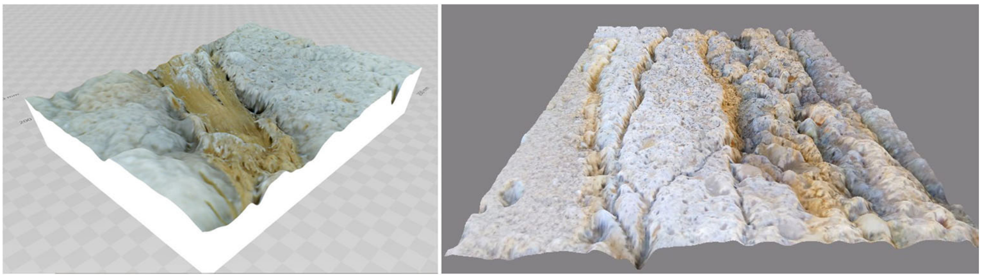

Fig. 1 Microphotographs taken with the N.I.M.H.R. technique. *Left image*: 3D-volumetry (50X) of a vegetal fibre in a historic plaster from a seventeenth century house in Chinchón (Madrid, Spain). *Right image*: Micro-photogrammetry (50X) of the fissured surface of a historic mortar from the façade of the Archbishop's Palace in Alcalá de Henares (Madrid, Spain), restored at the end of the nineteenth century. Courtesy of Dr Pablo Guerra García (National University of Distance Education, Spain)

thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Digital Image Analysis (DIA) must be performed.

2) Highly diluted solutions often only partially separate the binder (Casadio et al. 2005).
3) Soluble silica may also come from the aggregate. This possibility must be excluded by performing mineralogical and petrographic analyses (which will clarify if the silica originates from hydraulic binders, brick dust, volcanic ash, flint or clay minerals, Middendorf et al. 2005b).

Chemical and mineralogical study

The chemical and mineralogical analytical techniques described in this section are mainly used to investigate the composition of historic mortars, in order to ascertain the type of binder and aggregate used, as well as to examine the presence of inorganic and organic additives and admixtures (when possible), and the formation of decay phases (e.g. soluble salts, phases formed from the reaction with air pollutants, etc.). In the specific case of historic hydraulic mortars, the use of chemical and mineralogical analyses is essential for differentiating lime-pozzolan binders, hydraulic limes and cements, as highlighted by Van Balen et al. (1999).

The chemical and mineralogical analyses described here are all destructive techniques, with the exception of certain portable instruments that can be used on site for preliminary diagnoses (Alberghina et al. 2020), as will be discussed below.

Thermal analyses

Thermogravimetric analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are commonly used in the study of historic hydraulic mortars, as they can determine the presence and amount of hydrated phases in the binder fraction of these mortars (Pecchioni et al. 2018). These analyses involve heating 20–60 mg (Chiari et al. 1996) of a powdered sample. The temperature is increased from 25 to 1000 °C (at a rate of 5, 10 or 20 °C/min) under air or in a N_2 atmosphere. The instrument measures the variation in the weight of the sample as temperature increases (TGA) and/or the differences in weight loss between the analysed sample and an inert standard (DTA and DSC) (Ramachandran et al. 2012; Middendorf et al. 2005a), both of which are plotted as a function of temperature. TGA and DTA or DSC can be carried out simultaneously if the instrument so permits. Carrying out all three techniques is recommended as they each provide different complementary information. TGA enables us to semi-quantify the chemical compounds/mineral phases present in the sample, whilst DTA and DSC provide information for the qualitative identification of the components that undergo weight loss (Chiari et al. 1996) and allow us to identify polymorphic transformations of compounds that do not involve weight loss (e.g. vaterite and calcite[5], Maciejewski et al. 1994). The DTA and DSC curves also show both endothermal (heat absorption) and exothermal (heat evolution) effects (Chiari et al. 1996).

The typical temperatures at which dissociation of the common mineral phases found in hydraulic binders (Table 1) takes place are reported in the literature and summarised below. The weight loss in the TGA curve corresponds to endothermic peaks in the DSC curve at the same temperature range.

Around 100 °C, hygroscopic water

150–250 °C, dehydration of gypsum ($Ca_2SO_4 \cdot 2H_2O$) in two steps (Földvári 2011)

200–600 °C, loss of structurally bound water from CSH and CAH (Diekamp et al. 2012; Philokyprou 2012; Frankeová and Koudelková 2020). The endothermic peak in the DSC curve between 250 and 300 °C is due to CSH (Földvári 2011)

480–620 °C, portlandite ($Ca(OH)_2$) (Földvári 2011)

650–890 °C, calcite ($CaCO_3$) (Földvári 2011)

693 °C, phase transition of belite (C_2S, Table 1) only detectable in the DSC curve (Middendorf et al. 2005a)

750–800 °C, dolomite ($MgCa(CO_3)_2$) (Földvári 2011)

---

[5] Calcite, vaterite and aragonite are all polymorphs, i.e. mineral phases with the same chemical formula ($CaCO_3$) but different crystalline structures.

800–850 °C, sharp exothermic peak in the DSC curve due to recrystallization of amorphous CSH into wollastonite ($CaSiO_3$, Table 1) (Földvári 2011)

1425 °C, phase transition of alite (C_3S, Table 1) only detectable in the DSC curve (Middendorf et al. 2005a)

These ranges may vary slightly according to the crystallinity and the particle size of the mineral phases.

When studying historic hydraulic mortars, it is useful to plot and find the exponential correlation of CO_2 to the structurally bound water/CO_2 ratio, which is inversely related to the degree of hydraulicity of the mortar (Moropoulou et al. 1995; Moropoulou et al. 2005; Bonazza et al. 2013).

Main limitations:

1) Water loss from CSH takes place at a similar temperature to other silicates (Middendorf et al. 2005a).
2) The mortar could be made of other compounds whose decomposition could interfere with the H_2O release pattern (e.g. organic substances, hydrated salts, hydrated magnesium carbonates coming from dolomitic lime, Lanas and Alvarez 2004).

X-ray fluorescence

X-ray fluorescence (XRF) is commonly used to determine the chemical composition of historic mortars (with typical detection limits of 0.01% for major elements and 1–5 ppm for traces). A sample weighing approximately 6 g is ground into a fine powder (ideally with a grain size of less than 75 μm) and then prepared in different ways depending on the instrument type, e.g. loose powders (15 g of sample is needed for this preparation), pressed pellets and fusion beads, among others (Pecchioni et al. 2018). It is recommended to carry out the XRF analysis on the binder fraction of the mortar, so as to be able to identify the mortar as hydraulic or air-hardening. Hydraulic mortars can be distinguished from air-hardening mortars because the latter have a much higher $\%CaCO_3$ (calculated from the $\%CO_2$ and $\%CaO$) (Callebaut et al. 2001). In hydraulic mortars, it is also possible to determine the degree of hydraulicity, estimated by means of the *cementation index* (CI) (Eckel 1922). This value is calculated from the percentages of various oxides, as determined by XRF, according to the following equation:

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

According to their cementation index, historic hydraulic mortars can be classified as *weakly hydraulic* ($0.3 < CI < 0.5$), *moderately hydraulic* ($0.5 < CI < 0.7$) and *eminently hydraulic* ($0.7<CI< 1.1$). These three ranges correspond to hydraulic mortars prepared with NHL or HL with indexes 2, 3.5 and 5, respectively (EN 16572 2015). Lime-pozzolan binders show a cementation index of around 1 (Mertens 2009), whilst natural cement mortars show CI values of between 1.1 and 1.7 (Holmes and Wingate 1997).

According to Mertens (2009), hydraulic binders such as NHL and lime-pozzolan mixes have a higher CaO content (62.61 ± 6.88) compared to quick-setting natural cements such as Roman cement (44.69 ± 9.11) and lower SiO_2 (19.26 ± 4.21) and Al_2O_3 (4.34 ± 2.28) contents (compared to $SiO_2 = 24.52 \pm 4.43$, $Al_2O_3 = 9.21 \pm 3.15$ for quick-setting natural cements). There is not much difference between natural cements and artificial cements in terms of SiO_2content, which ranges between 22 and 25% in both binders. Similar values were also reported by Mertens (2009) when comparing the CaO content in hydraulic limes and lime-pozzolan binders with slow-setting cements (CaO is around 62% in both). However, there is a difference between, on the one hand, hydraulic limes and lime-pozzolan binders and on the other, natural and artificial cements, in terms of their Al_2O_3 content, which is always higher in the latter.

Some authors argue that portable XRF instruments are valid tools for the chemical study of historic mortars from archaeological sites and museums (Donais et al. 2010) and that their use is highly recommended in the preservation of cultural heritage objects (Donais et al. 2020). However, it is important to make clear that portable instruments are not always as accurate as their non-portable counterparts, so their use should be restricted to preliminary diagnostic work or to studies in which samples cannot be taken.

X-ray diffraction

This technique enables us to identify the mineralogical composition of historic mortars. Prior to this analysis, the binder fraction should be mechanically separated from the aggregate, in order to obtain more precise information about the mineralogy of each fraction (Middendorf et al. 2005a). Quantitative determination of mineral content is only possible if the Rietveld method is used (Gualtieri et al. 2006; Mertens et al. 2007; Isebaert et al. 2016).

X-ray diffraction (XRD) can highlight the presence of hydraulic limes, pozzolanic admixtures, or cement thanks to the identification of the mineral phases described in section 1.4. The Rietveld method can be used to identify hydraulic limes (HL) and natural hydraulic limes (NHL), thanks to their different C_2S/C_3S ratio, given that C_2S is more abundant than C_3S in NHLs, whilst the opposite is true in hydraulic limes and other cementitious binders (Gualtieri et al. 2006).

