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Occurrences of thaumasite in laboratory and field concrete

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Abstract

The mineral thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) has been observed by the authors in a number of concrete samples including (i) an 80 year-old aqueduct in Manitoba, (ii) a 33 year-old pavement in Ontario, (iii) test samples exposed to marine (tidal) conditions, and (iv) laboratory samples exposed to wet–dry cycles in sulphate solution. The source of carbonate differed for these cases being variously derived from de-dolomitization of dolostone aggregate, carbonate ions in the seawater, or atmospheric CO_2 through the process of carbonation. In some cases the thaumasite mineral was found in close association with the mineral ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$).

The paper discusses the results of detailed analyses using optical and electron microscopy. Although the mineral thaumasite can be readily identified by these techniques, it is possible that the thaumasite form of sulphate attack is frequently misdiagnosed as conventional sulphate attack due to the similarities in crystal structure and appearance of the minerals thaumasite and ettringite.

Keywords: Carbonate; Dolomite; Ettringite; Thaumasite; Case histories

1. Introduction

Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) formation was first diagnosed as a symptom and cause of deterioration in concrete in Canada about a decade ago [1]. Since this time, only a few other instances of thaumasite formation have been reported in Canada (e.g. [2]) and in these cases the precise role of thaumasite in the deterioration process has not been established unequivocally. The apparent scarcity of the thaumasite form of sulphate attack (TSA) seems somewhat surprising since sulphate-bearing soils and groundwater exist in certain parts of Canada and the relatively cool climate, which favours the formation of thaumasite, is usually present. TSA probably occurs more often but has not been recognized for two reasons. First, because deteriorated concrete is seldom submitted to detailed petrographic examination. Second, because thaumasite is very similar to ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) in crystal structure and appearance and may be overlooked during examination. To confirm the presence of suspected thaumasite there are a number of techniques. Detailed measurement of refractive index is the classical technique but requires skill and patience. A more common technique used today is to conduct examination under an SEM with EDX to look for the characteristic chemistry. X-ray diffraction (XRD) of powder mounts may also be undertaken but the pattern obtained is very similar to that of ettringite and it may be difficult to obtain sufficient material for study.

This paper summarizes the results of detailed analyses of both laboratory and field concrete samples where thaumasite has been identified. The laboratory cases include mortar samples exposed to wet–dry cycles in sulphate solution and laboratory-produced concrete samples exposed to tidal conditions in a marine exposure site. The field cases include concrete from an aqueduct in Manitoba suspected of being affected by sulphate attack and a concrete pavement in Ontario apparently suffering from D-line cracking. Analysis was performed using a combination of optical and electron microscopy techniques.

2. Laboratory mortars exposed to sulphate solution

As part of a wider study on the deleterious effects of sulphate-bearing fills on embedded concrete [3], a series

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of mortar bars were exposed to cycles of wetting and drying in sulphate solution. The mortar bars were produced using quartz sand and three different cements (CSA Types 10, 20 and 50) or blends of either Type 10 with 50% slag or Type 20 with 30% fly ash. After moist curing for 28 days the bars were exposed to various aggressive solutions. For the first 20 months of exposure, the bars were removed each day and dried in an oven at 38 °C, until approximately 410 cycles had been achieved. Beyond this period, the mortar bars were continuously stored in solution.

A discussion of the results of these tests and other tests on concrete samples has been presented elsewhere [3]. However, of interest here are the observations made regarding the performance of the mortar cast using CSA Type 50 cement (equivalent to sulphate-resisting Portland cement) and exposed to weak sodium sulphate solution (2000 ppm SO_4^{2-}). The mortar bars cast using this cement exhibited deleterious expansion (>0.10%) after 3 years storage (20 months wet/dry + 16 months constant immersion) and had expanded by 0.375% after 10 years. Surprisingly, these mortars showed inferior performance compared with those cast using Types 10 and 20 cement despite the low-C_3A content of the Type 50 cement (calculated as 0.7% by Bogue). In addition to volumetric expansion, the deterioration of these mortars took the form of severe surface softening to a depth of approximately 3–5 mm.

