

A petrographic study of mortar hydraulicity.

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SUMMARY: *The nature of the binder determines the mortar cohesiveness and its intrinsic bond, therefore it greatly impacts its physical properties and durability. In a binder, the hydrated material is mainly responsible for the strength. Mortars containing hydrated material are hydraulic. Hydraulicity is coupled to faster hardening, higher ultimate strengths and a greater durability, and is probably the most important feature to be determined in order to replicate historic mortars for repair. The aim of this paper is to explore mortar hydraulicity through petrographic analysis. Hydraulicity can reside either in the binder or in other mortar components such as the aggregate or pozzolanic additions. The paper evidences these instances through case studies.*

This paper concludes that very similar hydration products to those formed in mortars made with hydraulic lime and Roman cements are present in lime/brick mortars due to pozzolanic reaction. These include amorphous C-S-H cements and crystalline and layered C-S-H). This work also suggests that the C-S-H formed during hydration of hydraulic lime and lime-brick mortars may exhibit a higher crystallinity than that in portland cement pastes, and this may be due to the higher free lime content of the hydraulic lime and lime-brick pozzolan systems, where more calcium is available for reaction. The results also indicate that the hydrates resulting from pozzolanic reaction in lime/brick mortars are more determined by the pozzolan's composition and the conditions of the reaction, than by its specific surface. This paper also concludes that clay-bearing aggregate such as shale and greywacke; microsilica-bearing aggregate such as chert and even crystalline igneous rocks such as dolerite are reactive, and can bind substantial amounts of lime being therefore pozzolanic.

Finally, the paper states that even though petrographic analysis does not allow us to precisely quantify mortar hydraulicity, it enables to discern whether a mortar is hydraulic and conclude on the hydraulicity source. The presence of both crystalline and amorphous C-S-H; portlandite crystals, relicts of unhydrated clinkers; hydration layers and pozzolanic reaction rims as well as the arrangement of new-formed amorphous silica and aluminosilicates can be determined with petrography, and these conform evidence of hydraulicity.

KEY-WORDS: *hydraulicity, petrographic analysis, C-S-H, unhydrated clinker, lime-brick mortar, hydraulic lime, cement.*

1. INTRODUCTION

The nature of the binder determines the mortar cohesiveness and its intrinsic bond therefore it greatly impacts the physical properties and durability of a mortar. In a binder, the hydrated material is mainly responsible for the strength. Mortars containing hydrated material are hydraulic. Other mortar components such as unhydrated residual material and carbonated lime also exhibit the capacity to resist external stresses. However, at a constant porosity, the strength increases with an increasing amount of hydrates in the paste (Odler [1]).

Contemporary industrial and historic binders can be divided into two groups: hydraulic and non-hydraulic. When water is added to a hydraulic binder such as hydraulic lime or cement, the C_3S (alite) and C_2S (belite) react with water and hydrated calcium silicate is formed (C-S-H). The C-S-H is responsible for the binding properties of hydraulic composites and therefore their cohesiveness and strength. Hydraulicity is coupled to faster hardening, higher ultimate strength and a greater durability, and is probably the most important feature to be determined in order to replicate historic mortars for repair. Mortars made with non-hydraulic binders may also contain hydrated material because hydraulicity can reside not only in the binder, but also in other mortar components such as the aggregate, kiln fuel contamination or pozzolanic additions.

It is generally accepted that the hydraulicity of a mortar is better estimated with chemical methods (Middendorf [2]). However, this paper demonstrates that even though petrographic analysis does not allow us to precisely quantify hydraulicity, it enables to assess the presence of hydrated material and determine its source, thus allowing making a significant qualitative evaluation of mortar hydraulicity.

A great deal of detailed, high-quality research has been undertaken on the kinetics and mechanism of hydration of Portland cement binders and the structure of the resultant hydrated cement paste. In a cement paste, hydration consists of a series of reactions between individual clinker minerals, calcium sulfate and water which progress both simultaneously and successively at different rates and influencing each other. The progress of these reactions is determined by the rate of dissolution of the involved phases, the rate of nucleation and crystal growth of the hydrates to be formed and the rate of diffusion of water and ions through the hydrated material already formed (Odler [1]). According to this author, the kinetics of the hydration process is complex and depends on the composition of the clinker; its heating and cooling rates and burning temperature; the quantity and form of calcium sulfate in the cement; the fineness of the cement; water/cement ratio of the mix; curing conditions; hydration temperature and presence of admixtures or other additives.

