

Sulfation of a decrepit Portland cement mortar and its adjacent masonry.

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Abstract

This paper concentrates in the phenomenon of sulfate formation within an old cement paste dating from c.1878, leading to damage of the mortar and its adjacent masonry. Samples of mortar and salt efflorescence were taken for XRD, XRF, petrographic and SEM/EDAX analyses. SEM/EDAX revealed detail on the clinker microstructure and the presence and arrangement of sulfates including kieserite, syngenite and calcium langbeinite. Gypsum, thenardite, picromerite, aphthitalite, ettringite, niter and potassium calcium carbonate were detected by XRD analysis. Under the petrographic microscope, the mortars displayed strong damage by expansion with abundant, fractured, residual cement clinkers, extensive sulfate replacement, carbonation and alkali-aggregate reaction.

The paper concludes that damage is caused by sulfation (mainly by gypsum and thenardite). Sulfate damage is closely related to the location of the portland cement (PC) repair, suggesting that the sulfate source is internal, originating from a sulphur-rich clinker phase in the cement. However, ground contamination is probably a further source for sulfate. Based on the nearly total absence of ettringite and other calcium sulfoaluminates and the abundance of alkali sulfates such as thenardite and aphthitalite, the paper suggests that the original cement clinker was low in aluminium and probably high in alkalis. Gypsum was the most common phase recorded in the solid mortars whereas thenardite was the most abundant phase in the efflorescence. This may be due to the lower solubility of gypsum when compared to that of thenardite. This paper also concludes that, despite the vast amount of outstanding research on the reactions responsible for sulfate release from primary cement phases such as primary ettringite and C-S-H, the 'time elapsed' is an important parameter that is often overlooked. For example, does decomposition of primary ettringite take place only at high temperatures ($>70^{\circ}\text{C}$) or can this take place at ambient temperatures over long time periods i.e. 100 years?

Keyword

Alkali cement, high-sulfur clinker, gypsum, thenardite, picromerite, aphthitalite.

1. Introduction

Sulfate attack to PC composites and masonry has been studied by many authors. This process is associated with expansion leading to fracturing and spalling induced by the crystallization of sulfates within the pores of solid material. For example, crystallization of calcium and sodium sulfates i.e. thenardite and gypsum is considered to be responsible for significant damage to masonry and concrete and has been studied in detail.

In addition, sulfate attack to PC composites by ettringite formation has been known, at least, since the last century (Eckel 1905), and is considered to be the cause of most of the expansion and disruption of PC bound structures (Collepardi 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 (Collepardi 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 by cracking and spalling. This paper concentrates in the phenomenon of delayed sulfate formation within an old cement paste leading to strong damage.

The occurrence of sulfates (and other soluble salts) in walls is strongly connected with water migration. They become concentrated and precipitate when water moves in one direction and evaporates, this is the case in the upper zone of rising damp (Arnold 1984). Conditions necessary for masonry/ mortar and or concrete damage by salt crystallization are permeability, a source for salt and the presence of moisture. The types and concentrations of salts found in concrete and masonry vary greatly and depend on the material type and the environment around the building.

The source of the sulfate ions required for sulfate formation can be internal or external. External sulfate attack occurs when environmental sulfate arising from atmospheric pollution, ground water or contaminated soil enters the material whereas internal sulfate attack occurs, in a sulfate-free environment, when the sulfate source is inside the material. Internal sulfate sources can be sulfur-rich cement clinkers, contaminated aggregate and the stone or brick masonry.

Salt attack to masonry has been related to mortar types. For example, sulfate attack has been linked to the presence of cement mortars as well as pozzolanic mortars (hydraulic but not cementitious); and alkali carbonates are indicative of the use of Portland cement in restoration (Arnold 1984).

This paper investigates sulfate damage at Christchurch Cathedral, a National Monument dating from Mediaeval times and largely rebuilt in the 19th century. The work concentrates on one of the remaining sections of original masonry: the crypt's piers. These limestone masonry structures, originally built with calcium lime mortar in the 12th century, were later repaired with a low aggregate: binder ratio Portland cement mortar circa 1878.

2. Materials and Methods

A condition assessment of the masonry evidenced significant material loss coupled to salt efflorescence, the damage being stronger at the plinth of the piers. In order to conclude on the cause of stress and disruption, samples of mortar and salt efflorescence were taken for analysis. The analytical techniques focussed on the assessment of the damage as explained below.

2.1 Sampling

Samples of PC mortars and salt efflorescence were taken for analysis. As aforementioned, all the materials were sourced from the plinth of the Medieval masonry piers at the Cathedral's crypt. The height above the ground varied between 10 cm and 1 m.