Main limitations:

1) XRD cannot distinguish between carbonatic minerals in the aggregate and in the binder, which is why this analysis should be carried out on separate fractions of each (Middendorf et al. 2005a).
2) XRD detects crystalline phases but the majority of CSH phases in hydraulic mortars are amorphous (Richardson 2008). Although it is possible to quantify the total amorphous phase content by means of Rietveld analysis, it is impossible to identify the different phases.
3) XRD can only clearly identify phases when they are present in amounts in excess of the minimum detectable by the equipment (usually 3–5% of total sample weight). According to Mertens et al. (2007), in hydraulic binders, most hydraulic phases are present in small amounts (less than 3 %.wt), and in bulk samples, the resolution of XRD is insufficient to accurately identify these minor phases. To overcome this obstacle, these authors proposed three selective dissolution techniques as possible methods for enriching calcium aluminates, calcium silicates and acid insoluble phases before their quantification using the Rietveld method. With this approach, the overlapping of certain hydraulic phases (e.g. C_2S and C_3S, Lanas et al. 2004) is also reduced, making identification of the mineral phases unambiguous.

Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) can be useful for the study of historic mortars, especially hydraulic ones and mortars that contain organic additives (Pecchioni et al. 2018), as it enables the functional groups of the chemical compounds present in the sample to be identified. Despite this, FTIR data must always be processed in combination with other chemical and mineralogical analyses (Middendorf et al. 2005a), as interpretation of the spectra can be complex (Pecchioni et al. 2018). FTIR analysis can be carried out on the whole mortar or on just the binder fraction, reduced to powder and mixed with KBr to obtain pressed pellets. When the Attenuated Total Reflection (ATR) mode is applied, a very small powdered sample (around 50 mg) can be analysed without the need for prior preparation and with the possibility of reuse in other analyses.

When the binder fraction of hydraulic mortars is analysed using FTIR, calcium silicates and CSH can be identified. Indeed, C_3S give characteristic absorption bands between 880 and 950 cm^{-1} (this makes it easier to distinguish C_3S from C_2S, which may overlap in X-ray diffraction patterns, as commented above), and CSH give typical bands between 900 and 1120 cm^{-1} (Diekamp et al. 2012). Another advantage of FTIR compared to other common techniques is that it enables us to identify the presence of organic compounds (e.g. varnishes, pigment binders, waxes, and other organic additives).

Portable FTIR instruments can be used for a preliminary, non-destructive, diagnostic analysis always bearing in mind that portable instruments are less accurate.

Drawbacks The processing and interpretation of FTIR data should always be carried out on the basis of the chemical and mineralogical data obtained through thermal analyses and/or XRD.

Other chemical and mineralogical analytical techniques

Although the chemical and mineralogical techniques described above are the most widely used and accepted for the study of historic mortars according to the literature (GCI 2003) and European regulations (EN 17187 2020), other analytical techniques can also be useful in specific investigations or when the aforesaid techniques are not available. These other techniques include the following:

- *Atomic Absorption Spectroscopy* (*AAS*), *Ionic Chromatography* (*IC*) and measurements of *electric conductivity* for the analysis of the soluble salts present in historic mortars (Pecchioni et al. 2018);
- *Laser Ablation Inductively Coupled Plasma Mass Spectrometry* (*LA-ICP-MS*), for the study of the provenance of the raw materials, as it enables the trace components of mortars, including rare earth elements, to be identified very precisely (Pecchioni et al. 2018).
- *RAMAN and micro-RAMAN spectroscopy* can be used as a complementary technique together with FTIR (Ghosh and Handoo 1980) above all for the identification of the aggregate (Pecchioni et al. 2018).
- *Mortar dating* by studying stable isotopes of C and O to obtain data about the period in which the mortar was manufactured (Kosednar-Legenstein et al. 2008; Pesce 2010). This method can be invalidated by the presence of carbonatic aggregates or of secondary precipitations of carbonates, among others. To overcome these limitations, dating should ideally be carried out on a lump of pure carbonated lime (Pecchioni et al. 2018). Lubritto et al. (2018) also highlighted that a preliminary mineralogical and petrographic characterisation of the mortar must be carried out so as to ensure correct selection of the most suitable samples for radiocarbon dating.

Petrographic study

Polarized optical microscopy

The study of historic mortars under the optical microscope is an essential step in their characterisation (Elsen 2006; Ingham 2011), as it enables us to observe the main textural and compositional features of these materials, from which important information can be gleaned about the mortar manufacturing and application conditions. In particular, polarized optical microscopy (POM) enables us to:

- distinguish between the binder and the aggregate;
- identify the type of binder;
- identify the type of aggregate on the basis of its mineralogy, texture and shape;
- describe the grading and even dosage of the aggregate (B/A ratio, Casadio et al. 2005);
- identify organic fibres, pozzolanic materials and other admixtures;
- observe the porosity and texture of the mortar;
- observe the cohesion between the matrix and the aggregate;
- identify deterioration morphologies.

Optical microscope observation of historic mortars can be carried out under reflected (RL) and transmitted (TL) light. RL should be used in the presence of painted layers, in order to identify the pigments used. TL should always be used for the complete characterisation of the mortar, investigating both the binder and the aggregate fractions. In the literature, the term “matrix fraction” is also found in petrographic studies of the binder fraction.

As regards the aggregate fraction, the following aspects need to be studied:

- The mineralogical composition and petrographic features, which provide information on the provenance of the raw materials used (Fig. 2);
- The grading and shape;
- The distribution within the matrix, which provides information on how evenly the components were mixed (Pecchioni et al. 2018);
- The orientation of the grains, which offers certain indications regarding the pressure exerted during mortar application (Pecchioni et al. 2018).
- The B/A ratio (RILEM TC 167-COM-C1 2001).

As regards the binder (or matrix) fraction, the following aspects need to be studied (Pecchioni et al. 2014):

- The mineralogical composition (identified on the basis of the optical properties of each mineral phase);
- The texture (micritic, sparitic);
- The presence of newly formed phases;
- The presence of reaction rims around the aggregates providing hydraulic features (Fig. 3) or microcrystalline silica;
- The porosity, i.e. the shape, content and size of the pores, and the presence of shrinkage fissures or trapped air bubbles, which may be related with the water-to-binder ratio of the mortar (Middendorf et al. 2005a; Pecchioni et al. 2018). Only the macroporosity can be studied under POM as the minimum detectable pore size is 10 μm.
- The presence of lime lumps, which can provide information about the firing temperature inside the kiln, the lime slaking process, or the conditions in which the mortar was applied in the masonry (Elsen 2006; Pecchioni et al. 2018). In the case of natural hydraulic limes and cements, small inclusions of non-hydrated hydraulic phases (C_2S and C_3S) can be observed. These phases can be differentiated by size (below 50 μm, Pecchioni et al. 2014), shape and colour, as C_3S phases appear darker than C_2S due to the fact that they are obtained at higher firing temperatures inside the kiln (Callebaut et al. 2001; Pecchioni et al. 2014).

For the petrographic study, a mortar fragment is embedded in an epoxide resin and then reduced to a thin section (30 μm thick) that must be polished before observation. The thin sections must be prepared perpendicular to the surface, especially in mortars with a clear stratigraphy, so as to be able to study the sequence of layers and the adhesion and contact between them, as well as to describe the petrographic features of each layer, or simply to observe the differences between the external and internal surfaces of a one-layer mortar (EN 11176 2006; EN 17187 2020).

The porosity study can be enhanced by impregnating the mortar samples with a fluorescent resin before observing them with fluorescent light microscopy (using ultraviolet light). The use of reflected light microscopy combined with surface etching by acid of polished sections of hydraulic mortars is also suggested as a useful tool for identifying non-hydrated hydraulic phases (such as C_2S, C_3S, C_3A, etc.) (Middendorf et al. 2005a; Elsen 2006).

Main limitations Binder phases are often very fine-grained and sometimes amorphous (e.g. CSH, CAH), which makes their identification challenging. In this case, the petrographic study must be completed by means of higher-resolution microscopy techniques (such as scanning electron microscopy, SEM). It is worth highlighting that, despite the fact that CSH and CAH are predominantly amorphous and shapeless, and therefore

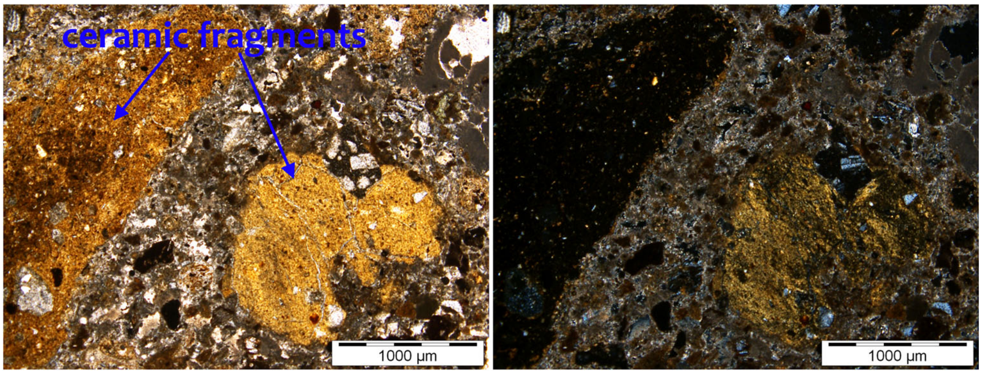

Fig. 2 Microphotographs taken with a transmitted light optical microscope with plane polarized light (*left image*) and crossed nicols (*right image*) of a historic hydraulic mortar from ancient Stabiae (Naples, Italy), showing the presence of ceramic fragments used as aggregates. Courtesy of the Group of Mineralogy and Petrography of the Department of Sciences and Technologies of the University of Sannio (Benevento, Italy)

difficult to detect using POM, some researchers have observed the presence of crystalline CSH phases that coexist with the amorphous ones, as reported by Pecchioni et al. (2014). The same authors have suggested that the CSH formed in natural hydraulic lime and in pozzolanic lime mortars may develop higher crystallinity than those formed in cement pastes, due to the fact that the former have larger amounts of free lime available for the hydration reaction.

