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Effect of cement C_3A content, temperature and storage medium on thaumasite formation in carbonated mortars

M.T. Blanco-Varela [a,*], J. Aguilera [a,b], S. Martínez-Ramírez [a]

[a] Instituto de Ciencias de la Construcción Eduardo Torroja, (CSIC), c/ Serrano Galvache 4, 28033 Madrid, Spain
[b] Cementos el Monte, c/ Muelle Ingeniero Juan Gonzalo s/n, 21810 Palos de la Frontera (Huelva), Spain

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Abstract

The purpose of this study is to determine the effect of cement C_3A content, temperature and composition of the immersion medium (water, gypsum and magnesium sulphate solution) on the rate of thaumasite formation in cement mortars. It also aims to ascertain how the C_3A content influences the composition of the salt formed.

The mortar prisms for this study were made with two different cements, one with low and the other with high Al_2O_3 content, with or without gypsum and/or calcium carbonate. After hydration, curing and carbonation, the prisms were partially immersed in distilled water and stored at temperatures ranging from 0 to 5 °C for up to 5 years. Some of the prisms were immersed in a 2% (w/w) gypsum solution or in 1.4% (w/w) magnesium sulphate solution at ambient temperature. Samples were taken at different ages and mineralogical and micro-structurally characterised.

Some of the specimens tested were observed to expand, in a process concurring with the formation of thaumasite or a solid solution of thaumasite and ettringite, at both ambient and cooler temperatures. A correlation was found between cement C_3A content and the composition of the deterioration product involved in the expansive process: thaumasite forms in mortars made with low C_3A cement, whereas mixed crystals or solid solutions of thaumasite and ettringite form in mortars made with high C_3A content cement.

Keywords: Thaumasite; Concrete durability; Expansive process; Sulphate attack

1. Introduction

Concrete attack by sulphates is a well known and widely studied phenomenon and an acknowledged cause of concrete deterioration [1–3]. For many years ettringite formation was regarded to be chiefly responsible for such attacks. The use of sulphate-resistant–i.e., low C_3A content–cement is recommended to minimise this process. In recent years, a new form of sulphate attack associated with thaumasite formation has been identified, more often although not exclusively in foundations and other underground structures [4].

A report [4] drafted by the Thaumasite Expert Group formed in the UK to address this problem defined two types of processes: TSA (Thaumasite form of Sulphate Attack), involving a sulphate attack on concrete or mortar with very destructive effects, and TA, consisting of not necessarily destructive thaumasite formation in pores and cracks. The report cites four primary risk factors that must be simultaneously present for TSA processes to take place in buried concrete. These factors are:

- presence of sulphates and/or sulfides in the ground,
- presence of mobile groundwater,
- presence of carbonate, generally in coarse and/or fine aggregates,
- low temperatures (since the formation of thaumasite is most active at below 15 °C).

It was initially thought that thaumasite form of sulphate attack process could be inhibited by using (low C_3A content) sulphate-resistant cement. Nonetheless, high quality concrete, made with such cement [4], was found to be affected by TSA.

In this regard Nobst and Stark [5] studied the performance of two types of highly sulphate-resistant Portland cements

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* Corresponding author.
E-mail address: blancomt@ietcc.csic.es (M.T. Blanco-Varela).

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(German standard DIN 1164 specifies a maximum C_3A content of 3%). Thaumasite formation was observed to be high in sulphate-resistant cements with very low C_3A contents (2.9% and 1.1%) at 6 °C, whereas at ambient temperature the amount of thaumasite formed was negligible.

Brown and Hooton [6] studied the performance of two types of sulphate-resistant cements, one ASTM Type V sulphate-resistant cement containing 3.5% C_3A and the other ASTM Type II moderate-sulphate resistant cement containing 7.1% C_3A. Based on their results, they concluded that sulphate attack occurred in both cements due to ettringite as well as thaumasite formation.

Aguilera et al. [7] studied thaumasite formation in mortars made with two cements, one with 1.24% C_3A and the other with 13.3% C_3A content, mixed with varying proportions of gypsum and/or calcite and submerged in water at 5 °C. They concluded that thaumasite forms in mortars made with C_3A-low cement, but the rate of formation is much slower than in mortars made from cement with a high C_3A content.

Higgins et al. [8] explored how cement-type, aggregate-type and curing conditions (at 5 and 20 °C up to 6 years) affect the susceptibility of concrete to the TSA. The cements were Portland cement (PC), sulphate-resisting Portland cement (SRPC) and a combination of 70% ground granulated blastfurnace slag (ggbs) with 30% PC. Deterioration, consistent with TSA, was observed on many of the PC and SRPC concretes that had been made with carbonate aggregate and stored in sulphate solutions at 5 °C, with SRPC providing no better resistance to TSA than PC. Good quality concretes made with 70% ggbs/30% PC showed high resistance to TSA and the presence of carbonate in the mix substantially improved their general sulphate resistance.

Mulenga et al. [9] studied the effect of fly ash on thaumasite formation. The presence of the ash was found to improve cement sulphate-resistance at 20 °C. At 8 °C, however, cement both with and without fly ash were vulnerable to the thaumasite form of sulphate attack.

Justnes [10] studied the behaviour of mortars with 20% limestone or quartz filler, respectively, stored in gypsum-saturated 5% sodium sulphate solution at 5 °C. The author concluded that mortars with 20% limestone filler form excessive amounts of thaumasite in the binder after 10 months of exposure, resulting in expansion and loss of mass and strength.

Sagrera et al. [11] observed thaumasite and ettringite in a decayed rendering mortar of lime, gypsum and cement from Canary Island; ettringite was found in the internal side of sample together with portlandite while thaumasite was located at the external carbonated zones were portlandite was not present.

Thaumasite formation kinetics appear to be enhanced at temperatures of less than 15 °C and low temperatures have been unanimously [4,7] reported to accelerate thaumasite formation. Although the process takes longer, the mineral also forms at temperatures of around 20 °C and, indeed, the literature contains accounts of such developments under both real [12] and laboratory [7] conditions. Diamond [5] reported that significant thaumasite deposits were found in buildings located in Southern California, where mild temperatures prevail [13].

The purpose of the present study is to compare the rate of thaumasite formation in cement mortars, varying the cement C_3A content, temperature and immersion medium (water, or gypsum or magnesium sulphate solution) used in the tests. Another aim of the study is to ascertain the effect of cement C_3A content on the composition of the salt formed.