2.2 X-Ray diffraction and X-Ray fluorescence analyses

Samples of salt efflorescence and weathered mortar were analysed by XRD (the powder method) with a diffractometer Philips PW 1710 using Cu K α radiation with a voltage of 40 kV and an intensity of 40 mA. The area was scanned between 5 and 60 degrees 2 θ . This technique provided a record of the mineral phases in the salt efflorescence. The samples were run in parallel through a X-Ray fluorescence meter in order to determine the major elements so as to facilitate X-ray identification.

2.3 SEM/EDAX analyses

The PC mortars were studied with a scanning electron microscope (SEM). The analytical system employed was a Zeiss DSM-950 SEM equipped with a backscattered electron detector and a LINK-QX 2000 energy dispersive X-ray analysis attachment (EDXA). Spectrums were taken with a voltage of 20 kV through a beryllium window. The system revealed detail on the clinker microstructure and the nature and extent of the sulfate damage. It provided high-resolution, three-dimensional images of relicts of cement clinker, aggregate, binder and secondary mineral phases allowing to record fracturing, aggregate-binder reaction and qualitative elemental analyses of specific areas.

2.4 Petrographic microscopy

Thin sections of PC mortars were prepared for petrographic analysis. The samples were cut with oils to avoid damage to water-soluble 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.

Petrographic analysis mainly focused on the detection of secondary reactions and fracturing; and on the identification and location of secondary compounds formed due to weathering. The extent of carbonation and the composition of relict cement phases were also investigated.

3. Results

3.1 X-Ray diffraction

Crystalline phases determined in the salt efflorescence are included in Table 2 and representative records shown in figures 1, 2 and 3. The predominant phase in the efflorescence was thenardite. Gypsum, picromerite, apththialite, niter and potassium calcium carbonate (probably fairchildite) were also recorded. Traces of ettringite and thaumasite may also be present. The low amount of ettringite and thaumasite and their nearly identical position of their XRD peaks did not allow for further discrimination.

sample	X-ray	notes
cch2s	T / P	results in fig. 1
cch3s	G / N/ F	results in fig. 2
cch5	E / th	traces
cch5s	T / A	results in fig. 3
cch6s	T / A	-
Sm2s	T / G	-

Table 2. Salts determined with XRD: T -Thenardite- Na_2SO_4 ; P-picromerite- $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; G -gypsum- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; N-niter- KNO_3 ; F- fairchildite - $\text{K}_2\text{Ca}(\text{CO}_3)_2$; E-ettringite- $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$; th- thaumasite- $\text{CaSO}_4 \cdot \text{CaCO}_3 \cdot \text{CaSiO}_3 \cdot 15\text{H}_2\text{O}$; A -apththialite- $\text{K}_3\text{Na}(\text{SO}_4)_2$;

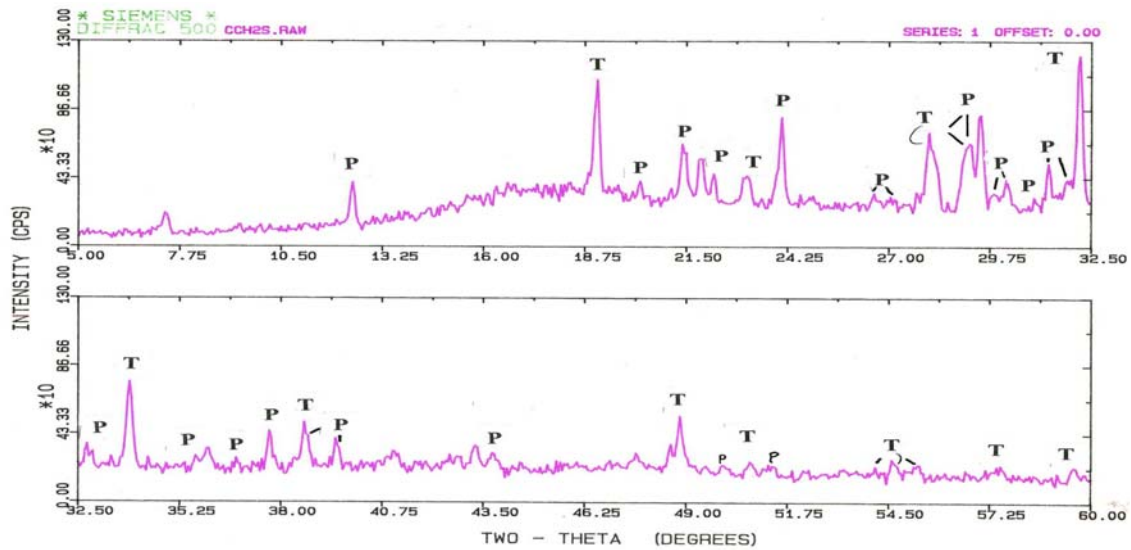


Figure 1. T -Thenardite- Na_2SO_4 ; P-picromerite- $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

