Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 36 (2006) 160–170

Cement and Concrete Research

The role of pH in thaumasite sulfate attack

Q. Zhou, J. Hill, E.A. Byars*, J.C. Cripps, C.J. Lynsdale, J.H. Sharp

Department of Civil Engineering and Centre for Cement and Concrete, University of Sheffield Mappin Street, Sheffield, S1 3JD, UK

Received 18 August 2003; accepted 17 January 2005

Abstract

The thaumasite form of sulfate attack (TSA) has been recognised in recent years as a distinct mechanism by which degradation of buried concrete can occur in the presence of an external source of sulfate ions. There is, however, disagreement about the role of pH. It has been proposed that attack by sulfuric acid, produced by oxidation of pyrite, is sometimes the primary cause of deterioration. Others believe that the acid is rapidly neutralised giving a higher concentration of sulfate ions in the ground, hence increasing the extent of attack. The aim of the laboratory study reported here was to understand the role of sulfuric acid in TSA by examining concrete cubes, made from three types of cement and two types of aggregate, immersed at low temperature in two solutions, one alkaline corresponding to BRE Design Sulfate Class DS-3 and the other acidic. It is concluded that the presence of acid does not promote the formation of thaumasite. Although degradation of the concrete was observed in acid conditions, the mechanism was not TSA as observed in alkaline conditions.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Degradation (C); pH (A); Sulfate attack (D); Thaumasite (D); X-ray diffraction (B)

1. Introduction

Until recently the thaumasite form of sulfate attack (TSA) was considered to be so rare as to be a curiosity and attracted only a brief mention in textbooks on the chemistry of cement and concrete. The identification of thaumasite in degraded foundation concrete of ten motorway bridges on the M5 motorway near Cheltenham in the west of England in 1998 completely changed this attitude. TSA is now recognised as distinct from "conventional sulfate attack", which results in formation of ettringite and gypsum, and it is likely that TSA is common in buried concrete subjected to sulfate-containing ground waters, especially at low temperatures (<15 °C). In the past TSA may sometimes have been wrongly diagnosed as conventional sulfate attack, since the X-ray diffraction (XRD) patterns of thaumasite and ettringite are similar. Positive identification of thaumasite by XRD depends on examination of peaks at d-spacings below 4 Å, which are of relatively low intensity and frequently overlap with peaks due to other phases present in the hydrated cement.

Over 80 cases of TSA have been reported in England [1] and elsewhere [2]. Perhaps the worst reported case is from the Canadian Arctic [3]. Many other cases, especially in Europe [4–6], were reported at the First International Conference on Thaumasite in Cementitious Materials, held at the Building Research Establishment in England in June 2002.

The conditions necessary for thaumasite formation have been discussed in several recent papers and were carefully considered by the Thaumasite Expert Group [7], set up by the UK Government to consider the risks, diagnosis, remedial works and guidance on new construction, after identification of TSA in the motorway bridge foundations referred to earlier. It is generally agreed [1,7] that thaumasite formation is favoured by:

- a source of C-S-H;
- an external supply of sulfate ions;
- a source of carbonate ions;
- mobile water; and
- cool temperatures (<15 °C).

---

* Corresponding author. Department of Civil and Structural Engineering, Concrete Materials Research Unit, Centre for Cement and Concrete, University of Sheffield, United Kingdom. Tel.: +44 114 2225715; fax: +44 114 2225700.

E-mail address: e.byars@shef.ac.uk (E.A. Byars).

0008-8846/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2005.01.003

It has also been suggested that calcium hydroxide is a reactant [8,9] and that storage in magnesium sulfate solutions is more detrimental than storage in other sulfate solutions [8,10].

While there is general agreement about the importance of the factors listed above, there is another issue that has led to disagreement and much discussion. This relates to the role of acid (or more correctly pH) in the formation of thaumasite and notably the degradation attributed to TSA in the M5 motorway bridges. During the construction of the motorway, unweathered Lower Lias clay containing pyrite, FeS_2, was excavated, stockpiled and replaced around the concrete foundations [2,7]. This disturbance to the clay resulted in oxidation of the pyrite, possibly accelerated by microbiological agents. According to the actual conditions, notably the specific bacteria present, iron(II) sulfate, iron(III) sulfate or iron oxy-hydroxide phases may be formed, but always accompanied by formation of sulfuric acid. The chemical equation for one of the more common oxidation reactions is

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \quad (1)$$

The sulfuric acid that has been generated may be neutralised, either by reaction with limestone to form gypsum or possibly by reaction with the cement at the surface of the concrete. There is no doubt that at the site of the M5 motorway bridges, the sulfate level of the ground increased from BRE Design Sulfate (DS) Class 1 or 2 (1.4 g/l of SO_4^{2-} as $CaSO_4$) to Class DS-3 (1.4 g/l of SO_4^{2-} as $CaSO_4$+1.6 g/l of SO_4^{2-} as $MgSO_4$) [11].

Controversy has arisen about the actual role of sulfuric acid in TSA. Does it act merely as an intermediate leading to increased levels of sulfates, notably gypsum, in the ground, or does the low pH initiate chemical attack at the interface with the concrete, facilitating subsequent formation of thaumasite? One aim of this project was to understand the role of sulfuric acid in TSA by examining concrete cubes made from ordinary Portland cement (OPC, equivalent to ASTM type I), Portland-limestone cement (PLC), and sulfate-resisting Portland cement (SRPC, equivalent to ASTM type V) after immersion at low temperature in two solutions containing sulfate ions but at very different levels of pH. The first solution contained calcium sulfate and magnesium sulfate made to meet the limits of BRE DS-3 sulfate solution with a pH > 12, whereas the second solution contained sulfuric acid, which was adjusted every week to provide an acidic environment as discussed in Section 2. Some preliminary results, based on examination of a subgroup of cubes stored for only 6 months, have already been reported [12].

2. Experimental work

2.1. Cementitious binders and concrete mixes

Concrete mixes were prepared using OPC, PLC and SRPC. It should be noted that the OPC contained 5% limestone filler, the PLC 20% and the SRPC none. Either Thames Valley gravel or an Oolitic limestone aggregate was used for both coarse and fine fractions. The gravel did not contain amounts of calcite detectable by XRD.

2.2. Specimen preparation and exposure

One hundred millimeter concrete cubes were cast according to BS 1881 using a water:binder ratio of 0.45, left for 18 h under wet hessian sheeting, demoulded and then individually double wrapped. These were then placed in a mist room at around 95% RH and 21 °C for 28 days. After curing, the cubes were unwrapped and transferred to their designated exposure solutions in small tanks maintained at 5 ± 0.5 °C. Each tank contained only one type of cement to avoid any interference. These were renewed with fresh solutions every 3 months.