2. Experimental

Two types of cement were used, one with low C_3A content (type BA), and the other (type AA) with high C_3A content. The chemical and mineralogical composition (according Bogue) of the two cements is given in Table 1.

The mortars were made with three types of binders, with the following composition:

- cement (1AA and 1BA),
- cement + 5% gypsum (2AA and 2BA),
- cement + 5% gypsum + 10% calcite (5AA and 5BA).

Fifty 1 × 1 × 6 cm mortar prisms were made with each of the above binders, using siliceous sand, a cement/sand ratio of 1:3 and a water/cement ratio of 0.7. These specimens were cured for 3 months at 21 °C and a relative humidity of 95–100% and subsequently subjected to accelerated carbonation for 3–4 days, being the carbonation conditions: RH = 60%, $T = 21 \pm 2$ °C, 100% CO_2. The carbonation was considered finished when the XRD patterns of mortars did not show the reflections of portlandite. The CO_2 content of mortars after carbonation process was determined by ATD/TG. Mortar specimens were grounded to less than 45 μm size and then studied by ATD/TG with the conditions that maximum temperature is at 1000 °C and heating rate is 4 °C/min. Table 2 shows the lost of weight of samples from 25 °C to 1000 °C together with the $CaCO_3$ content of mortars.

Thereafter the mortar specimens were partially submerged in distilled water and stored at temperatures ranging from 0 to 5 °C for up to 60 months. After 5 months of immersion in water, one sample of each type of mortar was submerged in $MgSO_4$ solution (1.4% w/w) and another in a $CaSO_4{\cdot}2H_2O$ (2% w/w) solution for 16 months at 21 °C.

XRD and FTIR of the mortars was performed at the following times: end of the hydration process; end of the

Table 1
Chemical composition of BA and AA type cements, in % by weight

	LOI	I.R	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	CaO_{free}
BA	1.66	0.57	20.44	3.07	4.08	66.43	0.94	2.90	1
AA	2.88	0.53	19.68	6.01	1.57	63.30	1.99	3.20	0,3

Phase composition using Bogue's calculation

	C_3S	C_2S	C_3A	C_4AF
BA	76.22	1.49	1.24	12.4
AA	55.1	15.16	13.27	4.77

Table 2
Loss of weight of mortars after carbonation process (from TG); percentage of calcite in mortars and percentage of CaO of cement transformed into $CaCO_3$

	Loss of weight (%)			$CaCO_3$	%CaO of cements transformed into $CaCO_3$
	25–700	700–1000	Total		
1AA	7.8	4.2	13.0	9.5	37.5
2AA	9.1	4.4	13.5	10.0	37.9
5AA	9.2	5.2	14.4	11.8	37.0
1BA	8.2	5.1	13.3	11.6	44.6
2BA	7.9	5.0	12.9	11.4	43.4
5BA	7.1	6.3	13.4	14.3	47.5

carbonation process; and at approximately 3-month intervals during immersion in H_2O at temperatures of 0–5 °C or in sulphate solutions at 21 °C. Sample 5AA, kept in water at 5 °C for 1 year, was further characterised using ^{29}Si [^1H]CP/MAS NMR techniques. Microstructural characterisation of samples was also performed in a SEM/EDX JEOL JMS-5400, operating at 20 kV, studying the cracking surface and the powder growing in the cracks or surface of samples.

3. Results

Post-curing XRD and FTIR mineralogical characterisation studies revealed the presence of calcite, gypsum (except 1AA and 1BA) and quartz in the mortars made with both types of cement, and of ettringite in cement with a high C_3A content. As a result of mortar dosing, the most intense absorption bands on the X-ray diffraction patterns and FTIR spectra for these samples were the quartz bands. FTIR spectra also showed absorption at about 970 cm^{-1} characteristic of C–S–H gel.

In all the mortar types, carbonation produced portlandite conversion to calcite, and consequently an increase in the intensity of reflection of calcite in the XRD pattern while a decrease of the gypsum reflections was also observed. The amount of $CaCO_3$ in hydrated samples was rather high between 9.5% and 14.3% w/w, this means that the amount of CaO of cement transformed into $CaCO_3$ was from 37% to 47% (Table 2). In the samples containing ettringite, the mineral was observed to decompose partially into gypsum, aluminium hydroxide and aragonite.

Table 3 lists the mineralogical composition obtained from the X-ray diffractograms of the mortars after storage at different times in the three solutions: (a) water (at 5 °C), (b) gypsum and (c) $MgSO_4$ solutions (at 21 °C). The main phases detected in all samples are quartz and calcite while gypsum is observed as traces. In many cases the low intensity and the high width of reflections did not allow to distinguish whether they corresponded to thaumasite and/or ettringite or a solid solution of both phases. Finally, the table specifies (marked with an asterisk) whether samples were cracked.

3.1. Microstructural characterisation

3.1.1. Cement mortars stored in water at 5 °C

The SEM/EDX study of these samples showed that all mortars were highly carbonated, with very well-formed calcite crystals. No ettringite or thaumasite needles were found in samples 1AA, 2AA, 1BA, 2BA or 5BA immersed in water for 26 months; at that age, only sample 5AA showed outward signs of deterioration in the form of cracks.

Sample 5AA (26 months) (Fig. 1) was also highly carbonated and covered with calcite crystals, with occasional acicular crystals in addition to the sand particles. The CSH matrix was difficult to distinguish. Under EDX analysis, the needle-shaped crystals found in areas where expansion had taken place proved to be composed primarily of calcium (60–80%), with the following minority elements: Al (3.2–5.5%), Si (12.4–14.4%) and S (6.8–9.6%). The band at $\delta = -179$ ppm on the ^{29}Si [^1H] CP/MAS NMR spectrum of sample 5AA (stored in water at 5 °C for 1 year) (Fig. 9) constitutes evidence of the presence of octahedrally coordinated silicon, an indication that after 1 year thaumasite or the solid solution between thaumasite and ettringite had already begun to form.

The 1BA and 2BA prisms, made with C_3A-low cement in the absence of any calcite additive, cracked after 60 and 36 months, respectively (Figs. 2 and 3). Their FTIR spectra (Fig. 4) and SEM/EDX results (Figs. 2 and 3) confirm the XRD findings showing that both samples contained thaumasite.

