Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 36 (2006) 384 – 394

Cement and Concrete Research

Microstructure of 5-year-old mortars containing limestone filler damaged by thaumasite

S.M. Torres [a], C.J. Lynsdale [a,*], R.N. Swamy [b], J.H. Sharp [c]

[a]Department of Civil and Structural Engineering and Centre for Cement and Concrete, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK
[b]Department of Mechanical Engineering and Centre for Cement and Concrete, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK
[c]Department of Engineering Materials and Centre for Cement and Concrete, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

Received 31 August 2004; accepted 24 February 2005

Abstract

This paper presents the findings of a long-term study on the microstructure of Portland cement mortar specimens containing 5%, 15% and 35% limestone filler, as cement replacement, after exposure to a solution of magnesium sulfate at a concentration of 1.44% SO_4, for 5 years at 5 °C. The findings are compared to results reported earlier, obtained from the same systems but after 1-year exposure. It was found that the deterioration due to thaumasite advanced with the increased exposure period and limestone content. Thaumasite solid solutions (Tss) formed as the dominant phases within the deteriorated cement matrix and at the paste-aggregate interface resulting in cracks and delamination. Thaumasite was also found as an inner product in various clinker grains. Interestingly, the control specimens, with no limestone filler, were found to exhibit cracks due to the formation of Tss, with atmospheric carbon dioxide being the most likely source for the carbonates.

Keywords: Thaumasite; Ettringite; Sulfate attack; Limestone filler; Microstructure

1. Introduction

Composite cements make an effective contribution to sustainable construction and the energy efficiency of the concrete industry. There are many examples of the successful utilisation of industrial by-products such as fly ash, ground granulated blast furnace slag and silica fume, as well as natural pozzolans, in concrete structures where durability is the prime concern. The use of cement replacement materials is also of great environmental importance, since Portland cement production is responsible for about 5–7% of the industrially emitted carbon dioxide to the atmosphere, and also nitrogen and sulfur oxides, all of which are known to contribute to global warming and acid rain.

For environmental benefits and efficiency gains, composite cements incorporating limestone filler (BS EN 197-1:2002) have been introduced in recent years. In these Portland–limestone cements, ordinary Portland cement (OPC) is partially replaced by limestone in the range from 6% to 35% by mass. The European standard (EN 197-1) also allows OPC to contain up to 5% filler by mass and usually limestone is used. Following the discovery of

Table 1
Chemical and mineralogical composition of raw materials

Oxides	Limestone (%)	OPC (%)	OPC phase composition	(%)
SiO_2	0.86	21.08	C_3S	48.70
Al_2O_3	0.08	5.13	C_2S	23.70
Fe_2O_3	0.34	3.00	C_3A	8.50
CaO	56.25	64.58	C_4AF	9.10
MgO	0.58	2.91		
SO_3	0.22	2.93	Gypsum	6.30
K_2O	0.05	0.74	Free CaO	1.70
Na_2O	0.08	0.32		
Loss on ignition	42.01	1.36		

---

* Corresponding author. Tel.: +44 1142225720; fax: +44 1142225700.
E-mail address: c.lynsdale@sheffield.ac.uk (C.J. Lynsdale).

0008-8846/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2005.02.007

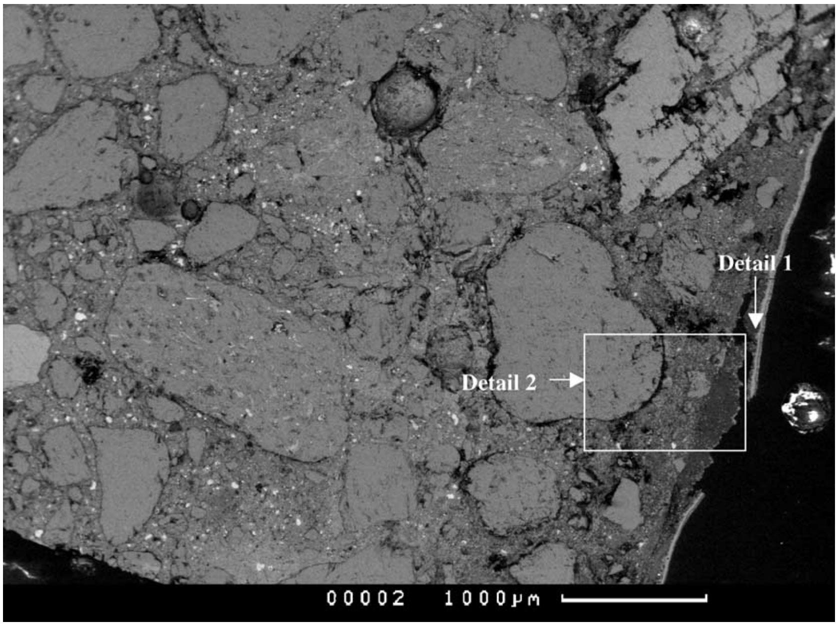

Fig. 1. SEM of control OPC mortar after 5 years at 5 °C in $MgSO_4$ solution.

