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The microscopical characterisation of thaumasite

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Abstract

BRE's Microscopy unit have been extensively involved in the identification of new and unusual occurrences of the thaumasite form of sulfate attack (TSA) and thaumasite formation (TF). Using both optical and scanning electron microscopy a substantial database of information describing the location, form, composition and characteristics of TSA and TF in a series of different examples both within the UK and abroad has been developed. This paper describes the form taken by the TSA/TF within these various localities, and compares it with the characteristic taken by naturally occurring thaumasite.

Earlier work on the M5 concrete bridges in Gloucestershire, UK defined a four-stage degradation process, resulting in the formation of at least three microscopically distinct forms of thaumasite. This paper takes these basic stages and assesses their presence and makes some revisions to the characteristics of the TSA reaction, and its evolution within lower quality cement-derived materials, such as mortars and masonry. Finally the observed strong association of TSA and TF, with the "Popcorn" calcite form of deposition within more depleted areas of affected cement paste from degraded concrete-based material is also discussed along with a proposed mechanism of deterioration.

Keywords: Thaumasite; Form of degradation; TSA; TF; Popcorn calcite carbonation (PCD)

1. Introduction

BRE's Microscopy unit have been extensively involved in the identification of new and unusual occurrences of the thaumasite form of sulfate attack (TSA) and thaumasite formation (TF). Using both optical and scanning electron microscopy (SEM) a substantial database of information describing the location, form, composition and characteristics of TSA and TF in a series of different examples both within the UK and abroad has been developed. This paper describes the microscopic form taken by the TSA/TF within these various localities, and compares it with the characteristics taken by naturally occurring mineral thaumasite. There are features of the mineral observed within both materials but there are also a number of characteristics, which differ between the two environments.

The optical characteristics of thaumasite occurring in concrete were first reported by Erlin and Stark [1]. The information in Table 1 shows the close similarity between thaumasite and ettringite. Even structurally there is little significant difference between thaumasite [$CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$] and ettringite [$3CaO \cdot Al_2O \cdot 3CaSO_4 \cdot 31H_2O$]. On the basis of this and other information, it is the authors' present view that a considerable number of previously reported cases of sulfate attack attributed to ettringite formation were in fact a result of the thaumasite form of sulfate attack.

2. Comparison of natural thaumasite with TSA in cementtious materials

A microscopical comparison has been made between a sample of naturally occurring thaumasite from Crestmore in California and the TSA affected concretes which the BRE have recently been looking at.

2.1. Natural thaumasite

Natural thaumasite crystallises in the hexagonal system usually as compact white or colourless masses with a vitreous lustre. The naturally occurring crystals are often acicular in appearance and have a hardness of 3.5 and specific gravity of 1.9 [2]. However, the examination at BRE of a naturally occurring thaumasite deposit

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Table 1
Optical characteristics of thaumasite and ettringite (from [1])

Property	Thaumasite	Ettringite
Crystal system	Hexagonal	Hexagonal
Crystal habit	Acicular	Acicular
Elongation and sign	Length fast Negative	Length fast Negative
O-ray	1.504	1.464
E-ray	1.468	1.458
Birefringence	0.036	0.006

from Crestmore, California, showed the crystal forms and optical characteristics to be more varied. Even the examination of natural thaumasite using the scanning electron microscope (SEM) showed it to have an apparently highly diverse appearance. The backscatter image of the large, well-formed thaumasite crystals within the sample showed a variety of backscattered electron intensity levels as represented by a range of grey shades for thaumasite crystals which were otherwise compositionally identical (Fig. 1). This suggests that the variations could be due to differences in crystal density (which seems unlikely in this sample), carbonate content (see later discussions), or water content of the thaumasite. The disappearance of these grey level intensities in the sample at a later age sometime after its preparation suggests that water content may be the most likely cause of the observed phenomenon.