3.1.2. Cement mortars stored in 2% gypsum solution at 21 °C

The prisms made with cement containing 13% C_3A and no calcite additive, namely 1AA and 2AA, showed no external cracking, but after 16 months their entire surface was covered with needle-shaped crystals. Under EDX analysis these needles proved to contain varying proportions of Si, Al, S and Ca.

Table 3
Mineralogical composition obtained from the X-ray diffractograms of the mortars after storage at different times in the three solutions: (a) water (at 5 °C), (b) gypsum and (c) $MgSO_4$ solutions (at 21 °C)

Storage time/T^a/immersion medium	Sample	Phases
26 months/5 °C/H_2O	1AA	Q+++ Calc++ Gy o Aft o
	2AA	Q+++ Calc++ Gy o Aft o
	5AA*	Q+++ Calc++ Aft ? Th?
	1BA	Q+++ Calc++ Aft ? Th?
	2BA	Q+++ Calc++ Gy o Aft ? Th?
	5BA	Q+++ Calc++ Gy o
60 months/5 °C/H_2O	1BA* (Fig. 2)	Q+++ Calc++ Th
36 months/5 °C/H_2O	2BA* (Fig. 3)	Q+++ Calc++ Th
16 months/21 °C/$CaSO_4 \cdot 2H_2O$ solution	1AA	Q+++ Calc++ Gy o Aft ? Th?
	2AA	Q+++ Calc++ Gy o Aft ? Th?
	5AA* (Fig. 5)	Q+++ Calc++ o Aft ? Th?
	1BA* (Fig. 5)	Q+++ Calc++ Th o
	2BA* (Fig. 5)	Q+++ Calc++ Gy o Th o
	5BA	Q+++ Calc++ Gy o Aft ? Th?
16 months/21 °C/$MgSO_4$ solution	1AA	Q+++ Calc++ Gy o Aft ? Th?
	1BA* (Fig. 5)	Q+++ Calc++ Th o

Q=Quartz; Calc Calcite; Gy=Gypsum; Aft=Etringitte; Th=Thaumasite.
+++=very much; ++=much; o=traces, ?=doubt; *=prisms cracked.

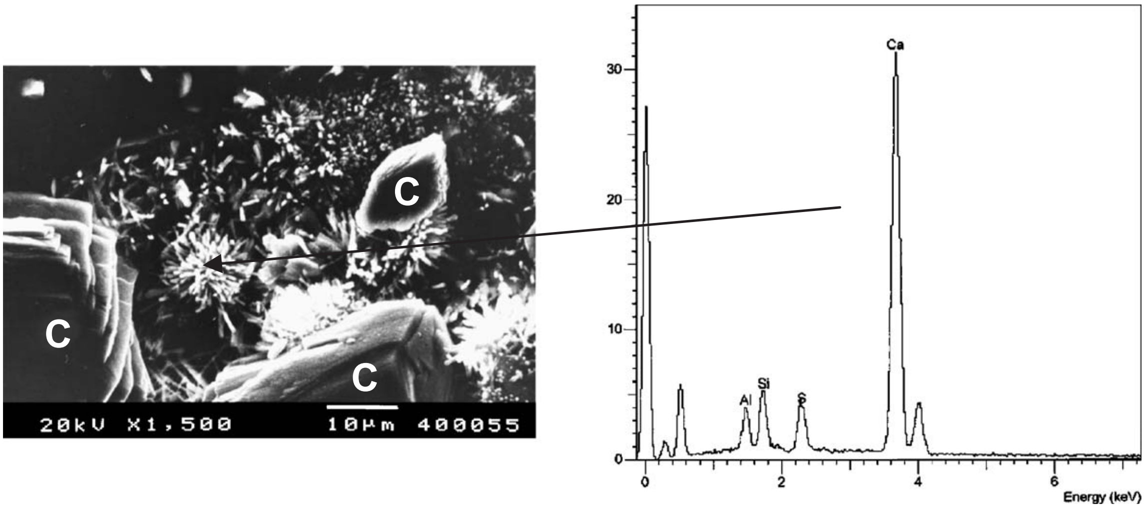

Fig. 1. SEM image of mortar 5AA after storage in water for 26 months. Calcite crystals © and thaumasite–ettringite solid solutions or mixed crystals. EDX analysis of the needles.

According to EDX analysis, the composition in the areas where the crystals were fully developed was: Al (7–13%), Si (9–11%), S (12–17%) and Ca (61–70%), all of which suggests that they may have been solid solutions or mixed crystals of ettringite and thaumasite.

After 16 months of immersion, the 5AA-type prisms–made with 13% C_3A cement plus 5% of gypsum and 10% calcite–exhibited expansion cracks visible to the naked eye. See Fig. 5. SEM observation of the samples shows that the surface morphology around the crack was very uneven, with highly carbonated areas covered by smooth and corroded calcite crystals. The areas with high carbonate content had fewer needles. There were also areas with many well-developed and crystallised needles, alongside others with bundles of small needles, as shown in Fig. 6. EDX results (Al, 4–8%; Si, 11.9–17.9%; S, 14.2–18.4%; and Ca, 52.56–61.74%) indicated that such crystals could be ettringite–thaumasite solid solution or to mixed crystals of the two phases.

Type 1BA and 2BA prisms, made with C_3A-low cement, expansion-cracked after 16 months in the test solution (Fig. 5). SEM/EDX studies confirmed FTIR (Fig. 4) finding and identified the needle-shaped crystals as thaumasite (Fig. 7),