2.3. Solutions

The solutions used were as follows:

BRE Class DS-3-calcium sulfate (1.4 g SO_4/l)+magnesium sulfate (1.6 g SO_4/l) [11]
Sulfuric acid-pH checked weekly to maintain acidic conditions (see Fig. 1).

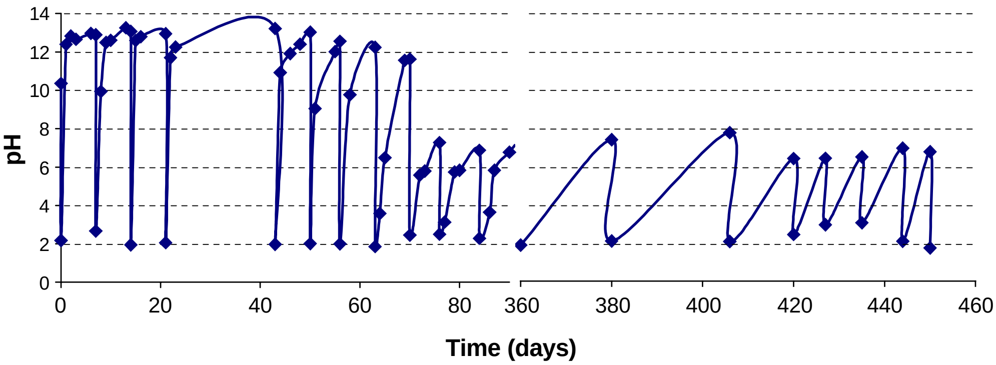
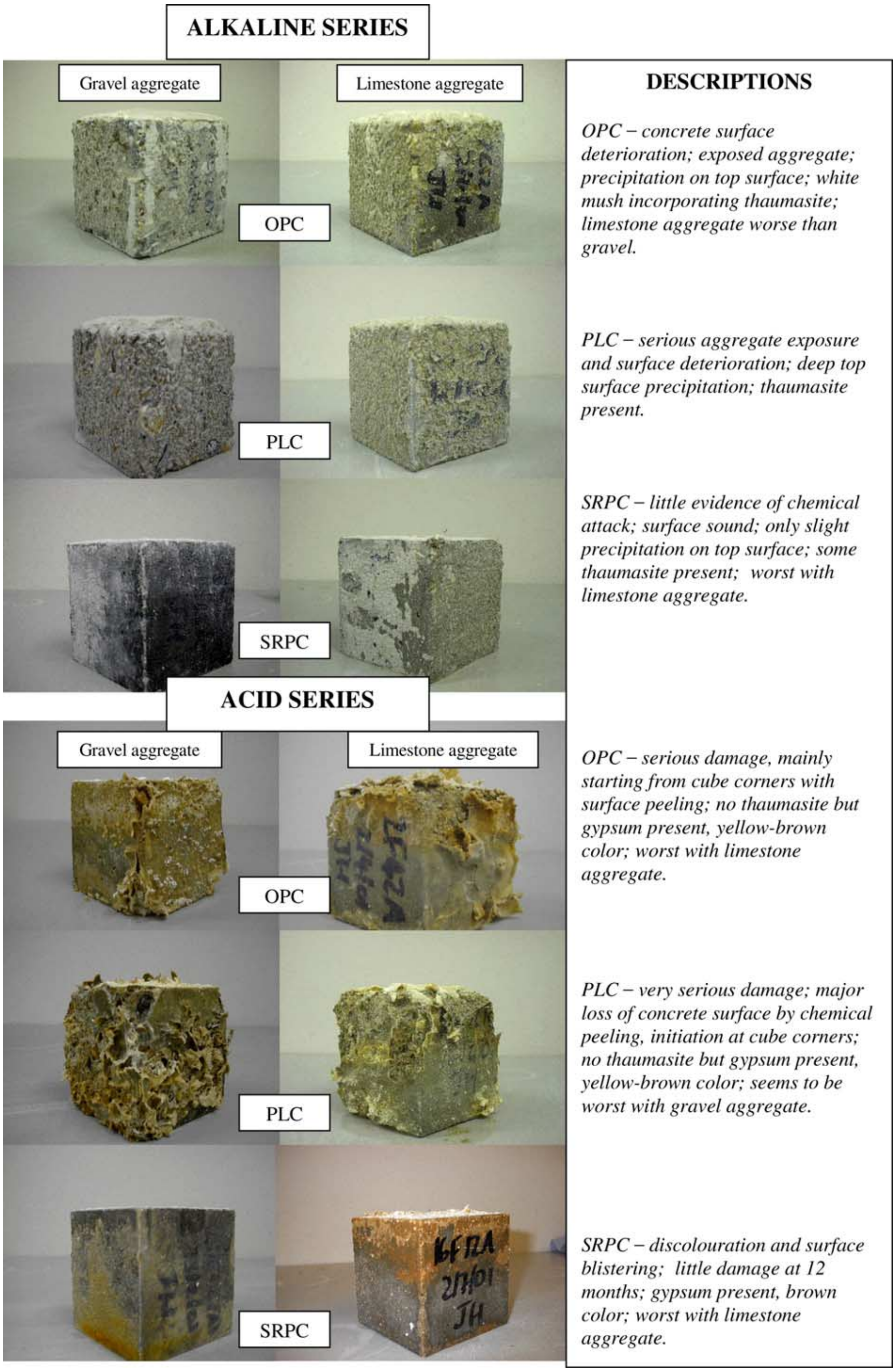


Fig. 1. Variation in pH with time of the acidified solution containing PLC concrete cubes.

The intention was to maintain a pH close to 4 in the acid solution, but this was not possible because of the alkaline nature of the cement hydration reactions taking place in the cubes. The pH of the acid solution was monitored weekly and whenever it exceeded 6, measured amounts of sulfuric acid were added to reduce the pH down to 2. During the early stages of hydration, it was impossible to maintain the pH continuously below 7, but after 70 days it became possible to maintain acidic conditions with a pH mostly between 2 and 6. The variation in pH during the first 90 days of storage in both year 1 and 2 for the solution containing the cubes made with PLC is shown in Fig. 1 and is typical of the results obtained with all the cements.

2.4. Concrete testing

At the age of 12 months (1 month curing and 11 months immersed in solution) the cubes were removed and



DESCRIPTIONS

OPC – concrete surface deterioration; exposed aggregate; precipitation on top surface; white mush incorporating thaumasite; limestone aggregate worse than gravel.