Morphological, textural and chemical study by electron microscopies

Various different types of electron microscopy are used in scientific analyses. The most commonly used in the study of historic mortars and binders are *scanning electron microscopy* (*SEM*) and *transmission electron microscopy* (*TEM*).

SEM observations can be carried out on either small pieces of mortar or on the same polished thin sections used for POM. Both types of samples need to be carbon-coated before SEM observation, in order to be conductive. For the morphological and topographic study, mortar fragments are better observed under secondary electrons (SE), as they provide a three-dimensional image (displayed on the screen with different shades of grey). Backscattered electrons (BSE) provide a flat image, in which the brighter areas usually correspond to chemical elements with a higher average atomic number (Golstein et al. 1992). The chemical composition of the samples can be analysed using an energy dispersive X-ray analyser (EDS) coupled to the SEM, which enables point, line and area analyses.

Another advantage of studying hydraulic mortar fragments with SEM is that it can identify hydrated phases which as they tend to be amorphous and very fine, cannot always be identified using XRD or POM (Middendorf et al. 2005a). Hydrated phases of calcium silicate (CSH) and calcium aluminate (CAH/CASH) must first be observed under SE and identified on the basis of their morphologies. As an example, in air-hardening lime-pozzolan mortars, CSH can be identified by its needle-shaped and packed particles (Fig. 4), or reticular grains (Fig. 5), whilst CAH phases (especially CAĈH, Table 1) are distinguishable because they form hexagonal platelets (Fig. 6) very similar to those in portlandite and brucite. The different phases identified are then analysed by EDS, in order to corroborate their chemical composition.

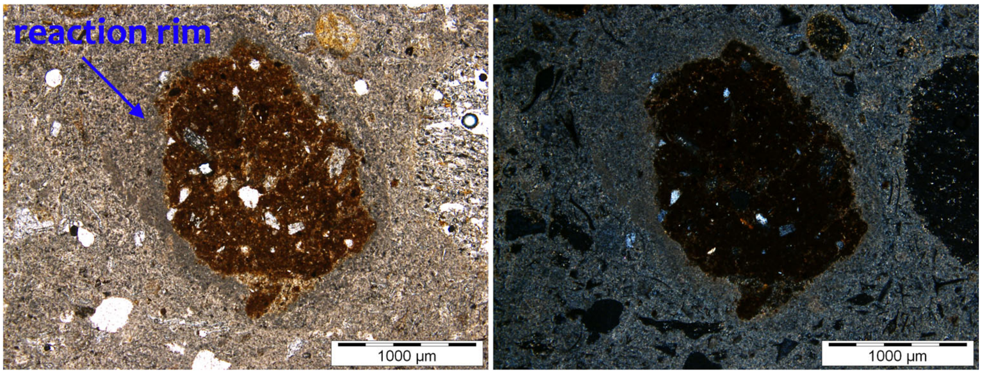

Fig. 3 Microphotographs taken with a transmitted light optical microscope with plane polarized light (*left image*) and crossed nicols (*right image*) of a historic hydraulic mortar from ancient Stabiae (Naples, Italy), showing a pozzolanic reaction rim around a ceramic fragment with hydraulic features. Courtesy of the Group of Mineralogy and Petrography of the Department of Sciences and Technologies of the University of Sannio (Benevento, Italy)

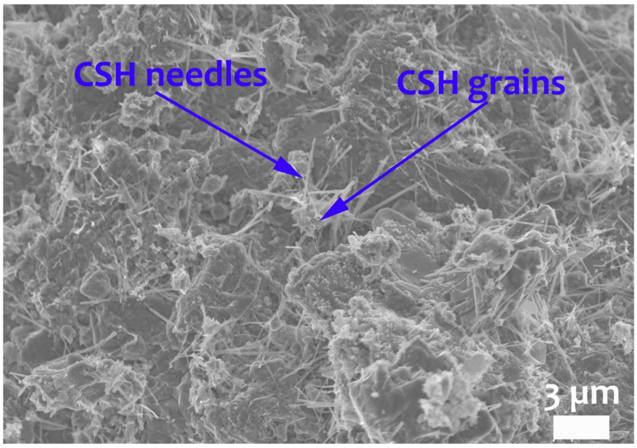

Fig. 4 High-resolution scanning electron microscopy (HRSEM) image taken with SE of a fragment of hydraulic mortar made with air-hardening lime and metakaolin (as the pozzolanic material), showing the morphology of calcium silicate hydrates (CSH), in the form of needles and packed particles

The study of polished thin sections of historic hydraulic mortars using SEM-EDS provides useful information about the chemistry of specific areas of the mortar that have previously been observed under POM, such as reaction rims between aggregates with hydraulic features (e.g. cocciopesto, Fig. 7) and the air-hardening lime in the matrix of the mortar.

An *Environmental Scanning Electron Microscope* (*ESEM*) can be also used for the textural study of the mortar pieces, the main advantage being that the samples do not need carbon-coating, as the observations are carried out at low vacuum conditions.

TEM is mostly used for the study of binders, as it provides information about the morphology, chemistry and crystalline structure (by means of *Selected Area Electron Diffraction*, *SAED*) of nanometric particles that are not easily detectable by SEM. However, it can also be used for the mineralogical study of the binder fraction of historic mortars, in order to investigate the presence of nanometric amorphous or crystalline CSH phases (Setti et al. 2021).

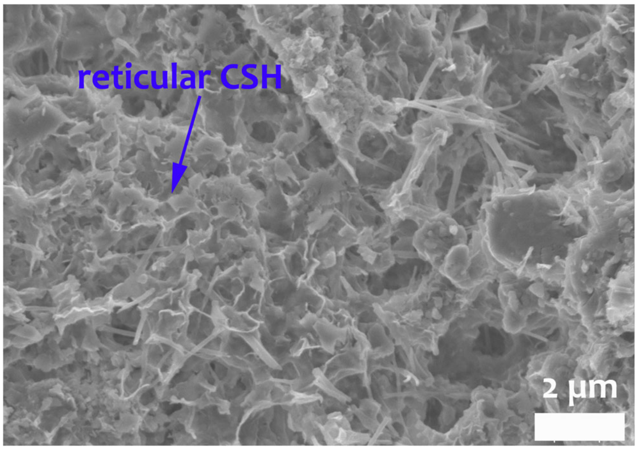

Fig. 5 High-resolution scanning electron microscopy (HRSEM) image taken with SE of a fragment of a hydraulic mortar made with air-hardening lime and metakaolin (as the pozzolanic material), showing the morphology of calcium silicate hydrates (CSH), in the form of reticular grains

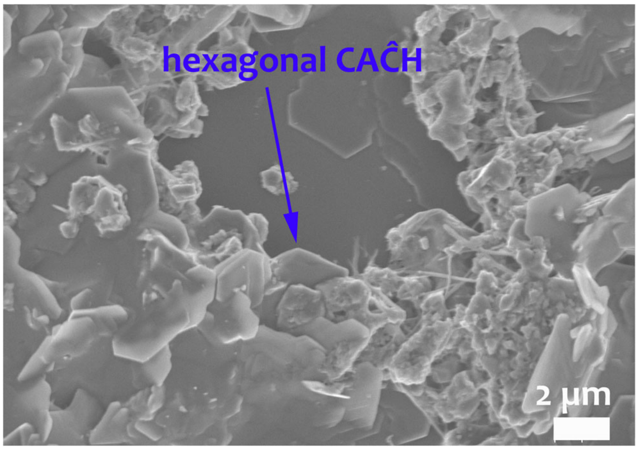

Fig. 6 High-resolution scanning electron microscopy (HRSEM) image taken with SE of a fragment of a hydraulic mortar made with air-hardening lime and metakaolin (as the pozzolanic material), showing the morphology of hydrated monocarbon aluminate hydrates (CAĈH), in the form of hexagonal platelets

Digital image analysis

The microphotographs taken under the optical and electron microscopes can be analysed using digital image analysis (DIA), which is a valuable additional tool for the petrographic characterisation of mortars (Casadio et al. 2005; Carò et al. 2006; Middendorf et al. 2017). DIA offers a quicker, more accurate alternative to traditional mechanical sieving, when it comes to determining the B/A ratio (Casadio et al. 2005) and the grading curve for the aggregate (Marinoni et al. 2005).

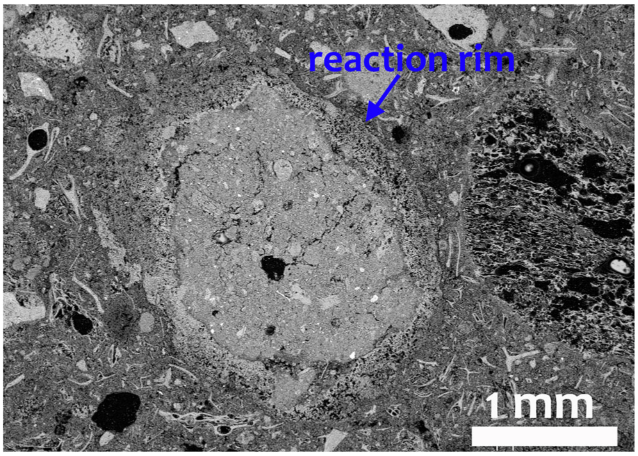

Fig. 7 High-resolution scanning electron microscopy (HRSEM) image taken with BSE on a polished thin section of a historic hydraulic mortar from ancient Stabiae (Naples, Italy), showing a pozzolanic reaction rim around a ceramic fragment used as an aggregate with hydraulic features. Courtesy of the Group of Mineralogy and Petrography of the Department of Sciences and Technologies of the University of Sannio (Benevento, Italy)

It can also be used as an indirect method for studying porosity, although it cannot always distinguish between open and closed pores on a bi-dimensional scale.