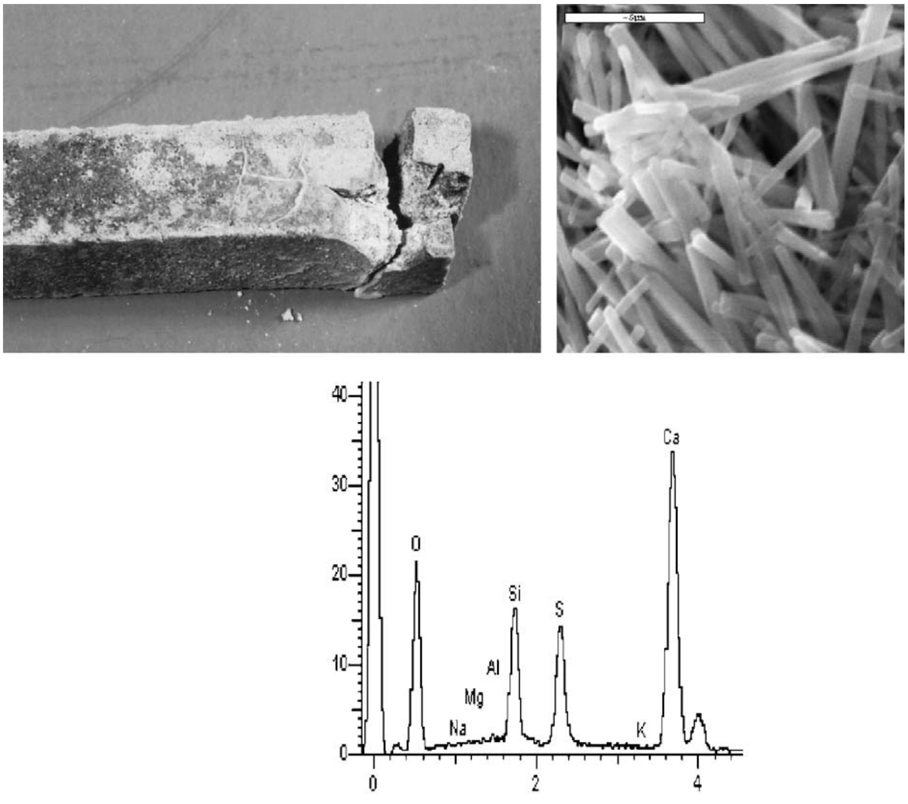

Fig. 2. Prism made with 1BA mortar, cracked after 60 months of storage in water; thaumasite crystals present around the crack and EDX analysis of these crystals.

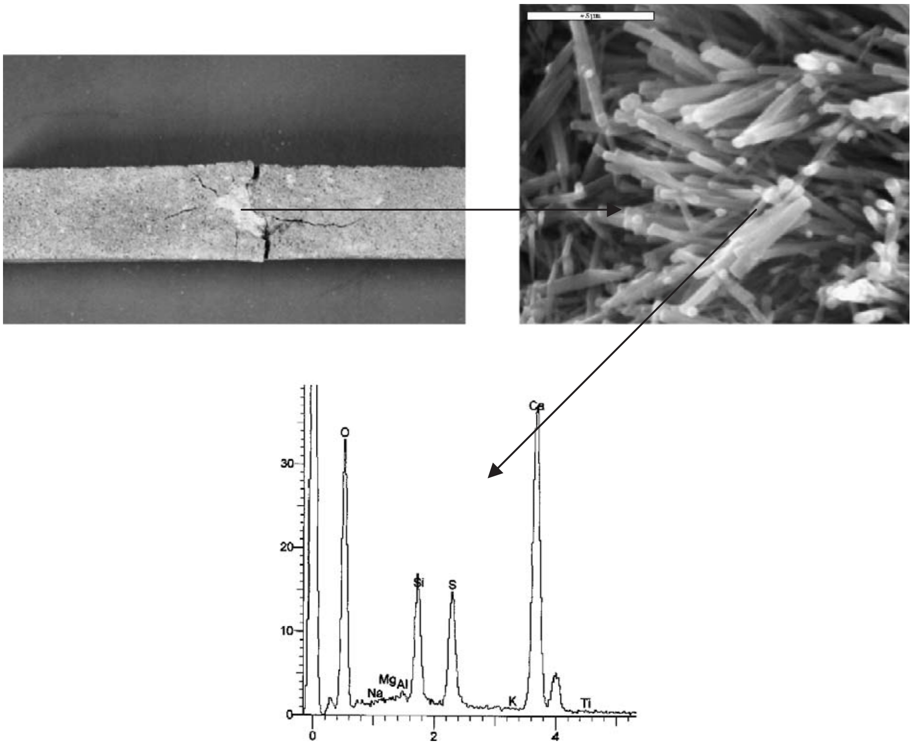

Fig. 3. Prism made with 2BA mortar, cracked after 36 months of storage in H_2O. EDX analysis of the needles.

whose composition was found to be as follows: Ca (60–63%), Al (0.5–2%), Si (16.9–18%) and S (17.6–20.6%).

3.1.3. Cement mortars stored in 1.4% magnesium sulphate solution at 21 °C

No cracks owing to the growth of expansive phases were observed in mortar type 1AA prisms made with 13% C_3A cement. Nonetheless, some incipient needle-shaped crystal growth was found in certain areas of the mortar, which EDX analysis did not clarify if it corresponds to thaumasite or ettringite or a solid solution between the two phases.

The type 1BA prisms were cracked and broken (Fig. 5), with a large number of sulphate-rich as well as calcite crystals along the cracked area (Fig. 8). SEM/EDX results revealed the presence of very well developed needles which were identified as thaumasite on compositional grounds: Ca (≈ 65%), Si (≈ 17%), Al (≈ 1.4%) and S (≈ 15%).

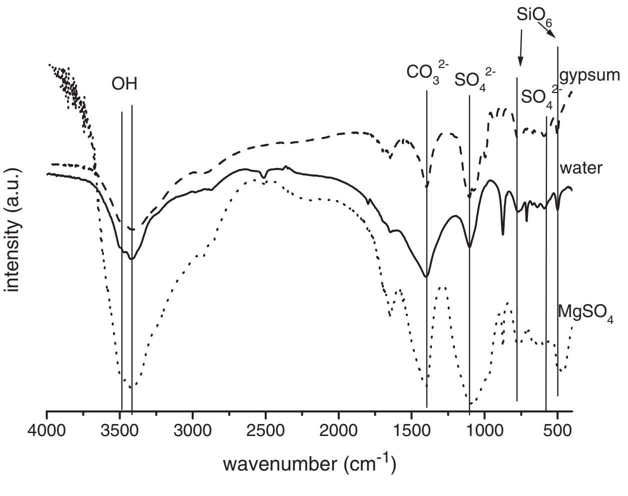

Fig. 4. FTIR of 1 BA samples in different storage medium.

4. Discussion

4.1. Cement mortar stored in water at 5 °C

The thaumasite forming on type 1BA (no additives, 60 months) and 2BA (5% gypsum added, 36 months) prisms immersed in water at temperatures of from 0 to 5 °C had proliferated sufficiently to have a destructive impact.