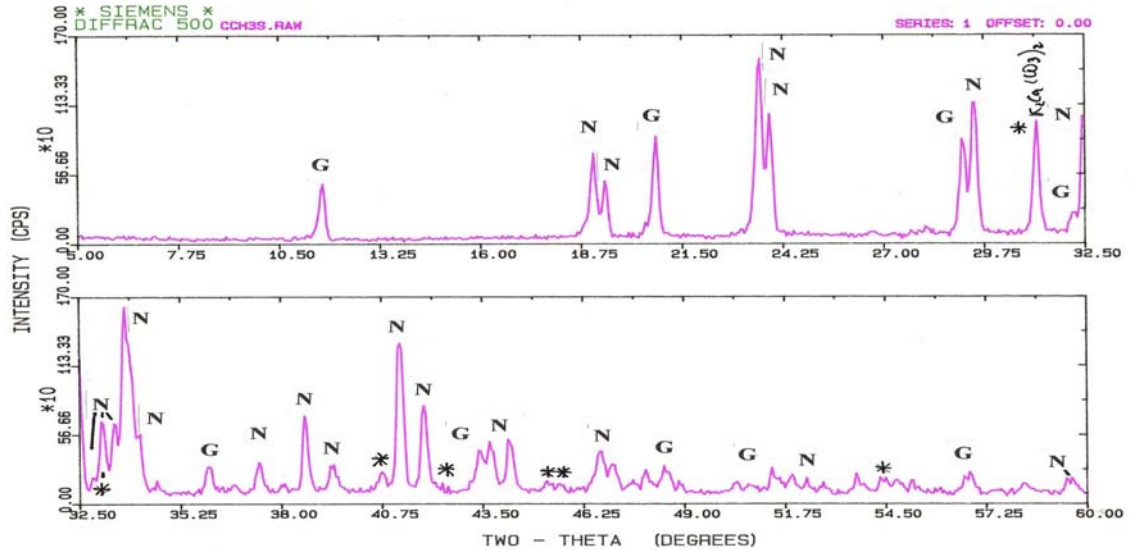


Figure 2. G-gypsum-Ca SO₄.2H₂O; F- fairchildite -K₂Ca (CO₃)₂ and N-niter-KNO₃

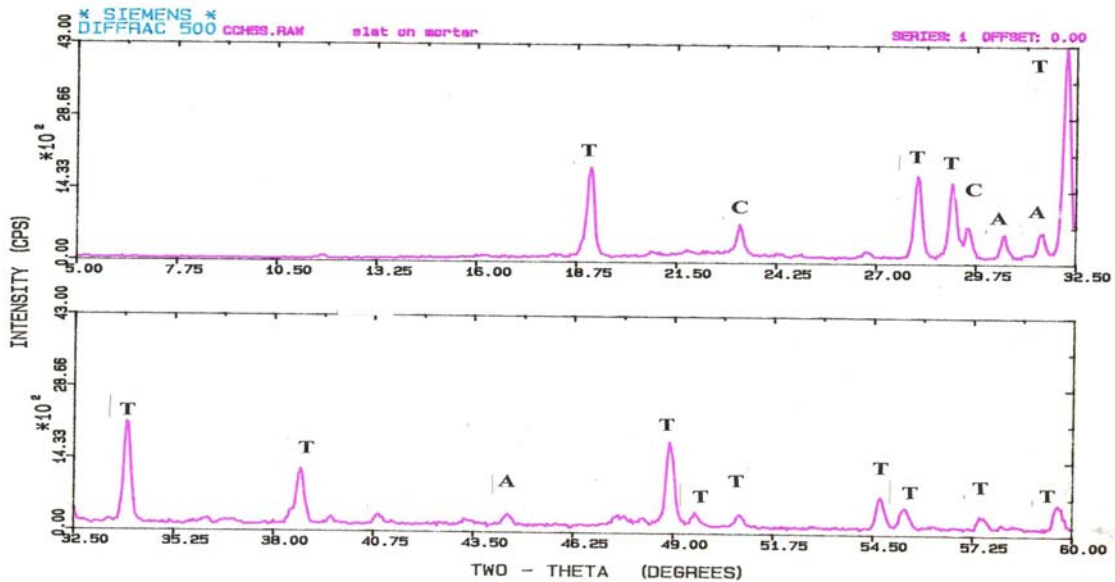


Figure 3. T -Thenardite- Na₂SO₄; C-calcite- Ca CO₃; A-apthitalite-K₃Na(SO₄)₂

3.2 SEM/EDAX

While the XRD analyses above evidenced specific sulfates, under the SEM, it was clear that these occurred in association, forming complex microstructures. Under the SEM, sulfates were found with different habits in various associations. For example, as illustrated in figures 4 and 5, gypsum often appeared as either fibrous or granular and massive as well as in euhedral plates; associated to a number of other sulfates including syngenite and Na and Mg sulfates.