Drawbacks and limitations:

1) In heterogeneous materials like mortars, a large number of representative microphotographs of different samples of the same mortar are needed in order to perform a systematic analysis.
2) According to Casadio et al. (2005), the automatic segmentation features are not effective when the difference in colour between the elements to be separated is negligible. The same authors suggest dyeing thin sections with Alizarin Red S, assuming that fine-grained crystals with a large surface area (binder fraction) etch more rapidly and therefore show more intense stain colours than coarser crystals with limited crystal boundaries (aggregate fraction). Nevertheless, selective staining is not successful when microcrystalline aggregate is present.
3) Reliable digital image analysis of poorly or very poorly sorted aggregates may not be possible (Carò et al. 2006).

Porosity study

Mortar porosity is strongly influenced by the binder fraction. The pore size distribution, in particular, is mainly shaped by the chemical and mineralogical composition of the binder (air-hardening or hydraulic, Silva et al. 2014), whilst the pore volume depends above all on the water-to-binder ratio (Arandigoyen and Alvarez 2007). The aggregate fraction of the mortar can also affect the pore system to some extent, because it generates new porosity, especially at the interface between the aggregate grains and the matrix (known as the interfacial transition zone or ITZ, Arandigoyen and Alvarez 2007, Lawrence et al. 2007). The particular characteristics of the aggregate, in terms of morphology (rounded or angle-shaped particles, Lanas et al. 2004), texture (rough or smooth surfaces, Arizzi and Cultrone 2013) and size, can also affect the pore system. It is therefore generally accepted today that the main factors affecting the pore system of a mortar are (1) the type and amount of binder; (2) the amount of kneading water and (3) the type and amount of aggregate. It is also worth mentioning the influence of inorganic admixtures, e.g. artificial pozzolans (Arizzi and Cultrone 2012, 2018; Grilo et al. 2014); organic additives, mainly because of the direct effect they have on the amount of kneading water; fine aggregates, which increase the porosity but do not change the PSD (Isebaert et al. 2016); curing conditions, as less porous hydraulic mortars are obtained under high relative humidity (Arizzi et al. 2015); and last but not least, decay processes, which can cause an increase in mortar porosity.

It is important to study the porosity of historic mortars in order to find out more about their hydric behaviour (e.g. in terms of water absorption and water vapour permeability), durability (e.g. against freeze-thaw and salt crystallisation phenomena) and mechanical properties. Mortar porosity can be studied using *indirect methods*, such as DIA on POM and SEM microphotographs (as commented above) and hydric tests (as detailed in section 2.8.1), or *direct methods*, as commented below.

Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) is the most widely used technique for studying mortar porosity because it assesses various different aspects of the pore system: the volume of open pores (*open porosity* or *porosity accessible to mercury*, P_o), real and bulk (or apparent) density values (EN 1936 2006), and pore size distribution (PSD) in a pore diameter range (d) of $0.004 < d < 400$ µm.

Different MIP studies on historic hydraulic mortars report the following:

- Hydraulic mortars from the Mediterranean area show porosity values ranging from 18 to 40%, a mean pore size of between 0.1 and 3.5 µm and bulk density values of 1.7–2.1 g/cm^3 (Pecchioni et al. 2018).
- Ancient Roman mortars show porosity values of between 20 and 45% (Klisinska-Kopacz et al. 2010).
- Lime-pozzolan mortars made with natural pozzolans show porosity values of 30–42%, a mean pore size of between 0.1 and 1.5 µm and bulk density values of 1.6–1.9 g/cm^3 (Pecchioni et al. 2018).
- Lime-pozzolan mortars made with artificial pozzolans, such as cocciopesto, show porosity values of 30–40%, a mean pore size of between 0.1 and 0.8 µm and bulk density values of 1.5–1.9 g/cm^3 (Pecchioni et al. 2018).

Drawbacks:

1) MIP analyses on historic mortar samples with poor cohesion (due to an advanced degree of deterioration, for example) can break the sample or produce micro-cracking due to the injection of mercury into the pore network at increasing pressures during the analysis. This can also create new porosity resulting in misleading porosity readings in the sample.
2) Despite being the most widely used technique for studying mortar porosity, MIP is gradually being abandoned due to environmental issues with the mercury residues it produces.
3) It is a highly destructive technique, which means that samples cannot be reused.

Micro X-ray computed tomography

As a result of these drawbacks, MIP is gradually being replaced by other more advanced, more environmentally friendly techniques, including micro X-ray computed tomography (μXCT) (Cnudde et al. 2015). This technique uses X-rays to perform a digital cut on the examined object, in order to provide a final 3D image of its internal structure. Unlike MIP, μXCT can detect closed pores (Divya Rani et al. 2021) and macro voids (Birgul 2008) and can also distinguish air voids from other pores or fissures (Koenig 2020). Lyu and She (2019) also studied the effect of aggregate surface morphology on the microstructure of the interfacial transition zone using μXCT.

Although closed pores and air voids do not contribute to water absorption, they do affect the air content of the mortar paste during application, which has direct consequences on its durability against freeze-thaw (air voids provide protection against frost damage, Su and Scherer 2010) or crystallisation salts phenomena. Data about the amount of air voids and closed pores inside a mortar is therefore useful to help understand its resistance to decay.

Main limitations Pores smaller than the spatial resolution of the μXCT technique (which mostly depends on the equipment used, among other factors) cannot be detected. This generally refers to pores of less than 1 μm (Coletti et al. 2016). The total porosity obtained may therefore be substantially lower than that determined by digital processing of SEM images, for example (Divya Rani et al. 2021).

Physical-mechanical study

The EN 17187 standard (2019) recommends carrying out the physical tests described in this section, providing that enough material can be collected. In spite of this, if sample materials are in short supply, in some tests, smaller samples than those specified in the standards may be used.

Hydric tests

The study of the behaviour of building materials in relation to water is fundamental in order to understand more about their durability, given that most masonry structures are affected by water-related decay phenomena (e.g. rising damp, salt crystallisation, microbial growth, and freeze-thaw cycles).

The study of the hydric behaviour of historic mortars is crucial when a repair mortar with the same petrophysical features as the original needs to be designed. As a general rule, the water absorption of the repair mortar should be similar to that of the masonry (Maurenbrecher 2004; Hughes 2010), so as to ensure homogeneous water movements throughout the different building materials, thus preventing water from accumulating in certain areas of the masonry, and the water vapour transmission rates should be higher in the repair mortar than in the masonry so as to enable correct drying through the mortar (Groot 2010). On this question, it is worth highlighting that mortars made with lime and pozzolans or with natural hydraulic lime show higher water vapour permeability than cement mortars (Silva et al. 2015).

Therefore, in order to guarantee the physical compatibility of the repair mortar, it is advisable first to carry out the following hydric tests on the historic mortar that is due for repair:

1) *Water absorption at atmospheric pressure* (EN 13755 2008) (by total immersion of samples under water) and *drying* (NORMAL 29/88 1988).
2) *Water absorption by capillary uptake* (EN 15801 2009).
3) *Permeability to water vapour* (EN 15803 2009).

The main limitations when performing hydric tests on historic mortars are due to their cohesion and size. Mortar samples cannot be brittle, or they would disintegrate under prolonged contact with water. Although the standards indicate the number, shape and size of the samples needed for each test, small deviations are accepted in the study of historic samples. For example, the samples used in the water absorption by total immersion test can have an irregular shape, whilst at least one smooth, regular surface is needed for the water absorption by capillary uptake test to ensure good, uniform contact with the water. The permeability to water vapour test is the most restrictive in terms of sample shape and size, which are limited by the size of the device used to perform the test.

As a general rule, water absorption hydric tests are performed on samples left drying at 60–70 °C until constant mass is reached, i.e. when the weight variation is $< 0.01\%$. Samples are then left in contact with water or submerged (depending on the hydric test) and their mass is weighed at regular time intervals until saturation is reached. When samples subjected to the water absorption by total immersion test reach saturation, they are left exposed to air, under laboratory-controlled conditions, and their weight variation during drying is measured again at the same time intervals (drying test). In the case of the water vapour permeability test, the variation in sample weight due to the transfer of water vapour through the sample is recorded every 24 h, until constant weight is reached.

The various hydric tests measure different hydric parameters. Representation on a graph of the variation in the weight of the samples over time enables us to calculate the mortar drying index and the capillary uptake and water vapour permeability coefficients, which are very useful for comparisons with other ancient mortars, or in the design of a compatible repair mortar.

However, the comparative study might not be reliable if:

1) the size, number and shape of the tested samples are different from those specified in European standards and from those used in previous research studies used for comparison purposes;
2) the unit of measurement used for the representation of the curve and, hence, for the determination of the coefficients is different from those indicated in the European standards.

With this in mind, it is best to use the units of measurement specified in the standard so as to ensure that the data obtained can be easily compared with the results of other studies. Thus, for example, the capillary uptake coefficient value must be presented as g m^{-2} $s^{-1/2}$ instead of kg (cm or mm)^2 (min or h)$^{-1/2}$, as can be found in some papers.

In historic hydraulic mortars in a good state of conservation and with high cohesion between the different components, *forced water absorption* (under vacuum) can be carried out, so providing additional porosity data about the mortar (i.e. degree of interconnection among the pores, saturation coefficient, real and bulk densities, porosity accessible to water) (EN 1936 2006; Ponce Antón et al. 2019).