Notably, thaumasite formed on prisms made with carbonated C_3A-low mortars and no additional or external source of sulphates (sample 1BA): in other words, the sole source of sulphates was the cement itself. The process was expansive and slow (60 months). No destructive process or thaumasite

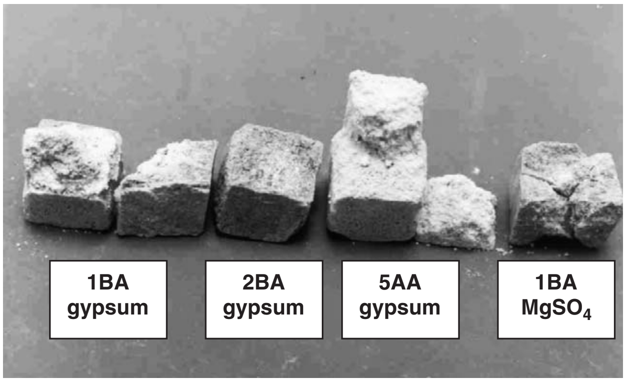

Fig. 5. Mortar prisms damaged after storage in different sulphate solutions.

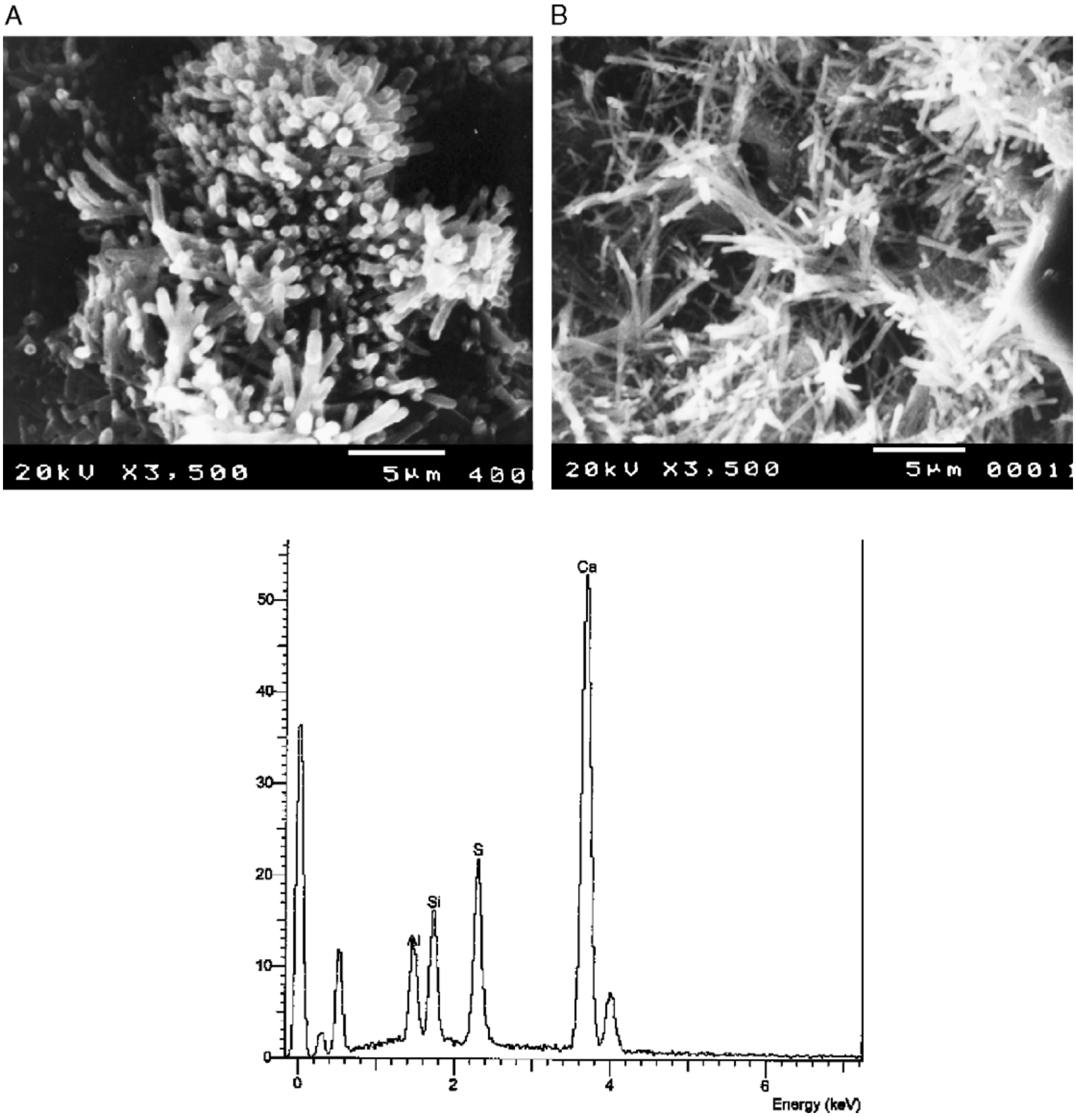

Fig. 6. Microphotograph of a cracked area in a 5AA mortar prism after 16 months in a 2% gypsum solution; (A) incipient needles and (B) fully crystallised needles attributable to a solid solution or mixed crystals of ettringite and thaumasite. EDX analysis of the needles.

formation was observed, however, in comparable prisms of the same age prepared with cement containing 13% C_3A (likewise containing no additional gypsum) (sample 1AA).

The addition of 5% gypsum to the cement accelerated the thaumasite-forming in mortars made with C_3A-low cement, which cracked showing an expansive deterioration process at the age of 36 months (sample 2BA), whilst prisms made from cement mortars containing 13% C_3A were unaffected by the inclusion of gypsum (sample 2AA).

The differential behaviour between mortars 1BA and 2BA on the one hand and 1AA and 2AA on the other provides evidence that internally generated sulphate attack and thaumasite formation are favoured in cements with low C_3A content.

It may be added that in mortars 1BA and 2BA, which cracked at 60 and 36 months, respectively, the carbonate required to form thaumasite was a product of the carbonation process. This indicates that the presence of limestone aggregates is not indispensable, and that the conditions necessary for the formation of this mineral may arise in older, carbonated concrete. These results concur with the data reported by Sahu et al. [14], who found thaumasite in concrete containing no limestone aggregate.