It can also be observed optically as shown in Figs. 2 and 3 that the crystalline form of the natural thaumasite was indeed varied and showed increasingly well-structured crystal forms, without any detectable changes in its composition. Fig. 4 shows how the thaumasite deposits relate to the rest of the mineral types in the sample, which appears to include calcium alumino silicates, calcium silicates, and calcium aluminates. XRD analysis detected small amounts of Afwillite ($Ca_3Si_2O_4(OH)_6$), Grossular ($Ca_3Al_2(SiO_4)_3$), and Jennite ($Ca_9H_2Si_6O \cdot 18(OH)_8 \cdot 6H_2O$) and possible traces of bredigite, ettringite, and gehlenite as well as an abundance of thaumasite. The naturally occurring crystalline thaumasite was observed to be colourless or white in the plane polarised light mode of optical microscopy. The well ordered prismatic and acicular forms of thaumasite shown in Figs. 2 and 3, show a clear colourless appearance with a range of birefringence close to 0.018. Birefringence is the effect on polarised light of variations in the refractive index of different minerals. The difference between mineral types are often manifested by different levels of birefringence (refraction) and thus the associated polarisation colour when viewed with cross polars under a polarising microscope. This is a complex area and greater details are given in Optical Microscopy by Paul Kerr [3].

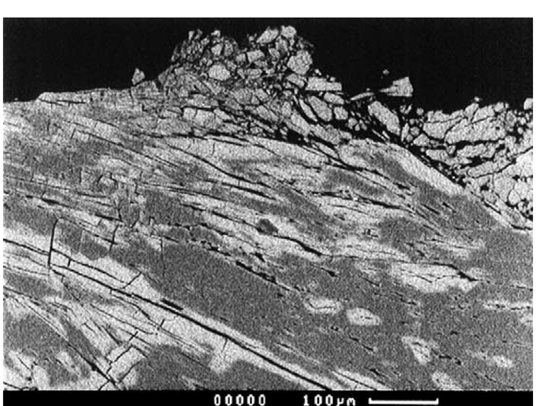

Fig. 1. BSE image of a natural thaumasite deposit showing differing detected X-ray intensity associated with the microcracks.

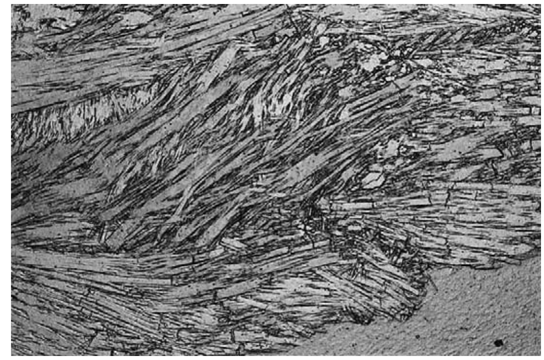

Fig. 2. Large more acicular well-formed thaumasite crystals from the centre of the Crestmore natural deposit. Magnification ×30 image taken in plane polarised light.

Fig. 3. Natural thaumasite sample showing the interface between the colourless well-formed acicular crystals (bottom) and the straw yellow, finely crystalline, and randomly orientated thaumasite mush typically observed within TSA-affected concretes (top). Magnification ×33 (PPL).

The fine-grained, more randomly orientated crystalline mass material observed on the top of the natural thaumasite sample was reminiscent of the thaumasite already observed by BRE within concretes affected by either TSA or TF [4]. This form of natural thaumasite was more randomly orientated and exhibited a more distinctive straw yellow colour when observed in plane