These sulfate associations could not be determined in detail due to the limitations of the chemical image provided by the EDXA detector. This detector, an energy-dispersive analytical system, is not completely accurate because, as a result of the interaction of the electron beam with the specimen, the spectrum obtained may

include chemical elements from adjacent minerals rather than only those specific from the area scanned.

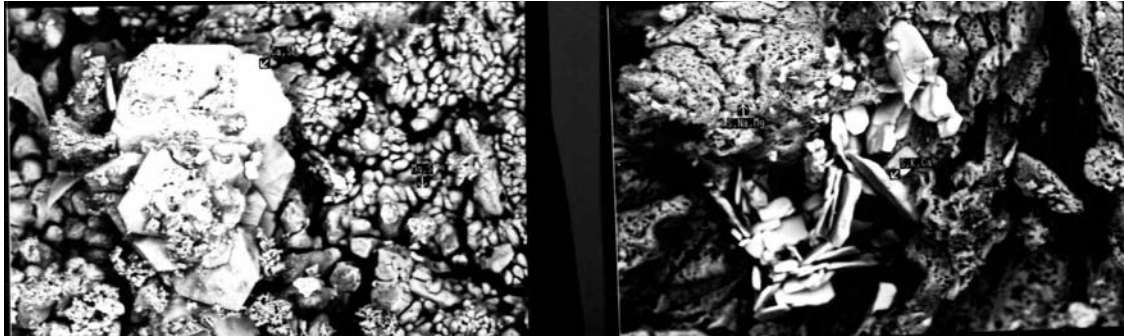


Figure 4: (left) Euhedral gypsum plates (approx. 100 μm across) and small magnesium sulfate crystals (probably kieserite $-\text{Mg SO}_4 \cdot \text{H}_2\text{O}-$ because of the granular to prismatic habit).

Figure 5: (right) Cross sections of tablets of K and Ca sulfate (possibly syngenite $-\text{K}_2\text{Ca} (\text{SO}_4)_2 \cdot \text{H}_2\text{O}-$ or calcium langbeinite $-\text{K}_2 \text{SO}_4 \cdot 2\text{Ca SO}_4-$) and massive clusters of interlocking fibres of Mg and Na sulfates. Field of view 0.20 mm.

According to the SEM analysis, the mortar matrix evidenced strong expansion. It was fractured and extensively replaced by secondary sulfates and carbonates (figs 6, 7, 8). Secondary reactions involving aggregate were also evidenced: calcite precipitate around aggregate (figure 9) may be the result of a combination of ASR-induced fracturing followed by crystallization of secondary calcite filling these fractures and partially replacing the surrounding matrix.

Unhydrated relics of cement clinker were common in the mortar. These often included hexagonal, pseudo-hexagonal and prismatic alite crystals in interstitial ferrite phases (Figure 6). The interstitial phases were not always ferrite but were often found to form calcium aluminate-ferrite series (figures 6 and 10).

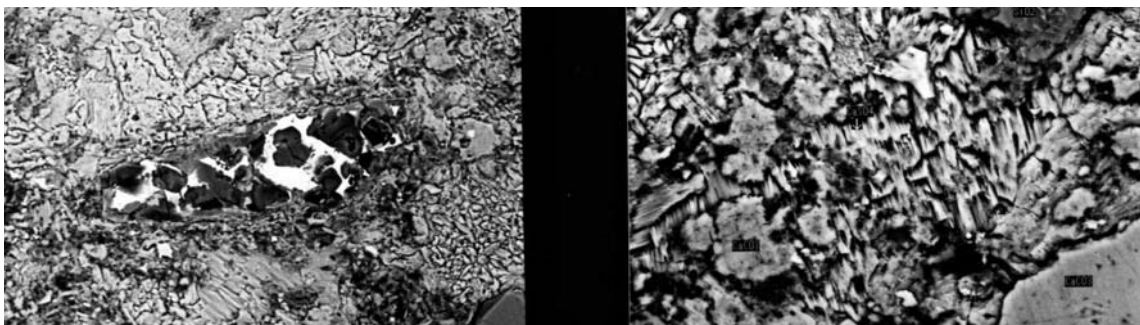


Figure 6: (left) Unhydrated relic of cement clinker (170 μm) including hexagonal and prismatic alite crystals in an interstitial ferrite phase. This is surrounded by an extensively sulfated and carbonated paste with gypsum, thenardite and calcite.

Figure 7: (right) Abundant fibrous gypsum surrounding 'islands' of carbonated paste (lower right corner) and silica gel (top right). Field of view 0.11 mm.

