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# The thaumasite form of sulfate attack in Portland-limestone cement mortars stored in magnesium sulfate solution

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## Abstract

Mortar prisms ($40 \times 40 \times 160$ mm$^3$) made at a water:solids ratio of 0.5 and a cement:aggregate ratio of 1:2.5 from Portland cement with 0%, 5%, 15% and 35% limestone additions were cured in water at 20 °C for 28 days. They were subsequently stored in air and submerged in 1.8% magnesium sulfate solution at 5 and 20 °C for a year. The prisms were inspected visually every 28 days, the solution was changed every 84 days, and selected samples were examined by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) after specified intervals. The thaumasite form of sulfate attack was readily identified in the ordinary Portland cement (OPC) – 35% limestone mortar after 126 days storage in magnesium sulfate solution. The surface layer of the prism had spalled and was mushy, while the core was still solid and sound. Gypsum, thaumasite and brucite were identified in the surface layer. Secondary electron images of polished sections of deteriorated Portland-limestone cement mortars revealed the microstructure of the cement to be suffering from the thaumasite form of sulfate attack. The extent of this attack was greater at 5 °C than at 20 °C, although some thaumasite was formed even at the higher temperature. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Thaumasite; Sulfate; Portland-limestone

## 1. Introduction

There has been much recent interest in the formation of thaumasite, both in the field [1–6] and in the laboratory [7–11] especially in the UK, and at least two reviews have been written recently [12,13]. Although the thaumasite form of sulfate attack (TSA) of Portland cement mortar and concrete has been reported intermittently for over 30 years, it is only recently that its occurrence has been suspected to be widespread, especially in cool damp conditions. How serious a durability problem it is still to be ascertained, but it is important to have a better understanding of the conditions under which it can form, and any deleterious properties associated with its formation.

The results presented here are based on a laboratory investigation of mortar prisms, made from Portland-limestone cements and a standard quartz sand, after immersion in 1.8% magnesium sulfate solutions. The experimental techniques used were X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

The engineering properties of these mortars, which have been reported elsewhere [11], indicated that prisms made from ordinary Portland cement (OPC) – 35% limestone cement mortars had suffered extensive damage and deterioration within a year, while prisms containing OPC – 15% limestone cement mortars showed signs of impending sulfate attack. In the prisms made from OPC – 35% limestone mortars stored in 1.8% magnesium sulfate solution at 5 °C, visible evidence of deterioration was apparent after 126 days, when the surface layer of the prism had become mushy.

The formation of appreciable amounts of thaumasite in Portland-limestone cement *pastes*, stored under similar conditions to the *mortars* reported in the present investigation, has been reported by the authors [8], and in several other studies (e.g., [7,9,10]). The objectives of this investigation were to monitor the formation of thaumasite and other hydration products in Portland-limestone

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cement mortars, and to try to correlate the formation of thaumasite with changes in the engineering properties already reported [11].

## 2. Experimental

A series of mortar prisms was prepared and tested, as reported elsewhere [11]. The mix design and storage conditions are summarised in Table 1. Four mixes were studied, with different levels of limestone replacement, and each batch was stored in air and in 1.8% magnesium sulfate solution at 5 and 20 °C. The results presented in this paper relate to prisms stored in magnesium sulfate solution at 5 °C, unless specified otherwise.

The OPC and the limestone were provided by Castle Cement (Ribblesdale, England) and typical compositions have been given elsewhere [8]. The limestone used was the same as that used in the manufacture of the cement and was very fine. The sand used was Normensand, a German standard quartz sand, conforming to BS EN 196-1 (British Standards Institution 1995). Each prism comprised 450 g sand, 180 g cement and 90 g water. For those prisms with limestone replacements, the amount of Portland cement was reduced by the appropriate percentage and replaced by an equivalent mass of ground limestone.