PLC – serious aggregate exposure and surface deterioration; deep top surface precipitation; thaumasite present.

SRPC – little evidence of chemical attack; surface sound; only slight precipitation on top surface; some thaumasite present; worst with limestone aggregate.

OPC – serious damage, mainly starting from cube corners with surface peeling; no thaumasite but gypsum present, yellow-brown color; worst with limestone aggregate.

PLC – very serious damage; major loss of concrete surface by chemical peeling, initiation at cube corners; no thaumasite but gypsum present, yellow-brown color; seems to be worst with gravel aggregate.

SRPC – discolouration and surface blistering; little damage at 12 months; gypsum present, brown color; worst with limestone aggregate.

Fig. 2. Visual observations of gravel and limestone concrete stored for 12 months in alkaline BRE DS-3 sulfate solution and sulfuric acid solution.

individually photographed. Any degradation products were easily removed with a spatula and left to air dry prior to grinding for examination by X-ray powder diffraction. Samples from the sound core of the concrete were also collected and crushed for X-ray diffraction analysis.

2.5. X-ray diffraction

Samples of the degraded surface material were believed to be free from core material because the latter could only be removed by crushing the cube. The dried samples from the surface layers were ground by hand to a fine powder (<63 µm) using an agate mortar and pestle. The powder was packed into a back-filled sample holder (to minimise preferred orientation) for examination in a Philips 1710 X-ray diffractometer using monochromatic CuKα radiation operating at a voltage of 50 kV and current of 30 mA. A scanning speed of 2°2θ/min and a step size of 0.02° were used to examine the samples in the range of 5–65°2θ.

3. Results

3.1. Visual observations

A montage of photographs of the cubes taken after storage in alkaline and acidic conditions is shown in Fig. 2. In general the extent of attack decreased in the sequence:

PLC>OPC>SRPC

Deterioration was generally greater in acidic solution than in alkaline, although the nature of the attack varied with pH, as discussed below. In alkaline DS-3 sulfate conditions, degradation commenced at the corners and edges of the cubes and was accompanied by formation of a white mushy deposit on the top surface of the cubes. The aggregate became exposed on each face of the cubes and some material was lost to the solution. The degree of deterioration in alkaline solutions was greater for cubes made with limestone aggregate rather than gravel. Only slight changes were observed in the case of the SRPC cubes.

After immersion in sulfuric acid solution all the cubes showed signs of attack, but this had different characteristics from those observed in alkaline conditions. Blistering, spalling and aggregate exposure were observed, although the cubes remained intact. The SRPC cubes were the least affected but showed blistering on all faces. Spalling commenced at the corners and edges of the cubes. One major difference from the cubes stored in alkaline conditions was the colour of the samples, which were orange-brown in acid, but grey in alkaline solutions. Very fine crystals were observed on the surfaces of the cubes stored in acid, which were shown by XRD to be gypsum.

3.2. X-ray diffraction

It is clear from Section 3.1 and from previous studies at Sheffield [8,9,12,13] that deterioration of the cubes commenced at the corners and edges of the cubes and progressed to the faces. A core of sound, unreacted material always remained in the cubes described here. The degradation products of interest were found in the surface layers of the cubes. XRD patterns of some such material found after six months have already been reported [12]. The XRD data shown here relate to samples that had been stored for 12 months.

An XRD pattern of the core material from the PLC concrete made using gravel aggregate is compared in Fig.

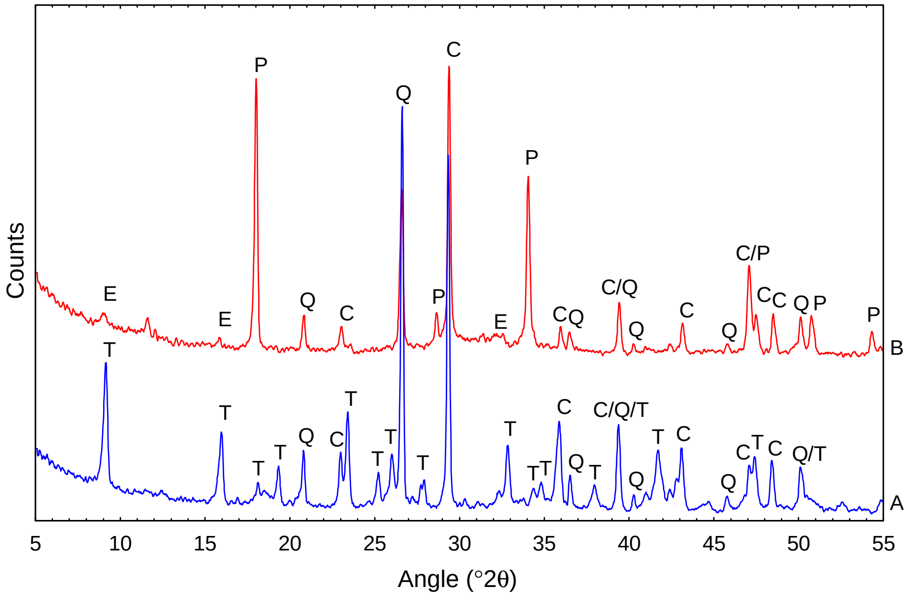


Fig. 3. XRD of PLC concrete cube made with gravel, stored in alkaline BRE DS-3 sulfate solution for 12 months, (A) surface layer and (B) core. E=ettringite, T=thaumasite, P=portlandite, Q=quartz, C=calcite.