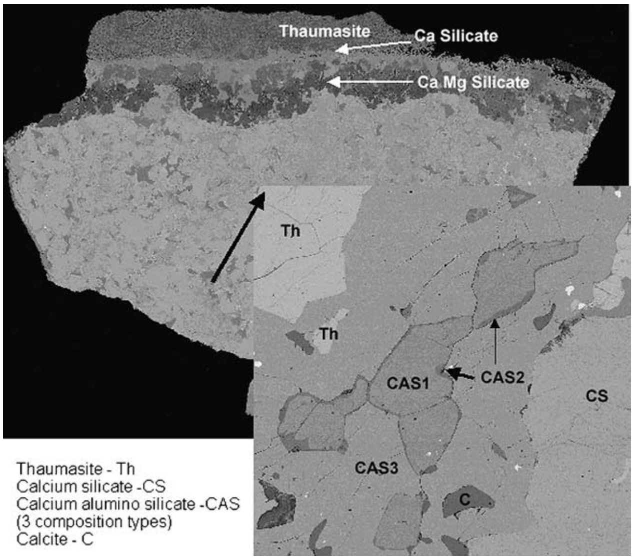

Fig. 4. SEM images of natural thaumasite showing the relationship of the surface thaumasite deposit (top) to other minerals. Internal well-formed prismatic crystals of thaumasite were found within the main mass, alongside calcium silicate and calcium alumino silicate phases. Close up area at bottom right is 1000 μm wide.

polarised light (Fig. 3). The range of birefringence observed within the natural thaumasite was also similar to the TSA thaumasite ranging between 0.000 and 0.027. The reason for the distinct straw yellow coloration was felt to relate to either minor impurities incorporated within the finer crystalline matrix, (after being expelled from the more well-formed and larger crystals), or differences in a constituent undetectable by SEM i.e. H_2O, CO_2, $CaCO_3$ or unspecified carbon compounds.

2.2. Thaumasite in TSA affected materials

Comparison by BRE of the natural thaumasite sample from Crestmore with the abundant examples of TSA-affected concretes confirm that some optical characteristics are common to both. TSA develops within hardened concrete through four progressive stages of degradation (zones 1–4). The characteristics of these zones are summarised in Table 2 and Fig. 5.

The development of zones 1–4 has been previously noted to occur on sharp very distinct fronts within high quality structural concrete. The thickness of the concrete solely affected by zone 1 deposition compared with zones 2–4 can often be negligible. More recently, it has also come to light that degradation zones 1–4 can be found within structural concrete below a distinct and still largely intact outer layer or crust of 'sound' concrete which will ultimately debond from the underlying degraded concrete extremely easily. Zones 1–4 are still apparent but less well defined within lesser quality cementitious materials, which generally have lower cement contents and higher capillary porosity and therefore higher apparent water to cement ratios. Such observations have been found in masonry mortars and external renders.

Thaumasite formation (TF) was found in zone 1 in which thaumasite was observed to fill available voidage, be it air voidage, entrapment voidage [4], or pre-existing microcracks and adhesion voids around aggregate particles. No associated degradation, or consumption of the surrounding cement paste and aggregate is associated with this form of thaumasite precipitation. Fig. 6 shows a typical example of the extent of severe TSA degradation, which can be observed within structural concrete under the optical microscope.

The information listed in Table 1 regarding birefringence is interesting as it fails to note the apparent significant range of birefringence recently observed by BRE within TSA-derived thaumasite deposits (0.000–0.027) and reported in the Thaumasite Expert Group Report [4]. BRE investigations have now shown no difference between natural thaumasite and TSA-induced thaumasite with respect to their crystallography. In particular the elongation of both sets of crystals was confirmed at BRE to be length fast and therefore negative.

