

A PETROGRAPHIC STUDY OF THE TECHNOLOGY OF HYDRAULIC MORTARS AT MASONRY BRIDGES, HARBOURS AND MILL PONDS.

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Abstract

Masonry mortars for underwater works such as bridge piers, harbours and mill ponds are of hydraulic nature. This paper investigates the raw materials and production technology of a number of these mortars. It focuses on the assessment of hydraulicity and the phenomena of delayed sulfate formation and alkali silica reaction (ASR) leading to damage.

Hydraulicity is probably the most important property of a binder. Not only it governs a mortar's cohesiveness and intrinsic bond therefore ruling physical properties and durability, but it also determines site application and performance. Samples of mortars from several structures including Annesley Bridge, St John's Bridge, Dun Laoghaire Harbour and Dundrum Millpond were analyzed with petrography and X-ray diffraction. All the mortars displayed evidence of eminent binder hydraulicity including unhydrated clinker relics of different composition and hydraulic minerals. The identification of specific hydraulic minerals was difficult under the microscope, however, both irresolvable C-S-H, portlandite and other unidentified hydraulic phases were recorded. Blast furnace slags undergoing hydraulic reaction were noted, suggesting the addition of artificial pozzolans; and reactive aggregate showing pozzolanic reaction was also found. In relation to mortar durability, secondary reactions involving microsilica aggregate (ASR) leading to fracturing by expansion were evidenced; and delayed ettringite formation was also common in the mortars studied.

Keywords: hydraulicity, clinker relics, ASR, sulfation, ettringite, pozzolans.

1. Introduction

The petrographic microscope is widely recognised as a powerful tool for the study of natural and artificial materials. Microscopy provides information on the composition of clinker, cement (and other binders), aggregate and additions in mortar, concrete and other composites. It is a powerful technique for the examination of the fabric of mortars and concrete, and can be an efficient means of checking compliance with specification and studying deterioration and failures (St John et al. 1998). This paper studies hydraulic masonry mortars from underwater works including bridges, harbours and mill ponds. Its objective is to explore the technology of these mortars by assessing the source of their hydraulicity (i.e. presence of hydraulic binder and/or pozzolans), as well as secondary reactions leading to damage including delayed sulfate formation and alkali silica reaction (ASR). This is undertaken through petrographic investigation of case studies including Annesley Bridge, Dun Laoghaire Harbour and Dundrum millpond (Dublin) and St John's Bridge (Kilkenny).

The nature of the binder determines a mortar's cohesiveness and its intrinsic bond, therefore, it greatly impacts physical properties and durability. Within the binder, the hydrated material is the main responsible for strength. Mortars containing hydrated material are hydraulic, capable of hardening underwater. 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 the main responsible for the binding

properties of hydraulic composites and therefore their cohesiveness and strength. Hydraulicity is coupled to a faster hardening, higher ultimate strengths and a greater durability. It is probably the most important property of a binder, and an essential feature to be determined in order to both diagnose mortar failure and replicate mortars for repairs. Hydraulicity not only determines the physical properties of a mortar but it also governs its application and site performance.

There are many industrial and traditional binders of hydraulic nature including artificial cements such as Portland cement, natural cements such as Roman cement, natural hydraulic limes and formulated limes. The degree of hydraulicity of these binders varies from feeble to eminent. However, mortars made with non-hydraulic binders can also be hydraulic: hydraulicity can not only reside in the binder, but also in other mortar components such as the aggregate, kiln fuel contamination or pozzolanic additions. 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. According to Massazza (2002), 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).

Even the strongest hydraulic binder can be disrupted by sulfate attack or ASR, and these can be clearly diagnosed with petrographic microscopy. Sulfate attack to hydraulic composites is associated with expansion leading to fracturing and spalling, and this is due to the crystallization of sulfates within the pores of solid material. Sulfate attack by ettringite formation has been known, at least, since the last century (Eckels 1905), and is considered to be the cause of most of the expansion and disruption of PC bound structures (Collepari 2003). However, sulfate formation within a cement paste does not necessarily involve damage by expansion: gypsum and anhydrous calcium aluminate react during the plastic state of the cement mixture to form ettringite. This occurs homogeneously and immediately (within hours) and does not cause any significant disruption but acts as a set retarder (Collepari 2003). However, when sulfates form later, after several months or years, within the rigid frame of a hardened composite, the associated expansion can produce disruption. This paper focuses on the phenomenon of delayed sulfate formation leading to damage.

A further well known problem affecting hydraulic binders in mortars and concrete is caused by the expansive reaction between cement alkalis (Na and K) and minerals in the aggregates. This is known as alkali-aggregate reaction (AAR), however, when the reacting phase is a siliceous component, the term alkali-silica reaction is used (ASR). Expansive silica gels are produced as a result of ASR. These expand as they absorb water into their structure, and the expansive pressure creates a tensile strain within the material that may lead to cracking.