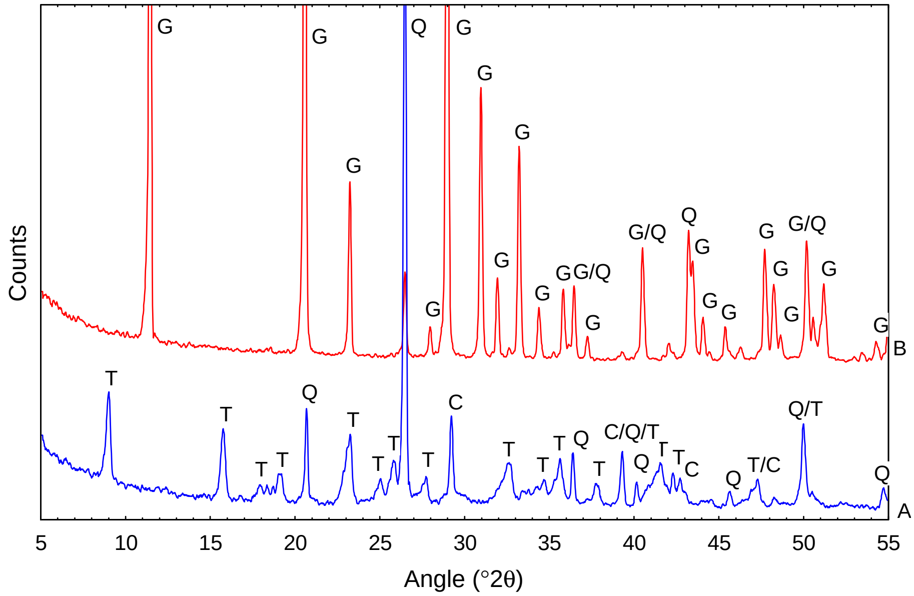


Fig. 4. XRD of OPC concrete cube made with gravel, stored in (A) alkaline BRE DS-3 sulfate solution and (B) sulfuric acid for 12 months. T = thaumasite, G = gypsum, Q = quartz, C = calcite.

3 with that of material from the surface layer of the same cube after storage in BRE DS-3 sulfate conditions at pH > 12 for 12 months at 5 °C. The core material consisted of quartz, gypsum, calcite, portlandite and ettringite, which are all phases expected to form during the normal curing of OPC. In the surface layer, however, thaumasite was observed, while gypsum, ettringite and notably portlandite were absent. More thaumasite and quartz were observed after 12 months, than after 6 months storage. This is attributed to the removal of some of the fine aggregate as the surface of the cubes became more degraded.

The XRD patterns of the degraded material taken from the surfaces of the OPC/gravel aggregate cubes after 11 months immersed in the two solutions are compared in Fig. 4. Both cubes were showing distinct signs of deterioration, but the surface layer of the cube stored in BRE DS-3 sulfate solution contained thaumasite and calcite, whereas the one stored at lower pH (acid solution) had intense gypsum peaks instead. Some quartz was observed in both samples.

The observations of formation of thaumasite were almost as clear cut when other concrete cubes were considered, including those made using OPC-limestone aggregate, PLC-gravel aggregate and PLC-limestone aggregate. Typical

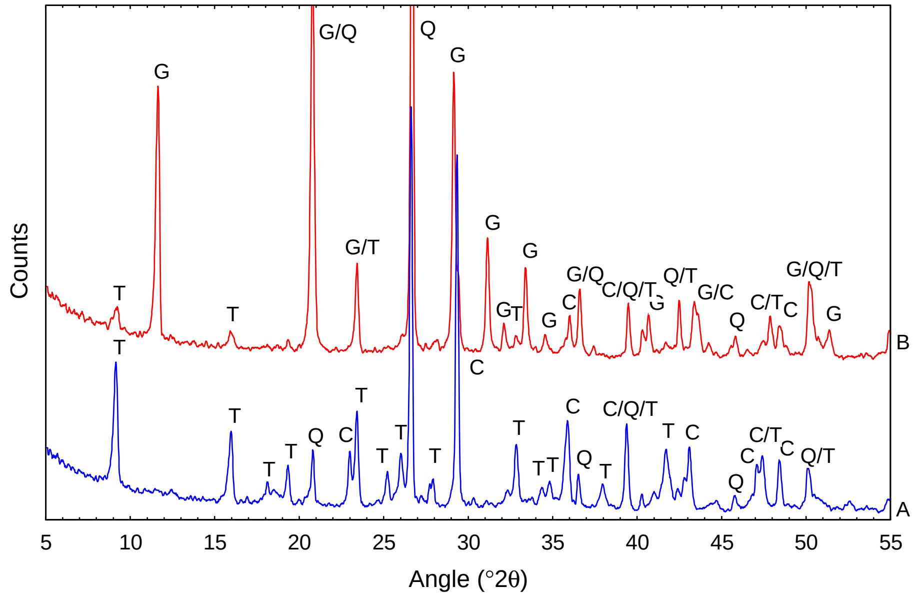


Fig. 5. XRD of PLC concrete cube made with gravel, stored in (A) alkaline BRE DS-3 sulfate solution for 12 months and (B) sulfuric acid for 12 months. T = thaumasite, G = gypsum, Q = quartz, C = calcite.

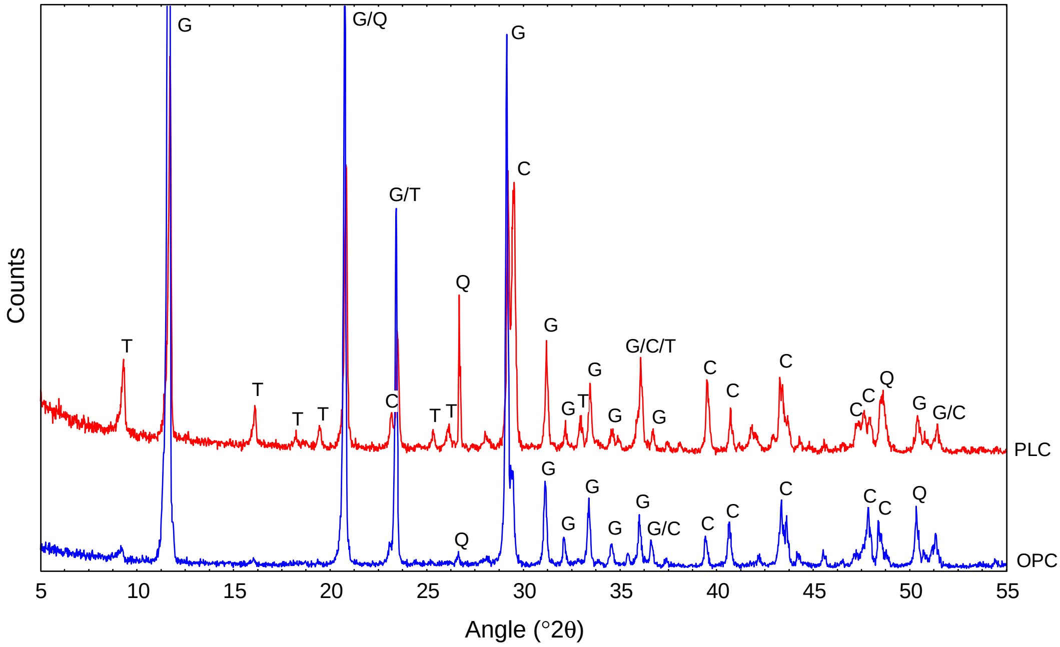


Fig. 6. XRD of (A) OPC and (B) PLC concrete cube made with limestone, stored in sulphuric acid solution for 12 months. T = thaumasite, G = gypsum, Q = quartz, C = calcite.