Cracks were observed in the prisms made with 5AA mortar after 26 months in water. The only prism made with high C_3A content cement that was destroyed was the sample in which 5% gypsum and 10% calcite were added to the cement (sample 5AA). Although slow (26 months), this expansive process nonetheless took place more quickly than in the two cases described in the preceding paragraph. XRD characterisation of the expansive agent causing the damage in these samples indicated that it might be ettringite, although the low intensity ($2\theta = 9.09$, $I/I_{max} = 0.9$) and width ($2\theta = 0.2°$) of its most intense reflection raised some doubts about whether it was ettringite, thaumasite or both phases. The SEM/EDX data suggested that the agent involved could be mixed crystals or a solid solution of ettringite and thaumasite. NMR confirmed the existence of octahedral silicon (Fig. 9). ^{29}Si [^{1}H] CP/MAS NMR afforded unequivocal information on the existence of silicon in an

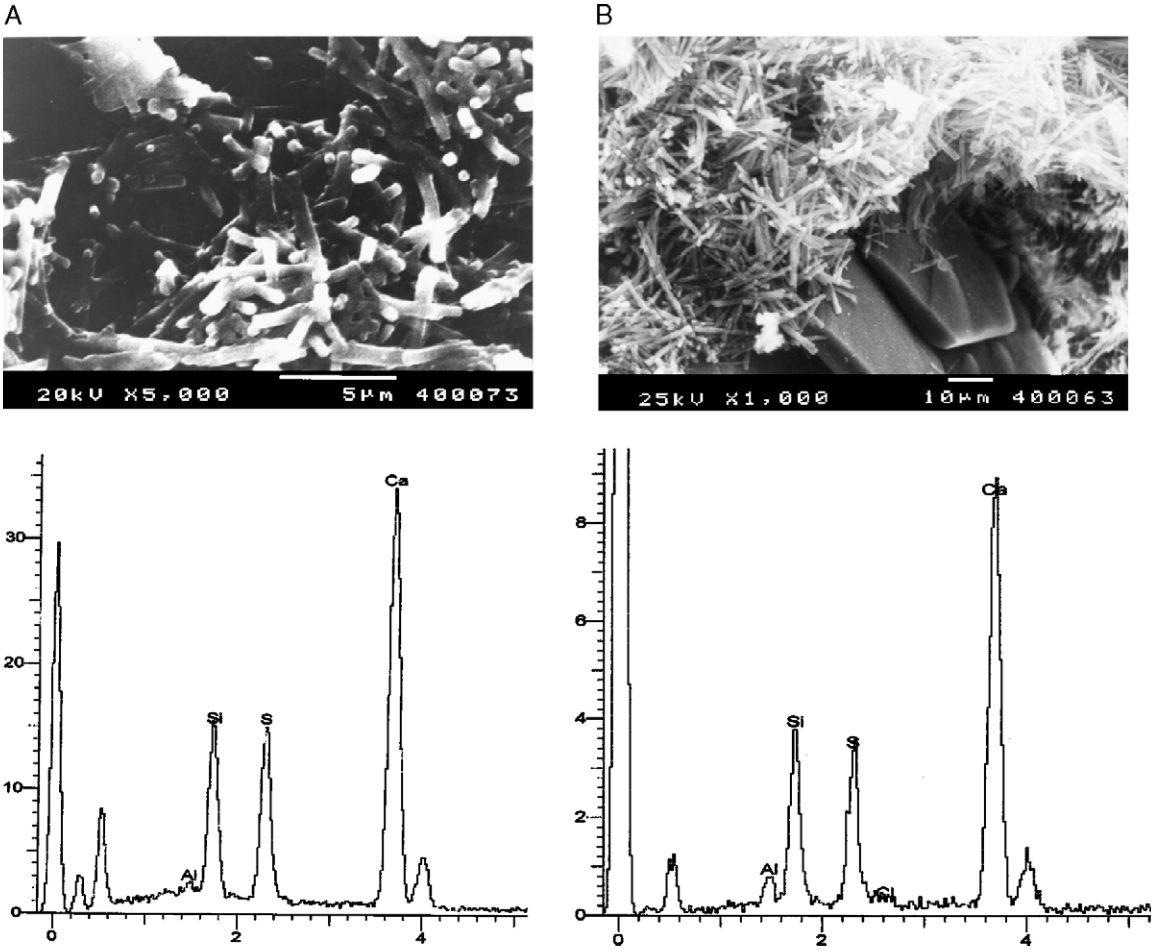

Fig. 7. Thaumasite needles in mortars kept in 2% gypsum solution at 21 °C for 16 months. (A) Mortar 1BA and (B) Mortar 2BA.

octahedral configuration [15]. Although the signal for the octahedrally coordinated silicon in thaumasite is well known, no description of the signal for such silicon in solid solutions of thaumasite and ettringite is to be found in the literature. But as the silicon is surrounded in both cases by 6 OH groups, the respective signals are likely to differ very little. Hence, the presence of the signal referred on the ^{29}Si [^{1}H] CP/MAS NMR spectrum would confirm the presence of thaumasite or thaumasite–ettringite solid solution crystals; the additional presence of ettringite cannot be ruled out on 5AA sample, however.