This paper studies mortars made with hydraulic binders including lime with hydraulic properties, Portland cement and Roman cement (the natural cement developed and patented in the 18th century, made by burning septaria nodules). It focuses on the identification, structure and arrangement of hydration products and unhydrated clinker remnants. Pozzolanic reactions involving slag and reactive aggregate, and secondary harmful reactions including ASR and delayed sulfate formation are also investigated.

2. Materials and methods

This study is largely based on petrographic analysis. The petrographic microscope 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 (St John et al. 1998). 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, and these allow examination with transmitted, both polarized and natural light. The petrographic microscope was first developed to study 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 et al. 1998). Today, petrographic microscopy is an established technique for mortar analysis (Charola et al. 1984; Middeldorf et al. 2005). It informs on the composition, origin and proportions of raw materials; and 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 and Bolton 2000). The petrographic microscope has limitations, as the grain size of interstitial components may be under the practical resolution limits of the optical system.

Thin section preparation for petrographic analysis often requires pre consolidation of friable material by impregnation in a resin under vacuum. The thin sections in this paper were impregnated in resin and cut with oils to avoid damage to water-soluble minerals. The samples were dyed with a chemical solution of alizerine and potassium ferrocyanide in order to differentiate carbonate minerals. They were polished to the thickness of approximately 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.

In addition, mortar samples were analyzed by X-ray diffraction (the powder method) with a diffractometer Philips PW 1710, using $Cu K\alpha$ radiation with a voltage of 40 kV and 40 mA intensity. The area was scanned between 3 and 40 degrees 2θ . The powder diffraction method is used for characterization and identification of polycrystalline phases (about 95% of all solid materials can be described as crystalline). When X-rays hit atoms in a crystalline substance, the electrons around the atom start to oscillate with the same frequency as the incoming beam (an electron in an alternating electromagnetic field will oscillate with the same frequency as the field). This produces a destructive interference in almost all directions within the substance (the combining waves are out of phase and there is no resultant energy leaving the solid sample), however, as the atoms in a crystal are arranged in a regular pattern, in a few directions, the interference will be constructive: the waves will be in phase and well defined X-ray beams will leave the sample at various directions (Scintag 1999). This diffracted beam generates a diffraction pattern, and this is recorded in order to characterize and identify the polycrystalline phases in the solid material in question.

3. Results

These concentrate on the assessment of the composition of the raw materials, in particular the type of binder, and on the assessment of deterioration and failure.

3.1 Diagnosis of the type of mortar binder: hydraulicity

Presence of presence of unhydrated clinker relicts

All mortars studied contain clinker relicts, and this is an infallible proof of binder hydraulicity (Figures 1-2). Clinker relicts can be resolved with petrography in Portland and Roman cements and hydraulic lime mortars. In theory, these relicts are more likely to consist of belite (as alite quickly reacts with water in the first stages of hydration) however, in practice, different clinker types can be identified with petrography and, among these, alite is common (Pavía 2008) (Figure 2). The nature of these clinkers depends on the kiln temperature; the composition of the raw kiln feed and the fineness of the grinding (Odler 2007).

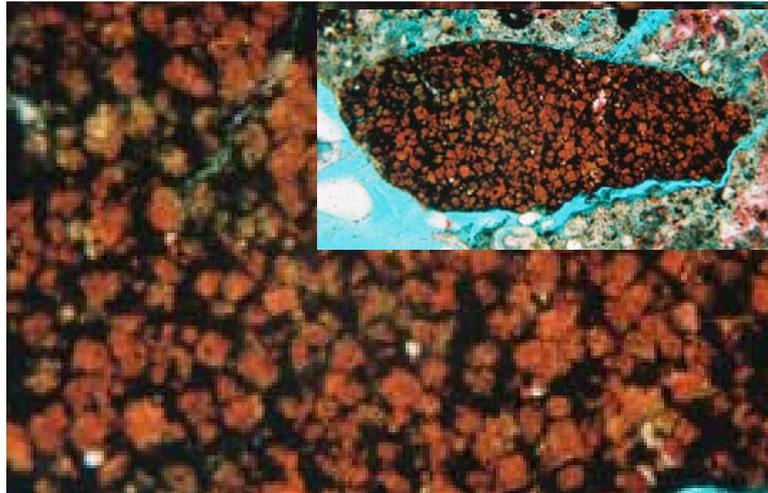


Figure 1 - Ferrite in unhydrated clinker relict. North pier, Dun Laoghaire Hbr. Insert: the clinker grain at a lower magnification (grain 0.9 mm length). Parallel polars.