Ultrasonic pulse velocity

The study of historic mortars sometimes requires the use of non-destructive techniques. Of all the testing methods available, *ultrasonic pulse velocity* measurement (*UPV*) is probably the most widely used non-destructive tool for the characterisation of the micro-structural properties of building materials (Cazalla et al. 1999; EN 14579 2005).

Ultrasonic measurements are carried out using portable instruments either on site or in the laboratory. Depending on the size of the samples, different types of transducers can be used, e.g. cylindrical, conical, pointed, or with different diameters. Ultrasound eco-gels are generally used to ensure a good coupling between the transducers and the material being studied. However, these gels can be hard to remove, as large amounts of water are required. An alternative method which also achieves good coupling would be to use surgical-type plastic films, which are flexible and adapt easily to the mortar surface.

The selected frequency and the position of the transducers (direct, semi-direct, indirect (surface), pulse echo) must be chosen on the basis of the metric dimensions of the materials and their accessibility on site.

Ultrasounds have proved to be a sensitive tool for determining the textural characteristics of mortars, especially as a function of matrix porosity, as UPV decreases in line with increasing porosity values (Ferreira Pinto et al. 2010) and hardening time. In addition, UPV increases in proportion with the age of the mortar (Arizzi et al. 2013). The effects of decay are also revealed by this technique, as decay usually increases mortar porosity, so resulting in a decrease of the UPV through the mortar. As a general rule, historic mortars with hydraulic features show higher ultrasonic pulse velocities than air-hardening mortars (Almeida et al. 2019).

Colorimetric measurements

Another non-destructive method used for evaluating aesthetic aspects of historic mortars is *colorimetry* (Cultrone et al. 2005; Díaz-Ramos 2020; Loke et al. 2020). The CIELab system is frequently used to assess chromatic parameters as it represents human sensitivity to colour better than other colour encoding systems (Grossi et al. 2007).

Taking colorimetric measurements on historic mortars is especially important during conservation studies, in order to guarantee that the repair mortar is aesthetically compatible with the ancient masonry and to assess possible chromatic changes caused by the application of consolidating products and protective treatments (Grossi et al. 2007) or due to cleaning of historic masonry.

The overall colour difference between two mortar samples (or the same mortar before and after treatment) is expressed by the numerical value ΔE, which is determined as follows (EN 15886 2010):

$$\Delta \mathrm{E} = \sqrt{\left(\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2\right)}$$

Where L_1^*, a_1^* and b_1^* are respectively the lightness and the chromatic coordinates of sample 1 and L_2^*, a_2^* and b_2^* are those of sample 2.

According to Mokrzycki and Tatol (2011), a ΔE over 3.5 represents colour changes that are visible to the human eye, which means that ΔE values must be less than 3.5 in order to be acceptable in conservation studies.

Mechanical tests

When large samples of historic mortars are available, as in the case of cylindrical cores collected from ancient walls, their mechanical performance can be assessed by measuring their *flexural and compressive strengths* with a mechanical press (EN 1015-11 2020). Despite being totally destructive, mechanical tests are especially useful during conservation studies, as they can guarantee the mechanical compatibility of the repair mortar with the ancient masonry.

When mechanical tests cannot be undertaken, other moderately invasive and portable methods can be used for the mechanical study of historic mortars *in situ*. The *Schmidt hammer* (Theodoridou and Torok 2019), the *micro-rebound tester* (*Equotip*), the *micro-drilling test* and the *indentation hardness measurement* (Broitman 2016) are the most frequently used methods for assessing the physical-mechanical parameters of natural stone at heritage sites where sampling is limited.

Both the Schmidt hammer and the Equotip devices measure hardness, which can be related to the mechanical resistance of a material. Both have proved to be useful tools in the study of weathered stones (Viles et al. 2010). The Schmidt hammer, in particular, seems to be extremely sensitive to discontinuities, which is why it would be suitable for the mechanical study of heterogeneous materials like mortars. However, certain kinds of Schmidt hammer cannot be used to study historic mortars, as they can be too aggressive on weak materials. The "N" or "P" type hammers are probably the most appropriate for testing materials with low or very low hardness (Viles et al. 2010).

The micro-drilling tool enables us to determine the resistance of a material to drilling, according to micro-structural modifications and the state of its surface at different depths. This method is mainly applied during *in situ* investigations and structural surveys for the diagnosis of building materials (Ruiz-Agudo et al. 2011), for the evaluation of the efficacy of a consolidating treatment (Molina et al. 2017; Zuena et al. 2018), for the identification of previous decay events or treatments (Delgado Rodrigues et al. 2002), and for the comparison of the mechanical performances of artificial building materials such as bricks (Saenz et al. 2019), among others.

The indentation hardness method seems to be the least appropriate method for use on historic mortars, as the data it provides might not always be reliable.

Concluding summary of key concepts

This review presents a complete, systematic methodology for the characterisation of historic mortars and plasters with hydraulic features. It covers the main investigations into hydraulic lime mortars over the last 30 years and discusses the most significant results, highlighting the advantages and drawbacks of the various analytical techniques and methods used in this field.

The following summarised conclusions can be reached:

1) Prior to any sampling on the historic masonry, building or monument, it is essential to establish the primary objective of the study, e.g. conservation, archaeological study or scientific research. Historic, artistic and architectural data on the structure must be collected and an initial visual inspection and photographic report must be carried out before sampling the historic mortars or plasters. Sampling methods and tools must always be selected on the basis of the particular characteristics of the mortar and the planned analyses.
2) A macroscopic study must be carried out prior to the preparation of samples for their study in the laboratory. This will reveal the macroscopic characteristics of the mortar: i.e. the general features of the materials, any visible pathologies, and the presence of decorations or previous treatments.
3) The binder and aggregate should always be characterised regardless of the purpose of the study. In order to obtain more reliable, more accurate results, these two fractions must be separated and analysed individually. The most suitable separation methods will vary according to the type of binder (air-hardening or hydraulic) and the type of aggregate (siliceous or carbonatic). If this information is not available, it can be obtained by carrying out a preliminary mineralogical analysis on the whole mortar sample using XRD.
4) For the study of the **binder** fraction, a preliminary chemical-mineralogical study must be carried out to identify (by XRD, DSC, FTIR and TEM) and semi-quantify or quantify (by TG and XRD) the amorphous and crystalline hydrated phases coming from the hydraulic binder. Information on the cementation index (by XRF) and the degree of hydraulicity (by TG) of the mortar can also be obtained. With these data, it will be possible to make a preliminary differentiation between lime-pozzolan binders from hydraulic limes, and natural or artificial cements. These results must then be completed with the petrographic study of the mortar (by POM and SEM), so as to obtain additional information on the binder nature, the raw materials used, the manufacturing conditions, the mixing and application methods, and the forms of decay. Porosity studies (by MIP, μXCT and hydric tests) also provide indications regarding the type of binder and the amount of kneading water used to make the mortar, and about the decay processes to which it has been exposed.
5) The **aggregate** must be analysed using XRF, XRD, POM, sieving and micro-RAMAN when available. A petrographic study under POM can provide useful information on the provenance of the aggregate and about how evenly the components of the mortar were mixed, as well as on aggregate grading, shape and content. DIA should be used to calculate the B/A ratio accurately.
6) The presence of **organic additives** can be detected using FTIR and RAMAN, whilst **other admixtures** can be identified using POM, e.g. in the case of mortars containing fibres, and XRD if the admixtures are crystalline, e.g. mineral pigments.
7) Physical-mechanical tests, ultrasonic pulse velocity and chromatic measurements on historic mortars are also recommended during conservation studies, to guarantee compatible repair work on historic masonry, buildings or monuments.

It is finally worth adding that most of the techniques used for mortar characterisation are destructive, except for ultrasonic pulse velocity and colour measurements, and certain other low-invasive devices. Although portable instruments can be used for preliminary diagnoses on site or when sampling is impossible, laboratory analyses are strongly recommended to ensure the most accurate results.

Acknowledgements We are grateful to Pablo Guerra García (National University of Distance Education, Spain) and Francesco Izzo (Group of Mineralogy and Petrography of the Department of Sciences and Technologies of the University of Sannio, Benevento, Italy) for providing some of the images. We thank Nigel Walkington for his assistance in revising the English used in the manuscript.

Author contribution A. Arizzi and G. Cultrone decided together on the structure of the article; A. Arizzi wrote the text, which was then carefully revised and corrected by G. Cultrone.

Funding This study was funded by Junta de Andalucía Research Group RNM179; Research Project MAT2016-75889-R, Spanish Ministry of Economy and Competitiveness.

Data availability Not applicable.

Code availability

Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

References

Aceto M (2021) The palette of organic colourants in wall paintings. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01392-3

Adriano P, Santos Silva A, Veiga R, Mirao J, Candeias AE (2009) Microscopic characterisation of old mortars from the Santa Maria Church in Évora. Mater Charact 60:610–620

Alberghina MF, Germinario C, Bartolozzi G, Bracci S, Grifa C, Izzo F, la Russa MF, Magrini D, Massa E, Mercurio M, Nardo VM, Oddo ME, Pagnotta SM, Pelagotti A, Ponterio RC, Ricci P, Rovella N, Ruffolo SA, Schiavone S, Spagnuolo A, Vetromile C, Zuchtriegel G, Lubritto C (2020) The Tomb of the Diver and the frescoed tombs in Paestum (southern Italy): new insights from a comparative archaeometric study. PLoS One 15(4):e0232375

Allen G, Allen J, Elton N, Farey M, Holmes S, Livesey P, Radonjic M (2003) Hydraulic lime mortar for stone, brick and block masonry. Donhead Publishing Ltd, Shaftesbury. ISBN: 1-873394-64-0, pp 3–4

Almeida L, Santos Silva A, Mirao J, Veiga MR (2019) Evolution of mortars composition and characteristics during the 20th century — study of Portuguese buildings awarded with architecture Valmor Prize. In: Proceedings of the 5th Mortars Conference, Pamplona (Spain).