XRD results are shown in Fig. 5 for the PLC-gravel aggregate cubes stored in acid and alkaline solutions for 11 months. Under alkaline conditions, thaumasite was readily observed, especially in the case of the PLC cubes. Although the XRD pattern of the sample stored in acid was again dominated by the peaks due to gypsum, weak peaks due to thaumasite and calcite were also observed. No thaumasite, however, was observed in the deteriorated surface layer of OPC cubes made with limestone aggregate after storage for 12 months in acid (Fig. 6).

Table 1
Phases identified by X-ray diffraction in degraded surface layers

Conditions	Binder	Aggregate	Time (m)	Ett	Thaum	Gyp	Qz	Calcite	Arag	MH	CH
Alkaline	OPC	gravel	6		x			xx			
			12		xx		xx	xx			
	OPC	limestone	6		x			xxx			
			12		x		x	xxx			
	PLC	gravel	6		xx		x	xxx			
			12		xxx		xx	xxx			
	PLC	limestone	6		xx			xxx			
			12		xxx		x	xxx		x	
	SRPC	gravel	6		x	x	x	x			
			12		xx		xx	x		x	
	SRPC	limestone	6								
			12		xxx	x	x	xx	x	xx	
	OPC	gravel	6			xxx					
			12			xxx	xx				
Acid	OPC	limestone	6			xxx		xx			
			12			xxx	x	xx	x		
	PLC	gravel	6		x	xxx	x	x			
			12		x	xxx	x	x			
	PLC	limestone	6		x	xxx		xxx			
			12		x	xxx	xx	xxx		x	
	SRPC	gravel	6	x		xxx	x	x			
			12			xxx	x				
	SRPC	limestone	6			xxx					
			12			xxx					
Alkaline	Core	PLC/gravel	6	x		x	x	xxx			xxx
			12			x	x	xxx			xxx

Ett = ettringite, Thaum = thaumasite, Gyp = gypsum, Qz = quartz, C = calcite, Arag = aragonite, MH = brucite, CH = portlandite.
Relative importance in sample: x = low, xx = medium, xxx = high (but see text).

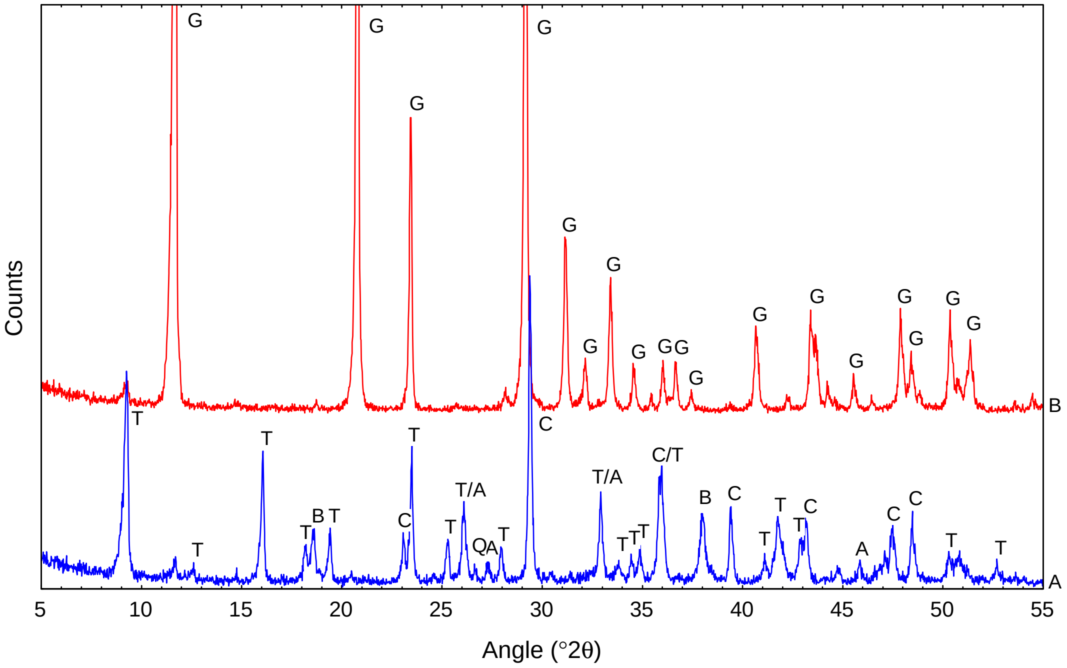


Fig. 7. XRD of SRPC concrete cube made with limestone, stored in (A) alkaline BRE DS-3 sulfate solution and (B) sulphuric acid for 12 months. A=aragonite, B=brucite, T=thaumasite, G=gypsum, Q=quartz, C=calcite.

When the XRD patterns of the cubes made with SRPC and stored in the two solutions were examined, the behaviour was again clear. Thaumasite was observed in cubes made from gravel and limestone, after 6 and 12 months in the alkaline solution (see Table 1), but not in the cubes stored at lower pH in the acidified solution, Fig. 7. The latter cubes gave X-ray patterns after 12 months that were dominated by the formation of gypsum and virtually free from all other phases except small amounts of quartz. On the other hand, the XRD patterns after storage in the alkaline solution indicated the formation of thaumasite, calcite and brucite in cubes made with gravel aggregate, while thaumasite, brucite, aragonite, and possibly gypsum formed in those made with limestone aggregate.