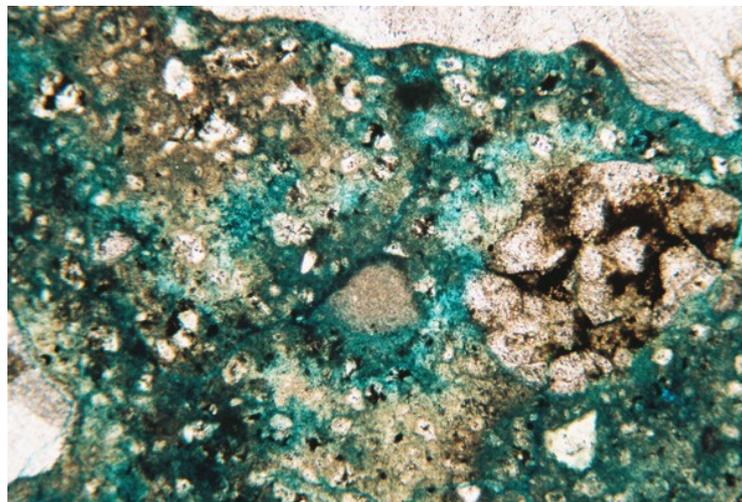


Figure 2 - Unhydrated clinker remnants (probably alite crystals in an interstitial ferrite phase) and abundant hydraulic phases in the paste suggest the use of a binder of eminent hydraulicity. Dundrum Millpond. Field of view 0.6 mm. Parallel polars.

In addition, a petrographic assessment of the composition of clinker remnants may help to resolve the type of hydraulic binder in a particular mortar. For example, iron-rich binders such as Roman cement contain abundant ferrite and, as a result, unhydrated ferrite/aluminoferrite clinker relicts are often evidenced under the microscope. This is the

case of Dun Laoghaire Harbour (Figure 1). Here, the presence of abundant ferrite relicts indicates that the binder was not only hydraulic but also iron-rich, and this suggests the use of natural Roman cement. However, sometimes, the relict grains may not represent the overall composition of the clinker, but exhibit variable petrographic features that do not allow concluding on the nature of the binder. (E.g. ferrite phases do not possess a constant composition but tend to form aluminato-ferrite series).

Presence of hydration products and secondary phases

Both portlandite ($\text{Ca}(\text{OH})_2$) and irresolvable C-S-H were recorded in the hydraulic mortars studied. The presence of portlandite (Figures 3 and 4) and C-S-H (Figures 5 and 6) also evidence the use of hydraulic binders as, in both hydraulic lime and cement, the clinker reacts with water to form hydration products of which C-S-H and portlandite are the most abundant. Clinker mineral C_3S (alite) quickly reacts with water, and C-S-H is formed together with a supersaturated solution of portlandite, from which portlandite 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 $2/3^{\text{rd}}$ less of $\text{Ca}(\text{OH})_2$ (Odler 2007).

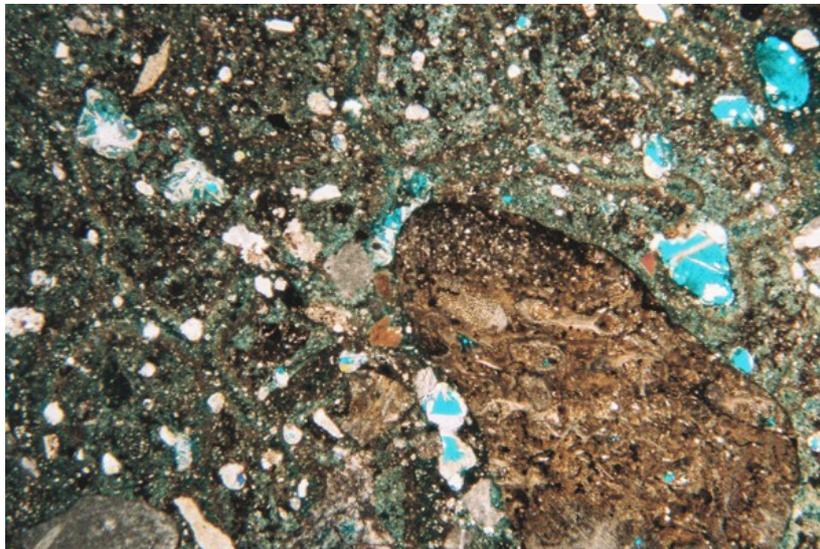


Figure 3 – Petrofabric of Dundrum Millpond mortar with abundant cavities partially filled with portlandite. Field 4.2 mm. Polarized light.

Irresolvable C-S-H, ranging from amorphous to crystalline, was also identified in the mortars. According to cement petrographers, it is difficult to optically resolve C-S-H because it is usually nearly amorphous and isotropic, featureless under the microscope. Furthermore, C-S-H exhibits a highly variable composition (structurally related to tobermorite and jennite and to poorly crystalline C-S-H(I) and C-S-H(II) (Odler 2007; Gartner et al. 2002 and others). In addition, only certain C-S-Hs form optically visible crystals: the high calcium type known as α -dicalcium silicate hydrate ($\alpha\text{-C}_2\text{SH}$) (St John et al. 1998) and afwillite (which only appears in specific conditions, Odler 2007). However, it has been proposed, that the C-S-H formed during hydration of both hydraulic lime and lime-pozzolan mortar may exhibit a greater crystallinity than that 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 (Pavía 2008). This may be the case in the mortar from the pier core of St John's Bridge, (post 1793), containing natural hydraulic lime (Figures 5 and 6).