Optical microscopy examination of thin sections prepared from an 11 year-old mortar containing Type 50 cement showed that the surface 5 mm had carbonated (presumably during the wet–dry cycling) and that the mineral ettringite appeared to be abundantly present throughout the cross-section of the mortar bar. Further examination of fracture surfaces by scanning electron microscopy indicated that the mineral in the carbonated layer, despite being of similar morphology to the ettringite found at greater depth from the surface (i.e. needle-shaped crystals) was of different composition. Fig. 1 shows an SEM image of the crystalline material in the carbonated layer together with an EDX spectrum from a spot analysis performed on one of the needle-shaped crystals. The principal chemical constituents (calcium, sulphur, and silicon) and the crystal form suggest that the mineral is thaumasite.

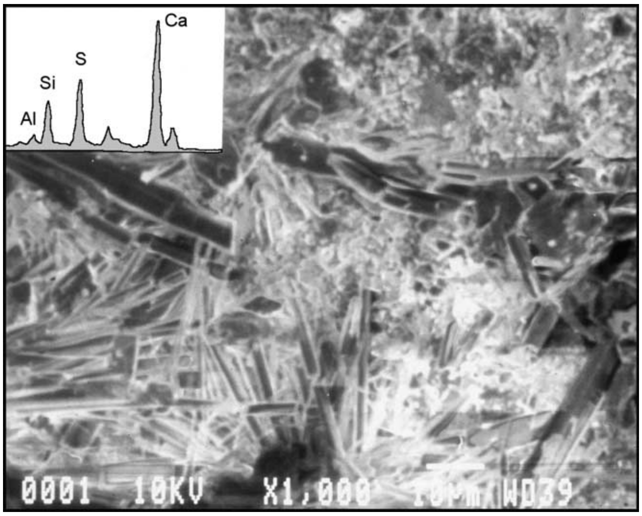

Fig. 1. SEM image of acicular needles in carbonated layer of mortar bar exposed to wet–dry cycling in sulphate solution (EDX spectrum shows spot analysis of needle-shaped crystal).

The only possible source of carbonate in the mortar bar is from interaction with atmospheric CO_2 during wet–dry cycling. There was no external source of carbonate as the original mortar bars were composed of laboratory-grade Ottawa (quartz) sand and Type 50 cement (CSA A5 does not permit carbonate additions in Type 50 cement). Furthermore, during sulphate-exposure period, bars were completely immersed in Na_2SO_4-solution in sealed containers. The participation of atmospheric CO_2 in thaumasite formation has not been reported previously. However, such a phenomenon is unlikely to be significant in practice as the rate of carbonation is generally slow in quality concrete and will be further inhibited in moist environments that are characteristic of aggressive sulphate conditions.

It is not known why the mortars prepared with the other Portland cements (Types 10 and 20) failed to exhibit similar deterioration during exposure to the same environments.

3. Laboratory concretes exposed to seawater

Thaumasite was also detected during an examination of 10 year-old marine-exposed concrete samples of various strength grade and composition [4]. All concretes were cast using a siliceous coarse and fine aggregate (Thames Valley) and combinations of ordinary Portland cement (8% C_3A) and fly ash meeting BS 12 and BS 3892, respectively, and were exposed in the tidal zone of a marine exposure site on the Thames Estuary in the UK Plain Portland cement concretes (100 mm cubes) of low to moderate strength grade (25–35 MPa) were found to lose strength during exposure and this was attributed to a slow progressive softening of the cement paste from the surface inwards. Examination by scanning electron microscope showed that the surface layers were characterized by a decalcification of the CSH with aragonite, magnesium silicate and thaumasite being the primary reaction products. Ettringite was only found beneath the softened surface zone, whereas gypsum was found both within and below the surface layers. Concrete of higher strength grade (e.g. 45 MPa) and concrete containing fly ash (especially replacement levels $\geqslant$30%) showed a lower degree of strength loss and the surface was generally hard and intact in such specimens.