In contrast, the kinetics and mechanism of hydration of hydraulic lime and lime-pozzolan mortars, and the structure of the resultant hydrated paste has not yet been investigated to a great extent. Pozzolans are materials rich in reactive silica, or alumina plus silica, that react with lime ($Ca(OH)_2$) and water forming calcium silicate and aluminate hydrates with cementing properties. The pozzolanic reaction is determined by the chemical and mineral composition of the pozzolan, its specific surface and the conditions of the reaction including water ratio and curing time and temperature (Massazza [3]).

According to Massazza [4], the reaction of pozzolan-lime mixes produces the same compounds as those which are found upon hydration of Portland cement since the overall composition of the two mixes falls in the same field (blends of silica, or silicates, with lime and water). Also according to this author, for the same reason, different types of pozzolans produce the same aluminate and silicate hydrates: differences are minor and, in general, affect the amount rather than the nature of the hydrated phases. However, petrographic identification of hydraulic components in lime-pozzolan mortars proves difficult, and this can be attributed to the conditions of the pozzolan-lime-water reaction and the rapid water loss during mortar setting resulting in very small minerals in low concentrations (Charola and Henriques [5]).

The aim of this paper is to explore mortar hydraulicity through petrographic analysis. This paper outlines petrographic evidence of hydraulicity in mortars made with hydraulic binders including lime with hydraulic properties, Portland cement, Roman cement (the natural cement developed and patented in the 18th century, made by burning septaria nodules). The paper also studies hydraulicity of mortars made with non-hydraulic binders (calcium lime/brick mortar of Roman age) where hydraulicity resides in the addition of brick as a pozzolan. The paper focuses on the identification, structure and arrangement of hydration products and unhydrated clinker remnants. Pozzolanic reactions involving reactive aggregate and brick fragments are also investigated.

2. METHODOLOGY

Microscopy has greatly developed since, according to Sobel [6], Galileo Galilei created what was probably the first microscope, by reversing the lenses of the telescope he used to watch the stars. According to St John [7] the polarising microscope itself was first designed as a chemical microscope for examining crystals by J. Lawrence Smith, and constructed and exhibited in Paris at the Great Exhibition of 1857. As with conventional microscopes, the objective enlarges the image and the eye piece magnifies the object further. However, the petrographic microscope differs in that it is equipped with two polaroids: a polarizer and an analyser, fitted above and below the specimen, and these allow examining specimens with transmitted, both polarized and natural light, using a light source below the stage. Minerals are identified by studying their optical properties, a graduated rotational stage allows angles to be measured and approximately twelve optical properties can be determined (Heinrich [8]). The petrographic microscope was first developed for the study of rock forming minerals, and the first reported application to artificial materials was by Le Chatelier in 1882, who studied cement clinkers concluding that their main constituent was C_3S (St John [7]). Today, petrographic microscopy is an established technique for mortar analysis (Charola [9]; Middeldorf [10]). It informs on the composition, origin and proportions of raw materials and mortar technology. It enables to assess aggregate size and shape; presence of additions such as pozzolans; binder type and pore structure; current condition; reasons for failure and decay processes such as fracturing, binder dissolution, aggregate/binder reaction and salt damage, thus providing valuable data to design improved mixes or mortar replicas for masonry repair (Pavía [11]).

Thin section preparation for petrographic analysis often requires pre consolidation of friable material by impregnation in a resin under vacuum. The thin sections shown in this paper

were impregnated in resin and cut with oils to avoid damage to water-soluble minerals. In addition, the samples were dyed with a chemical solution containing alizerine and potassium ferrocyanide in order to differentiate carbonate minerals. They were then polished to the standard thickness of 20 microns, covered with a glass slip and examined with a petrographic microscope incorporating eye pieces of 2, 10, 20 and 40 magnifications, using both natural and polarised light.