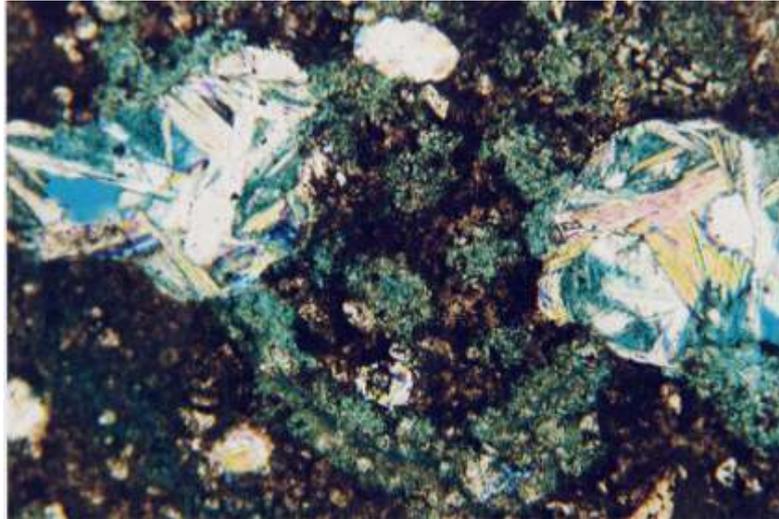


Figure 4 - Detail of figure 3 showing portlandite in the cavities. Field 1.2 mm. Polarized light.

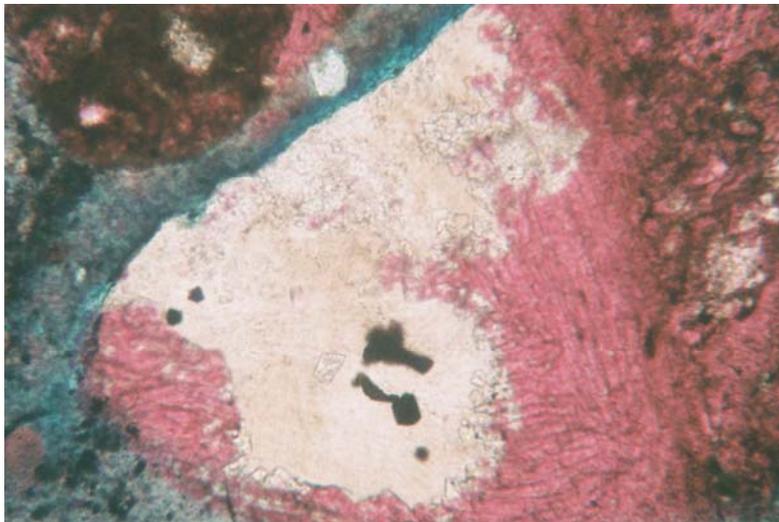


Figure 5 - Hydraulic phases (probably C-S-H) with hydration layers, pseudomorphing fragment of under burnt siliceous limestone. St John's Bridge. Field 1.2 mm. Parallel polars.

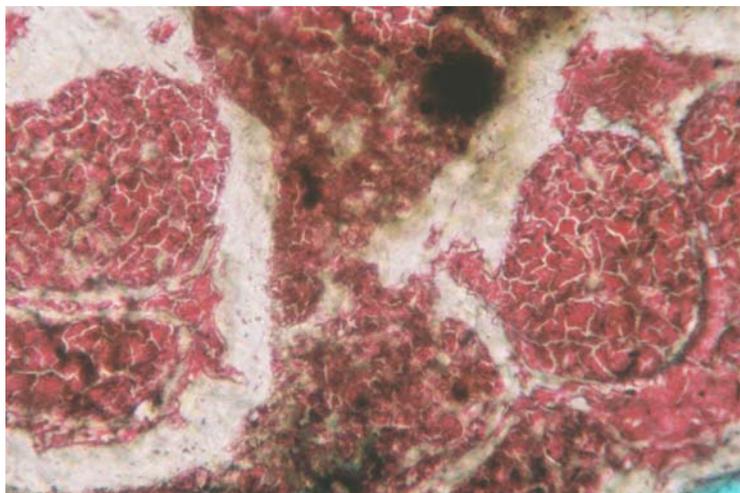


Figure 6 - Detail of the hydraulic material in figure 5. Field of view 0.3 mm. Parallel polars.

Hydraulic lime or Portland cement?