Fibrous gypsum was abundant in both the matrix (figure 7) and fractures (figure 8). In fractures, it was often found in association with alkali and magnesium sulfates (figures 8 and 10). Granular massive gypsum was also common in the matrix (figure 7).

Alite crystals within unhydrated clinker relicts were found to incorporate low, variable amounts of Mg and K (figure 9). Very little aluminium was recorded with the EDXA detector, this agrees with the XRD results, as these only evidenced traces of sulfoaluminates (ettringite).

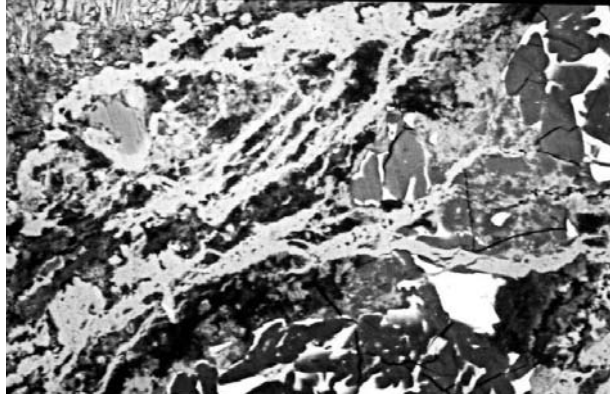


Figure 8. General view of the PC mortar showing strong expansion. Abundant fractures are filled with gypsum, alkali and magnesium sulfates such as picromerite $K_2Mg(SO_4)_2$. The remains of the cement paste include unhydrated clinker relicts (upper right corner) probably forming series including low, variable amounts of Mg and K) and carbonated areas (e.g lower right corner).

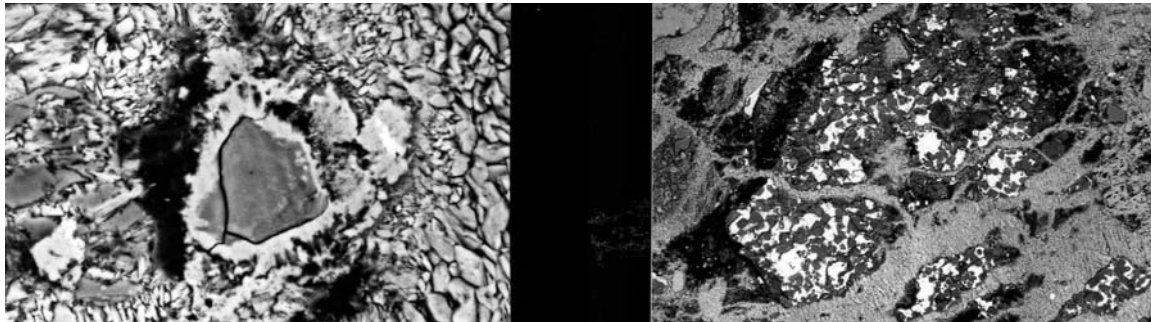


Figure 9. (left) Calcite precipitate around aggregate, surrounded by a sulfated and carbonated paste. Field of view 0.11 mm. Possible processes: secondary calcite filling fracture around aggregate and replacement of C-S-H by calcite.

Figure 10. (right) Fractured relic of cement clinker (approx 600 μm in length) including alite and, possibly, some belite in an interstitial phase of calcium aluminate. The general microstructure denotes strong expansion. Fractures are filled with thenardite and gypsum often combined with other sulfates.

3.3 Petrographic microscopy

Thin sections of the PC mortar revealed strong damage by expansion. In several areas, the original mortar was totally replaced by sulfate (mainly gypsum) and carbonate;

and it was clear that gypsum had gradually replaced the C-S-H, main responsible for the binding capacity of the cement paste. As reported by previous authors (Colleparidi referring to Mehta 1993), sulfate attack not only causes expansion but also decalcifies C-S-H transforming it into sulfate (gypsum, ettringite, thaumasite or Mg sulfate) thus causing the loss of strength and adhesion of the cement paste. In the mortars analysed, replacement by sulfates and calcite was so intense, that it was no longer possible to determine the original mortar components (figure 11).