Figs. 2 and 3 show the presence of the mineral thaumasite both within air voids and at the periphery of aggregate particles in 10 year-old, 25-MPa concrete (without fly ash). Thaumasite was commonly observed close to the surface (i.e. up to ~5 mm) in this concrete. Powder samples removed from the surface and analysed by XRD confirmed the presence of thaumasite in the surface layers [4]. Furthermore, LECO analysis indicated enhanced carbon and sulphur contents in the powder sample recovered from the depth increment between 1 and 6 mm from the surface [4]. This depth increment corresponded to the soft, weak layer of material. No evidence of thaumasite was detected by SEM, XRD or LECO analysis in samples recovered from depths greater than 5 mm from the surface.

Thaumasite has been found in marine-exposed concrete by other workers [5], sometimes leading to severe deterioration [1]. A common feature of thaumasite formation, whether in seawater or sulphate-contaminated groundwater, is that the concrete contains a source of carbonate ions, such as limestone aggregate [1,6]. This is not the case in the presence study since both the coarse and fine aggregates are siliceous materials with a negligible content of carbonate. In this study, it is possible that both the seawater and atmospheric CO_2 provided the source of carbonate required for thaumasite formation. LECO analysis indicated that significant levels of sulphate and carbonate ions penetrated the outer 5 mm thick layer of concrete during the 10 year exposure. The interaction of these ions with the cement hydrates produce, among other compounds, $CaCO_3$, $2SiO_2 \cdot H_2O$ and $CaSO_4 \cdot 2H_2O$. Since thaumasite is essentially comprised of these products, then the combined action of sulphates and carbonates has the potential to form thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$).

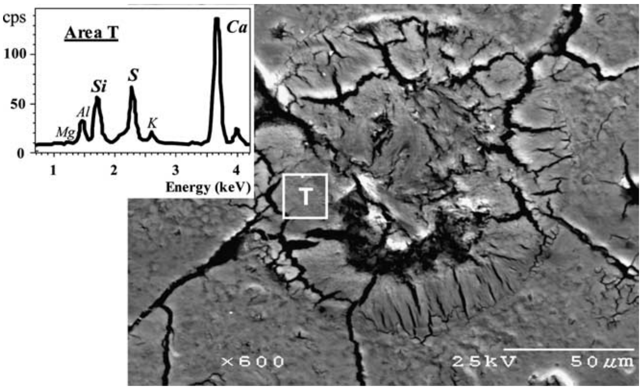

Fig. 2. BSE image and EDX spectrum showing thaumasite in void in 25 MPa OPC concrete after 10 years' exposure in marine tidal zone.

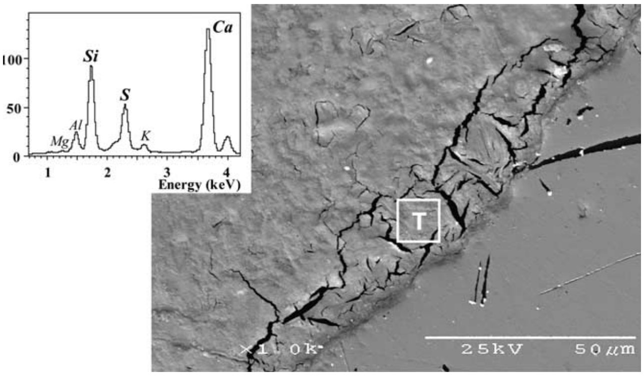

Fig. 3. BSE image and EDX spectrum showing thaumasite at cement–aggregate interface in 25 MPa OPC concrete after 10 years' exposure in marine tidal zone.