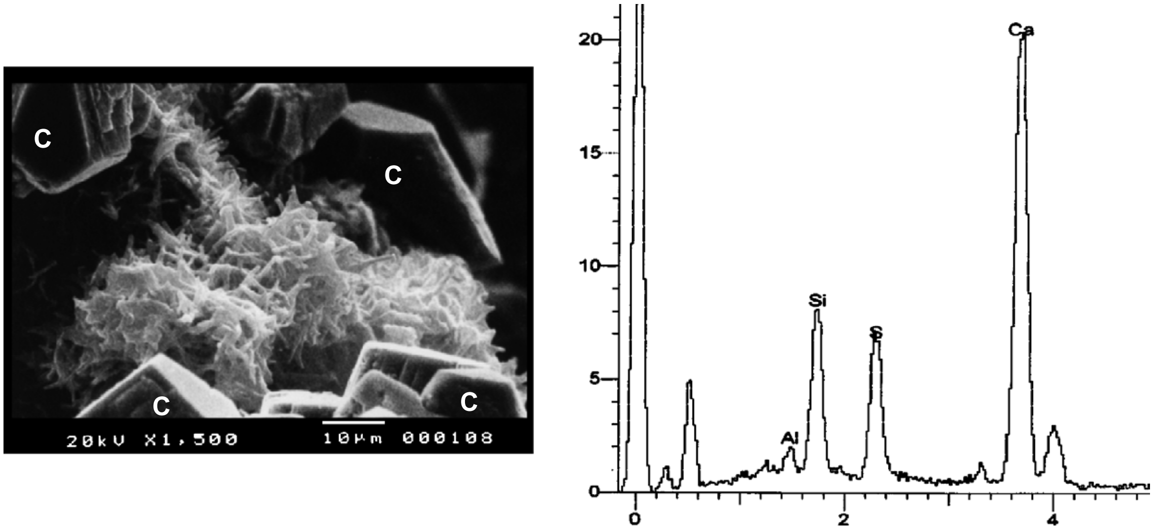

Fig. 8. Microphotograph of 1BA type mortars after 16 months in $MgSO_4$ solution at 21 °C, with fully crystallised thaumasite needles. C = calcium carbonate. EDX analysis of the needles.

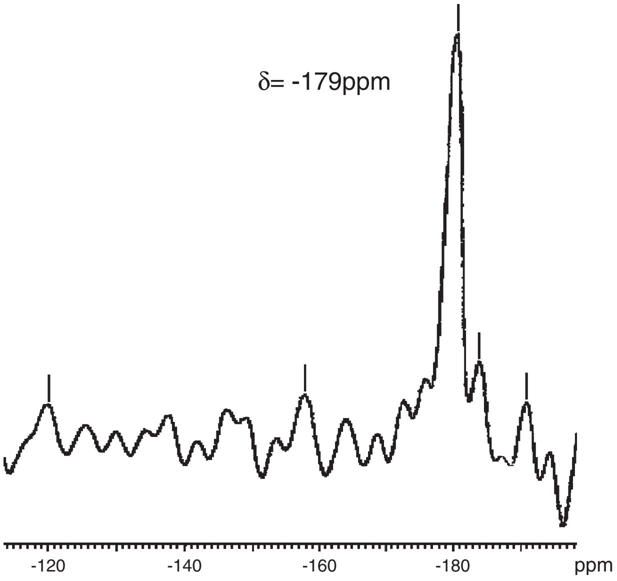

Fig. 9. ^{29}Si[^{1}H] CP/MAS NMR of 5AA mortar after storage in water for 1 year.

The simultaneous presence of thaumasite and ettringite in samples of damaged concrete, mortar or synthetic pastes after being subjected to accelerated sulphate attack in the laboratory has been reported by a number of authors [5,6,16,17]. Also both phases were simultaneously found in samples of structures actually in service—in deteriorated concrete taken from bridge foundations in the UK [1] and slabs in California [18].

The structural similarity between thaumasite and ettringite, in turn, may suggest the existence of solid solutions between the two phases [19]. Barnett et al. [20,21] determined the extent of the miscibility gap between the two phases (between 50% and 87% of Si substitution for Al). According to their revised results [22], thaumasite can tolerate little or no replacement of Si by Al in its structure, while ettringite tolerates a higher degree of solid solution, with up to 1/2 its Al being replaced by Si. By other hand, given the difference between the two phases in terms of the length of parameter *c* in the unit cell, some authors claim that there is no such solid solution and observe crystalline inter-growth in the samples, in addition to the mixed thaumasite and ettringite crystals [23]. In our studies the results can not confirm neither mix of crystals nor solid solutions in sample 5AA mortars.

It is therefore concluded from the literature that ettringite and thaumasite may co-exist but that solid solutions of the two phases may likewise form. The identity of the agent causing the expansive process observed in sample 5AA, kept partially submerged in water at 5 °C for 26 months, cannot be categorically established from the experimental results; it is believed to be ettringite and thaumasite or a solid solution between the two minerals.

Furthermore, the comparison of the behaviour of samples 1AA, 2AA and 5AA leads to the conclusion that internal sulphate attack involving the formation of thaumasite or a thaumasite–ettringite solid solution is favoured by the addition of calcite in mortars made with high C_3A content cements.

4.2. Cement mortars stored in 2% gypsum solution at 21 °C

When the samples were submerged in gypsum solutions at ambient temperature for 16 months, expansive thaumasite formation took place in mortars made with C_3A-low cement containing no extra gypsum (1BA), and in the mortars to which 5% additional gypsum had been added (2BA), but not in mortars made with cement containing both gypsum and calcite additives (5BA). No expansion was observed in 1AA and 2AA mortars while mortar 5AA cracked. Mixed crystals or a solid solution of ettringite and thaumasite formed in mortars 1AA, 2AA and 5AA, all made with cement containing 13% C_3A.

It may be noted that the samples submerged in the 2% gypsum solution were kept at ambient temperature. It is also to be remarked, that samples 1BA and 2BA, made with C_3A-low cement and immersed in this medium need less time to be damaged (16 months) by thaumasite formation than the same type of mortar and stored in water at 5 °C (60 and 36 months).

These results reveal how little is known about the effect of temperature on the thaumasite form of sulphate attack in cement mortars which, according to many authors, is hastened at low temperatures and has a threshold temperature of 15 °C, above which the process is believed to be very slow [4].

The findings of the present study confirm that high concentrations of the sulphate ion in solution drive sulphate attack [5,6,8] and concur in this regard with reports in the literature of concrete deterioration in warm climates [12,18,14].

In another vein, the C_3A content of the cement was also observed to affect the type of expansive salt produced and its formation process. In the mortars made with C_3A-low cement, the expansive process takes place together with the stoichiometric formation of well-crystallised thaumasite, a salt identifiable by FTIR, XRD, SEM/EDX, etc. In mortars made with high C_3A content cement, however, the carbonation process totally or partially destroys ettringite and the XRD, FTIR and SEM/EDX characterisation of the acicular crystals forming in subsequent recrystallisations does not clarify whether they are thaumasite–ettringite solid solutions or due to joint precipitation of the two phases.

Finally, it will be noted that thaumasite forms unevenly in the prisms, which in some cases are severely cracked in one area but sound in others, and that regardless of whether the source of the sulphate ions is internal or external, the mechanism causing the damage is expansion-driven.