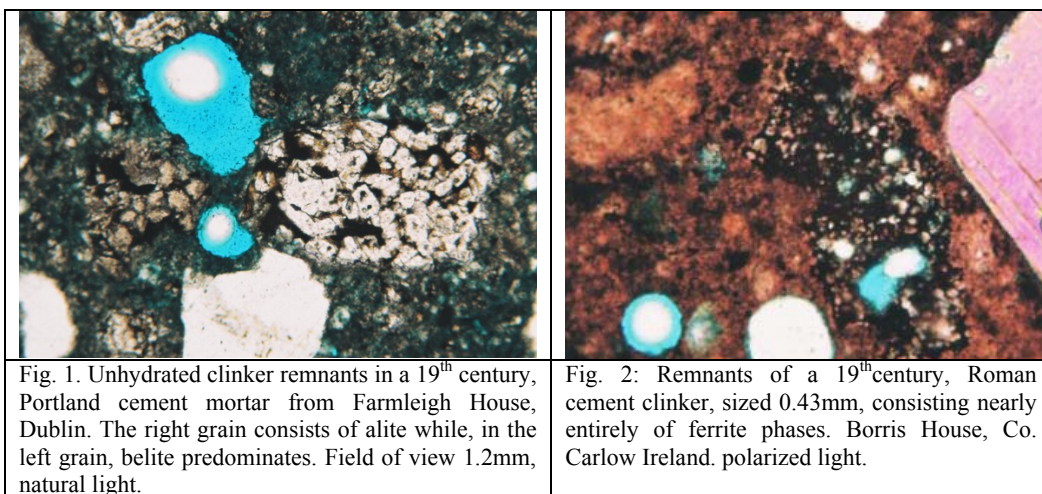
3. RESULTS

3.1 Petrographic evidence of hydraulicity in mortars made with hydraulic binders.

3.1.1 Presence of unhydrated clinker relicts

An infallible proof of binder hydraulicity is the presence of unhydrated clinker relicts. These can be resolved with petrography in Portland (Fig. 1) and Roman cements (Fig. 2) and hydraulic lime mortars both contemporary (Fig. 3) and historic (Fig. 4). In theory, unhydrated relicts are more likely to consist of belite (as alite reacts quickly with water in the first stages of hydration) however, in practice, a variety of clinkers can be identified with petrographic analysis, depending on the kiln temperature; the composition of the raw kiln feed and the fineness of the grinding.

Petrographic assessment of clinker remnants may help to discern the type of hydraulic binder in the mortar. However, this is not always the case and, sometimes, the relict grains may not represent the overall composition of the clinker. Iron-rich hydraulic binders such as Roman cement contain abundant ferrite and, as a result, unhydrated ferrite/aluminoferrite clinker relicts are often evidenced under the microscope (Fig. 2). These may exhibit variable petrographic features, consistent with the fact that ferrite phases do not possess a constant composition but tend to form aluminate-ferrite series (Figs 2 and 5).



In addition, petrographic analysis enables to estimate the fineness and amount of clinker remnants, and these are related to the binder's reactivity and the mortar technology, in particular to the grinding process and water/clinker ratio. Low water/clinker ratios lead to a lack of hydration and therefore enhance the presence of unhydrated relicts.

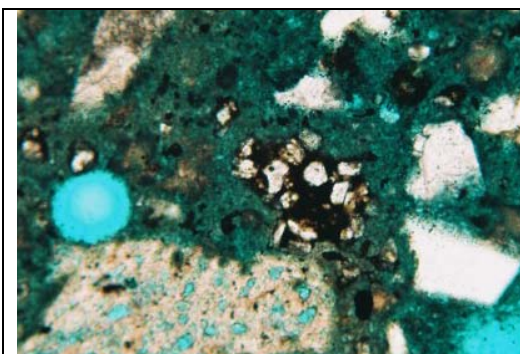


Fig. 3. Natural hydraulic lime (NHL3.5) mortar made in 2000, Royal Hospital Kilmainham. Clinker remnant of belite, sized 0.18mm, in an interstitial ferrite phase and scattered, partially hydrated clinkers. polarized light.