The preparation of the mortar prisms has been described in a previous paper [11]. The prisms were air cured for 24 h and water cured for a further 27 days at 20 °C, before being transferred to the appropriate storage conditions. For both temperatures studied, the prisms were stored, completely submerged, in 1.8% $MgSO_4$ solution (made by dissolving 38.2 g $MgSO_4 \cdot 7H_2O$ per litre of boiled distilled water, equivalent to a 0.1550 M solution of $MgSO_4$) in a large plastic tank. For 5 °C, a Grant immersion thermostat and cooling coil were used to maintain a constant temperature of $5 \pm 1$ °C. For 20 °C, the prisms were stored in a plastic tank and the ambient temperature monitored; this was found to be $20 \pm 2$ °C. In each case, the solution was changed every 84 days.

The prisms were monitored carefully every 28 days [11]. The hydration products were identified on selected samples, usually from broken prisms after compressive strength testing. The sample preparation and the experimental procedures for XRD, DSC and SEM were the same as those described for the cement pastes [8]. Spalled pieces of prisms were also examined, especially by XRD.

Table 1
Mix design and storage conditions for the mortars used in the present study

| | |
|---|---|
| Prism size | $40 \times 40 \times 160$ mm$^3$ |
| Cement/aggregate ratio | 1:2.5 |
| Water/(cement + limestone) ratio | 0.5 |
| Storage temperatures | 5 and 20 °C |
| Storage conditions | Air and magnesium sulfate solution |
| Limestone replacements | 0%, 5%, 15% and 35% |

## 3. Results

### 3.1. X-ray diffraction

Several deteriorated Portland-limestone cement mortars were examined by XRD after various periods of immersion in 1.8% magnesium sulfate solution at 5 °C. The XRD traces shown in Fig. 1 relate to an OPC – 35% limestone mortar that had been cured for 126 days. The surface layer of the sample had spalled and was mushy, whilst the core was sound and solid. The XRD trace indicates that gypsum, thaumasite and brucite were the only crystalline phases present in the surface layer in addition to quartz and calcite.

The main thaumasite peak (at 9.2 °$2\theta$) was very intense compared with the ettringite peak (at 9.1 °$2\theta$), obtained from the sound material in the core of the prism (Fig. 1(2)). The gypsum peak at 11.5° was also very strong, indicating that the surface layer was sulfate rich. The XRD trace of the core of the prism indicates the presence of ettringite, portlandite, quartz and calcite, i.e. the expected products of hydration of a Portland-limestone cement mortar. On the other hand, there was an apparent absence of portlandite in the surface layer. Instead a small amount of brucite was detected from its peaks at 18.5 and 38.0 °$2\theta$, both of which were absent in Fig. 1(2). The distinctive microstructural separation that always seems to follow the formation of ettringite and thaumasite under laboratory conditions is well emphasised by the curves shown in Fig. 1.

Quartz which was present as sand in the mortar was identified in both samples. The concentration of quartz in the surface layer was lower than in the core for two

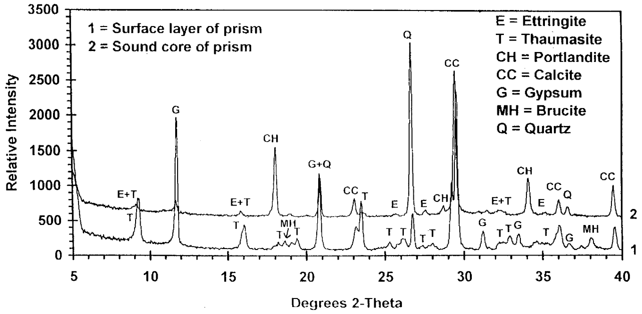

Fig. 1. XRD pattern of OPC – 35% limestone cement mortar stored in 1.8% $MgSO_4$ solution at 5 °C for 126 days.