Both hydraulic lime and PC mortars can contain unhydrated clinker relics of variable composition, therefore, this is not an argument for discrimination. However, in hydraulic limes, C_2S (belite) predominates over C_3S (alite) therefore, on thin section, belite relics should be more abundant than those of alite. Yet, in practice, this may not be the case, and a variety of clinkers can be identified in both hydraulic lime and Portland cement.

The presence of significant $Ca(OH)_2$ (and gehlenite) has been proposed as an argument to discriminate between hydraulic lime and PC (Callebaut et al. 2001). However, this may not always be the case as, a hydrated lime paste should exhibit less $Ca(OH)_2$ than hydrated cement paste because it contains more C_2S than C_3S , and C_2S produces $2/3^{rd}$ less $Ca(OH)_2$ than C_3S on hydration. Other petrographic features such as the presence of under burnt limestone (Figures 5 and 7) and the identification and arrangement of hydration products (see above) can assist to conclude on whether a mortar was made with hydraulic lime or cement. For example, the under burnt siliceous limestone in the St John's Bridge mortar suggests the use of natural hydraulic lime to make the mortars. This was evidenced in both the bridge destroyed by the flood of 1763 (Figure 7) and that built to replace it (Figure 5).

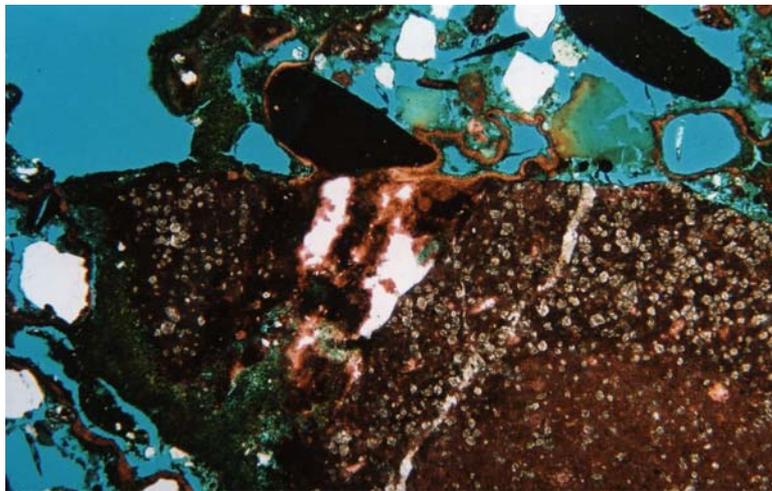


Figure 7 - Hydraulic phases inside under burnt siliceous limestone evidence the use of natural hydraulic lime as a binder. Mortar from the pier core of St John's Bridge (destroyed by the flood of 1763). Field of view 4.2 mm. Parallel polars.

Presence of pozzolans and pozzolanic aggregate

Pozzolans react with lime and water forming calcium silicate and aluminate hydrate cements (pozzolanic reaction). This reaction is usually fast, and the cements generated mechanically strong and water insoluble. Pozzolans are added to binders in order to enhance their cementation; speed up their initial hardening and increase the ultimate strength of their composites. This has been a common practice since, at least, the Roman times, and today, a wide range of artificial pozzolans (most of them industrial by-products) are added to Portland cement binders for concrete production. However, pozzolans can also be naturally present in a composite, for example, as reactive aggregate. Pozzolanic aggregate was recorded in the St John's Bridge mortar, destroyed during the 1763 flood (Figure 8); and pozzolanic additions (slag) evidenced in the mortar of the bridge post-dating the flood (Figure 9).

The silica and alumina need to be reactive for the mineral in question to be considered a pozzolan. Among the most reactive materials are disordered silica (opal and volcanic glass)

and thermally activated clays (thermal treatment of clays destroys their crystal structures resulting in an amorphous mixture of SiO_2 and Al_2O_3 available for hydration reactions). However, petrographic analysis suggests that minerals that are considered non-reactive may possess some reactivity (Pavía 1990-2006; Pavía 2008). For example, hydraulic reaction involving crystalline igneous rocks (Figure 8) was noted in the mortars from St John's Bridge. This agrees with Massazza (2007), who states that finely ground crystalline minerals such as alkali-feldspar can also bind substantial amounts of lime.

As aforementioned, the addition of slag as a pozzolan was also evidenced (Figure 9). The analysis suggests that this is probably a ferrous blast furnace slag (a waste product from the smelting of iron ores). The slags recorded are not fully crystalline, a plus to their hydraulic activity as, according to St John et al. (1998), crystalline blast furnace slag has little reactivity.



Figure 8 - Amorphous and crystalline hydrates formed in a pozzolanic aggregate (a fragment of crystalline rock, probably a dolerite). Top left insert shows detail of the pozzolanic reaction. St John's Bridge pier core, destroyed by the 1763 flood. Field of view 4.2mm. Parallel polars.