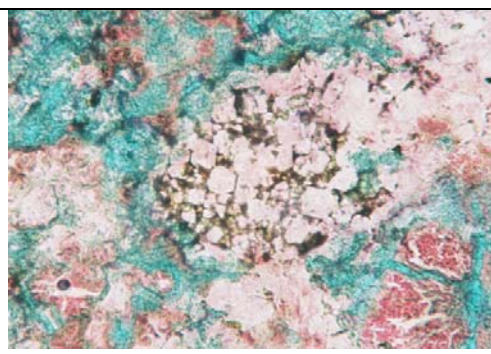


Fig. 4. Partially hydrated cluster of belite crystals with hydration layers in a mortar made with hydraulic lime in the 17th century. Limekiln, Bannow Bay, Co Wexford, Ireland. Field of view 0.3mm, natural light.



Fig. 5. Coarse remnant of unhydrated ferrite, 19th century mortars, Dun Laoghaire Harbour, Co. Dublin. Field of view 1.2 mm. natural light.

Clinker fineness is an important property that determines reactivity: coarse clinkers are resistant to hydration due to their large size (Fig. 5). Today, efficient mill systems grind to the level of fineness required for each cement and hydraulic lime strength class, however, in the past, the grinding process was not that efficient. Coarse clinkers including abundant relicts of unhydrated cement are common in old Portland cement composites (St John [7]), and can also be common in old hydraulic lime mortars and Roman cements. This is probably due to the lower efficiency of the grinding process of old clinker production systems (Livesey pers com 2008).

3.1.2 Presence of hydration products

When water is added to a hydraulic lime or cement, the clinker minerals react with water to form hydration products of which calcium silicate hydrate (C-S-H) and portlandite ($\text{Ca}(\text{OH})_2$) are the most abundant. The C_3S (alite) quickly reacts with water, and C-S-H is formed together with a supersaturated solution of portlandite, from which $\text{Ca}(\text{OH})_2$ crystals are subsequently precipitated in the space originally filled with water and pores. C_2S (belite) follows a similar process, however, at a much slower pace, and producing 2/3rd less of

Ca(OH)₂ (Odler [1]). According to this, a hydrated lime paste should exhibit less Ca(OH)₂ than a cement paste. However, in practice, this may not be the case, and the presence of significant Ca(OH)₂ and gehlenite (together with predominance of C₂S over C₃S) have been proposed to discriminate hydraulic lime from portland cement (Callebaut [12]).

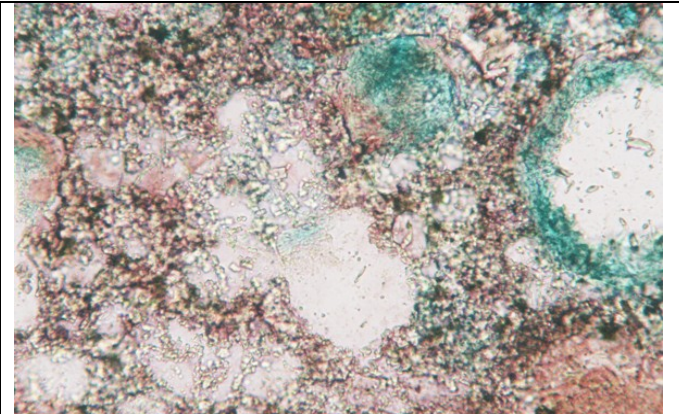


Fig. 6. Detail of crystalline hydration products, probably C-S-H associated to portlandite, and remnants of semi-hydrated clinker (belite). 17th century mortar made with hydraulic lime. Lime kiln, Bannow Bay. Field of view 0.3mm, natural light.

