

Review

Microscopy of historic mortars—a review

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Abstract

Mortars with mud, gypsum and lime as binder have, since ancient times, been used for very different applications. The characterisation of these historic mortars was until 1970–1980 mostly based on traditional wet chemical analyses but the interpretation of these results is difficult and often impossible without a good knowledge of the nature of the different mortar components. More recently developed mortar characterisation schemes have optical microscopy as a first step in identifying the aggregates, of the various mineral additions (latent hydraulic), binder type, binder-related particles and in describing the pore structure. Optical microscopy is also a valuable aid for damage diagnosis of degraded historic mortars and for the study of the interfacial zone, the bonding and possible reaction rims between aggregates, bricks or stone and the mortar. Automated image analysis techniques or manual point-count/linear traverse methods can be used to determine mix proportions, binder/aggregate ratio, aggregate size distribution and air void system.

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1. Introduction

Mortars with different binder types have been used since ancient times for different applications; masonry mortars

between bricks or stones, mortars as wall finishing materials internally (plaster) or externally (render), mortars as foundations for flooring, rubble mortars for the infillings of walls, mortars as casings of water conduits or jointing compounds from terracotta pipes, decoration mortars, etc. The compositional variation in historic mortars is surprisingly large with great differences both geographically and during different time

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periods. Mud, gypsum and lime had traditionally been the three most common binder types during the construction history of mankind until about two centuries ago, when their use was replaced gradually by different natural cement types and later by Portland cement, which is nowadays the dominant binder type in the construction industry. Mud is probably the oldest binder type in mortars, the use of clay has been identified for example in Catal Hüyük in Turkey, 6000 BC [1]. The use of lime as a binder dates back to the 6th millennium BC. A terrazzo floor excavated in Canjenü in Eastern Turkey laid with a lime mortar has been dated between 12 000 and 5000 BC [2]. A lime mortar used for flooring fishermen's huts excavated at Livinski Vir in Serbia–Montenegro has been dated at about 5600 BC [3]. Although mud and gypsum have been used in Europe during certain time periods and in certain regions, the majority of ancient mortars in Europe are lime-based and most of this review will therefore handle historic lime mortars. Gypsum was used for most applications in Pharaonic Egypt [4] and in other countries in the Middle East, but also in medieval times for masonry mortars in the region around Lübeck in Northern Germany [5,6] and in the Paris region. Mortar samples from several Gothic cathedrals in and around Paris have been analysed by Adams et al. [7] and their study showed that gypsum mortars were used for the cathedrals of Chartres and Bourges in the early 13th century. A review of the use of gypsum mortar in historic buildings in Europe can be found in Livingston et al. [8].

Until 1970–1980 the characterisation of historic mortars was mostly based on traditional wet chemical analyses [9–12]. The interpretation of these results however is difficult and often impossible without a good knowledge of the nature of the different mortar components [1,13,14]. The majority of later mortar characterisation and/or identification schemes propose optical microscopy and X-ray diffraction techniques as a first step in the qualitative identification of the different components of the mortar. These procedures describe several chemical and other analytical techniques for further qualitative and quantitative analyses like SEM-EDX, microprobe, DSC/DTA/TGA, FTIR, etc. [15–18]. The choice of the appropriate analytical technique depends mainly on the questions that have to be answered and on the amount of material available. There are at least three distinct fields of interest with different approaches and different requirements; namely the conservation field of historic monuments, the archaeological field and the academic material research field. The conservation field is *inter alia* interested in specific information about a historic mortar to formulate compositions for compatible repair mortars [19–21], to know possible causes of degradation of old mortars and to distinguish different building phases through history. The requirements for building conservation regarding formulations for a repair mortar are mainly the hydraulicity of the binder, the mixture proportions (aggregate/binder ratio) and the aggregate grading in order to identify the necessary components to produce a compatible mortar [22]. The archaeological field is interested in the chronology and spatial distribution of the raw materials and of the finished products and can use the information obtained to draw socio-economic conclusions on

the provenance of the raw materials and on the production processes (lime burning, mortar mixing, etc.) [10,14,23,24]. More fundamental material research studies use several advanced analytical techniques with the aim of enhancing our knowledge of the burning, the mixing, the hydration and the carbonation processes and of identifying the different mineral phases formed.