thaumasite in deteriorated bridge foundations in the UK [1,2], the durability of concrete incorporating limestone is being extensively investigated. In these foundations, the buried concrete was made using either OPC or sulfate-resisting Portland cement (SRPC) and limestone aggregates. The involvement of limestone in the thaumasite form of sulfate attack (TSA) has been identified as a major factor responsible for the deterioration. Until recently, it has been widely believed that the amount of aluminate phases present in Portland cement controlled sulfate attack through the formation of secondary ettringite and gypsum. However, it is now established that restriction of the tricalcium aluminate phase content in cement does not mitigate against the occurrence of TSA [3].

The incorporation of fine limestone as filler, partially replacing some of the Portland cement, is known to bring about even greater susceptibility to thaumasite formation than does the presence of limestone as aggregate [1]. The onset and progress of deterioration in cement paste and mortar, due to TSA, have been found to increase with the

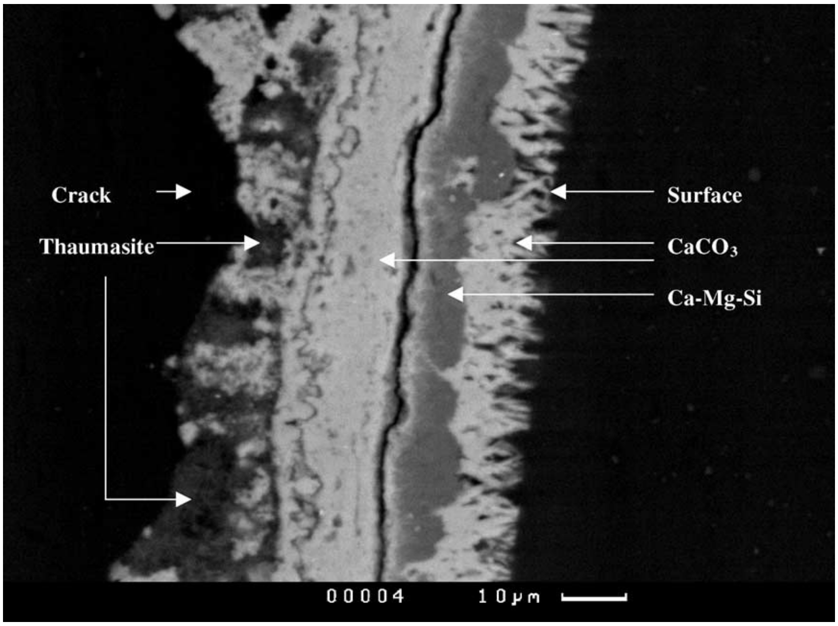

Fig. 2. Detail 1 in Fig. 1.

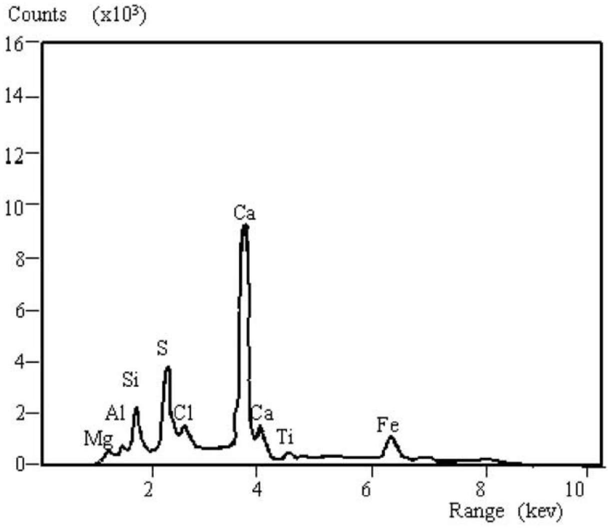

Fig. 3. EDS of thaumasite in OPC control shown in Fig. 2.

increase in limestone filler content in prisms stored in magnesium sulfate solution at 5 °C [4–7]. Furthermore, it was established that thaumasite forms as a solid solution rather than as the pure phase [8]. The solid solution is between thaumasite, $Ca_6[Si(OH)_6 \cdot 12H_2O]_2(SO_4)_2(CO_3)_2$, and ettringite, $Ca_6[Al(OH)_6 \cdot 12H_2O]_2(SO_4)_3 \cdot 2H_2O$, and has a miscibility gap associated with a change in the crystallographic space group [8–10].