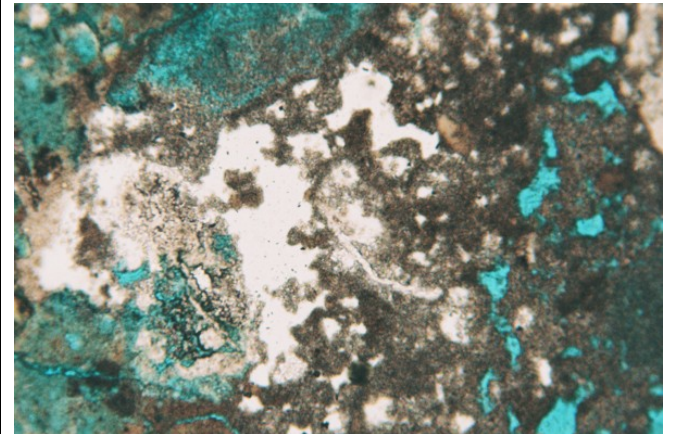


Fig. 7. Remains of an underburnt siliceous limestone particle including amorphous and crystalline hydration products. Mortar made with hydraulic lime c.16th, Williamstown Castle, Co. Westmeath. Field of view 1.2mm, polarized light.

According to Odler [1], Gartner [13] and others, C-S-H is nearly amorphous and isotropic, featureless under the microscope, and exhibits a highly variable chemical composition (structurally related to tobermorite and jennite and to poorly crystalline materials called C-S-H(I) and C-S-H(II)). St John [7] reports that the only C-S-H forming crystals large enough to become optically visible is the α -dicalcium silicate hydrate (α -C₂SH), a high calcium type. In addition, Odler claims that, under ball milling conditions at ordinary temperatures, C₃S hydrates to a crystalline C-S-H known as afwillite.

According to the above, C-S-H is considered by cement petrographers to be mostly amorphous and featureless, however, the author has recorded instances where abundant crystalline hydrates (that can be ascribed to C-S-H) have formed, usually co-existing with amorphous C-H-S. These crystalline

hydrates are colorless (to pale yellow/green) and appear as fibers and plates of high relief (Fig. 6). They have been recorded in hydraulic lime, lime/pozzolan and Roman cement mortars in different forms including: 1- pseudomorphing the silica of underburnt, siliceous limestone particles (Fig. 7); 2- on reaction rims of both pozzolans and aggregate of greywacke, dolerite (Fig. 8) and chert; 3- pseudomorphing semi-hydrated belite relicts (Figs. 6 and 9). This suggests that the C-S-H formed during hydration of hydraulic lime and lime-

pozzolan mortar may exhibit a higher crystallinity than that formed in cement pastes, and this may be due to the higher free lime content of the hydraulic lime and lime-pozzolan systems, where more calcium is available for reaction.



Fig. 8. Amorphous and crystalline hydrates formed in fragment of crystalline rock (probably dolerite), consisting of skeletal olivine and branching plagioclase crystals in a groundmass of plagioclase needles (pozzolanic reaction). Late Medieval lime mortar, St John's Bridge Kilkenny. Field of view 1.2mm, natural light.

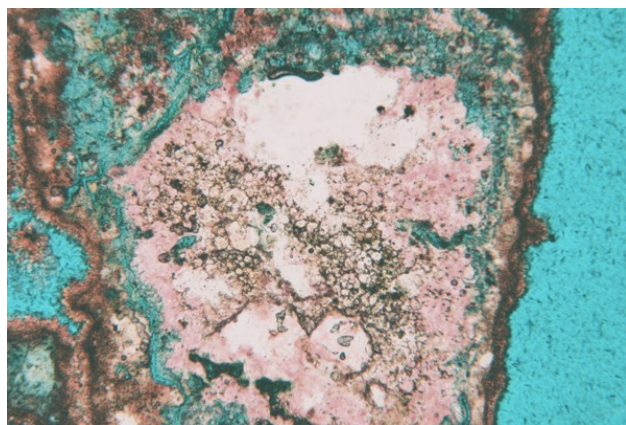


Fig. 9. Hydration layers on belite crystals plus crystalline and amorphous hydrates in a semi hydrated clinker remnant. 17th c. hydraulic lime mortar. Lime kiln, Bannow Bay. Field of view 1.2 mm, polarized light.

The co-existence of crystalline and amorphous C-S-H agrees with previous authors: Massazza [4] evidenced the co-existence of C-S-Hs of different optical properties, and stated that this is consistent with the non-stoichiometry of the C-S-H (determined by the chemical composition of the pore solution).