2.3. Petrographical identification of three different types of thaumasite

Three types of thaumasite have been identified within the TSA-affected concretes examined by BRE. These are

Table 2
The simple four-stage degradation sequence for TSA development

Zone 1: No visual evidence of attack; petrographic examination can reveal occasional voids and adhesion cracks around aggregate particles lined with thaumasite or ettringite.
Zone 2: Thin cracks lined with white thaumasite begin to appear running sub-parallel to the concrete surface. Calcium carbonate is sometimes precipitated into these cracks. Little portlandite is observed within the cement paste matrix. There is no evidence of other sulfate-bearing minerals.
Zone 3: An abundance of sub-parallel cracks filled with thaumasite become wider and the amount of unattacked cement paste matrix is greatly reduced. Haloes of white thaumasite can be seen around coarse and fine aggregate particles. Calcium carbonate is sometimes precipitated into the cracks. Little portlandite is observed in the still unattacked cement paste. There is no evidence of other sulfate-bearing minerals.
Zone 4: Complete transformation of the cement paste matrix to thaumasite. All that remains are occasional aggregate particles embedded in extremely soft white mush (thaumasite) and a few residual 'islands' of heavily depleted cement paste.

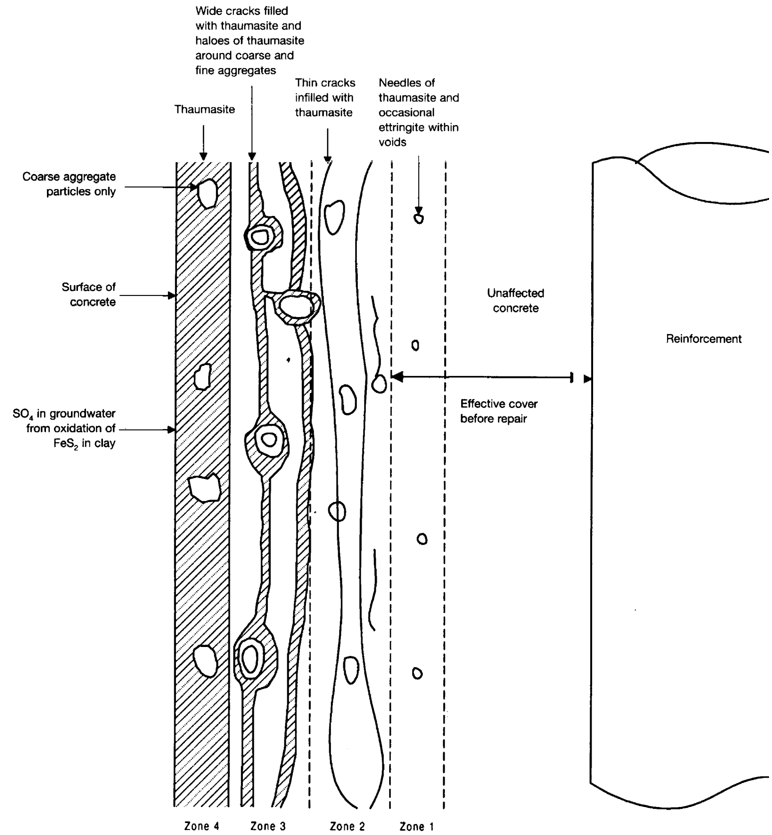

Fig. 5. Sketch of the idealised form taken by TSA degradation with high quality structural concrete.

Fig. 6. Zone 3 and 4 TSA development within structural concrete. Thaumasite shown is light yellow coloured, quartz sand grains are white and the remaining cement paste matrix is brown. Image width 4 mm taken in plane polarised light.

described below. They all have a certain amount of co-habitation, intermixing and variation in colour etc.

Type I: A needle-like crystalline material. These crystals were more poorly formed, randomly orientated and associated with large amounts of voidage. Crystals were colourless to very pale yellow in plane polarised light. The birefringence of most crystals ranged between virtually isotropic/black (0.000) and first order white (0.000–0.005) when examined under crossed polars. The material was closely associated with Type II crystals, and might have represented an extremely porous or more poorly crystalline form of that material.