Álvarez Galindo JI, Ontiveros Ortega E (2006) Morteros. In: PH cuadernos 19 “Programa de normalización de estudios previos aplicado a bienes inmuebles”. Junta de Andalucía, Conserjería de Cultura, 92-145. ISBS: 84-8266-588-X

Alvarez JI, Veiga R, Martínez-Ramírez S, Secco M, Faria P, Maravelaki PN, Ramesh M, Papayianni I, Válek J (2021) RILEM TC 277-LHS report: a review on the mechanisms of setting and hardening of lime-based binding systems. Mater Struct 54 (63)

Arandigoyen M, Alvarez JI (2007) Pore structure and mechanical properties of cement-lime mortars. Cem Concr Res 37:767–775

Arizzi A, Cultrone G (2012) Aerial lime-based mortars blended with a pozzolanic additive and different admixtures: a mineralogical, textural and physical-mechanical study. Constr Build Mater 31:135–143

Arizzi A, Cultrone G (2013) The influence of aggregate texture, morphology and grading on the carbonation of non-hydraulic (aerial) lime-based mortars. Q J Eng Geol Hydrogeol 46(4):507–520

Arizzi A, Cultrone G (2018) Comparing the pozzolanic activity of aerial lime mortars made with metakaolin and fluid catalytic cracking catalyst residue: a petrographic and physical-mechanical study. Constr Build Mater 184:382–390

Arizzi A, Martínez-Martínez J, Cultrone G (2013) Ultrasonic wave propagation through lime mortars: an alternative and non-destructive tool for textural characterization. Mater Struct 46:1321–1335

Arizzi A, Martínez-Huerga G, Sebastián-Pardo E, Cultrone G (2015) Mineralogical, textural and physical-mechanical study of hydraulic lime mortars cured under different moisture conditions. Mater Constr 65(318):e053

Artioli G (2010) Scientific methods and cultural heritage. An introduction to the application of materials science to archaeometry and conservation science. Oxford University Press, CPI Group LTd, Croydon ISBN: 978-0-19-954826-2

Becker H (2021) Pigment nomenclature in the ancient Near East, Greece, and Rome. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01394-1

Birgul R (2008) Monitoring macro voids in mortar by X-ray computed tomography. Nucl Instrum Methods Phys Res Sect A 596(3):459–466

Blatt H, Tracy RJ (1996) Petrology: igneous, sedimentary, and metamorphic, 2nd edn. WH Freeman, New York ISBN: 0716724383

Bonazza A, Ciantelli C, Sardella A, Pecchioni E, Favoni O, Natali I, Sabbioni C (2013) Characterization of hydraulic mortars from archaeological complexes in Petra. Period Mineral 82(2):459–475

Borsoi G, Santos Silva A, Menezes P, Candeias A, Mirao J (2010) Chemical, mineralogical and microstructural characterization of historical mortars from the Roman villa of Pisões, Beja, Portugal. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 43-54

Broitman E (2016) Indentation hardness measurements at macro-, micro-, and nanoscale: a critical overview. Tribol Lett 65(1):23

Burgio L (2021) Pigments, dyes and inks — their analysis on manuscripts, scrolls and papyri. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01403-3

Callebaut K, Elsen J, Van Balen K, Viaene W (2001) Nineteenth century hydraulic restoration mortars in the Saint Michael’s Church (Leuven, Belgium). Natural hydraulic lime or cement? Cem Concr Res 31:397–403

Carò F, Di Giulio A, Marmo R (2006) Textural analysis of ancient plasters and mortars: reliability of image analysis approaches. Maggetti M, Messiga B (eds) Geomaterials in Cultural Heritage, Geological Society of London, Special Publications, 257, pp 337-345

Caroselli M, Ruffolo SA, Piqué F (2021) Mortars and plasters — how to manage mortars and plasters conservation. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01409-x

Casadio F, Chiari G, Simon S (2005) Evaluation of binder/aggregate ratios in archaeological lime mortars with carbonate aggregate: a comparative assessment of chemical, mechanical and microscopic approaches. Archaeometry 47(4):671–689

Cavallo G, Riccardi MP (forthcoming) Glass-based pigments in painting. Archaeological and Anthropological Sciences (this Topical Collection)

Cazalla O, Sebastián E, Cultrone G, Nechar M, Bagur MG (1999) Three-way ANOVA interaction analysis and ultrasonic testing to evaluate air lime mortars used in cultural heritage conservation projects. Cem Concr Res 29:1749–1752

Chiari G, Torraca G, Santarelli ML (1996) Recommendations for systematic instrumental analysis of ancient mortars: the Italian experience. In: Kelley SJ (ed) Standards for preservation and rehabilitation, ASTM STP 1258. American Society for Testing and Materials, West Conshohocken, pp 275–284

Cizer O (2009) Competition between carbonation and hydration on the hardening of calcium hydroxide and calcium silicate binders. PhD Thesis, Katholieke Universiteit Leuven, Belgium

Cnudde V, De Kock T, Boone M, De Boever W, Bultreys T, Stappen JV, Vandevoorde D, Dewanckele J, Derluyn H, Cárdenes V, Van Hoorebeke L (2015) Conservation studies of Cultural heritage: X-ray imaging of dynamic processes in building materials. Eur J Mineral 27(3):269–278

Coletti C, Cultrone G, Maritan L, Mazzoli C (2016) Combined multi-analytical approach for study of pore system in bricks: how much porosity is there? Mater Charact 121:82–92

Collepardi M (1990) Degradation and restoration of masonry walls of historical buildings. Mater Struct 23:81–102

Collepardi M (1999) Thaumasite formation and deterioration in historic buildings. Cem Concr Compos 21:147–154

Cowper AD (1927) Lime and Lime Mortars, vol 14. Donhead Publishing Ltd, Shaftesbury . ISBN:1-873394-29-2, pp 6–8

Cultrone G, Cazalla O, Rodríguez C, de la Torre MJ, Sebastián E (2005) Técnicas no destructivas aplicadas a la conservación del patrimonio arquitectónico. Colorimetría PH Boletín del Instituto Andaluz del Patrimonio Histórico 53:6–10

DeLaine J (2021) Production, transport and on-site organisation of Roman mortars and plasters. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01401-5

Delgado Rodrigues J, Ferreira Pinto AP, Costa D (2002) Tracing of decay profiles and evaluation of Stone treatments by means of microdrilling techniques. J Cult Herit 3(2):117–125

Demelenne M, Dagrain F, Scaillet JC (2010) Development of a methodology for characterisation of historical mortars in the Walloon region (Belgium). In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 99-110

Díaz-Ramos I (2020) The Architectural Finishes of the Cloister of the Bramante Temple in Rome. An Approach by the Use of the Munsell Colour System. Ge-conservation 18(11):69–81

Diekamp A, Stalder R, Konzett J, Mirwald PW (2012) Lime mortar with natural hydraulic components: characterisation of reaction rims with FTIR imaging in ATR-mode. In: Válek J, Hughes JJ, Groot CJWP (eds) Historic Mortars. Characterisation, assessment and repair, RILEM Bookseries, vol 7. Springer, Dordrecht. ISSN: 2211-0844, ISBN: 978-94-007-4634-3, pp 105–113. https://doi.org/10.1007/978-94-007-4635-0

Divya Rani S, Rahul AV, Santhanam M (2021) A multi-analytical approach for pore structure assessment in historic lime mortars. Construction and Building Materials 272121905. https://doi.org/10.1016/j.conbuildmat.2020.121905

Domingo Sanz I, Chieli A (2021) Characterising the pigments and paints of prehistoric artists. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01397-y

Donais MK, Duncan B, George D, Bizzarri C (2010) Comparisons of ancient mortars and hydraulic cements through in situ analyses by portable X-ray fluorescence spectrometry. X-Ray Spectrom 39:146–153

Donais MK, Alrais M, Konomi K, George D, Ramundt WH, Smith E (2020) Energy dispersive X-ray fluorescence spectrometry characterization of wall mortars with principal component analysis: phasing and *ex situ versus in situ* sampling. J Cult Herit 43:90–97

Eckel EC (1922) Cement, limes and plasters: their materials, manufacture and properties. Wiley, London

Edison MP (2010) Rosendale natural cement: reintroduction of an authentic North American historic binder. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 599-607

Elsen J (2006) Microscopy of historic mortars — a review. Cem Concr Res 36:1416–1424

Elsen J, Balen K, Mertens G (2012) Hydraulicity in historic lime mortars: a review. Historic Mortars:125–139. https://doi.org/10.1007/978-94-007-4635-0_10

EN 1015-11 (2020) Methods of test for mortar for masonry. Part 11: determination of flexural and compressive strength of hardened mortar

EN 11176 (2006) Cultural heritage. Petrographic description of a mortar

EN 13755 (2008) Natural stone test methods — determination of water absorption at atmospheric pressure

EN 14579 (2005) Natural stone test methods — determination of sound speed propagation

EN 15801 (2009) Conservation of cultural property — test methods — determination of water absorption by capillarity

EN 15803 (2009) Conservation of cultural property — test methods — determination of water vapour permeability (δp)

EN 15886 (2010) Conservation of cultural property — test methods - Colour measurement of surfaces

EN 16085 (2012) Conservation of Cultural property — methodology for sampling from materials of cultural property — general rules

EN 16572 (2015) Conservation of cultural heritage — glossary of technical terms concerning mortars for masonry, renders and plasters used in cultural heritage

EN 17187 (2020) Conservation of cultural heritage — characterization of mortars used in cultural heritage

EN 1936 (2006) Natural stone test methods — determination of real density and apparent density, and of total and open porosity

EN 459-1 (2011) Limes for construction. Part 1: definitions, specifications and conformity criteria

EN 80305 (2012) White cements

EN 933-1 (1998) Test for geometrical properties of aggregates. Part 1: determination of particle size distribution. Sieving method

Ergenç D, Fort R, Varas-Muriel MJ, Alvarez de Buergo M (2021) Mortars and plasters — how to characterise aerial mortars and plasters. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01398-x

Ferreira Pinto AP, Nogueira R, Gomes A (2010) In situ techniques for the characterization of rendering mortars. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 475-482.