Hydration layers also provide petrographic evidence of hydraulicity. These have been recorded on clinker minerals (Fig. 9), at aggregate /paste interfaces (Fig. 10) and on incipient hydrate phases scattered in the paste (in both lime (Figs.11 and 13) and hydraulic pastes). The structure of a hydrated paste in the vicinity of rock surfaces differs from that in the bulk material. This transition zone has been studied in Portland cement pastes. According to Odler [1], most investigators report the presence of a thin continuous film of $\text{Ca}(\text{OH})_2$ adhering to the aggregate surface, covered by a second layer of C-S-H gel. However, Odler refers to work by Scrivener reporting that the phase in contact with the

aggregate is most often C-S-H. The results in this paper seem to agree with Scrivener's work, an example is shown in Fig. 10. The presence of ettringite can also constitute a clue to a mortar's hydraulicity because this mineral can form (provided sulfur and calcium are present) as a hydration product, from either the aluminates and silicates of hydraulic binders or the aluminium silicates in pozzolans. However, due to its high solubility, ettringite can also arise from adjacent materials.

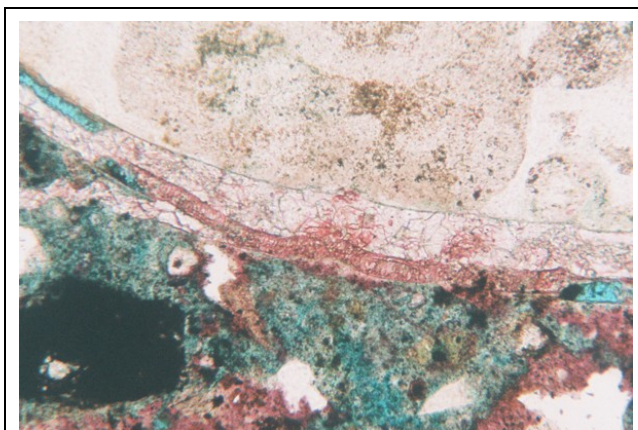


Fig. 10. Hydration layer on chert aggregate, 19th c. mortar, Dun Laoghaire Hbr, Dublin. Field of view 0.6mm, natural light.

3.2 Petrographic evidence of hydraulicity in mortars made with non-hydraulic binders.

3.2.1 Presence of hydration products and pozzolanic reaction in lime-pozzolan mortars

While pozzolans cover a wide range of materials such as natural diatomite, pumicite, tuff and trass, burned clay and shale; and artificial slags, silica

fume, brick and others; according to St John [7], the reactive constituents they contain are restricted to three mineral groups: 1-amorphous silica; 2-glassy and amorphous aluminosilicates; 3-altered aluminosilicates of a zeolitic nature. Therefore, the minerals arising from pozzolanic reaction are very similar to those formed in the hydration of limes and cements, since the overall composition of the two groups fall in the same chemical field. For the same reason, different types of pozzolans produce the same aluminate and silicate hydrates, differences are minor and, in general, affect the amount rather than the nature of the hydrated phases (Massazza [4]). Charola and Henriques [5] report prehnite, leucite, gehlenite, diopside, analcime, melilite as minerals that can be found in lime-pozzolan mortar as a result of pozzolanic activity. They refer to experimental work by Lewin, who identified calcium aluminate and silicate reaction products as chunky polygonal crystals, growing out of pozzolans, in pre-set laboratory conditions. The occurrence of hydrogarnet is associated with the presence of clay minerals and long curing (Massazza [3]).