Type II: Needle-like crystals similar to Type I, but more closely spaced and exhibiting more massive structures which have developed into fans, bands and other flow-like structures around aggregate particles and microcrack edges. Internal porosity within the material was noticeably reduced. These structures exhibited sweeping extinction when examined under cross polars, which have resulted from the closer adjacent crystal orientations within these fans and masses. This thaumasite usually had a distinctly yellow colour in plane polarised light, ranging from light straw yellow to bright yellow. These variations in normal light colour appeared to be dependent on the particular location of the deposit concerned. Under crossed polars the thaumasite appeared to range between 1st order creamy white and pale yellow (0.005–0.07). SEM examination indicated that these crystals were better structured compared with Type I thaumasite. Transitional areas were observed between Type II thaumasite and the other two types.

Type III: Much denser, well ordered needle-like crystals, running in preferentially orientated sheets around aggregate particles and within microcracks. This material was also yellow tinted in plane polarised colour. Under crossed polars the thaumasite appeared to have a much higher birefringence, of up to at least second order green in the particularly dense crystal areas (0.007–0.027).

The different thaumasite types often appeared preferentially in certain locations within the concrete. All three types are also observed in close association with each other. The most common type being Type II. The various shades of yellow colour observed for these three habits of TSA-related thaumasite in plane polarised light are probably due either to a minor optical effect or impurities. The larger well-formed crystals from the natural Crestmore thaumasite were colourless under plane polarised light. These optically different forms of thaumasite were observed to preferentially develop in certain localities. The large deposits primarily formed presumably from the consumption of the cement matrix were usually composed of types I and II thaumasite. Whereas the haloes features developed around carbonate and siliceous aggregates particles were usually composed of Type III thaumasite. Cement paste air void and adhesion crack thaumasite fill deposits were also usually composed of Type III thaumasite. However, many cases were still noted where these basic observations do not apply. [This transition from Type I through to Type III is associated with a progressive increase in birefringence (higher polarisation colours)] [4,5].

The SEM analyses indicated that the concentrations of calcium, silica and sulfur within the thaumasite remained largely consistent for all three types of thaumasite, with only slight increases in calcium content in the haloes surrounding the carbonate aggregates (Type III). At present the best explanation for the increasing birefringence is an increasing carbonate content, with an associated increase in the thaumasite crystal lattice stability and/or increased capillary porosity.

2.4. Comparison

The overall forms taken by the TSA-related microcrack networks and the associated thaumasite deposits within these cracks were highly indicative of the internal expansion release on the outer surfaces. Such expansion is often associated with conventional sulfate attack, which is also due to an externally derived source of sulfates. The growth of the thaumasite crystals perpendicular to the crack walls is also highly suggestive that it is the formation of these crystals which has induced the microcracking resulting in the associated surface expansion and lifting. On a macro-scale, TSA-affected concrete often-demonstrates characteristics indicative of an expansive force being present. Whilst the natural thaumasite deposit though including the crystal forms and characteristic described above for the TSA affected materials often exhibited larger well-formed subhedral and euhedral crystals associated with a suite of other related calcium aluminate and calcium silicate minerals. There was obviously also no associated deleterious action within these deposits.

3. Scanning electron microscope and energy dispersive X-ray analysis (EDXA) of TSA-affected concrete

Examination of the various TSA-affected concretes using the SEM has established some additional observations regarding the mechanisms involved in the reaction. Thaumasite haloes have often been observed to surround the quartz fine aggregate particles in a similar manner to those observed around carbonate aggregates, but the quartz grains do not appear to be involved in the TSA reaction. These thaumasite haloes of Type III material appeared slightly enriched in calcium. However the most calcium-enriched thaumasite was found surrounding the oolitic limestone fine aggregate particles. Thaumasite deposits have been analysed in numerous locations and all habits within the concrete samples have been examined in order to determine whether compositional differences accounted for the variation in birefringence. The chemical composition of all three types of thaumasite appeared to be remarkably constant throughout. However, the fact the SEM cannot accurately detect carbon implies that an undetectable increase in carbonate content could account for the raised birefringence levels observed within the thaumasite. The three different thaumasite types observed under the optical microscope could also be demonstrated clearly under the SEM as shown in Fig. 7.