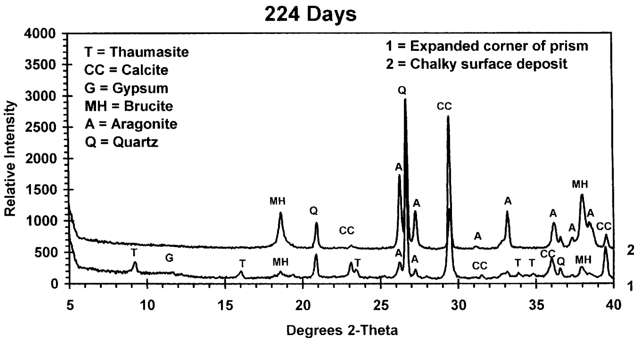

Fig. 2. XRD pattern of OPC – 35% limestone cement mortar stored in 1.8% $MgSO_4$ solution at 20 °C for 224 days.

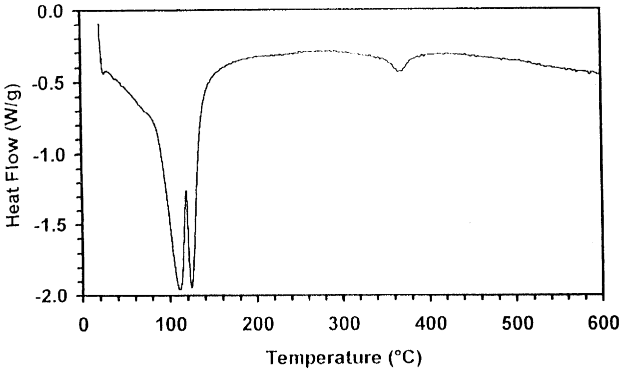

Fig. 3. DSC curve of OPC – 35% limestone cement mortar stored in 1.8% $MgSO_4$ solution at 5 °C for 196 days.

reasons. Firstly, the nature of the reaction products in the surface layer was such that the sand grains were easily dislodged because of lack of cohesion, and secondly, during sample preparation many of the larger grains were removed by sieving. Calcite was present in both samples, as expected from a 35% limestone mortar. These assemblages remain, almost unchanged, up to 364 days.

XRD of a similar mortar containing 35% limestone but stored at 20 °C for 224 days showed similar results, except that the thaumasite peaks were of lower intensity, indicating that less thaumasite had formed (Fig. 2). Once again, the sound core of the prism contained ettringite, portlandite, gypsum, calcite and quartz. The deteriorated surface material, in this case, was an expanded corner. The XRD trace of material from this corner (Fig. 2(1)) was found to contain thaumasite, gypsum (trace) and brucite, in addition to quartz and calcite. A number of previously unseen peaks were observed, e.g., at 26.3 and 27.2 °2$\theta$. These can be attributed to aragonite, a polymorphic form of calcium carbonate that is known to precipitate in the presence of magnesium ions. The sample had a chalky surface deposit, which was shown to consist of aragonite, brucite, calcite and quartz (Fig. 2(2)).

### 3.2. Differential scanning calorimetry

The DSC curve of deteriorated material from an OPC – 35% limestone mortar prism that had been stored in 1.8% magnesium sulfate solution at 5 °C for 196 days exhibited three endothermic peaks as shown in Fig. 3. The endotherms at 110 and 124 °C were attributed to thaumasite and gypsum, which were both shown to be present in large amounts by XRD, perhaps augmented by CSH gel. The smaller endotherm at 366 °C was attributed to the presence of brucite. There were no additional peaks that could be attributed to the presence of ettringite or portlandite. A closely similar DSC curve was obtained from a badly deteriorated OPC – 35% limestone mortar which had been stored under the same conditions for 364 days. This sample was also examined by differential thermal analysis (DTA), which confirmed the DSC endotherms, and also showed a large endothermic peak at 860 °C due to the loss of carbon dioxide from the limestone present in the sample.