Pozzolans are materials rich in reactive silica (or alumina plus silica) that react with $\text{Ca}(\text{OH})_2$ and water forming calcium silicate and aluminate hydrates with cementing properties. Pozzolanic reaction involves a reduction of $\text{Ca}(\text{OH})_2$ coupled to an increase in the silica and alumina dissolved. The percentage of $\text{Ca}(\text{OH})_2$ combined by a pozzolan depends on the composition of the pozzolan (mainly on its alkali and active silica content), its specific surface and the conditions of the reaction (water ratio and curing time and temperature) (Massazza [3]). In this paper, the presence and arrangement of hydration products was studied in twenty Roman, brick/lime mortars, ranging from 1500 to over 2000 years in age, originating from twelve structures from six different locations in La Rioja, Spain (Pavía and Caro [14]). Clay brick fragments were abundant in the samples, ranging from approximately 20 to 95% of the total aggregate. The brick size was approximately 10 down to 0.1mm, and its composition variable (most were fine grained calcareous ceramics). It was evidenced under the microscope, that the presence and arrangement of hydration products in the mortars was extremely variable. Some showed no reaction rims at the ceramic-matrix interface (Fig. 11), while others showed wide rims including featureless and crystalline hydrates (Fig. 12). Minerals, new formed as a result of the pozzolanic reaction

(probably diopside/gehlenite), were identified in the carbonated matrix next to brick fragments. In addition, both amorphous and crystalline hydrates, similar to those found in hydraulic lime and Roman cements (Fig. 6, 7 and 9), were present in reaction rims and as cement patches within the binder (Fig. 12). Therefore paper agrees with previous authors on the fact that the hydrates arising from pozzolanic reaction are very similar to those formed in the hydration of hydraulic limes and cements. It was also noted that the mortars whose brick fragments had no reaction rims, included abundant scattered hydraulic phases and new-formed minerals with hydration layers, interspersed within the lime binder, a material sometimes difficult to identify due to its low crystallinity (Fig.13).



Fig. 11. Brick fragments showing no reaction. Abundant hydrate phases in the lime binder. Celtic mortar, I c. B.C., Inestrillas, La Rioja, Spain. 2X (field of view 4.2mm), natural light.

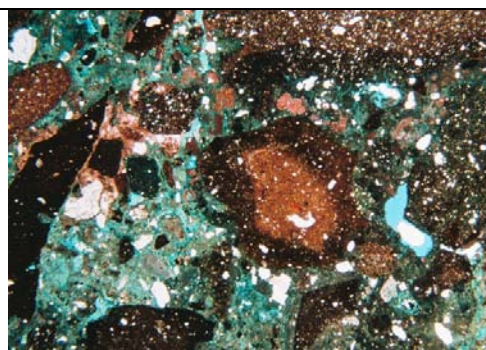


Fig. 12: Brick fragments with wide reaction rims and segregation of hydrates in a Roman mortar dating from V c. AD, Calahorra, La Rioja. 2X natural light.

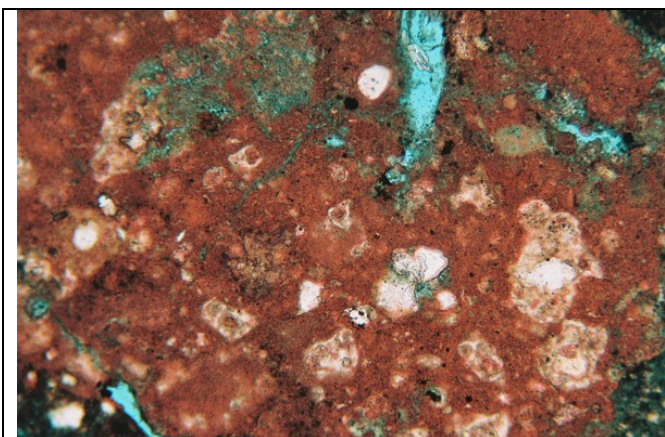


Fig. 13. Scattered hydraulic phases and hydration layers interspersed in the carbonated lime binder in the lime/brick mortar in Fig.11. Field of view 1.2 mm, natural light.

The presence of C-S-H and calcium aluminate hydrate (C-A-H) either at interface reactions or in the lime admixture in lime/brick mortars was outlined by Moropoulou [15]. These authors recorded reaction rims at the ceramic-matrix interface, dispersed as veins in the matrix and filling pores. Their chemical analyses concluded that carbonates are replaced by calcium-silicates and aluminates at the reaction rims. In addition, Baronio and Binda [16] and Baronio

[17] on similar reaction rims, demonstrated the predominance of Ca and Si concluding on the replacement of carbonates by calcium silicates and thus the occurrence of pozzolanic reaction.