The phases observed by X-ray diffraction in the degraded surface layers of all the cubes reported in this paper are summarised in Table 1. The number of crosses in each column gives an indication of the relative peak

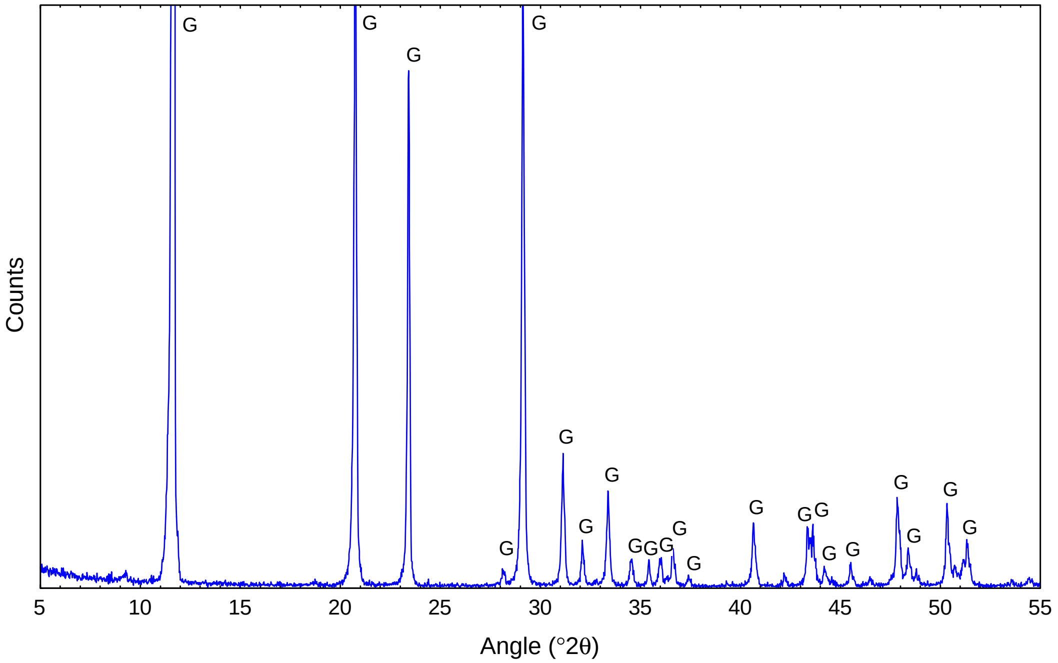


Fig. 8. XRD of SRPC concrete cube made with limestone, stored in acidified BRE DS-3 sulfate solution for 12 months. G=gypsum.

intensities. Three crosses for both thaumasite and calcite do not mean that there was as much thaumasite present as there was calcite, but rather give an indication that there was more thaumasite (or calcite) present in that sample than in others with only one or two crosses. The core material within all the cubes examined was similar and was found to be comprised of portlandite, ettringite, a trace of gypsum, quartz and calcite. The relative amounts of the last two phases varied according to the amount of limestone filler present in the cement and the particular aggregate used.

To ensure that the differences in mineralogy reported above were due to differences in pH, rather than to the presence or absence of Mg^{2+} and Ca^{2+} ions, a further set of concrete cubes made with SRPC was stored in DS-3 sulfate solution (containing calcium sulfate and magnesium sulfate) that was acidified every week. A typical XRD pattern of the degraded surface layer of one of these cubes is shown in Fig. 8. The product of the degradation was almost entirely gypsum, consistent with the results obtained in the sulfuric acid solution presented in Fig. 7.

3.3. Infra-red spectroscopy

An infra-red spectrum of the surface material from the cube made from SRPC cement with limestone aggregate after storage in alkaline BRE DS-3 sulfate conditions at 5 °C for 11 months is shown in Fig. 9, where it is compared with the IR spectrum of material from the core of the same cube. The spectra have some clear differences, indicating that there are differences in the composition of the samples. The key observation for the present purposes is the peak at 500 cm^{-1} evident in the surface layer, but hardly apparent in the core material. This peak is associated with silicon in octahedral coordination with respect to oxygen atoms [14] and is diagnostic for the presence of thaumasite, since octahedral silicon in other mineral silicates and cement hydrates is very rare. The other peaks observed can be attributed to carbonate and sulfate ions or to water molecules, as summarised in Table 2.

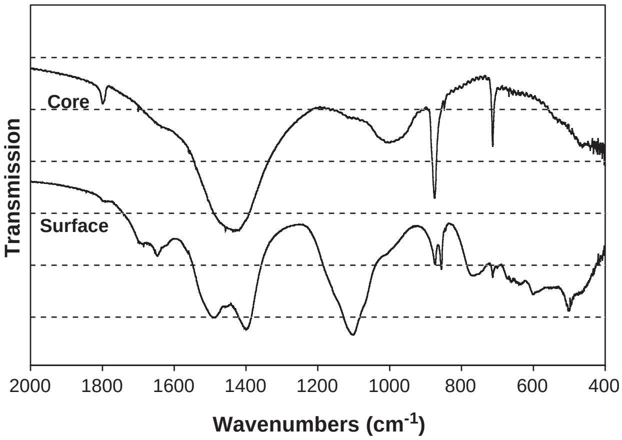


Fig. 9. IR spectra of SRPC concrete cube made with limestone, stored in alkaline BRE DS-3 sulfate solution for 12 months, (A) surface layer and (B) core.

Table 2
Summary of IR data and comparison with literature data

Thaumasite peaks (cm^{-1})	Bensted and Varma [14]	White [15]	Assignment [14]
497	500 s		SiO_6 bending
592	590 m		SO_4 bending
637	640 m		SO_4 bending
660	673 w		SiO_6 stretching
711		706 a, 712/724 c	
756	750 b,s		SiO_6 stretching
854		857 a	
872	887 m	873 a, 872 c	CO_3 bending
1096	1100 vs	1085 a, 1099 c	SO_4 stretching
1393	1400 s	1407 cc	CO_3 stretching
1476		1490 a, 1444 c	
1638	1650 m		H_2O bending
1677	1700 m		H_2O bending
1786			

vs = very strong, s = strong, m = medium, w = weak, b = broad, c = calcite, a = aragonite.

4. Discussion

4.1. Ordinary Portland cement

Cubes made using OPC (containing 5% limestone filler as permitted by European standard ENV197-1) that were stored in BRE DS-3 sulfate solution showed signs of deterioration after 6 months that had progressed further after 12 months. The attack commenced at the corners of the cubes and then progressed to the edges and finally to the faces. Similar cubes stored in sulfuric acid solution were also attacked, but the nature of the deterioration differed from that in alkaline DS-3 conditions. In the alkaline solution a soft, grey-white mush was formed in the expanded region and it fell away from the sides of the cube when it was lifted. The top layer of the cube was gradually raised until it became separated from the bulk of the cube. The material remaining on the top surface of the cube was examined by XRD and found to contain thaumasite. Clear differences were observed in acidified solutions. The sides of the cube had a distinct orange-brown coloration, typical of that associated with the presence of iron(III) ions. The top and side faces of the cubes became blistered and the hollows exposed when the blisters were broken contained gypsum and sometimes small amounts of thaumasite.