Comprehensive information on the historical use of lime-based mortars, about the burning of lime or on the production process of historic mortars can be found in Furlan and Bissegger [1], Sbordoni-Mora [25], Adam [26], Mallinson and Davies [3], Wisser [27], Knöfel and Schubert [28], Middendorf [29], Teutonico et al. [30], Lamprecht [31], Callebaut [32], Pallazzo-Bertholon [14] and Blezard [33].

2. Polarisation fluorescence microscopy (PFM)

In this paper the attention will be focused on polarised light microscopy of resin-impregnated thin sections although for some purposes other techniques might be better suited. Polarised light microscopy (PLM) is one of the fundamental techniques used in petrology for the study of minerals and rocks. The Scottish geologist, William Nicol, constructed in 1827 the first polarising microscope and Sorby's [34] significant paper on the microscopical structure of crystals started the huge interest in the study of rocks in thin section. Although this PLM-technique using thin sections was applied sporadically by some individual researchers to samples of concrete in the first half of the 20th century, it was not until appropriate epoxy resins became available that good quality thin sections could be prepared from concrete and mortar samples. The resin is necessary to bind together the heterogeneous components of the material with, sometimes, extreme differences in hardness. Traditionally, in sedimentary petrographical work, a blue dye is mixed with the resin to depict the porosity clearly. An additional technique introduced by Romer and Dobrolubov [35] is the use of fluorescence microscopy applied to concrete petrography. The fluorescence allows the high lighting of the cracks and pores filled with the fluorescent resin. Fluorescence combined with polarisation, nowadays, often described as Polarisation-Fluorescence-Microscopy (PFM) [36] is a suitable technique for studying any kind of porous building material. The most commonly used fluorochrome is fluorescein isothiocyanate (FITC) with mean excitation and fluorescence emission wavelength respectively at about 490 nm and 525 nm [37]. Incident light illumination (EPI-fluorescence) using a filter block on the microscope with an exciting filter of 450–490 nm and a barrier-filter of 515 nm gives satisfying results [38]. Although most laboratories use transmitted fluorescence light, EPI-fluorescence has the advantage of minimizing the 20–30 µm section thickness effect.

The preparation of fault free thin sections with a constant and homogeneous thickness requires precision work. The first step in manufacturing thin sections is the reduction of the sample to a small block of about 30×50×20 mm. This prism is impregnated under vacuum with a low-viscous resin containing a fluorescent dye. After the hardening of the epoxy resin one side

of the block is carefully ground and then glued to a glass plate. Afterwards the thickness of the block is reduced, first by sawing off the material which sticking out more than half a millimetre above the glass plate, and then by grinding or polishing the material in different steps until the desired thickness is obtained. Finally the thin section can be covered with a cover glass or polished if further analyses with the Scanning Electron Microscope (SEM) or with Cathodoluminescence are to be performed. Detailed information about thin section preparation can be found in Murphy [39], Jornet [40], Miller [41], Walker and Marshall [42] and in Camuti and McGuire [43]. Objects of controversy in thin section preparation are the possible introduction of microcracks as artefacts and secondly the use of water versus non-aqueous fluids as coolant lubricant during cutting, grinding and polishing. The former has been studied and discussed in detail by Jornet et al. [44] and one of the conclusions of their study was that no differences could be observed between specimens dried at 30 °C and those dried at 60 °C, while a significant increase in size and amount of microcracks was observed in specimens dried at 105 °C. A temperature of 40 °C should moreover not be exceeded for the drying of mortar samples to minimize dehydration of hydrous minerals as ettringite or gel products. An alternative procedure is first to replace the pore-water with ethanol and then to replace ethanol with epoxy. The use of non-aqueous fluids is preferred by several authors [42,45], while many laboratories, mainly in Scandinavia, with a long experience in thin section preparation of mortars and concrete, use water with good results. As a conclusion, (a minimum amount of) water can be used if the mortar is well impregnated with resin.