The mortars studied here had been prepared from Portland cement incorporating various levels of limestone filler and stored for 5 years in magnesium sulfate solution at 5 °C. The samples are the same as those reported on previously [4–6,8]. The aim of this paper is to report the microstructure of these specimens and elucidate the changes associated with the formation of thaumasite that have lead to the bulk physical deterioration exhibited by the samples, as shown previously [6].

2. Experimental work

The samples were obtained from test specimens, which were prepared about 5 years previously [6,7]. Mortar prisms (40 × 40 × 160 mm) were made with a cement to aggregate ratio of 1: 2.5 and a water to binder ratio of 0.5. The aggregate used was Normensand, a German standard quartz sand complying to BS EN 196-1. The chemical and mineralogical composition of the Portland cement and limestone used are shown in Table 1. The mineralogical composition of the cement was calculated by the Bogue method. Limestone powder replaced 5%, 15% and 35% of the Portland cement on a mass to mass basis. The test specimens were cured in water for 27 days after demoulding at 1 day, and were then submerged in a solution of magnesium sulfate at a concentration of 1.44% SO_4, at 5 °C. The solution was changed every 3 months in order to simulate mobile ground water. The prisms were kept in these conditions for a minimum of 4 years, after which the solution was allowed to evaporate, and the test specimens were exposed to a drying environment at 5 °C for several months. The results reported in this work refer to an overall period of exposure of just over 5 years.

The microstructure of the polished surface was examined using a CamScan scanning electron microscope (SEM) in backscattered electron image mode (BEI) with an accelerating voltage of 15 kV. Cubes of 20 mm size were cut from

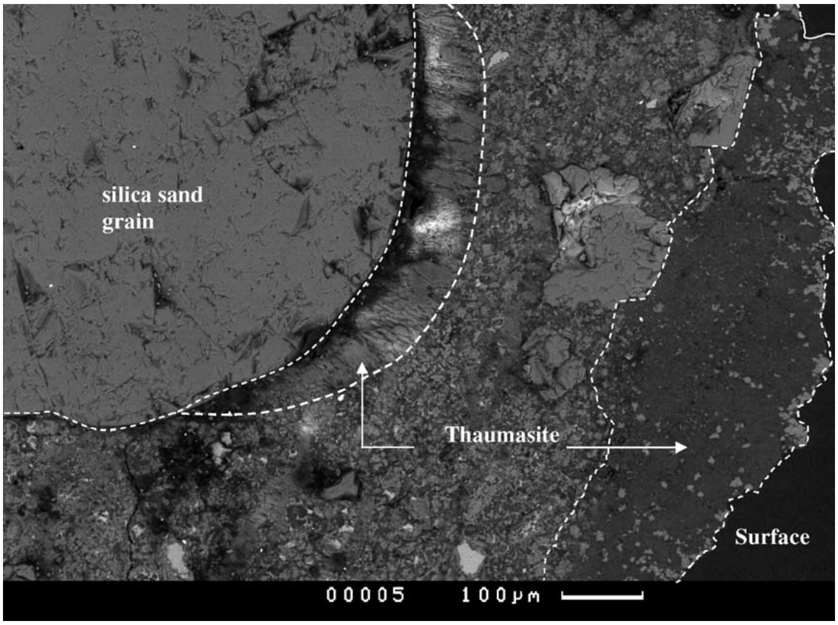

Fig. 4. Detail 2 in Fig. 1.