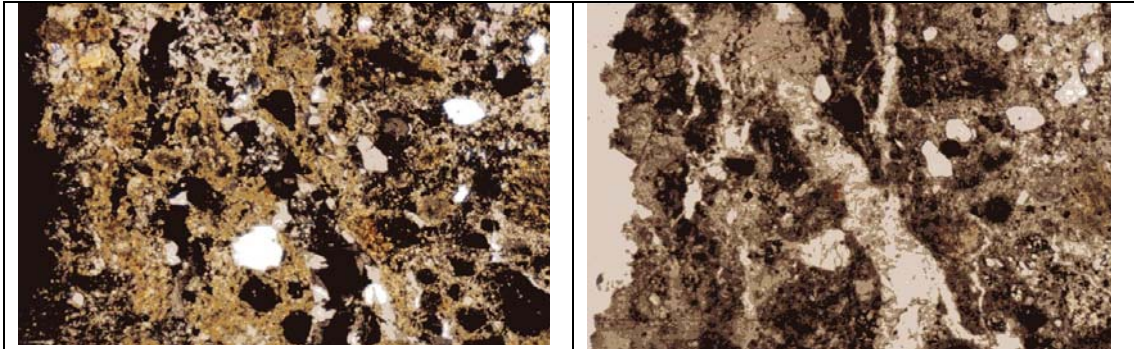


Figure 11. General microfabric of PC mortar with abundant fractures filled with sulfates, mainly gypsum (see text). Scarce quartz aggregate in a heavily sulfated and carbonated matrix. Left polarised light. Right natural light. 2.5X. Field of view approx. 5 mm.

Very abundant, both colourless and brown clinker were recorded with petrographic analysis. Together with the original clinker, a wide variety of secondary minerals formed as a result of weathering were identified. These include brucite ($Mg(OH)_2$), portlandite ($Ca(OH)_2$) and zeolites as well as gypsum, thenardite, ettringite and other salts that were not identified. The analysis also revealed reactive microsilica (chert) within the aggregate. The microstructure of fractured aggregate suggests sulfate expansion rather than alkali-silica reaction (ASR) (figure 12). However, it is possible that, initially, ASR had induced cracking, and these cracks were later filled with sulfates leading to the strong expansion now featured by the cracked aggregates.

In summary, petrographic analysis evidenced that the attack had taken many forms including sulfate formation, ASR and the formation of other secondary mineral phases such as zeolites, amorphous silica and the insoluble brucite.

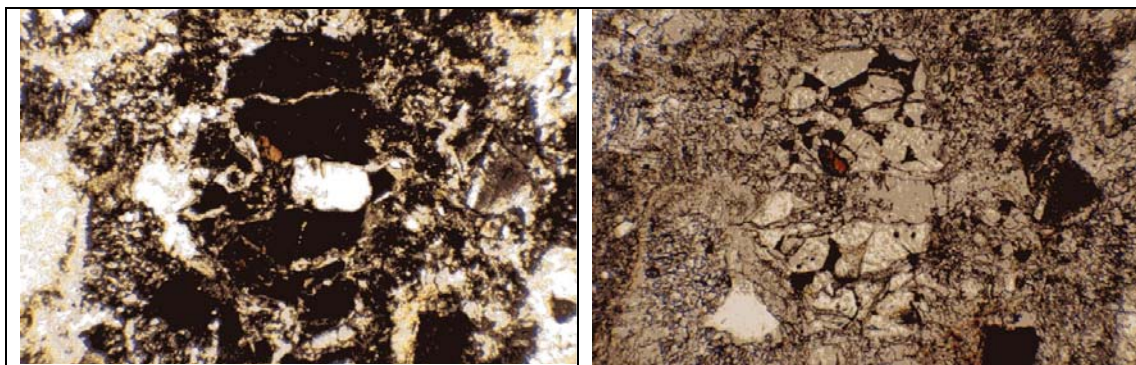


Figure 12. Cracking of aggregate in PC mortar (see text). Surrounded by a heavily sulfated and carbonated matrix. Fractures filled with mainly gypsum. Left polarised light. Right natural light. 10X. Field of view 1.2 mm.

3.4 Damage to masonry

The piers were originally built with Calp Stone (a shaley to siliceous limestone, the bedrock in Dublin) and oolitic limestone (a calcium carbonate limestone) bound with calcium lime mortars. As aforementioned, a condition assessment of the masonry evidenced significant material loss coupled to salt efflorescence. It was also noticed that the damage was stronger at the plinth of the piers, and that the most permeable masonry blocks (shale and oolitic limestone) showed the greatest damage. Analytical results evidenced that salt phases similar to those in the PC mortars were present in both the mortar/limestone interface and the limestone masonry (Pavía 1995). It was further noted that the PC mortars were high-cement mixes with a low aggregate:binder ratio, overly strong and brittle, and the imprevious nature of these mixes was probably exacerbating damage by driving salt solutions and ground capillary moisture into the more permeable masonry. Finally, it was observed that the strongest damage was clearly linked to the position of the PC repair: material loss and salt efflorescence did not occurred in the masonry piers which were not repointed.

4. Discussion

According to the results obtained, most of the damage to the PC mortars at the crypt is caused by the crystallization of sulfates, mainly gypsum and thenardite.