3. Other microscopical techniques

The study of polished sections using reflected light microscopy can be very useful for identifying different mineral hydraulic phases (C_2S , C_3S , C_4AF , etc.). This technique is most often used in Portland cement clinker studies and requires the use of selective etching techniques, details of which can be found in the handbook of Campbell [46]. The application of this technique to historic mortars is rather rare [1,33,47] and is mostly limited to the study of historic mortars from the 18th to 20th century.

A SEM analysis is, together with an XRD-analysis, the most valuable second step in the characterisation process of historic mortars. SEM analyses can be performed on mortar fragments or on polished epoxy-impregnated sections. The same sections can be used as those used for optical microscopy, if well polished and eventually coated with Au, C, etc. With a SEM equipped with an EDX-detector (Energy Dispersive X-ray) and BSE detector (Back-Scattered Electron), valuable information can be obtained on the mineral phase composition and on the pore structure of the historic mortar. These techniques were already used for a considerable time to characterise hydraulic phases in Portland cement and concrete research [48–50] and their use is increasing in historic mortar research. First results were published on mortar fragments [51–53] and later on polished sections [54–58].

Several sophisticated and recently developed microscopic techniques can be used to characterise historic mortar samples, but most published measurements are either on recent hydraulic materials or on restoration mortars (X-ray microscopy, AFM, Cathodoluminescence microscopy, TEM, etc.). Cathodoluminescence microscopy can be a valuable tool for the identification of calcium silicate minerals formed in historic hydraulic mortars [59].

4. Applications using PFM qualitative analysis

The most straightforward application of PFM for the study of historic mortars is the identification of the inorganic and organic aggregates (inert) and of the various mineral additions (latent hydraulic).

4.1. Inert aggregates

The nature of the inorganic aggregates found is very diverse because they are derived from very different types of geological deposits including several types of sand resources, crushed rock formations, etc. The identification of the aggregates and other possible observations that can be useful are carried out in the same way as those used in standard petrographical methods in geological sciences. More detailed information specifically on concrete petrography can be found in Jornet [40], in French [60] and in St John et al. [45]. The mineralogy of these aggregates reflects their geological origin and thus can give valuable information about their provenance. Other groups of inert aggregates are larger ceramic and slag fragments (see Fig. 1). Sometimes reaction rims can be observed at the interface between these particles and the binder [61,62]. Slags are either glassy amorphous or (partly) crystalline showing a complex mineralogy of calc-silicates of the melilite group (Äkermanite–Ghelenite), rankinite, etc. [58]. It is not clear whether these slag particles are formed in the burning process.

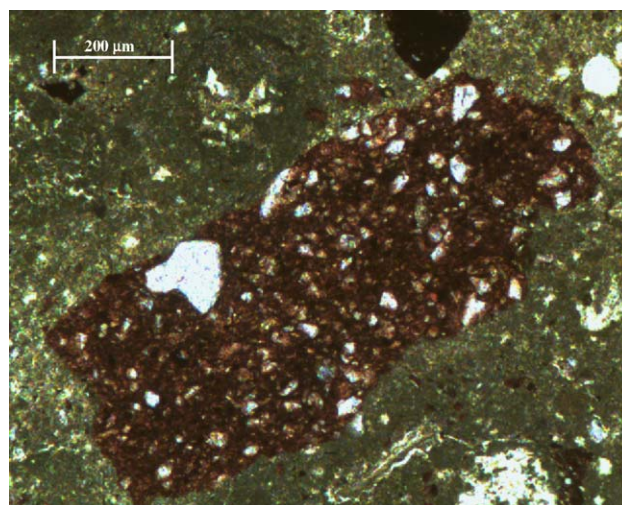


Fig. 1. Thin section photomicrograph (plane polars) of a historic lime mortar from the cathedral of Tournai (Belgium) with centrally in the image a ceramic fragment, without clear reaction rims.