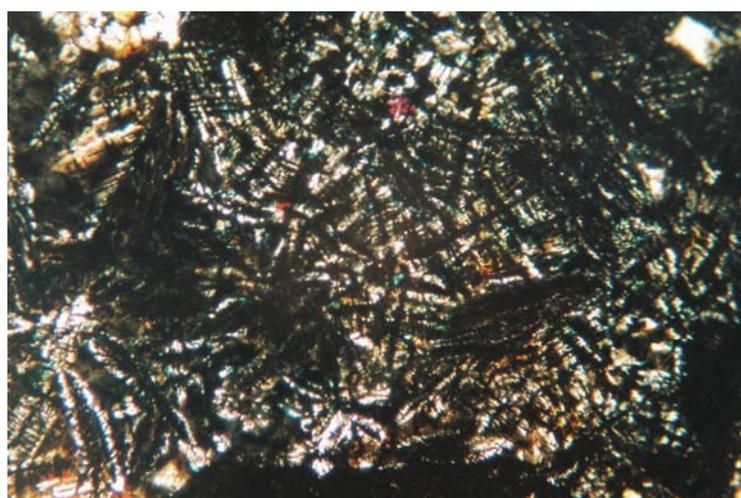


Figure 9 - Blastfurnace slag evidencing the use of artificial pozzolans to make the mortars of St John's Bridge piers, built after the flood of 1763. Field of view 1.2mm. Parallel polars.

3.2 Diagnosis of deterioration and failure: sulfate attack and AAR.

Sulfate attack

As aforementioned, the expansion associated to the crystallization of sulfates within the pores of hydraulic composites is currently considered to be the cause of most of the disruption of PC bound structures. Delayed sulfate formation leading to damage was recorded in the mortars from Annesley Bridge, Dun Laoghaire Harbour and Dundrum Millpond. The sulfates detected are ettringite and gypsum (Figures 10 and 11). Their microscopic fabrics (large crystals in cavities and fractures- Figures 12 and 13) suggest that these have not crystallized during the plastic state of the paste but they have formed later, within the rigid frame of the hardened composite. Fractures recorded within the paste (Figure 12), suggest that sulfate formation is associated to expansion and disruption.

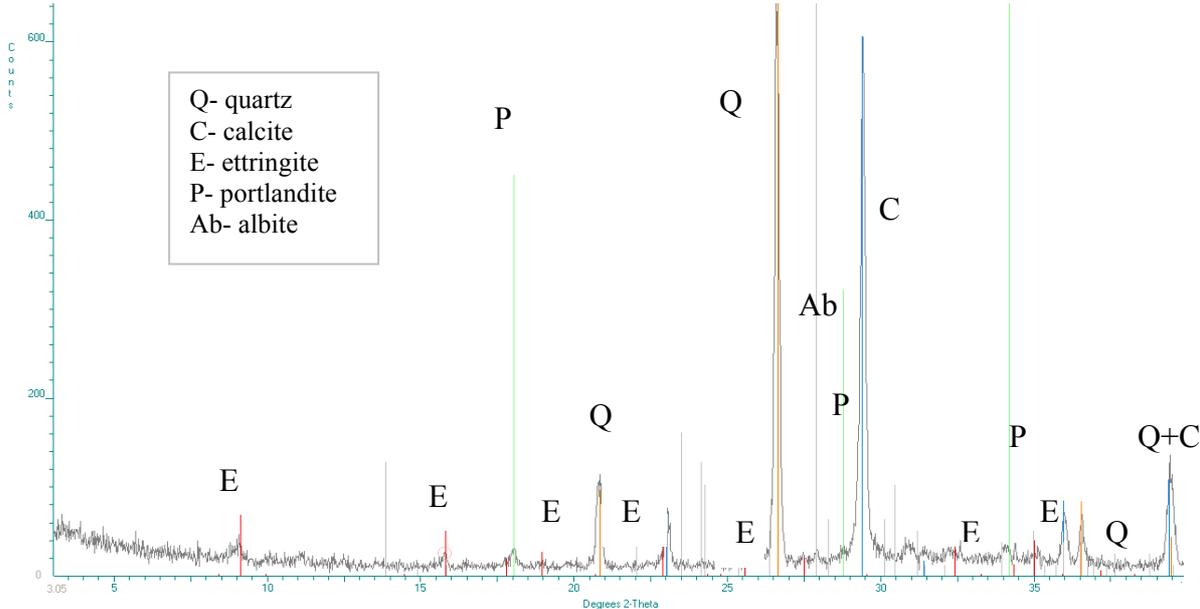


Figure 10 – X-ray diffraction pattern of the Annesley Bridge mortar showing ettringite.