X-ray diffraction of the surface layers of the cube stored in the alkaline solution, such as that shown in Fig. 4, indicated that the degradation was clearly due to TSA after both 6 and 12 months storage, irrespective of whether gravel or limestone aggregate was used. These observations provide further confirmation of the danger of TSA developing in OPC containing only 5% limestone filler as discussed by Torres et al. [13]. No evidence was obtained for the presence of ettringite in these surface layers. The intensity of any peaks due to portlandite was so weak that its presence was uncertain even in low concentrations, confirming previous reports that it is not a product of TSA [8,9]. After 12 months storage, more quartz from the fine aggregate was observed in the XRD patterns, indicating that the extent of degradation had increased compared with that after 6 months, such that loosening of the aggregate had occurred.

The XRD patterns of the cubes stored in sulfuric acid solution were dominated by the presence of considerable amounts of gypsum, $CaSO_4.2H_2O$. Thaumasite was not observed after 6 months, but trace amounts were observed after 12 months in one or two cubes made with either limestone or gravel. The replacement of calcite (present in alkaline conditions) by gypsum is expected as the pH changes to acid conditions, according to the equation:

$$CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + H_2CO_3 \quad (2)$$

Although very small amounts of thaumasite were sometimes formed in the acidified solution, it was much more readily observed in the solution maintained at high pH.

4.2. Portland-limestone cement

The observations made on cubes made with PLC (containing 20% limestone filler) differed from those made with OPC in degree, but not in kind. The extent of the deterioration and the amount of thaumasite formed were greater with PLC than with OPC. Strong peaks due to calcite were observed at high pH, replaced by strong peaks due to gypsum at low pH. The presence of brucite (and the absence of portlandite) were observed after storage of the PLC limestone-aggregate cubes for 12 months in alkaline DS-3 sulfate solution (Table 1).

4.3. Sulfate-resisting Portland cement

The effect of pH was very clear in the cubes made with SRPC, although they were only somewhat degraded in both solutions. The SRPC cubes resisted the acid solution better than those made with OPC or PLC. The slight deterioration at low pH was due to classic acid attack and the XRD patterns of the degraded surface material (in cubes made with either gravel or limestone aggregate) were dominated by the presence of gypsum. No peaks due to the presence of thaumasite were observed.

By way of contrast, the degradation at high pH could be attributed to TSA. Even with gravel aggregate, thaumasite formation was apparent after 6 months and had intensified after 12 months. Greater attack occurred in the cubes made with limestone aggregate, and the XRD pattern obtained after 12 months (Fig. 7) indicated the presence not only of thaumasite, but also of brucite and aragonite. The latter phase is a metastable form of calcium carbonate that has been observed previously (e.g. Ref. [9]) in association with thaumasite formation. Its formation is almost certainly via a through solution mechanism (see below).

In the tests on cubes immersed in BRE DS-3 sulfate solution that was acidified weekly to maintain a similar range of pH to that of the acidified solutions without added Ca or Mg, no thaumasite was observed and the product of the degradation was gypsum (Fig. 8) as in the sulfuric acid solution. The same result was obtained for cubes made with gravel or limestone aggregate. These observations indicate that the differences between the cubes were due to changes in pH rather than to the concentration of Ca^{2+} and Mg^{2+} ions.

4.4. The role of acid in TSA

Understanding the role of acid in TSA is of great importance and urgency because of the instances of serious chemical attack, including that on the foundations of motorway bridges in the West of England. The affected concrete was in contact with a large volume of Lower Lias clay backfill, leading Hobbs and Taylor [10] to propose that sulfuric acid, formed by oxidation of pyrites within the backfill, reduced the pH of the groundwater resulting in attack on the foundations and in reactions that raised the groundwater sulfate level. They concluded that sulfuric acid attack was the probable primary cause of deterioration.

Crammond [1,2] distinguished TSA as a separate form of sulfate attack that has the potential to affect a wide variety of components and a range of building materials. She reserved the term TSA for cases where there is significant damage to the matrix of a concrete or mortar as a consequence of the replacement of cement hydrates by thaumasite, referring to thaumasite formation (TF) when thaumasite is observed in preformed voids and cracks without necessarily causing deterioration of the mortar or concrete. TSA-affected concrete turns into a soft, mushy mass with a distinctive white coloration, as observed in the present work in alkaline solutions (Fig. 2).

Based on the experimental work reported by Gaze and Crammond [15], Crammond [1] concluded that TSA will continue if the pH is maintained above 10.5. In contrast to Hobbs and Taylor [10], she suggested that the higher the pH, the greater the likelihood of TSA, although she did propose a mechanism through which deterioration of the cement matrix can still continue even if the pH drops below 10.5 [1].

On the basis of preliminary evidence, we concluded [12] that it is neither acidic conditions nor high concentration of sulfate ions alone that brings about the formation of thaumasite, but the combination of relatively high sulfate levels and alkaline conditions. The fuller investigation presented here confirms this conclusion. The phases observed in BRE DS-3 sulfate solution at high pH are listed in the top half of Table 1. All of the cubes stored in this solution showed symptoms of TSA and thaumasite was observed in the surface layer of each cube. The amount of thaumasite formed increased after 12 months compared with 6 months storage; cubes made from PLC or OPC contained more thaumasite than did SRPC after 12 months. Small amounts of brucite were detected in some of the cubes, generally those with the highest amounts of thaumasite. Calcite was always present, varying to some extent depending upon the amounts of limestone filler and limestone aggregate present. As the TSA progressed into the cube, the matrix holding the fine quartz aggregate was loosened with the consequence that quartz was detected in some of the X-ray patterns, particularly in those containing gravel aggregate after 12 months.

The phases observed in acidified solution are listed in the bottom half of Table 1. By comparison with the phases observed in alkaline solution, the effect of pH can be readily seen, notably by the dominant presence of gypsum in the degraded surface layers of all the cubes. In some cases, gypsum was the only phase present, but in others, notably those made with PLC, small amounts of thaumasite were detected, and, on one occasion only, ettringite. The amounts of thaumasite formed in acid solution were very much less than those observed in the alkaline solution, although the extent of deterioration tended to be greater.

Although small amounts of thaumasite were observed in some of the cubes stored at low pH, the overall evidence does not support the hypothesis that TSA is favoured by acid conditions. It is possible that thaumasite formation took place during the periods that the cubes were subjected to a pH above 10.5, in line with Crammond's views set out above, but we have no evidence to prove or disprove this. There is, however, clear evidence that TSA occurred readily in all the cubes stored at a pH of 12 and above in DS-3 sulfate solution. Cubes made from all three cements (OPC, PLC and SRPC) and both aggregates (gravel and limestone) were significantly degraded after 12 months. This is particularly noteworthy in the case of the SRPC/gravel system because there is no immediately obvious source of carbonate. Limestone filler was incorporated in the OPC (5%) and the PLC (20%), but not in the SRPC. Small amounts of calcite could be present in the gravel aggregate, but these were below the level detectable by XRD, so that it seems likely that the principal source of carbonate in the cubes made using SRPC was from the storage water or via atmospheric carbonation.