When a sample containing both deteriorated outer surface material and sound core material from an OPC – 35% limestone mortar prism that had been stored in 1.8% magnesium sulfate solution at 5 °C for 224 days was examined by DSC, additional endothermic peaks were observed at 76 and 421 °C. Differences in the XRD patterns of this sample and that discussed in Fig. 3 indicated that the additional peaks were due to the presence of ettringite and portlandite, respectively. A very small endotherm was also observed at 571 °C due to the polymorphic transformation of quartz present in the sand used to make the mortar. Quartz was not always observed by thermal analysis because the energy change associated with the transformation is of low intensity, and attempts were made to select only the cementitious parts of the samples.

### 3.3. Scanning electron microscopy

A secondary electron image of a polished section of a deteriorated Portland-limestone cement mortar is shown in Fig. 4 at relatively low magnification. The mortar was made with OPC – 35% limestone and, following the initial 28 day water curing, was stored in 1.8% $MgSO_4$ solution until the age of 168 days. The micrograph is from an area close to the edge of the prism. The large sub-elliptical, dark grey areas are sand grains. The lighter grey matrix material is the cement paste. The most striking feature of the micrograph is the presence of numerous white lines, criss-crossing the field of view. These lines are cracks in the sample, highlighted by the secondary electrons. The cracking is extensive and pervasive. Whilst there are large cracks around some of the sand grains, the cracks also permeate through the cement paste.

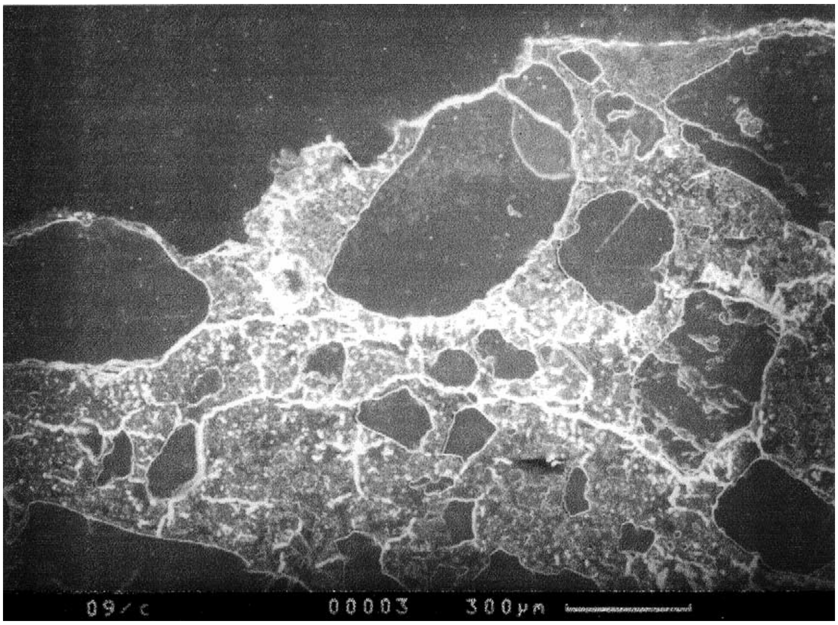

Fig. 4. Secondary election image of a deteriorated OPC – 35% limestone cement mortar stored in 1.8% $MgSO_4$ solution at 5 °C for 168 days.