4.1 Origin of the sulfates

The environment

Sulfates are widely distributed in nature and present virtually in all soils, however, they can also arise from the atmosphere (pollution and sea spray) or from building stone, brick and mortar. No data are available on sulfate concentration in the Christchurch Cathedral's soil. Nevertheless, industrial and domestic activites that tend to introduce sulfates in the ground and ground waters have taken place in this area for over a thousand years (the Cathedral is located next to the old Viking settlement of Dublin city). Therefore, the ground probably contains sulfates as well as other elements capable of forming salts.

However, it is unlikely for the sulfate source to be entirely external (arising from the soil) because the strongest sulfate damage is clearly linked to the position of the PC repair: masonry piers which were not repointed with PC mortar in 1878 do not display sulfate damage.

The original PC clinker and the decomposition of primary ettringite

Therefore, a highly possible source for the sulfate is the original PC clinker. The addition of calcium sulfate (gypsum) is required for all PC binder types in order to regulate their setting time. Nevertheless gypsum addition is limited: currently, the maximum permitted level is generally 4% except for exceptional cement types (EN196-1:2002). However, 100 years ago, when the kilns typically ran at lower

temperatures and the sulfur content of the fuel was often uncontrolled, a sulfur-rich clinker could have been produced (Paul Livesey pers. com. 2008), and this may have led to the formation of, not only primary sulfates in the fresh cement paste, but also delayed, disruptive gypsum, alkali-sulfates and ettringite.

This hypothesis (the source for the sulfate to be the PC clinker) is supported by previous research. For example, according to (Hime 1996) some PCs incorporate large amounts of sulfate in their clinker phase. Some of this sulfur is insoluble, and thus not available for harmless early ettringite formation but later available to produce disruptive sulfates. In contrast, other authors (Michaud et al 1997) claim that, even in sulphur-rich cements, all the clinker sulfate is rapidly available for primary ettringite formation within several minutes/days. However, these authors base their statement on PCs with a relatively low sulfate content (2.5-3%), and PCs can contain over twice this amount: standard sulfate limits (EN196-1) are characteristic limits rather than absolute maxima and, in practice, sulfate may exceed these limits in 10% of produced cements (Lawrence 1990).

Michaud et al 1997 also indicate that the internal sulfur source for secondary disruptive sulfates to form is the thermal decomposition of primary ettringite. However, in Christchurch, it is unlikely for the sulfur to originate from the thermal decomposition of primary ettringite for two reasons. First, the decomposition of primary ettringite only takes place at high temperatures $>70^{\circ}\text{C}$ (Miller and Tang 1996, Klemm et al. 1997, Michaud et al. 1997) and, in the Crypt, the temperature remains relatively constant throughout the year ranging between 15 and 20°C . Second, the low aluminium content detected by XRF and EDAX suggests that the clinker was low in aluminium therefore a great amount of primary ettringite was probably never formed.

The aggregate / The masonry

Other possible internal sources of sulfate ion release can be either gypsum-contaminated aggregate or the masonry itself. The mortars studied do not contain gypsum-bearing aggregate and, in addition, the limestone in the masonry does not include significant amounts of sulfur-bearing minerals (Pavía 1995): the piers were built with Calp Stone (the bedrock in Dublin) and an oolitic limestone (a more or less pure calcium carbonate limestone). The Calp is a shaley to siliceous limestone containing pyrite (S_2Fe) as an accessory mineral, however, the decomposition of this pyrite would not have been sufficient to provide the amount of sulfate recorded.

4.2 The nature of the clinker

The low aluminium content detected by XRF and EDAX coupled to the nearly total absence of sulfoaluminates determined by XRD suggest that the cement was low in aluminium. This agrees with old PC accounts by Eckel (1905). In the early times of the cement industry, it was advised to keep the aluminium content as low as possible for two reasons: first to ensure a slower setting and, second, for a higher strength and durability. At this time, the initial setting of a cement was ascribed to the calcium aluminates (rather than the gypsum) and, in addition, the aluminium compounds in the cement were assumed to be the direct cause of its destruction: Eckel, referring to Le Chatelier, accounts for the aluminous compounds in the PC to be the direct cause of

its destruction by sea-water *'by the formation of sulfoaluminate of lime which swells considerably on hydration and thus disintegrates the cement mass'*.

The abundance of alkali sulfates such as thenardite and aphthitalite, and the aggregate reaction recorded suggest that the original cement clinker was probably high in alkalis.

Both petrographic and SEM analyses evidenced the coarse nature of the PC clinker including abundant relicts of unhydrated cement. Clinker fineness is an important property that determines cement reactivity and, today, efficient mill systems grind to the level of fineness required for each strength class. The fineness of the cement depends on the rate at which clinker and gypsum are introduced in the mill (Lawrence 1988) and the clinker's grindability which is a function of its own chemistry and the burning conditions. Coarse PC clinkers including abundant relicts of unhydrated cement are common in old cement composites (St John et al. 1998), and this is probably due to the lower efficiency of the grinding process of old cement production systems (Livesey pers com 2008).