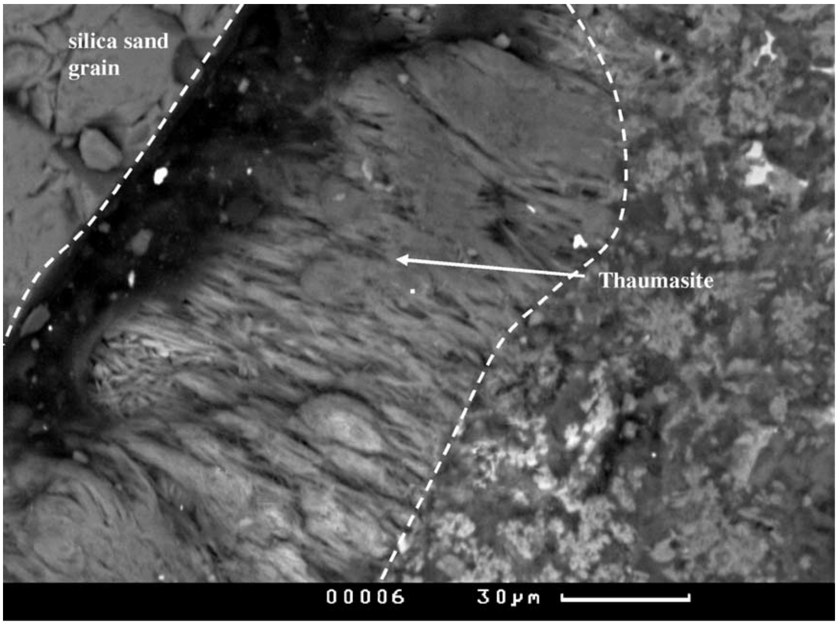

Fig. 5. Enlarged part of Fig. 4 showing thaumasite surrounding a silica sand grain.

the edges of each prism and dried in a desiccator for 36 h at room temperature. The samples were subsequently impregnated with a cold setting resin under vacuum. They were then polished down to 1 μm and carbon coated. The chemical analysis was carried out by energy dispersive spectroscopy (EDS) equipped with Link analytical facilities.

3. Results and discussion

3.1. Control OPC mortar

Fig. 1, obtained at low magnification, shows the features close to the edge of the control mortar, which contained no limestone filler. Expansion and cracks could be seen near the surface of the sample. A sub-surface parallel crack pattern had developed along the expanded part of the surface, as can be seen in the magnification of the detail shown in Fig. 2. The external layer consisted of needle-like calcium carbonate, a magnesium-containing hydrate region probably incorporating brucite, and thaumasite. Fig. 3 shows the chemical composition of the thaumasite, which contained Ca, Si, $\bar{S}$ and also some Al that is probably indicative of solid solution, in accordance with the XRD data reported previously [8].

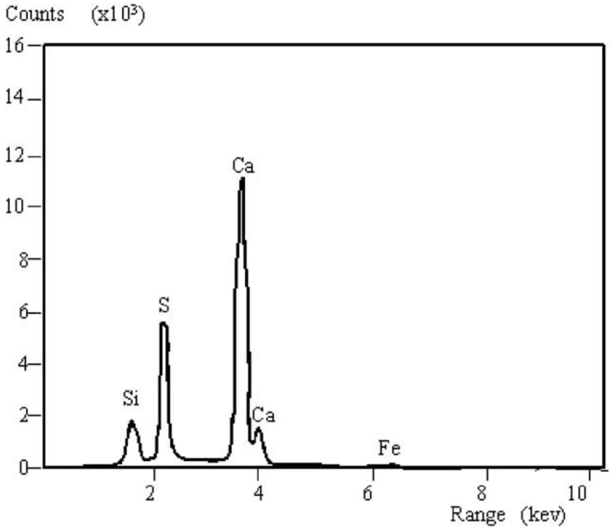

Fig. 6. EDS of thaumasite shown in Fig. 5.

Fig. 4 presents the magnified image of detail 2 in Fig. 1. It shows an expanded dark grey area close to the external surface, which is predominantly thaumasite. A closer examination reveals that a 60 μm band of material, of a texture different to that of the dark grey area, has crystallised close to the surface of the quartz aggregate (Fig. 5). As shown in Fig. 6, the EDS analysis of these needles shows Ca, Si and $\bar{S}$. Since no aluminium was observed, the chemical composition of these needles is characteristic of thaumasite. The extent and distribution of the thaumasite within the matrix and interface suggest that the control OPC sample is suffering from TSA and not merely thaumasite formation (TF) as defined by the Thaumasite Expert Group Report 1999 [1].

Thaumasite texture in a sample appears to vary depending on where it is formed; dark grey areas were found in the matrix near the surface, whilst needle-like bands were formed at the interface. It seems, therefore, from a comparison of the EDS analyses shown in Figs. 3 and 6 that the chemical composition of the thaumasite solid solution (Tss) may vary in different regions of the same sample.