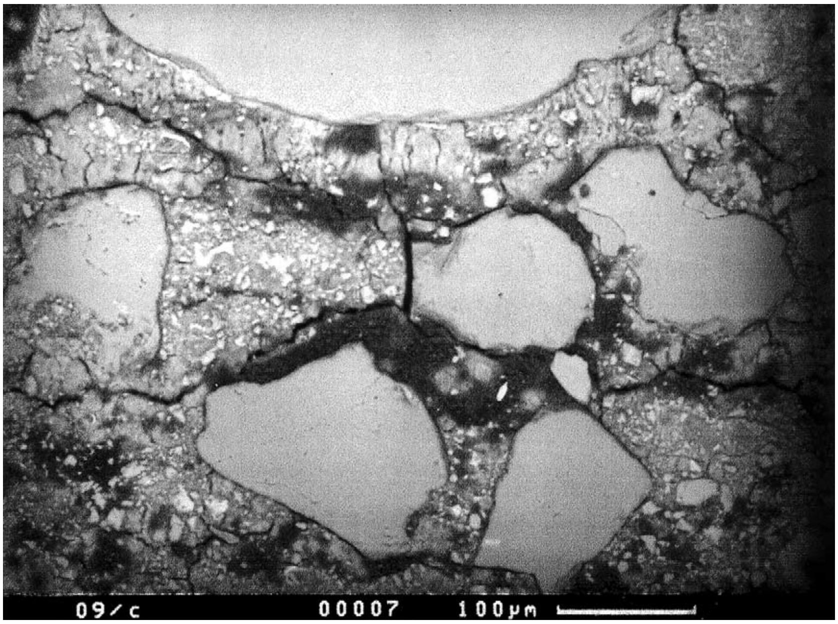

Fig. 5. Back scattered electron image of the same mortar at higher magnification.

There appears to be a concentration of small, subparallel cracks near the centre of the micrograph, at the base of the large sand grain. Examination of this area at higher magnification and using backscattered electron imaging (Fig. 5) clearly shows a cracked band of a different phase, approximately 30–40 µm wide, running along the edge of the sand grain and into the paste matrix. It is likely that this band is composed of a sulfate-bearing phase, gypsum, ettringite or thaumasite, found as a result of sulfate attack of the mortar. The XRD results presented above make it unlikely that the band is due to ettringite.

Sections of a deteriorated OPC – 35% limestone mortar stored in 1.8% $MgSO_4$ solution at 5 °C for 364 days were examined by SEM, as stub samples, in order to assess the external morphology of the prisms. A relatively low magnification, secondary electron image of the surface is shown in Fig. 6. Large subhedral gypsum

Fig. 6. Secondary electron image of a deteriorated OPC – 35% limestone cement mortar stored in 1.8% $MgSO_4$ solution at 5 °C for 364 days.

Fig. 7. Secondary electron image of the same mortar.

tabulae (∼50 mm) can be seen in the centre of the micrograph, surrounded by a mixture of smaller gypsum crystals and long thin needles of epsomite (up to 200 µm in length). Epsomite had formed as a result of direct precipitation from magnesium sulfate solution, whereas gypsum had formed from sulfate attack of the cement matrix. To the centre right of the micrograph is a phase with a different morphology. Further examination of the specimen showed that this phase was common throughout the sample.

A different view of the surface of the same sample is shown at higher magnification in Fig. 7. This micrograph shows more of the euhedral, tabular gypsum crystals surrounded by a mass of clusters of short, fine acicular crystals. Whilst the morphology of the gypsum was evident, that of the needle-like phase warranted

Fig. 8. Secondary electron image of the same mortar.