Apart from these inorganic aggregates, a very diverse group of organic components can be identified in historic mortars. Ubiquitous is charcoal, which is most probably a remnant of the burning process (see Fig. 2), but it can also be added in some cases as a pigment to darken the mortar [5]. Peat, wood, coal, etc., have been used in the past as fuels depending on the availability. The limestone and the fuel were laid in alternate layers in traditional kilns. Vertical shaft kilns were designed in the nineteenth century with separate charges of fuel and limestone resulting in ash-free lime. Different organic fibres, (animal hair, straw, etc.) are also often found, especially in plasters and renderings. These fibres have traditionally been used to improve the tensile strength.

4.2. Mineral additions (latent hydraulic)

A substance is said to be latent hydraulic, or pozzolanic when it combines with hydrated lime to form hydration products of cementitious value. These reaction products are often very similar to the calcium silicate hydrate compounds found in hydrated natural hydraulic lime. One group of mineral additions used since ancient times by both Greeks and Romans is certain volcanic pyroclastic rocks which are natural pozzolana. Well known deposits in Europe are the volcanic tuffs from Santorini (Santorini earth), those found near the Bay of Naples from the neighbourhood of Pozzuoli and the Rhenish volcanic tuffs known as Trass [31,63]. These pozzolanas were finely ground and mixed with the lime, making their identification by PFM often difficult depending on the progress of their reaction. The presence of the fine pozzolanic material has often to be verified with XRD [18,55]. Other rocks that have been used as pozzolanic materials are diatomaceous earth [64] as for example the Danish ‘Moler’ and other sedimentary rocks like the French ‘Gaize’, found to the east of Paris in the French Ardennes and Meuse region. The pozzolanic properties of both these materials improve remarkably after calcination [65]. An excellent overview of natural pozzolanas can be found in Massazza [66].

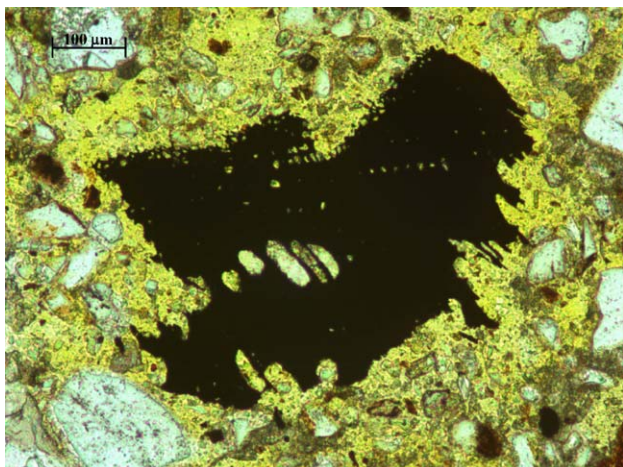


Fig. 2. Thin section photomicrograph (plane polars) of a historic lime mortar from the cathedral of Tournai (Belgium) with quartz grains and centrally in the image a charcoal fragment. Field of view 0.87 mm across.

Powdered ceramic material from tiles and pottery was also used as pozzolana since early Hellenistic time and has since been used in Europe especially in the Mediterranean countries. Romans used it also as pozzolanic material when there was no volcanic material in the region as was probably the case for the Roman mortars used for the Hadrian's wall in Britain, where crushed ceramic material was added to the lime binder [3]. Crushed ceramics seem also to be preferred from early Hellenistic to early Byzantine times in mortars related to water-bearing constructions and to protect the inside of walls from moisture, typically in baths, canals and aqueducts [25,67]. These often pink lime mortars with crushed brick fragments are often named ‘cocciopesto’ in southern Europe and ‘terrazzetto’ in Venice where this highly hydraulic lime has been used since Roman time for the rendering and plastering of buildings situated in places with a high relative humidity [25]. Crushed pottery and tiles have been used but clay minerals themselves can gain a distinct pozzolanic activity when fired at temperatures between 600 and 900 °C. The presence of intentionally calcined clays in historic hydraulic mortars is difficult to confirm but it is traditionally used in India and is described for the medieval ‘alla porcellana’ mortars in Genua, where kaolin clay, probably calcined to metakaolin, was added to lime to improve the hydraulic properties [68]. The use of burnt, improved pozzolana (carbunculus) in mortars by the Romans has been claimed by Davidovits [69,70] based on the interpretation of ancient texts of Vitruvius.