It is remarkable that magnesium sulphate medium shows less aggressivity than gypsum medium and it is also confirmed that thaumasite formation is high in the samples of the cement low in C_3A, immersed in this medium.

5. Conclusions

The main conclusions of the paper can summarized as follow:

1. Thaumasite or a solid solution between ettringite and thaumasite forms in carbonated mortars kept in water at 5 °C for several months, whether the cement used has a high

C_3A content or is C_3A-low. The process also takes place in mortars kept at ambient temperature in gypsum or magnesium sulphate solutions.

2. Mortar carbonation provides sufficient carbonates for the process to occur.
3. As the gypsum in C_3A-low cement affords a sufficient supply of sulphates for thaumasite to form, no additional or external source of these ions is required. Although slow (5 years), the process under such circumstances is very destructive.
4. Providing additional sulphates, either as the mortar is mixed or in the storage media, hastens thaumasite formation in some cases and triggers the appearance of thaumasite or thaumasite–ettringite solid solutions in others.
5. In all cases, the processes involve expansion, irrespective of the C_3A content in the cement or whether the sulphates are from an internal source or found in the storage/test solutions.
6. The composition of the expansive phase depends on the C_3A content in the cement. Thaumasite forms in mortars made with C_3A-low cement, whereas mixed crystals or solid solutions of thaumasite and ettringite form in mortars made with high C_3A content cements.
7. The amount of C_3A is a parameter to be considered for internal and external sulphate attack in terms of thaumasite formation.
8. Low C_3A cement produce higher amounts of thaumasite than high C_3A cement independently of immersion medium. Calcite addition decreases thaumasite formation in samples of high C_3A.

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References

[1] H.F.W Taylor, Sulphate Reactions in Concrete – Microstructural and Chemical Aspects, in: E. Gartner, H. Uchikawa (Eds.), Cement Technology, The American Ceramic Society, Westerville, OH, 1994, pp. 61–78.

[2] H.F.W. Taylor, Cement Chemistry, Thomas Telford Publishing, London, 1997.

[3] J. Skalny, V. Johansen, N. Thaulow, A. Palomo, DEF as a form of sulphate attack, Mater. Construcc. 46 (244) (196) 5–29.

[4] Report of the Thaumasite Expert Group, The thaumasite form of sulphate attack: risks, diagnosis,remedial works and guidance on new construction, London: Her Majesty's Stationery Office, 1999.

[5] P. Nobst, J. Stark, Investigations on the influence of cement type on thaumasite formation, Cement and Concrete Composites 25 (2003) 899–906.

[6] P. Brown, R.D. Hooton, Ettringite and thaumasite formation in laboratory concretes prepared using sulphate-resisting cements, Cement and Concrete Composites 24 (2002) 361–370.

[7] J. Aguilera, S. Martinez-Ramirez, I. Pajares, M.T. Blanco-Varela, Formation of thaumasite in carbonates mortars, Cement and Concrete Composites 25 (2003) 991–996.

[8] D.D. Higgins, N.J. Crammond, Resistance of concrete containing ggbs to the thaumasite form of sulphate attack, Cement and Concrete Composites 25 (2003) 921–929.

[9] D.M. Mulenga, J. Stark, P. Nobst, Thaumasite formation in concrete and mortars containing fly ash, Cement and Concrete Composites 25 (8) (2003) 907–912.

[10] H. Justnes, Thaumasite formed by sulphate attack on mortar with limestone filler, Cement and Concrete Composites 25 (8) (2003) 955–959.

[11] J.L. Sagrera, et al., Estudio po DRX de muestras de enfoscado deterioradas, Expediente n° 16.895-B.

[12] P.W. Brown, A. Doerr, Chemical changes in concrete due to ingress of aggressive species, Cement and Concrete Research 30 (2000) 411–418.

[13] S. Diamond, Microscopic Features of ground water induced sulphate attack in highly permeably concretes, in: V.M. Malhotra (Ed.), Proceedings of the Fith CANMET/ACI International Conference on Durability of Concrete, Barcelona, Spain, Am. Conr. Inst. SP-192, vol. 1, 2000, pp. 403–416.

[14] S. Sahu, S. Badger, N. Thaulow, Evidence of thaumasite formation in Southern California concrete, Cement and Concrete Composites 24 (2002) 379–384.

[15] J. Skibsted, L. Hjorth, H.J. Jakobsen, Quantification of thaumasite in cementitious materials by 29Si{1H} cross-polarization magic angle spinning NMR spectroscopy, Advances in Cement Research 7 (1995) 69–83.

[16] P.W. Brown, R.D. Hooton, B.A. Clark, The co-existence of thaumasite and ettringite in concrete exposed to magnesium sulphate at room temperature and the influence of blast-furnace slag substitution on sulphate resistance, Cement and Concrete Composites 25 (8) (2003) 939–945.

[17] M.E. Gaze, N.J. Crammond, The formation of thaumasite in a cement: lime: sand mortar exposed to cold magnesium and potassium sulphate solutions, Cement and Concrete Composites 22 (2000) 209–222.

[18] S. Sahu, S. Badger, N. Thaulow, Mechanism of thaumasite formation in concrete slabs on grade in Southern California, Cement and Concrete Composites 25 (8) (2003) 889–897.

[19] R.A. Edge, H.F.W. Taylor, Crystal structure of thaumasite, $[Ca_3Si(OH)_6 12H_2O](SO_4)(CO_3)$, Acta Crystallography B 27 (1971) 594–601.

[20] S.J. Barnett, C.D. Adam, A.R.W. Jackson, Solid solutions between ettringite and thaumasite, Journal of Materials Science 35 (2000) 4109–4114.

[21] S.J. Barnett, D.E. Macphee, E.E. Lachowski, N.J. Crammond, XRD, EDX and IR analysis of solid solutions between thaumasite and ettringite, Cement and Concrete Research 32 (2002) 1–12.

[22] S.J. Barnett, D.E. Macphee, N.J. Crammond, Extent of immiscibility in the ettringite-thaumasite system, Cement and Concrete Composites 25 (2003) 851–855.

[23] J. Bensted, S.P. Varma, Studies of Thaumasite: Part II, Silicates Industriels 39 (1974) 11–19.