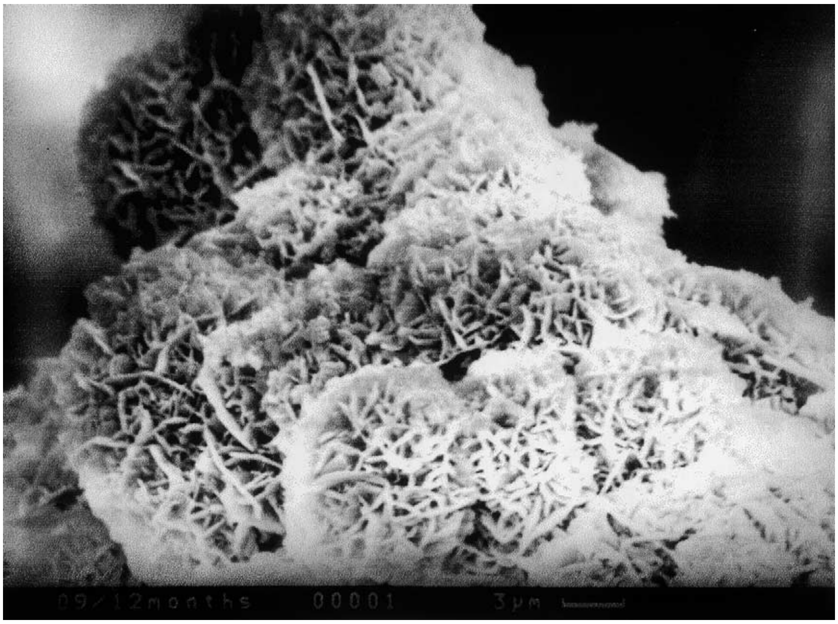

Fig. 9. Secondary electron image of the same mortar.

closer inspection. A cluster of these needles is shown in Fig. 8 at higher magnification. The needles were very fine ($\ll 1$ μm) and up to 3 μm in length. They appeared, in many cases, to taper and were joined together in a large, open felted mass. At still higher magnification, the needles sometimes appeared to have joined together to form platy rosettes (Fig. 9), where the edges of the rosettes had fused. EDS analysis of the needles showed large calcium and sulfur peaks, along with small silicon peaks. Since there was no evidence for the presence of aluminium, the phase was identified as thaumasite. This identification is supported by the XRD traces which indicated thaumasite and gypsum as the sulfate-bearing phases present. There was no evidence for the presence of ettringite.

SEM of further samples of deteriorated OPC – 35% limestone mortars after storage in magnesium sulfate solution for 364 days showed similar features. The sec-

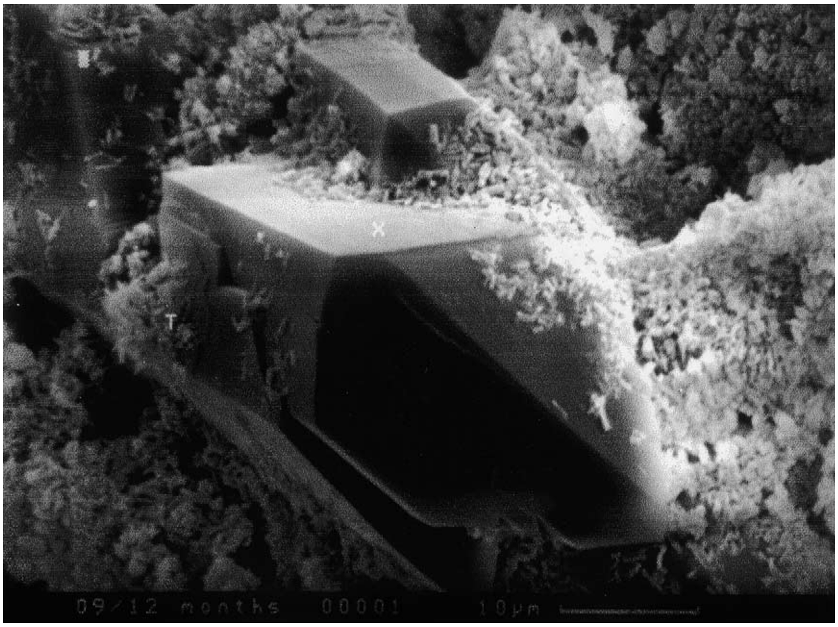

Fig. 10. Secondary electron image of the large tabular gypsum crystal surrounded by fine needles of thaumasite (T = thaumasite, X = gypsum).

ondary electron image (Fig. 10) shows a large tabular gypsum crystal with fine interwoven needles of another phase. EDS analysis of the acicular phase (labelled T) showed large calcium and sulfur peaks, a smaller silicon peak and a trace of magnesium, but no evidence for aluminium. It was concluded that the phase was thaumasite rather than ettringite. EDS of the large tabular phase (labelled X) showed the presence of only calcium and sulfur, confirming the identification of gypsum. These conclusions are supported by XRD analysis of the specimen.