4.3. Binder

The binder type can in most cases be determined by PFM. Gypsum-based-binders can easily be distinguished from lime-based mortars. Detailed information about historic gypsum mortars can be found in Middendorf and Knöfel [5,6]. PFM methods are also useful in the characterisation of historic mortars made with natural cement. Natural cement can be considered as highly hydraulic natural lime, these cements are prepared by calcining naturally occurring rocks, containing a mixture of argillaceous or siliceous and calcareous components, for example marls or septaria found in certain geological strata. The temperature is kept below the sintering point during the burning process with the result that natural cements vary considerably in composition [71,72]. Nowadays, a quick-setting natural cement is still produced by the company Vicat in the French Rhône-Alpes region [71,73] and according to Hadley [71] small-scale production continues in Switzerland and Spain. The use of natural cements in historic mortars can be identified by PFM by the observation of unhydrated cement grains, belite (dicalcium silicate) is the most common mineral phase observed (see Fig. 3). More difficult to determine by PFM is the hydraulic character of natural lime binders. In ideal conditions, a hydraulic one has a more cloudy appearance (parallel polars). Other analytical techniques (chemical, XRD, microprobe methods, etc.) can be used to confirm or to quantify the hydraulicity of the binder. The binder matrix in historic lime mortars as observed by PFM consists in most cases of very finely crystallised calcite derived from the carbonation of the

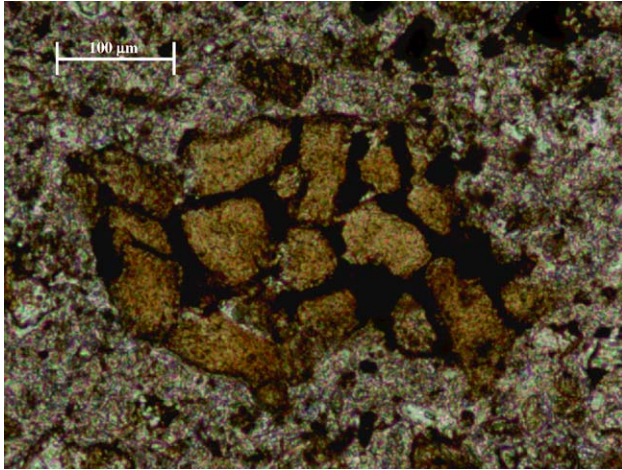


Fig. 3. Thin section photomicrograph (plane polars) of a historic lime mortar from the Saint-Michael's church of Leuven (Belgium) with rounded unhydrated C_2S -belite crystals centrally in the image.

slaked lime. The size and texture of the calcite crystals formed is probably related to the environmental conditions of carbonation. Solution–reprecipitation phenomena can often be observed in historical mortars masking original characteristics of the mortar. This can result in significant secondary binder porosity that could compromise measurements of binder/aggregate proportions [54].

4.4. Binder-related particles

Several authors mention the presence of smaller or greater binder-related particles often called 'lime lumps' (see Fig. 4) in historical lime mortars [54,74–79]. One difficulty of the presence of these lime lumps is that they are binder-derived, but appear to act as a form of aggregate. Their quantification, which is important for calculating a correct binder/aggregate ratio, is at the moment possible only using microscopical methods. Methods of analysis ignoring the presence of these lime lumps [77] have to be interpreted with great care. Different