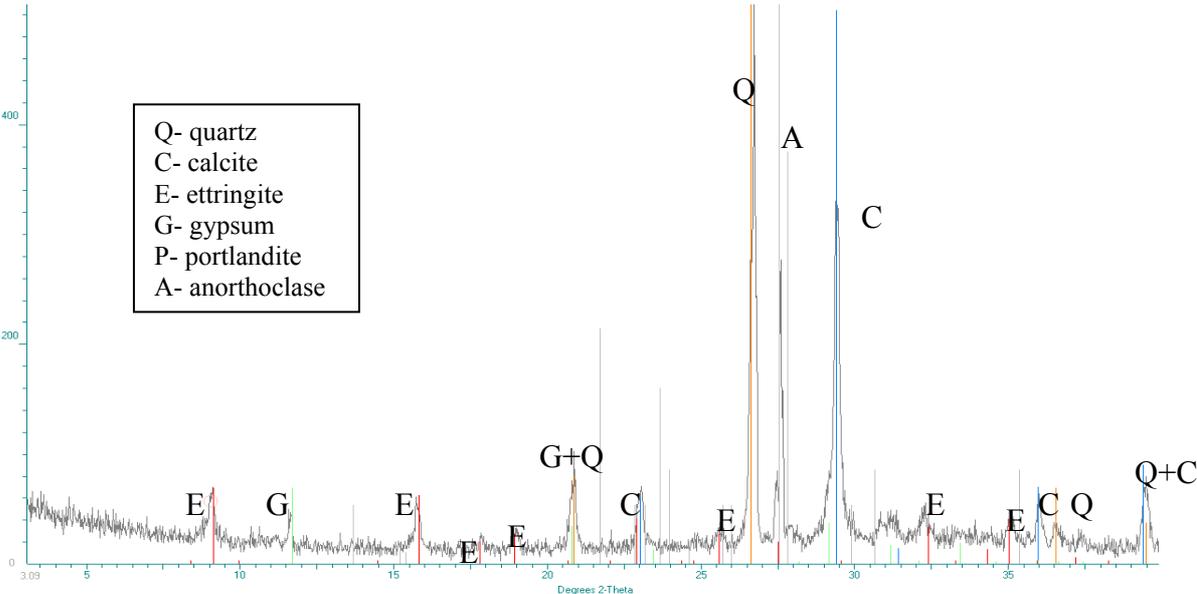


Figure 11 – X-ray diffraction pattern of Annesley Bridge mortar showing ettringite and gypsum together with other minerals in the aggregate and the paste.

The occurrence of these sulfates is strongly connected with water migration (all mortars investigated belong to water related structures). No specific research to determine the source of the sulfate ions was undertaken. However, it is likely that external sources including sea water and contaminated soil (sulfates are widely distributed in nature and present virtually in all soils) have contributed to the sulfation of the Dun Laoghaire and the Dundrum mortars respectively; while an internal source probably a sulfur-rich cement clinker may be responsible for the damage to the Annesley Bridge.

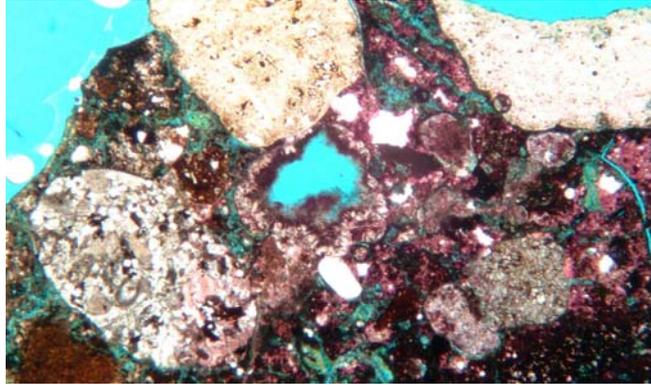


Figure 12 - Dun Laoghaire Harbour. Fractures within the paste evidence that sulfate formation (centre) is associated to expansion. Field of view 4 mm. Parallel polars.

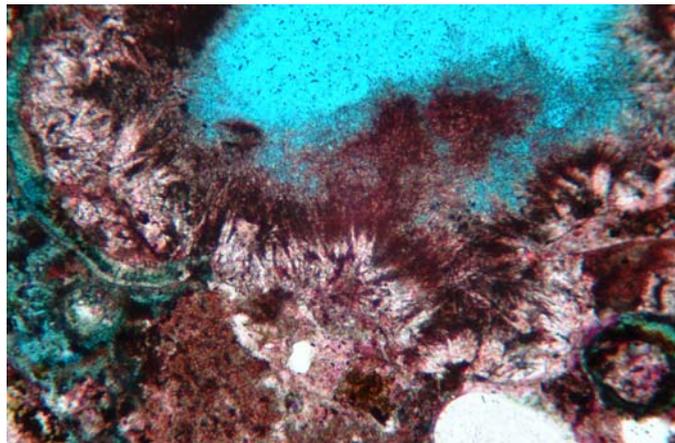


Figure 13 - Detail of figure 12 showing ettringite in the central cavity. Field of view 0.6 mm. Parallel polars.