As presented in the results, both the interstitial phases and the alite crystals within unhydrated clinker relicts were often found to incorporate small amounts of additional chemical elements. Among these, interstitial ferrite was found to form calcium aluminate-ferrite series and alite crystals were found to incorporate low, variable amounts of Mg and K. This agrees with work by previous authors as it has been demonstrated that aluminates (C_3A) and ferrites (C_4AF) accommodate alkalis, for example Na_2O , K_2O , MgO and TiO_2 can be included within the C_3A structure (Day 1965).

4.3 Methodology

There are small discrepancies between the salt phases determined by SEM/EDXA and petrographic microscopy and those determined by XRD. For example, XRD results revealed that thenardite was the predominant phase in the efflorescence whereas SEM and petrographic microscopy revealed gypsum as the predominant sulfate in the solid samples. The main reason for this is probably the different solubility of the sulfates: thenardite is more soluble than gypsum and therefore can easily form efflorescence.

In addition, some phases may have not been recorded due to the nearly identical position and overlap of XRD salt peaks; while others may be misinterpreted due to the scatter of the energy-dispersive detector in the SEM system, leading to the collection of information from adjacent areas in addition to those subject to analysis.

In relation to the methodology, probably the most important limitation of this research is that no long-term monitoring of salt efflorescence over time was undertaken and, according to Zehnder (2007) this is a key element in the dynamics of salt crystallization. Even though the crypt is unheated and the environmental conditions remain more or less constant throughout the year, ground moisture rising by capillary action will vary according to rainfall, and this may induce changes in the salts recorded. As a result, salt phases such as mirabilite (the hydrated stable form of thenardite) or epsomite and hexahydrate (hydrated forms of kieserite) may have been

overlooked due to a lack of monitoring during moist conditions. In addition, hydrated forms may have dehydrated during or following sampling.

5. Conclusion

The main cause of damage of the PC mortars and their adjoining masonry is probably sulfate formation, in particular gypsum and thenardite. Gypsum was the most common phase recorded in the solid mortars whereas thenardite was the most abundant phase in the efflorescence. This may be due to the lower solubility of gypsum when compared to that of thenardite.

Much importance has been given to sulfate attack to PC composites and masonry by thenardite and delayed ettringite/thaumasite formation: the formation of ettringite is often considered as the predominant cause of weathering of hydrated cement systems in the presence of sulfate solutions. However, as evidenced in this paper, the formation of gypsum and thenardite can significantly contribute to expansion of hydrated cement pastes and should not be underestimated.

Picromerite, apthitalite, ettringite, niter, potassium calcium carbonate, kieserite, syngenite and calcium langbeinite were determined. Of these, most are sulfates. Most of the salts evidenced are typically linked to PC clinkers (kieserite, syngenite, calcium langbeinite, potassium calcium carbonate, ettringite, apthitalite). Although, the main cause of damage is sulfate formation, due to the complex geochemistry of both the PC and the sulfate-bearing ground, the attack has taken other forms including ASR and the formation of further secondary mineral phases such as zeolites, amorphous silica and the insoluble brucite.

The location of the sulfate damage, closely related to the location of the PC mortar repair, suggests that a significant sulfate source is internal, probably originating from a sulphur-rich clinker phase in the cement. However, ground contamination is probably a further source for sulfate.

Based on the nearly total absence of ettringite and other calcium sulfoaluminates and the abundance of alkali sulfates such as thenardite and apthitalite, this paper suggests that the original cement clinker was low in aluminium and probably high in alkalis.

This paper also concludes that, despite the vast amount of outstanding research on the reactions responsible for sulfate release from primary cement phases such as primary ettringite and C-S-H, the 'time elapsed' is an important parameter that is often overlooked. For example, does decomposition of primary ettringite take place only at high temperatures ($>70^{\circ}\text{C}$) or can this take place at ambient temperatures over long time periods i.e. 100 years?

Finally, damage to the Medieval masonry piers of Christchurch Cathedral crypt is, at least, partially triggered by PC mortar repairs. Therefore, this rises the usual 'compatibility subject' between PC mortars and certain types of masonry. According to petrographic examination, the original masonry mortars used to built the crypt pillars were CL mortars of low aggregate:binder ratio, including local aggregate of quartz, chert, limestone, sandstone, lutitic and igneous rocks (Pavía 1995). Therefore,

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in order to ensure compatibility and avoid potential damage, the repair mortars should have been CL rather than PC-based.

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