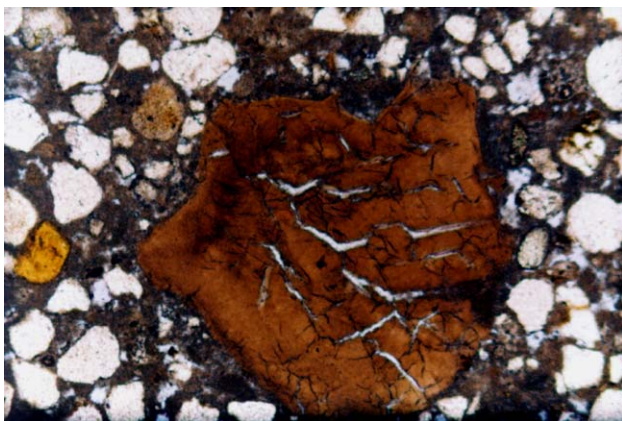


Fig. 4. Thin section photomicrograph (plane polars) of a historic lime mortar from the city hall of Ghent (Belgium) [32] with centrally in the image a very fine-grained, porous, pure $CaCO_3$ lime lump showing shrinkage cracks. Field of view 1.8 mm across.

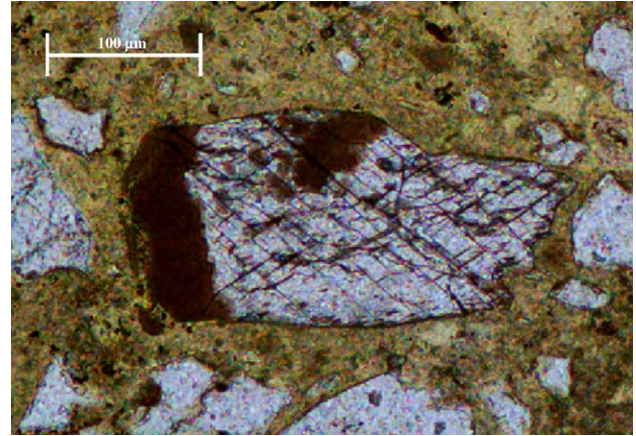


Fig. 5. Thin section photomicrograph (plane polars) of a historic lime mortar from the cathedral of Tournai (Belgium) with quartz grains and centrally in the image an example of an underburned limestone fragment. The darker part of the fragment (left) is partly burned.

types of these binder-related particles probably occur in ancient mortars with a different origin. A great number of these particles were investigated by Elsen et al. [57] in more detail using SEM/EDX and microprobe methods to investigate the nature of these particles. Three types of binder-related particles can be distinguished; underburned fragments, overburned fragments and lime lumps *sensu stricto*. Underburned fragments (see Fig. 5) can provide information about the type of limestone that had been used to burn the lime [77] and thus also about the hydraulicity of the lime. Other binder-related particles are considered to be partly sintered particles formed in traditional kilns where there are hot zones sufficient to initiate fusing or sintering of the lime. When sintered the lime is weakly reactive, or dead burned and when in a mortar, it will slowly hydrate and carbonate (see Fig. 6). Results of mineralogical analyses on overburned fragments can provide information about maximum burning temperatures used [32,56]. The most commonly

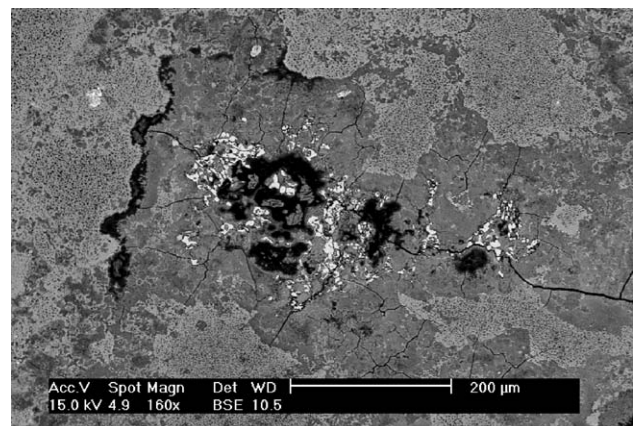


Fig. 6. BSE-image of the central part of a binder-related particle [57]. Two main zones can be distinguished, an outermost carbonated zone (pure $CaCO_3$) and a central, dark-grey zone with a chemical composition corresponding to a calcium silicate hydrate phase. In the central part of the figure, porous zones (black) and white particles with a chemical composition corresponding to a calcium silicate phase can be distinguished.