Földvári M (2011) Handbook of thermogravimetric system of minerals and its use in geological practice. In: Occasional Papers of the Geological Institute of Hungary, vol 213, Budapest (Hungary). ISBN: 978-963-671-288-4

Frankeová D, Koudelková V (2020) Influence of ageing conditions on the mineralogical micro-character of natural hydraulic lime mortars. Constr Build Mater 264:120205

Frankeová D, Slizkova Z, Drdacky M (2010) Characteristics of mortars from ancient bridges. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 147-155

GCI (2003) Preservation of lime mortars and plasters. In: the Getty Conservation Institute Bibliographies Series. http://www.getty.edu/conservation/publications/pdf_publications/lmpbib_categories.pdf. Accessed Jan 2021

Ghosh SN, Handoo SK (1980) Infrared and Raman spectral studies in cement and concrete (review). Cem Concr Res 10:771–782

Gliozzo E (2021) Pigments — mercury-based red (cinnabar-vermilion) and white (calomel) and their degradation products. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01402-4

Gliozzo E, Burgio L (2021) Pigments — arsenic-based yellows and reds. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01400-6

Gliozzo E, Ionescu C (2021) Pigments — lead-based whites, reds, yellows and oranges and their alteration phases. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01407-z

Gliozzo E, Pizzo A, La Russa MF (2021) Mortars, plasters and pigments - research questions and sampling criteria. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01393-2

Golstein JI, Newbury DE, Echlin P, Joy DC, Romig AD, Lyman JCE, Fiori C, Lifshin E (1992) Scanning electron microscopy and X-ray microanalysis. A text for biologists, materials scientists, and geologists, 2nd edn. Plenum Press, New York

Grilo J, Faria P, Veiha R, Santos Silva A, Silva V, Velosa A (2014) New natural hydraulic lime mortars — physical and microstructural properties in different curing conditions. Constr Build Mater 54:378–384

Groot CJWP (2010) Performance and repair requirements for renders and plasters. In: International workshop on "Repair mortars for historic masonry", RILEM TC 203-RHM, Prague

Grossi CM, Brimblecombe P, Esbert RM, Alonso FJ (2007) Color changes in architectural limestones from pollution and cleaning. Color Res Appl 32(4):320–321

Gualtieri AF, Viani A, Montanari C (2006) Quantitative phase analysis of hydraulic limes using the Rietveld method. Cem Concr Res 36:401–406

Guerra-García P (2015) Sola Romani: morteros hidráulicos romanos en la península ibérica. PhD Thesis, Universidad Politécnica de Madrid (Spain)

Guerra-García P, Morín de Pablos J, Sánchez Ramos I (2019) M.N.I.A.R. techniques of macroscopic characterization for the colorimetry and chromatographies analysis applied to the mortars in the archaeological site of Los Hitos (Arisgotas, Toledo, Spain). In: Proceedings of the 5th Historic Mortars Conference. 19-21 June 2019, Pamplona, Spain, pp 695-712

Gulotta D, Goidanich S, Tedeschi C, Nijland TG, Toniolo L (2013) Commercial NHL-containing mortars for the preservation of historical architecture. Part 1: compositional and mechanical characterisation. Constr Build Mater 38:31–42

Gulotta D, Goidanich S, Tedeschi C, Nijland TG, Toniolo L (2015) Commercial NHL-containing mortars for the preservation of historical architecture. Part 2: durability to salt decay. Constr Build Mater 96:198–208

Holmes S, Wingate M (1997) Building with lime. A practical introduction, vol 12-14. Intermediate Technology Publications Ltd, Warwickshire, pp 280–281

Hughes JJ (2010) The role of mortar in masonry: an introduction to requirements for the design of repair mortars. International Workshop on "Repair mortars for historic masonry". RILEM TC 203-RHM, Prague

Hughes JJ, Callebaut K (2002) In-situ visual analysis and practical sampling of historic mortars. RILEM TC 167-COM: "Characterisation of old mortars with respect to their repair". Mater Struct 35:70–75

Hughes DC, Weber J, Kozlowski R (2010) Roman Cement for the Production of Conservation Mortars. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 1043-1050

Hurst L (2002) The properties and uses of roman cement. Construction Hist 18:21–35

Ingham JP (2011) Geomaterials under the microscope. A colour guide. Manson Publishing Ltd, Frome ISBN: 978-1-84076-132-0

Isebaert A, De Boever W, Descamps F, Dils J, Dumon M, De Schutter G, Van Ranst E, Cnudde V, Van Parys L (2016) Pore-related properties of natural hydraulic lime mortars: an experimental study. Mater Struct 49:2767–2780

Izzo F, Grifa C, Germinario C, Mercurio M, De Bonis A, Tomay L, Langella A (2018) Production technology of mortar-based building materials from the Arch of Trajan and the Roman Theatre in Benevento, Italy. Eur Phys J Plus 133:363

Jackson M, Scheetz BE, Marra F (2010) Micromorphological textures and pozzolanic cements in Imperial Age Roman Mortars. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 207-215

Klisinska-Kopacz A, Tišlova R, Adamski G, Kozłowski R (2010) Pore structure of historic and repair Roman cement mortars to establish their compatibility. J Cult Herit 11:404–410

Knapp CW, Christidis GE, Venieri D, Gounaki I, Gibney-Vamvakari J, Stillings M, Photos-Jones E (2021) The ecology and bioactivity of some Greco-Roman medicinal minerals: the case of Melos earth pigments. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01396-z

Koenig A (2020) Analysis of air voids in cementitious materials using micro X-ray computed tomography (μXCT). Constr Build Mater 244:118313

Kosednar-Legenstein B, Diezel M, Leis A, Stingl K (2008) Stable carbon and oxygen isotope investigation in historical lime mortar and plaster — results from field and experimental study. Appl Geochem 23:2425–2437

Kramar S, Zalar V, Urosevic M, Körner W, Mauko A, Mirtic B, Lux J, Mladenovic A (2011) Mineralogical and microstructural studies of mortars from the bath complex of the Roman villa rustica near Mošnje (Slovenia). Mater Charact 62:1042–1057

La Russa MF, Ruffolo SA (2021) Mortars and plasters — how to characterise mortars and plasters degradation. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01405-1

Lanas J, Alvarez JI (2004) Dolomitic limes: evolution of the slaking process under different conditions. Thermochim Acta 423:1–12

Lanas J, Pérez Bernal JL, Bello MA, Alvarez Galindo JI (2004) Mechanical properties of natural hydraulic lime-based mortars. Cem Concr Res 34:2191–2201

Lancaster LC (2021) Mortars and plasters — how mortars were made. The Literary Sources. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01395-0

Lawrence RM, Mays TJ, Tigby SB, Walker P, D'Ayala D (2007) Cem Concr Res 37:1059–1069

Loke M, Kumar P, Haldenwang R (2020) Physical characterization of heritage mortars for restoration interventions. Proceedings of 2020 IEEE 11th International Conference on Mechanical and Intelligent Manufacturing Technologies, ICMIMT 2020

Lubritto C, Ricci P, Germinario C, Izzo F, Mercurio M, Langella A, Salvatierra Cuenca V, Montilla Torres I, Fedi M, Grifa C (2018) Radiocarbon dating of mortars: contamination effects and sample characterisation. The case-study of Andalusian medieval castles (Jaén, Spain). Measurement 118:362–371

Lyu K, She W (2019) Determination of aggregate surface morphology at the interfacial transition zone (ITZ). J Vis Exp 154:e60245

Maciejewski M, Oswald H-R, Reller A (1994) Thermal transformations of vaterite and calcite. Thermochim Acta 234:315–328

Maravelaki-Kalaitzaki P, Bakolas A, Karatasios I, Kilikoglou (2005) Hydraulic lime mortars for the restoration of historic masonry in Crete. Cem Concr Res 35:1577–1586

Marinoni N, Pavese A, Foi M, Trombino L (2005) Characterisation of mortar morphology in thin sections by digital image processing. Cem Concr Res 35:1613–1619

Mastrotheodoros GP, Beltsios KG, Bassiakos Y (forthcoming) Pigments — iron-based red, yellow and brown ochres. Archaeological and Anthropological Sciences (this Topical Collection)

Matschei T, Lothenbach B, Glasser FP (2007a) The role of calcium carbonate in cement hydration. Cement and Concrete Research 37(4) 551–558 https://doi.org/10.1016/j.cemconres.2006.10.013

Matschei T, Lothenbach B, Glasser FP (2007b) The AFm phase in Portland cement. Cement and Concrete Research 37(2):118–130. https://doi.org/10.1016/j.cemconres.2006.10.010

Maurenbrecher AHP (2004) Mortars for repair of traditional masonry. Pract Period Struct Des Constr 9(2):62–65

Megna B, Rizzo G, Ercoli L (2010) The mortars and plasters under the mosaics and the wall paintings of the Roman villa at Piazza Armerina, Sicily. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 275-283

Mertens G (2009) Characterisation of historical mortars and mineralogical study of the physic-mechanical reactions on the pozzolan-lime binder interface. PhD Thesis, Catholic University of Leuven

Mertens G, Madau P, Durinck D, Blanpain B, Elsen J (2007) Quantitative mineralogical analysis of hydraulic limes by X-ray diffraction. Cem Concr Res 37:1524–1530

Mertens G, Lindqvist JE, Sommain D, Elsen J (2008) Calcareous hydraulic binders from a historical perspective. In: Proceedings of the 1st Historical Mortars Conference “Characterization, Diagnosis, Conservation, Repair and Compatibility” HMC08, Lisbon (Portugal).