Alkali-aggregate reaction

Reactions between cement alkalis and minerals in the aggregate (AAR) had taken place in all mortars studied. In most of these reactions, microsilica aggregate was the reactive phase (ASR) (Figures 14 and 15). Crystalline rocks (probably dolerite) were also found to have reacted with the binder, and amorphous and crystalline hydrates pseudomorphing the aggregate had formed (Figure 8). However, as explained above, this particular reaction was resolved as pozzolanic, and no expansion or damage was associated to it.

Not all ASRs were associated to cracking. This may be due to either the nature of the compounds generated as a result of the reaction (only some compounds may be expansive) or differences of tensile strength within the material (locally, the material's tensile strength may be greater than the tensile strain generated). The lack of cracking, despite ASR taking place,

can also be ascribed to the use of hydraulic lime a binder with a greater elasticity that can accommodate tensile strain within the hardened paste. This may be the case in the mortar from the core of St John's Bridge pier (Figure 15).

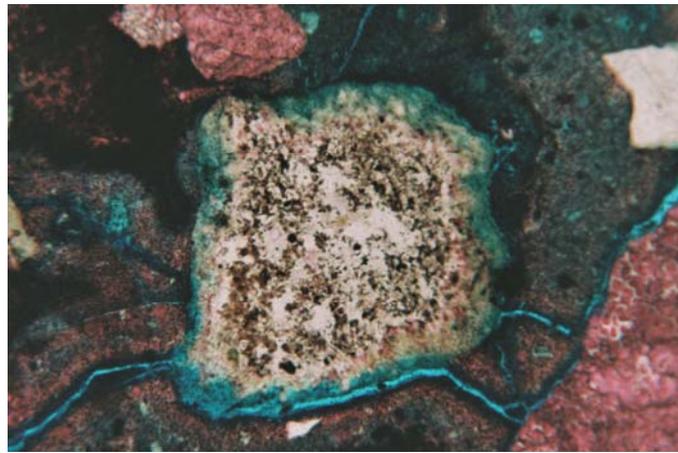


Figure 14 - Cracking probably associated to expansive reaction between alkalis in the paste and microsilica aggregate (ASR). Mortar core of St John's Bridge pier (post 1763). Field of view 1.2 mm. Parallel polars.

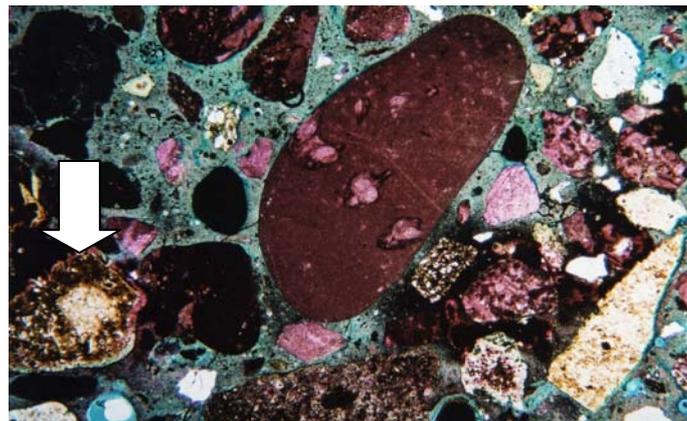


Figure 15 - Petrofabric of a mortar from the core of St John's Bridge pier (post 1763). Chert aggregate has reacted with the binder (ASR at lower left corner), however, there is no expansive cracking in the paste. Field 4.2 mm. Parallel polars.

4. Conclusion

All the mortars displayed petrographic evidence of eminent binder hydraulicity including unhydrated clinker relics of different composition and hydraulic minerals. The identification of specific hydraulic minerals was difficult under petrographic examination, however, both irresolvable C-S-H, portlandite and other unidentified hydraulic phases were noted. Blast furnace slags undergoing hydraulic reaction evidenced the addition of artificial pozzolans; and reactive aggregate showing pozzolanic reaction was also recorded. The study revealed that the mortars of St John's Bridge (both the bridge destroyed by the flood of 1763 and that built to replace it) were made with natural hydraulic lime and strengthened by adding blast furnace slag as a pozzolan. In addition, the analyses indicate the use of Roman cement to

make the mortars of Dun Laoghaire Harbour. In relation to mortar durability, secondary reactions involving microsilica aggregate (ASR) were confirmed not to always lead to fracturing by expansion. Delayed sulfate formation (ettringite and gypsum) was recorded in the mortars from Annesley Bridge, Dun Laoghaire Harbour and Dundrum Millpond. The microscopic fabrics of these sulfates and the expansion associated suggest that these have not crystallized during the plastic state of the paste but they have formed later, within the rigid frame of the hardened composite.

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