observed binder-related particles, the lime lumps *sensu stricto*, are often rounded porous structures, appearing distinctly in the mortar matrix. The origin of these is not agreed upon, but there are explanations proposed by different authors. According to Knöfel [74], Hughes et al. [54], Callebaut and Van Balen [80] and others, the presence of well-rounded porous lime lumps indicates that the lime used was dry-slaked, i.e. is slaked with a minimum amount of water to convert all CaO into Ca(OH)_2 . A method mentioned in literature for the production of dry-slaked lime is the thorough mixing of wet sand with burnt lime fragments [81]. From experimental work, these lime lumps are indeed formed by such dry-slaking method [80]. Another explanation formulated by Bruni et al. [76] is that the lime lumps are derived from the carbonate crust that forms on top of lime putty when maturing. We can conclude that these binder-related particles can provide information on the nature and the provenance of the raw materials and on the historic technologies which were used in lime production and mortar preparation.

4.5. Porosity

The following three values are fundamental for the description of porous materials: total porosity (TP), pore size distribution (PSD) and specific surface (SS). These values are traditionally used to assess the influence of porosity on mechanical properties, moisture transport and durability [82]. However, the complexity of the pore structure of historic mortars makes an interpretation of these porosity values difficult. The mortar consists of a porous binder together with different, often porous aggregates. These include various types of stone aggregate and lime lumps, each component having a different pore structure. These difficulties and the fact that often only a small sample is available makes the PFM a valuable technique but rather as an observational tool [22]. Different pore types can be distinguished. Capillary pores range in size from 0.1 to 100 μm and are found within the binder and at aggregate/binder interfaces. This porosity is developed in the first hardening phase during the drying and hydration processes and is influenced in a second phase by the carbonation process [83]. Coarse pores are greater than 100 μm in diameter and are generally formed by entrapped or entrained air. Entrained air pores are irregular in shape and distribution; they form by the entrapment of air during the mixing process. The entrained air pores (see Fig. 7) are round voids (bubble-like) formed by the introduction of admixtures (surfactants) which are probably organic materials in historic mortars containing proteins [84]. Spherical pores well distributed over the mortar matrix have been described in historic mortars by several authors [57,85].

Other interesting observations that can be easily made by PFM are the visualisation of cracks using parallel light and of microcracks ($< 10 \mu\text{m}$) using fluorescent illumination. Cracking may be caused by a large variety of factors. Cracks within the binder with irregular form and rather randomly oriented are typical for drying shrinkage cracks. Cracks with a rather sharp appearance are assumed to have formed after the initial hardening of the mortar due to several possible damaging processes such as frost action, mechanical actions, ASR, salt

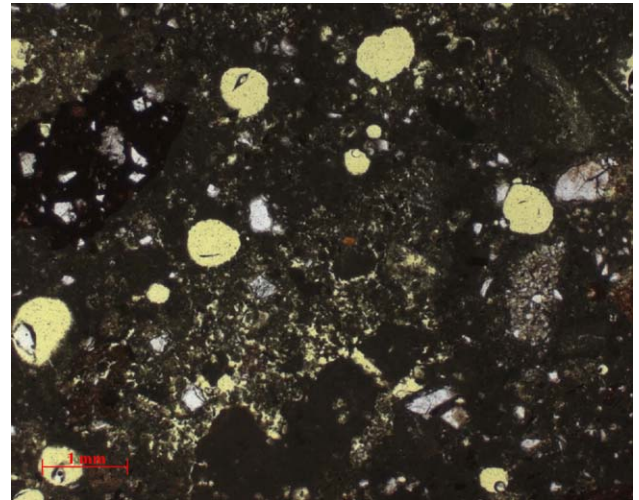


Fig. 7. Thin section photomicrograph (plane polars) of a historic lime mortar from Sagalassos (Turkey) showing spherical air pores well distributed over the mortar matrix. Field of view 7.2 mm across.

damage, etc. PFM is used as an important tool for diagnosing the degradation mechanism. More detailed information about this subject can be found in Van Balen et al. [18] and in Van Hees [86]. A valuable aid for damage diagnosis is the identification of secondary minerals and products which may be present in these cracks such as ettringite, gypsum, etc. Other valuable observations that can be made by PFM are the formation of secondary porosity and dissolution–reprecipitation phenomena. Ring-like textures of calcite are common along the interior of larger voids and at the exterior of mortar. Narrow cracks may heal by calcite precipitation, known as autogeneous healing. Finally PFM is also used to study the interfacial zone, the bonding and possible reaction rims between aggregates, bricks or building stones and the mortar.