It is interesting that thaumasite was not detected in specimens containing 30% or 50% fly ash in spite of the presence of similar concentrations of sulphate and carbonate in the surface 5 mm layer as those found in the OPC concrete [4]. It is not quite clear how fly ash inhibits the formation of thaumasite in the presence of sulphate and carbonate ions, although it is possibly due to the consumption of lime by the pozzolanic reaction. The presence of aragonite (or calcite), silica gel and gypsum is not sufficient to form thaumasite without an additional source of lime, which may be provided by calcium hydroxide; for example Eq. (1)

$$2CaCO_3 + 2SiO_2 \cdot H_2O + 2(CaSO_4 \cdot 2H_2O) + 2Ca(OH)_2 + 23H_2O \rightarrow 2(CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O) \tag{1}$$

The need for additional lime might also explain why thaumasite was detected at the cement–aggregate interface where increased levels of calcium hydroxide are generally found.

4. Concrete pavement in ontario

An investigation of a 33 year-old concrete pavement near Chatham, Ontario, which was suffering from D-line cracking, revealed the presence of thaumasite in concrete cores removed from the westbound lanes [2]. The deterioration was attributed to the frost susceptibility of the coarse aggregate, a crushed dolostone.

Petrographic examination of the concrete revealed extensive cracking principally in the form of a series of horizontal fractures between 0.1 and 1.0 mm wide and generally consistent with freeze–thaw deterioration (despite the presence of an apparently adequate air void system). Many of the coarse aggregate particles had undergone a de-dolomitization process with the result that the surrounding cement paste had carbonated. Thaumasite was found filling air voids in discrete areas of the concrete and the paste in these areas was characterized by a light-coloured mottled appearance as shown in Fig. 4. Typically these areas of mottling were

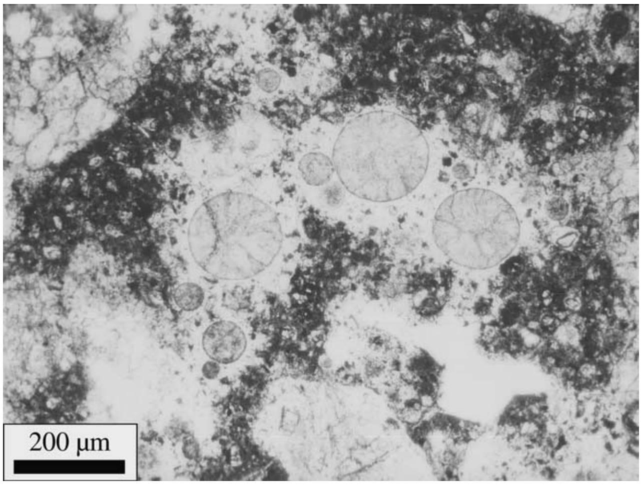

Fig. 4. Thin section of concrete pavement in plain light showing characteristic mottled appearance adjacent to thaumasite-filled air voids.

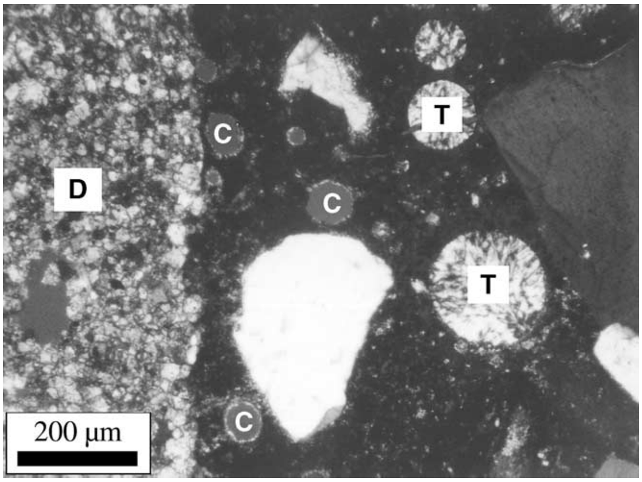

Fig. 5. Thin section of concrete pavement in cross-polarized light showing calcite-lined air voids (C) adjacent to dolostone particle (D) and thaumasite-filled air voids (T).

about 20–50 mm in size and occurred irregularly throughout the concrete. In these areas, every air void was filled with thaumasite. Thaumasite was present as acicular hexagonal crystals and agglomerations of these crystals, and showed characteristic upper first and lower second order birefringence. In reflected light, the thaumasite-affected areas had a white chalky appearance and could be easily carved with a knife. XRD testing of material plucked and extruded from the voids indicated the mineral was thaumasite.