## 4. Discussion

There is no doubt, based on the results presented here, that thaumasite is readily formed in OPC – limestone cement mortars stored in 1.5% $MgSO_4$ solution. The amount of thaumasite formed was greater at 5 °C than at 20 °C, although mortars stored at 20 °C eventually showed a mixture of gypsum and thaumasite to be products of sulfate attack. The extent of deterioration was, however, less marked than at 5 °C, with only the corners of the prisms being affected after 364 days immersion.

The mortar prisms containing 35% limestone stored in $MgSO_4$ solution at 5 °C were, however, seriously damaged. After only 126 days immersion, the surfaces of the prisms had spalled, accompanied by loss of a large amount of material [11]. Up to 7% of the 28 day mass had been lost by the age of 280 days. XRD analysis of the spalled material compared with the remaining core of the prism showed distinct changes in mineralogy (Fig. 1). The core of the prism was comprised of the expected assemblage of ettringite, portlandite, calcite and quartz, whereas the surface layer was composed of mostly thaumasite, gypsum, calcite and quartz, with some brucite.

The presence of brucite, and the absence of portlandite, was confirmed by DSC (Fig. 3). These changes correlated well with small changes in the dynamic modulus and pulse velocity, and larger changes in mass and strength at around the same age [11]. The expansion measurements showed no great change, indicating that the deterioration evident at the surface of the specimens was not affecting the interior. The XRD evidence suggested that the external sulfate had not yet penetrated to the interior, as thaumasite was not found in the core. The decrease in compressive strength was associated with the loss in cohesion of the cement matrix at the surface. Spalling of the surface layers continued, with the loss of almost 14% of the original mass after one year [11]. A similar clear separation of a surface region affected by TSA and a core unaffected has been reported in field samples [1].

Thaumasite formation in the laboratory-stored samples reported here was accompanied by formation of gypsum and brucite. At 20 °C, but not at 5 °C, aragonite was also observed (Fig. 2). The amount of calcium hydroxide present in the samples containing thaumasite was drastically reduced compared with the samples from the core. These results are the same as those previously reported [8] for cement pastes. In that paper, the equation for the formation of thaumasite was shown to be

$$\mathrm{C_3S_2H_3 + CH + 2C\overline{C} + 2M\overline{S} + 28H} \\ \rightarrow \mathrm{2C_3S\overline{C}\overline{S}H_{15} + 2MH}$$

The observations presented here are in accordance with this equation. It is believed that the reaction proceeds via a through-solution mechanism. The ions required in solution are as follows:

$$\mathrm{3Ca^{2+} + SiO_3{}^{2-} + CO_3{}^{2-} + 2(OH)^- + Mg^{2+} + SO_4{}^{2-}} \\ \rightarrow \mathrm{CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O + Mg(OH)_2}$$

A through-solution mechanism in which small amounts of calcite dissolve also accounts for the observed precipitation of aragonite at 20 °C, because the crystallization of aragonite from solution is favoured by higher temperatures and the presence of calcium sulfate in solution [14]. The depletion in the amount of C–S–H gel and CH present in the mortar affected the engineering properties in the manner reported elsewhere [11].

The results obtained on Portland-limestone cement mortars allow an estimate to be made of their age at the onset of thaumasite formation when stored in 1.8% magnesium sulfate at 5 °C. The estimates are shown in Table 2. Although the ages are approximate, the trend is clear; thaumasite was observed at an earlier age as the amount of limestone replacement increased. Crammond and Halliwell [5] also reported that the sulfate resistance of limestone-filled cements was largely determined by the amount of limestone incorporated in the cement.

In the present study, deterioration of the mortars was observed at earlier ages than in the corresponding cement pastes. Cracks that formed around the aggregate grains provided channels for the sulfate solutions to penetrate more readily (Fig. 4). The precipitation of expansive sulfates within these cracks led to rapid disintegration of the mortar prism. The pastes, being essentially homogenous, contained fewer cracks, thereby preventing rapid ingress of sulfates.