Ettringite has been found in close association with thaumasite within the cement paste of a degraded concrete sample. However, this ettringite has usually formed within the residual cement paste, and appeared to be primary in origin and was not formed as a result of external sulfate attack. The associated thaumasite remained remarkably pure and had not mixed with the ettringite.

4. Observations of TSA mechanism

Since the early stages of the BRE investigations into TSA, it was always felt that the carbonate requirements of the chemical reaction forming thaumasite did not necessarily have to come from carbonate aggregates or limestone fillers within the concrete/mortar itself. Other possible sources of carbonate, including groundwater [6], surface water or seawater, would be just as viable. A number of recent field cases have been reported to the authors in which zone 4 TSA had developed in concrete containing carbonate-free aggregates [7]. Three-year results from the BRE's thaumasite field trials and

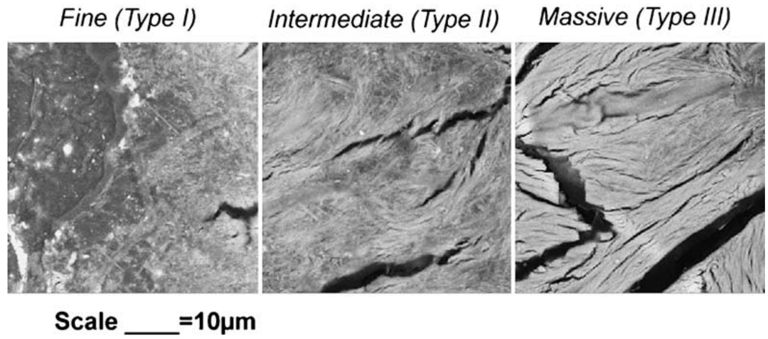

Fig. 7. Showing close up of forms exhibited by the three physically and optically different types of thaumasite.

associated parallel laboratory studies also confirm this observation. (The results from the BRE field trial to date will be presented at this conference). Similarly a range of different sulfate sources have also been identified and these include sulfates derived from plasterwork, sulfate-bearing bricks, seawater, and industrial by-products [8]. A significant number of cases are now documented in which full zone 4 TSA has developed within mortars and concretes within less than 18 months after construction, [6].

5. Association of TSA degradation with other deleterious processes

During the BRE investigation of TSA degradation it has increasingly come to light that it can be observed associated with other degradation mechanisms, for example:

(1) A number of Motorway bridge structures in south-west England, which were affected by severe TSA, were also slightly affected by the alkali-silica reaction (ASR) derived from a minor inclusion of chert particles within the fine aggregate [internal BRE report].
(2) Masonry mortar found within a sea wall, which was showing the effects of magnesium ion attack/seawater attack of the cement paste matrix was also showing advanced signs of TSA [8].
(3) TSA can occur alongside conventional sulfate attack where the products of deterioration are ettringite and gypsum in masonry mortars and renders [8].

However, the most interesting associated degradation mechanism is a phenomenon known either as cornflake [8] or popcorn [9] calcite deposition. Even though BRE has used ‘cornflake calcite’ to describe this mechanism, a decision has been made to adopt the term ‘popcorn calcite’ as it provides a better description of the calcite crystals habit. The finer details of the mechanism remain the subject of debate. It is clear that with time, de-calcification of cement paste can occur under certain conditions and that this is associated with a reduction in the internal pH of the concrete. De-calcification can affect all of the calcium-rich phases within concrete, which primarily include the cement paste hydrates, but can also include sulfate minerals, such as thaumasite. As the pH drops towards neutral calcite becomes the only stable calcium-bearing compound and it precipitates as popcorn calcite deposition (PCD) as shown in Fig. 8. This form of secondary calcite deposition produces a highly friable, easily lost and degradable material, con-