Middendorf B, Hughes JJ, Callebaut K, Baronio G, Papayianni (2005a) Investigative methods for the characterisation of historic mortars – Part 1: mineralogical characterisation. Mater Struct 38(282):761–769

Middendorf B, Hughes JJ, Callebaut K, Baronio G, Papayianni (2005b) Investigative methods for the characterisation of historic mortars – Part 2: chemical characterisation. Mater Struct 38(282):771–780

Middendorf B, Klein D, Hogewoning S, Schmidt SO (2010) The new group of formulated limes (FL) of lime standard EN459 – Bane or boon? In.: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 1087-1095

Middendorf B, Schade T, Kraus K (2017) Quantitative analysis of historic mortars by Digital Image Analysis of thin sections. Restoration of Buildings and Monuments 23(2):83–92

Mileto C, Vegas López-Manzanares F, García-Soriano L (2018) La restauración de la tapia monumental: pasado, presente y futuro. Inf Constr 69(548):231. https://doi.org/10.3989/ic.16.160

Mokrzycki WS, Tatol M (2011) Colour difference σE — a survey. Mach Graph Vis 20(4):383–411

Molina E, Rueda-Quero L, Benavente D, Burgos-Cara A, Ruiz-Agudo E, Cultrone G (2017) Gypsum crust as a source of calcium for the consolidation of carbonate stones using a calcium phosphate-based consolidant. Constr Build Mater 143:298–311

Moriconi G, Castellano MG, Collepardi M (1994) Mortar deterioration of the masonry walls in historic buildings. A case history: Vanvitelli’s Mole in Ancona. Mater Struct 27:408–414

Moropoulou A, Bakolas A, Bisbikou K (1995) Characterisation of ancient, byzantine and later historic mortars by thermal and X-ray diffraction techniques. Thermochim Acta 269(270):779–795

Moropoulou A, Bakolas A, Anagnostopoulou S (2005) Composite materials in ancient structures. Cem Concr Compos 27:295–300

Murat Z (2021) Wall paintings through the ages. The medieval period (Italy, 12th-15th century). Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01410-4

Navrátilová E, Rovnaníková P (2016) Pozzolanic properties of brick powders and their effect on the properties of modified lime mortars. Constr Build Mater 120:530–539

NORMAL 29/88 (1988) Misura Dell’indice di Asciugamento (Drying Index). CNR-ICR, Rome

Oleson JP, Brandon C, Cramer SM, Cucitore R, Gotti E, Hohlfelder RL (2004) The ROMACONS project: a contribution to the historical and engineering analysis of hydraulic concrete in Roman maritime structures. Int J Naut Archaeol 33(2):199–299

Ordóñez Agulla S (2017) Morteros, cales y otros materiales de construcción vistos por los propios romanos: su tratamiento en fuentes literarias y epigráficas. In the unpublished proceedings from the Seminar: “El empleo de morteros y cales en la arquitectura romana. De sus antiguas propiedades a las nuevas técnicas de análisis para su caracterización”. Sevilla (Spain), 23-25 November 2017. Universidad de Sevilla, Instituto Andaluz del Patrimonio Histórico

Pacheco-Torgal F, Faria J, Jalali S (2012) Some considerations about the use of lime–cement mortars for building conservation purposes in Portugal: a reprehensible option or a lesser evil? Constr Build Mater 30:488–494. https://doi.org/10.1016/j.conbuildmat.2011.12.003

Pecchioni E, Fratini F, Cantisani E (2014) Atlas of the ancient mortars in thin section under optical microscope. Atlases of Conservation of Cultural Heritage. Nardini Ed, Firenze

Pecchioni E, Fratini F, Cantisani E (2018) Le malte antiche e moderne tra tradizione e innovazione. Pàtron Ed., Bologna. 2nd edn., ISBN: 9788855534147.

Pérez-Arantegui J (2021) Not only wall paintings — pigments for cosmetics. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01399-w

Pesce GLA (2010) Radiocarbon dating of lumps of not completely mixed lime contained in old constructions: the sampling problem. In: Proceedings of the 2nd Conference on Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop. Válek J, Groot C, Hughes JJ (eds). e-ISBN: 978-2-35158-112-4, pp 301-308

Philokyprou M (2012) The earliest use of lime and gypsum mortars in Cyprus. In: Válek J, Hughes JJ, Groot CJWP (eds). Historic Mortars. Characterisation, assessment and repair. RILEM Bookseries, vol 7, pp 25-35. Springer Dordrecht Heidelberg New York London. ISSN: 2211-0844, ISBN: 978-94-007-4634-3. https://doi.org/10.1007/978-94-007-4635-0

Ponce Antón G, Arizzi A, Zuluaga MC, Cultrone G, Ortega LA, Agirre Mauleon J (2019) Mineralogical, textural and physical characterization to determine deterioration susceptibility of Irulegi Castle lime mortars (Navarre, Spain). Materials 12(584):1–17

Ramachandran VS, Paroli RM, Beaudoin JJ, Delgado AH (2012) Handbook of thermal analysis of construction materials. Noyes Publications, William Andre Publishing, Norwich

Richardson IG (2008) The calcium silicate hydrates. Cem Concr Res 38:137–158

RILEM TC 167-COM-C1 (2001) Characterization of old mortars. Assessment of mix proportions in historical mortars using quantitative optical miscroscopy. Mater Struct 34:387–388

Ruiz-Agudo E, Lubelli B, Sawdy A, van Hees R, Price C, Rodríguez-Navarro C (2011) An integrated methodology for salt damage assessment and remediation: the case of San Jerónimo Monastery (Granada, Spain). Environ Earth Sci 63:1475–1486

Saenz N, Sebastián E, Cultrone E (2019) Analysis of tempered bricks: from raw materials and additives to fired bricks for use in construction and heritage conservation. Eur J Mineral 31:301–312

Salvadori M, Sbrolli C (2021) Wall paintings through the ages. The Roman period: Republic and early Empire. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01411-3

Sánchez de Rojas MI, Frías M, García N (1993) Normas europeas de cementos. Mater Constr 43(231):29–40

Setti M, Arizzi A, Nieto P, Velilla Sánchez N, Cultrone G, d'Alfonso L (2021) From ancient construction, through survival, towards modern conservation: characterization of fine-grained building material at Niğde-Kınık Höyük (Cappadocia, Turkey). Archaeol Anthropol Sci 13:79. https://doi.org/10.1007/s12520-021-01309-0

Silva BA, Ferreira Pinto AP, Gomes A (2014) Influence of natural hydraulic lime content on the properties of lime-based mortars. Constr Build Mater 72:208–218

Silva BA, Ferreira Pinto AP, Gomes A (2015) Natural hydraulic lime versus cement for blended lime mortars for restoration works. Constr Build Mater 94:346–360

Su Z, Scherer GW (2010) Pore size and shape in mortar by thermoporometry. Cem Concr Res 40:740–751

Švarcová S, Hradil D, Hradilová J, Čermáková Z (2021) Pigments — copper-based greens and blues. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01406-0

Theodoridou M, Torok A (2019) In situ investigation of stone heritage sites for conservation purposes: a case study of the Székesfehérvár Ruin Garden in Hungary. Prog Earth Planet Sci 6:15

Van Balen K, Toumbakari EE, Blanco MT, Aguilera J, Puertas F, Sabbioni C, Zappia G, Riontino C, Gobbi G (1999) Procedure for a mortar type identification: a proposal. In: Bartos PJM, Groot CJW, Hughes JJ (eds.) Proceedings of the RILEM International workshop Historic Mortars: characteristics and tests, Paisley, pp 63–72

Varas MJ, Alvarez de Buergo M, Fort R (2005) Natural cement as the precursor of Portland cement: methodology for its identification. Cem Concr Res 35:2055–2065

Vazquez P, Carrizo L, Thomachot-Schneider C, Gibeaux S, Alonso FJ (2016) Influence of surface finish and composition on the deterioration of building stones exposed to acid atmospheres. Construction and Building Materials 106392–403. https://doi.org/10.1016/j.conbuildmat.2015.12.125

Viles H, Goudie A, Grab S, Lalley J (2010) The use of the Schmidt Hammer and Equotip for rock hardness assessment in geomorphology and heritage science: a comparative analysis. Earth Surf Process Landf 36:320–333

Vitruvius P, Morgan MH (1960) Vitruvius: The ten books on architecture. Dover Publications, New York Volume II, paragraph VI

Vitti P (2021) Mortars and masonry — structural lime and gypsum mortars in antiquity and Middle Ages. Archaeological and Anthropological Sciences. https://doi.org/10.1007/s12520-021-01408-y

Weber J, Bayer K, Pintér F (2012) Nineteenth century "novel" building materials: examples of various historic mortars under the microscope. In: Válek J, Hughes JJ, Groot CJWP (eds). Historic Mortars. Characterisation, assessment and repair. RILEM Bookseries, vol 7, pp 89-103. Springer, Dordrecht. ISSN: 2211-0844, ISBN: 978-94-007-4634-3. https://doi.org/10.1007/978-94-007-4635-0.

Zhang D, Zhao J, Wang D, Xu C, Zhai M, Ma X (2018) Comparative study on the properties of three hydraulic lime mortar systems: natural hydraulic lime mortar, cement-aerial lime-based mortar and slag-aerial lime based mortar. Constr Build Mater 186:42–52

Zuena M, Tomasin P, Costa D, Delgado-Rodrigues J, Zendri E (2018) Study of calcium ethoxide as a new product for conservation of historical limestone. Coatings 8:103