It is possible that the de-dolomitization process provided the source of carbonate required for formation of thaumasite in this concrete. Although an unusual feature that was observed in this concrete was that the air voids in the carbonated paste adjacent to de-dolomitized coarse aggregate particles were lined with calcite with no sign of thaumasite, whereas immediately outside this zone the air voids were filled with bundles of thaumasite crystals (see Fig. 5). The source of the sulphur for thaumasite formation is unknown but could be from internal sources (up to 15% sulphide-bearing shale present in the fine aggregate) or possibly from the small amounts of sulphate known to be present as either anhydrite or gypsum in de-icing salt.

The eastbound lane of the same highway, which was built 2–3 years later by the same contractor using the same sources of materials, showed similar but less extensive deterioration, but with no evidence of thaumasite formation. It is possible that the formation of thaumasite in the westbound lanes contributed to the deterioration process by reducing the resistance of the concrete to the action of freezing and thawing by weakening the cement paste or partially filling air voids. However, the reason why thaumasite formation occurred in this concrete and not in the concrete in the eastbound lanes has not been established.

5. Concrete aqueduct in manitoba

Sections of a concrete aqueduct, built between 1915 and 1919 to supply water to the City of Winnipeg, Manitoba, which were suspected of suffering from "classical" sulphate attack in areas where the 156-km long structure passes through subsoils with a high sulphate content [7], were found to be exhibiting signs of the thaumasite form of sulphate attack when examined by optical and electron microscopy [2].

Petrographic examination revealed abundant deposits of thaumasite filling continuous sinuous cracks parallel to the outside face of the concrete (Fig. 6); these cracks varied from 20 to 120 μm in width and occurred at the edges of coarse aggregate particles (Fig. 7) and within the matrix (Fig. 6). Thaumasite occurred as bundles of hexagonal crystals 1 μm wide and up to 120

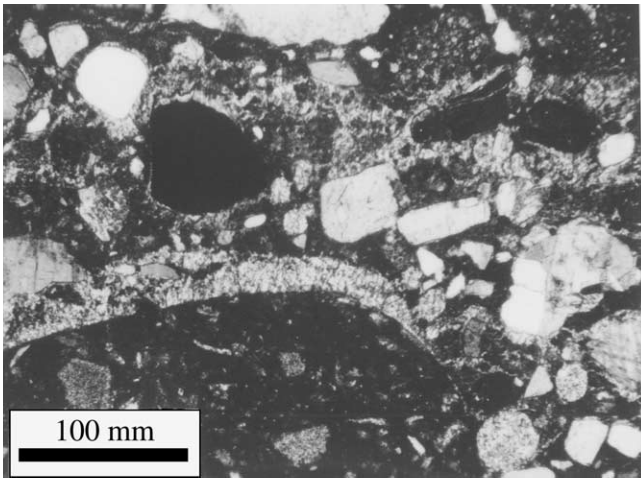

Fig. 6. Thin section of concrete aqueduct in cross-polarized light showing sinuous cracks filled with thaumasite.

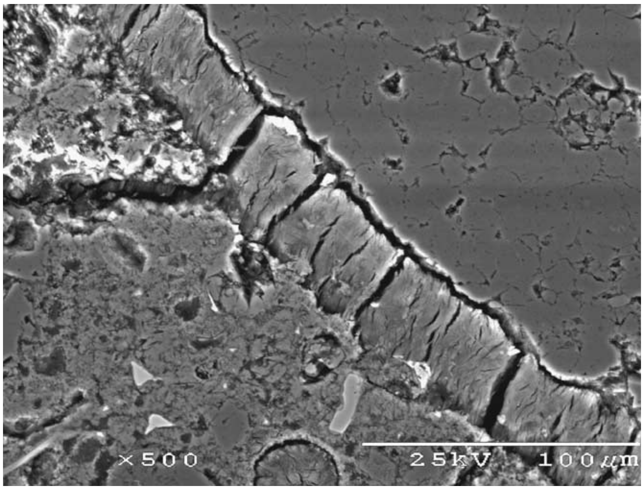

Fig. 7. BSE image showing thaumasite at cement–aggregate interface in concrete from Shoal Lake Aqueduct.