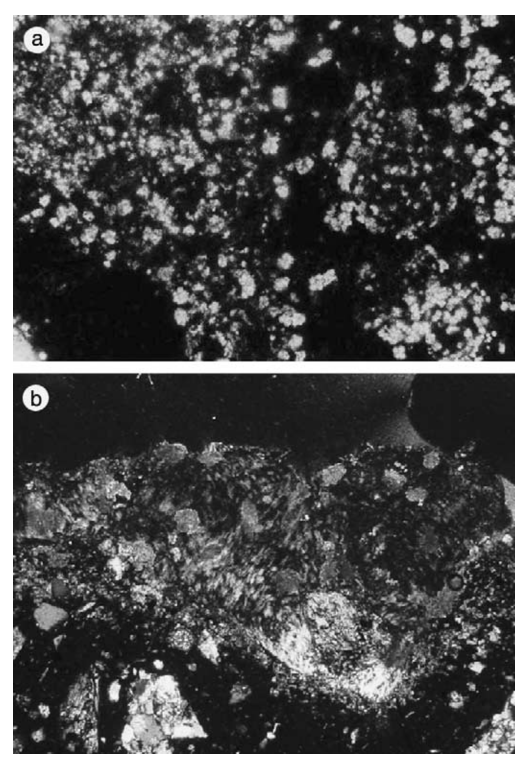

Fig. 8. (a) Close up of TSA degraded cement paste matrix affected by Popcorn calcite carbonation (PCD). (b) Locations can also be noted were calcite crystals have begun to form within the thaumasite product itself.

sisting of an evenly distributed mottled pattern of distinct individual clusters of calcite crystal growths (rosettes). In the case shown, these were surrounded by the residual decalcified product derived from the calcium silicate hydrate matrix (CSH gel), namely hydrous silica gel or hydrous magnesium silica gel.

A case also exists in which classic 'popcorn calcite deposition' was actually found developing within the Zone 4 thaumasite deposits. This may confirm that with a continuing reduction in the pH of the degraded concrete, the calcium-rich degradation products of TSA and other forms of chemical attack of cement based materials will finally succumb to decalcification with the final result being PCD. Ultimately there will usually be little or no evidence of the phenomenon that initiated the degradation in the first place. The quality (capillary porosity) of the concrete/mortar involved probably has a significant affect on the rate of development of the PCD.

6. Conclusions

1. The characteristics of the thaumasite crystals as observed within a natural sample are more diverse than the single fine grained form associated with the TSA reaction in degraded concrete. Whilst the natural thaumasite was observed in a number of different crystal forms the TSA-related thaumasite found in concrete consisted of very fine crystalline deposits which only varied in their density, extent of crystal lattice development and orientation.
2. The TSA and TF are associated with a four-stage degradation process, which proceeds inwards into affected concrete. The front between TSA degraded material and 'sound' concrete can be extremely sharp. These four stages are less well defined in lower quality cementitious materials such as renders and mortars.
3. Three types of thaumasite which form a complete and continuous spectrum of crystal lattice order, birefringence and porosity can be observed throughout the thaumasite deposits within TSA affected concrete. The variability of birefringence could be connected with carbonate content but this fact still needs to be verified.
4. The present on-going BRE investigations of new and differing cases of TSA and TF have shown that:
   - The reaction does not require the specific presence of carbonate within the concrete as limestone aggregate or filler; other sources include carbonate or bicarbonate ion from groundwater, surface water or seawater.
   - Sources of the sulfate other than external sulfate-rich ground conditions have been identified, including gypsum plaster contamination, seawater, sulfate-bearing bricks and industrial by-products.
   - Full zone 4 TSA can occur in concrete and mortars less than 18 months old.
   - TSA has been noted associated with other deleterious processes (ASR, conventional sulfate attack and popcorn calcite deposition).
5. The association of TSA degradation with popcorn calcite deposition which may be the ultimate end product, is extremely easily lost by coring and other sample collection procedures and can therefore be more often missed than collected.

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