5. Applications using PFM quantitative analysis

Quantitative image analysis applications using PFM are limited because of the complexity of the composite material. Therefore point-count methods or linear traverse methods (Rosiwal) are often used especially to determine the volume of the different components of the mortar, what is known as a modal analysis. These methods are based on the mathematical field called stereology. Comprehensive references to stereological interpretations can be found in DeHoff and Rhines [87], Underwood [88] and Weibel [89]. The tools as such for microscopy and applications are in detail described by Russ [90] and combined with image analysis techniques by Russ [91].

Mix proportions and binder/aggregate ratios of historic mortars are traditionally determined by wet chemical methods. However, these methods give unreliable results for mortars containing carbonate aggregates or with a high content of binder related particles such as lime lumps. A detailed procedure for an assessment of the mix proportions using quantitative optical microscopy has been published by the RILEM Technical Committee TC167-COM [92].

Quantitative optical microscopy methods can be used to determine the aggregate size distribution of historic mortars and are very useful when only a limited amount of sample is present or when the aggregate may not be resistant to acid attack. This method should only be applied to mortars with a rather uncomplicated composition such as pure aggregate grains with no mineral additions. Most results of aggregate size distribution that have been published using quantitative optical microscopy are on recent mortars or concrete [93–96].

The total pore volume and the pore size distribution have a major influence on the freeze/thaw durability of a mortar. The entrapped air pores and the entrained air pores (cf. supra) of the pore structure can be measured using quantitative optical microscopy for which fully automated image analysis techniques have been more frequently used during the last decennium. Detailed information on recent mortar and concrete analyses with the description of the different methods used can be found in Elsen et al. [97], Elsen [98] and Schouenborg et al. [99].

6. Discussion and conclusions

The Polarisation–Fluorescence–Microscopy (PFM) technique using thin sections is of primary importance for the characterisation of ancient mortars both because of the complex nature of these composite materials and of the fact that these mortars are dynamic materials. Ancient mortars are complex composite materials and show a very large variation in aggregate and pozzolanic mineral addition contents and the PFM-method is most suitable as a first step to identify these different inorganic and organic materials. Mortars are also dynamic materials, they continue to interact with their environment after the hardening and carbonation process. Dissolution/precipitation phenomena, such as isopachous calcite linings of pores and crack healings, result in enhanced secondary porosity formations [54,100]. In trying to quantify the mix proportions of an ancient mortar a PFM analysis will always be useful for a proper evaluation of any result obtained by another analysis (chemical, TGA, etc.) method [101]. Several authors [56,57,75,79,102] describe a much higher binder/aggregate ratio than the often mentioned, classical 1:3 ratio described by Vitruvius for quarry sand [26,31] and prescribed classically for restoration mortars. These high binder/aggregate ratios are probably related to the presence of lime lumps and other binder-related particles in ancient mortars [57,75,77]. These binder-related particles need to be considered as a separate phase for a quantitative characterisation of any historic mortar.

We can conclude that PFM is indispensable as a first step in the characterisation of ancient mortars, especially the identification of the different inorganic and organic aggregates (inert), the different mineral additions (latent hydraulic), the binder type, the binder-related particles and in the to description of the pore structure. Optical microscopy is also a valuable aid for damage diagnosis of degraded historic mortars and for the study of the interfacial zone, the bonding and possible reaction rims between aggregates, bricks or building stone and the mortar. Quantitative analyses using optical microscopy are more limited

because of the complexity of the composite material. Automated image analysis techniques or manual point-count/linear traverse methods can be used to determine mix proportions, binder/aggregate ratio, the aggregate size distribution and the air void system.

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