3.3 Further petrographic evidence of mortar hydraulicity

3.3.1 Presence of relict fragments of underburnt limestone

Traditional lime production results in both overburnt and underburnt limestone fragments within the mortars. This is well known and has been reported by many authors including Perander [18]; Hughes and Leslie [19] [20]; Pavia and Caro [21] [22]. The presence of relict fragments of underburnt limestone can inform on the type of limestone used as the raw kiln feed and, therefore, the hydraulicity of the resultant lime. For example, the remains of an underburnt siliceous limestone in the mortars of Williamstown Castle (Fig. 6) indicate that the mortar binder is hydraulic lime.

3.3.2 Presence of pozzolanic aggregate

The silica and alumina in minerals need to be reactive for the mineral in question to be considered a pozzolan. However, the results from petrographic analysis suggest that minerals that are generally considered non-reactive may actually possess some reactivity. Both opaline silica and volcanic glass are the most reactive forms of silica because they are the most disordered forms, however, petrographic analysis has evidenced microcrystalline silica such as chert to often react with lime [Pavia 22].

With respect to the alumina, it is generally accepted that clay minerals need to be thermally activated to become pozzolans. Thermal treatment of clays destroys their crystal structures resulting in an amorphous mixture of SiO_2 and Al_2O_3 available for hydration reactions (capable of combining with $\text{Ca}(\text{OH})_2$ and water to form hydrates). However, in lime mortars, reaction rims have been found on clay-bearing rock fragments such as shale or greywacke [Pavia 22]. This may be due to the fact that clay minerals in rocks may naturally contain some amorphous SiO_2 and Al_2O_3 (nature can thermally activate minerals through diagenesis or metamorphism) and thus possess pozzolanicity. Furthermore, Moropoulou [15], reporting on clay-lime reactivity assessed with MAS spectroscopy, concludes that crystalline phyllosilicates are reactive, and can be attacked by lime (although poorly when compared to those on the amorphous state). Finally, the author of this paper has found evidence of hydraulicity involving crystalline igneous rocks such as dolerite (Fig. 8). This agrees with Massazza [3], who states that finely ground crystalline minerals such as alkali-feldspar can also bind substantial amounts of lime.

4. CONCLUSION

Despite the vast amount of research on the kinetics and mechanism of hydration of cement, and the microstructure of the resultant hydrated paste, not many publications seem to be available on equivalent studies on hydraulic limes and lime-pozzolan mortars.

This paper concludes that very similar hydration products to those formed in mortars made with hydraulic lime and Roman cements are present in lime/brick mortars due to pozzolanic reaction. These include amorphous C-S-H cements and crystalline and layered C-S-H.

This work also suggests that the C-S-H formed during hydration of hydraulic lime and lime-brick mortars may exhibit a higher crystallinity than that in portland cement pastes, and this may be due to the higher free lime content of the hydraulic lime and lime-brick pozzolan systems, where more calcium is available for reaction.

In addition, this paper suggests that pozzolanic reaction in lime/brick mortars may be more determined by the chemical and mineral composition of the pozzolan and the conditions of the reaction, than by its specific surface. (In some mortars, no reaction rims were evidenced at the ceramic-paste interface, not even in the fine brick fragments sized down to 0.1 mm).

This paper also indicates that clay-bearing aggregate such as shale and greywacke; microsilica-bearing aggregate such as chert and even crystalline igneous rocks such as dolerite are reactive, and can bind substantial amounts of lime being therefore pozzolanic.

Finally, the paper concludes that even though petrographic analysis does not allow us to precisely quantify mortar hydraulicity, it enables to discern whether a mortar is hydraulic or not and the source of its hydraulicity. The presence of both crystalline and amorphous C-S-H; portlandite crystals, relicts of unhydrated clinkers; hydration layers and pozzolanic reaction rims as well as the identification and arrangement of amorphous silica and aluminosilicates can be determined with petrography providing evidence of hydraulicity.

A chemical study of the mortars in this paper is needed in order to bring any conclusions further.

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