There must be considerable concern about the possibility of TSA in mortars and concretes containing substantial amounts of limestone. It is still to be established how great the danger of TSA is when associated with the incorporation of only 5% limestone in OPC. The results of our studies indicates that in the presence of 5% limestone filler only small amounts of thaumasite are formed in the first year, and that the engineering properties are not much affected [11]. The duration of the experiments was, however, limited to only one year. Furthermore, long-term carbonation of the portlandite formed might increase the danger of TSA. It would be prudent for engineers to consider the threat of TSA in mortars and concretes with any level of replacement of Portland cement by limestone, whether or not a coarse limestone aggregate is also used. This threat is clearly greater in the presence of higher concentrations of external sulfate ions, especially if the source of these ions is magnesium sulfate which leads to the precipitation of brucite.

Table 2
Approximate age at onset of thaumasite formation in Portland-limestone cement mortars stored in 1.8% magnesium sulfate solution at 5 °C

| Limestone replacement (%) | Onset of thaumasite formation (days) |
|---|---|
| 0 | Not detected |
| 5 | 252 |
| 15 | 196 |
| 35 | 126 |

## Acknowledgements

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## References

[1] Thaumasite Expert Group. The thaumasite form of sulfate attack: Risks, diagnosis, remedial works and guidance on new construction, Report of the Thaumasite Expert Group, Department of the Environment, Transport and the Regions: London, January 1999.

[2] Crammond NJ, Nixon PJ. Deterioration of concrete foundation piles as a result of thaumasite formation. In: Nagataki S, editor. Proceedings of the 6th International Conference on Durability of Building Materials and Components, vol. 1. London: E. and F.N. Spon; 1993. p. 295–305.

[3] Hobbs DW, Taylor MG. Nature of the thaumasite sulfate attack (TSA) mechanism in field concrete. Cem Concr Res 2000;30:529–33.

[4] Brown PW, Doerr A. Chemical changes in concrete due to the ingress of aggressive species. Cem Concr Res 2000;30:411–8.

[5] Crammond NJ, Halliwell MA. The thaumasite form of sulfate attack in concretes containing a source of carbonate ions – a microstructural overview. In: Advances in Concrete Technology, 2nd CANMET/ACI Symposium on Advances in Concrete Technology, Las Vegas, 1995. p. 357–80.

[6] Yang R, Buenfeld NR. Microstructural identification of thaumasite in concrete by back scattered electron imaging at low vacuum. Cem Concr Res 2000;30:775–9.

[7] Gaze M. The effects of varying gypsum content on thaumasite formation in a cement:lime:sand mortar at 5 °C. Cem Concr Res 1997;27:259–65.

[8] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland-limestone cement pastes. Cem Concr Res 1999;29:1331–40.

[9] Barnett SJ, Adam CD, Jackson ARW, Hywel-Evans PD. Identification and characterisation of thaumasite by XRPD techniques. Cem Concr Composites 1999;21:123–8.

[10] Gaze ME, Crammond NJ. The formation of thaumasite in a cement: lime: sand mortar exposed to cold magnesium and potassium sulfate solutions. Cem Concr Composites 2000;22: 209–22.

[11] Hartshorn SA, Swamy RN, Sharp JH. Engineering properties and structural implications of Portland limestone cement mortar exposed to magnesium sulfate attack. Adv Cem Res 2001;13:31–46.

[12] Grijalvo JA, Blanco-Varela MT, Maroto FP, Sanchez AP, Moreno TV. In: Malhotra VM, editor. ACI/CANMET Conference on Durability of Concrete, Barcelona, June 2000 ACI SP 192-71, vol. II. 2000. p. 1173–92.

[13] Crammond NJ. The occurrence of thaumasite in modern construction – a review. Cem Concr Composites 2002;24:393–402.

[14] Deer WA, Howie RA, Zussman J. In: An Introduction to the Rock-forming Minerals. London: Longmans, Green and Co.; 1966. p. 498.