The relevance of this laboratory study to field instances of TSA, notably the M5 motorway bridge foundations, is that the primary cause of the deterioration observed in field studies is unlikely to be the low pH, but instead the increased levels of sulfate ions present in the ground due to the oxidation of pyrite. The sulfate level in the case of the motorway bridges is believed to have increased from BRE Class DS-2 to Class DS-4B [7].

It may be possible that storage in acid conditions could result in enhanced leaching accompanied by modification of the pore structure, resulting in increased surface area otherwise inaccessible in alkaline conditions. The reinstatement of alkaline conditions after acid leaching could give rise to enhanced formation of thaumasite in the presence of increased sulfate concentration derived from the gypsum precipitated at low pH. Such circumstances might result in substantial TSA.

4.5. Through solution mechanism

Many previous workers have suggested that thaumasite formation occurs via a through solution mechanism, in which ions from the reactants enter solution, which then becomes supersaturated with respect to thaumasite and other reaction products (notably gypsum and brucite). Whether or not thaumasite precipitates from this solution depends on the relative solubility products of thaumasite, ettringite, gypsum, calcite, portlandite and brucite, which vary with temperature and the various ions present in solution.

The observation that aragonite was formed from the SRPC concrete used in this investigation is evidence in favour of the through solution mechanism. It is indicative that carbonate ions are entering solution in sufficient quantities to permit the transformation of calcite into aragonite. This transformation has also been observed in our previous studies [9,13] and is believed to be favoured by the presence of Mg^{2+} ions in solution [16]. In other circumstances, a similar through solution mechanism can lead to the precipitation of massive coarse crystals of “popcorn” calcite [1,6].

5. Conclusions

- TSA occurred within 5 months in concrete cubes stored in DS-3 sulfate solution at 5 °C at pH of 12 or above and caused significant damage to the cubes within 12 months.
- This attack was particularly severe in the case of cubes made with PLC (containing 20% limestone filler), but was also evident in those made from OPC (incorporating 5% limestone filler) and SRPC (with no added filler or limestone aggregate). Both SRPC and Portland cement incorporating 5% limestone filler should be used cautiously in buried concrete liable to come into contact with sulfate containing ground water.
- The presence of acid does not promote the formation of thaumasite. Although thaumasite was observed in lesser amounts in cubes immersed in sulfuric acid solution at 5 °C, the nature of the corrosive attack was different.
- Both C-S-H gel and portlandite are consumed during the formation of thaumasite, which is often accompanied by the formation of gypsum and, when magnesium is present, brucite.
- Initial attack of concrete by acid could result in it being highly vulnerable to TSA should this be followed by alkaline, high sulfate conditions.

- The observation that aragonite was formed in some cubes supports the hypothesis that the reaction proceeds via a through solution mechanism.
- It is likely that the TSA observed in buried concrete associated with the M5 motorway in the West of England is due to the increased sulfate content of the ground associated with the oxidation of pyrite, rather than due to low pH associated with the production of sulfuric acid.

Acknowledgements

We acknowledge EPSRC for a grant to support this research. We are grateful to scientists and engineers from BRE, BCA, Castle Cement, CSMA, RMC and UKQAA for supply of samples and helpful discussions.

References

[1] N.J. Crammond, The thaumasite form of sulfate attack in the UK, Cem. Concr. Compos. 25 (2003) 393–402.

[2] N.J. Crammond, The occurrence of thaumasite in modern construction—a review, Cem. Concr. Compos. 24 (2002) 393–402.

[3] J.A. Bickley, R.T. Hemmings, R.D. Hooton, J. Balinsky, Thaumasite related deterioration of concrete structures, Proc. Concr. Technol.: Past, Present and Future ACI SP 144-8 (1995) 159–175.

[4] E. Freyburg, A.M. Berninger, Field experiences in concrete deterioration by thaumasite formation, possibilities and problems in thaumasite analysis, Cem. Concr. Compos. 25 (2003) 1105–1110.

[5] M. Romer, L. Holzer, M. Pfiffner, Swiss tunnel structures: concrete damage by formation of thaumasite, Cem. Concr. Compos. 25 (2003) 1111–1118.

[6] P. Hagelia, R.G. Sibbick, N.J. Crammond, C.K. Larsen, Thaumasite and secondary calcite in some Norwegian concretes, Cem. Concr. Compos. 25 (2003) 1131–1140.

[7] Thaumasite Expert Group, The Thaumasite Form of Sulfate Attack: Risks, Diagnosis, Remedial Works and Guidance on New Construction, Department of the Environment, Transport and the Regions, London, 1999 (January).

[8] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, Thaumasite formation in Portland-limestone cement paste, Cem. Concr. Res. 29 (1999) 1331–1340.

[9] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, The thaumasite form of sulfate attack in Portland-limestone cement mortars stored in magnesium sulfate solutions, Cem. Concr. Compos. 24 (2002) 351–359.

[10] D.W. Hobbs, M.G. Taylor, Nature of thaumasite sulfate attack mechanism in field concrete, Cem. Concr. Res. 30 (2000) 529–533.

[11] BRE Special Digest 1, Concrete in aggressive ground. Building Research Establishment, CRC Ltd, London, UK, 2001.

[12] J. Hill, E.A. Byars, J.H. Sharp, J.C. Cripps, C.J. Lynsdale, Q. Zhou, An experimental study of combined acid and sulfate attack of concrete, Cem. Concr. Compos. 25 (2003) 997–1003.

[13] S.M. Torres, J.H. Sharp, R.N. Swamy, C.J. Lynsdale, S.A. Huntley, Long term durability in Portland-limestone cement mortars stored in magnesium sulfate solution, Cem. Concr. Compos. 25 (2003) 947–954.

[14] J. Bensted, S.P. Varma, Studies of thaumasite—Part II, Silictes Industriels 39 (1974) 11–19.

[15] M.E. Gaze, M.J. Crammond, The formation of thaumasite in a cement:lime:sand mortar exposed to cold magnesium and potassium sulfate solutions, Cem. Concr. Compos. 22 (2000) 209–222.

[16] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock-forming Minerals, Longmans, Green and Co., London, 1966, p. 498.