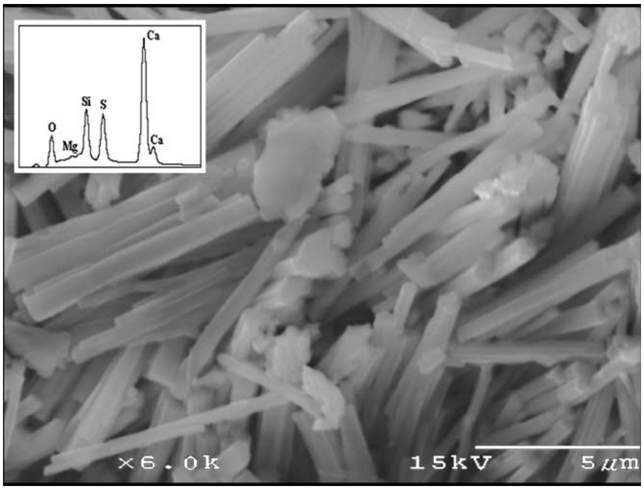

Fig. 8. SEM image of fracture surface showing thaumasite-filled air void in concrete from Shoal Lake Aqueduct.

μm long (Fig. 8). Thaumasite was also found as randomly oriented crystal bundles filling air voids near the cracks. The thaumasite showed high first order (bright yellow) to low second order (red/purple to sky blue) birefringence colours except in thin areas where individual crystals, which showed very low birefringence, could be resolved. The paste in areas near cracks showed complete or partial alteration to thaumasite. Cracks and voids in dolomite coarse aggregate particles were sometimes filled with thaumasite. The presence of thaumasite was confirmed by EDS spectra of crystals which showed the presence of Si, S and Ca and the complete absence of Al (Fig. 8). XRD analysis and refractive index measurements (lowest RI was estimated as 1.48 in contrast to published values of about 1.47) of powdered material plucked from air voids also confirmed the presence of thaumasite.

The likely source of the sulphur is reported [7] to be from adjacent ground water although there were potential sources of sulphur within the concrete. The concrete contained adequate sources of calcium carbonate from the aggregate, either as a result of dedolomitization or as carbonate dust (<75 μm) included with the aggregates [2].

6. Discussion

Thaumasite occurs in concrete in a variety of exposures. Thaumasite may be fairly easily identified in conventional thin sections by its crystal form, mode of occurrence and its higher birefringence than that of ettringite. Further confirmation of the presence of thaumasite may be obtained by determination of the refractive index, XRD of powder samples, or microanalysis using SEM and EDX techniques. Thaumasite probably occurs more frequently than suspected at present but is not recognized because of its superficial similarity to ettringite and also because of the failure to conduct comprehensive petrographic examination of distressed concrete.

Of specific interest here is the variety of sources of the carbonate required for the formation of thaumasite. In most cases of TSA limestone aggregate has been identified as the principal source of calcium carbonate [8] and there is little information available on the possible role of external sources of carbonate. The observations presented here indicate that CO_3^{2-} from seawater or CO_2 from the atmosphere may be potential sources of carbonate. However, in both cases examined here that involve external sources of carbonate, the rate of deterioration was relatively slow affecting only the outer (5 mm) layer of concrete or mortar after a decade. There are indications from these studies that the de-dolomitization of magnesium carbonate aggregate in concrete may also provide an alternative internal source of carbonate ions.

Concretes containing 30% or more fly ash did not exhibit surface deterioration when exposed to tidal marine conditions, and thaumasite was not readily detected at any location within such concretes. More work is required to determine the effect of materials such as fly ash, other pozzolans and slag on the thaumasite form of sulphate attack.

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