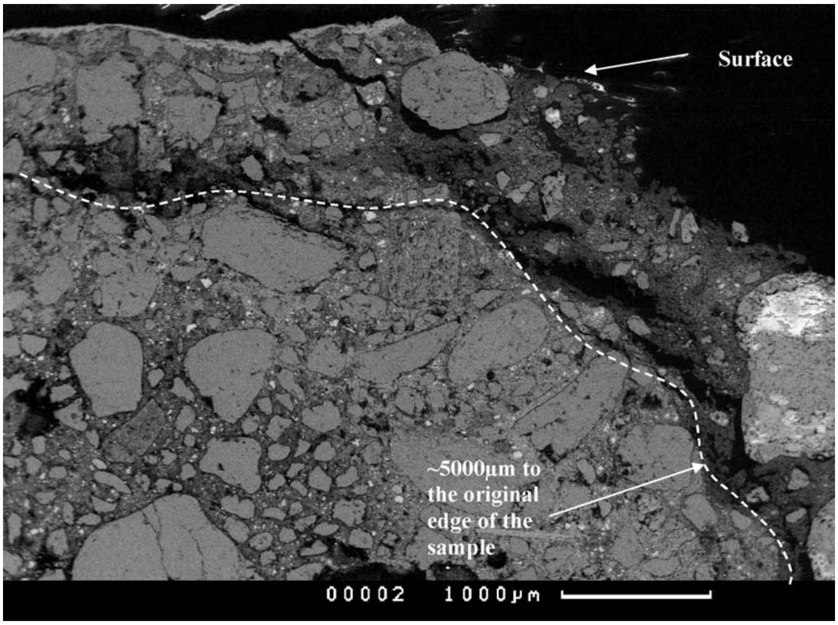

Fig. 7. SEM of microstructure at the corner of a 5% limestone mortar specimen.

The question arises, as to how does Tss form in a mortar sample that was made without incorporating limestone as filler or as aggregate? Inevitably the source of carbonates has to be atmospheric carbon dioxide, as has been demonstrated elsewhere [11].

3.2. Mortar with 5% limestone filler

The corner of a sample containing 5% limestone replacement of cement is shown in Fig. 7 at low magnification. Larger zones of disruption than those observed in the control specimens can be seen in this figure. Large cracks (dark area inside) are easily detected and the material had started to detach from the bulk sample at about 1000–2000 µm away from the corroded edge.

The transition zone between the cement paste and the aggregate is shown in Fig. 8 at higher magnification. Instead of just filling pores and cracks, a dark grey layer attributed to thaumasite is seen to surround the silica

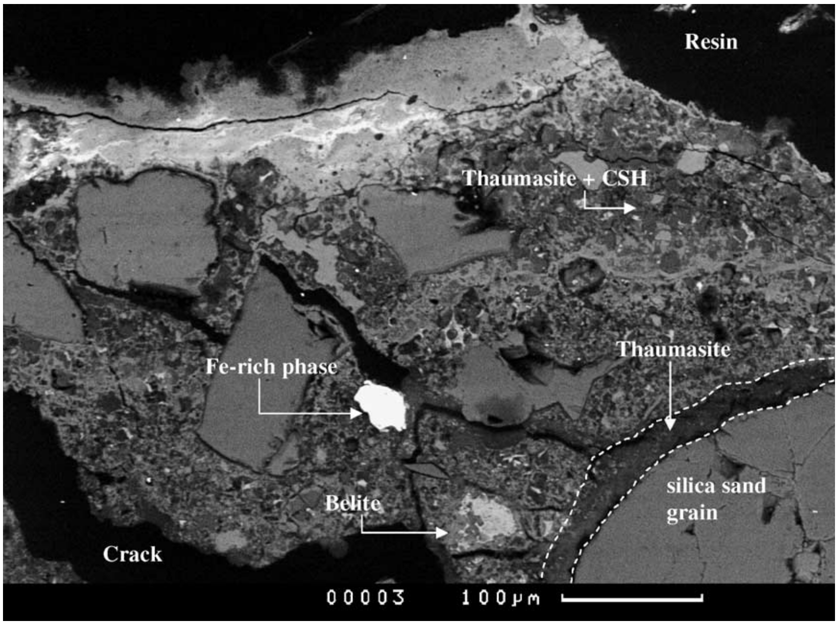

Fig. 8. SEM of cement matrix of corroded parts of 5% limestone filler mortar.

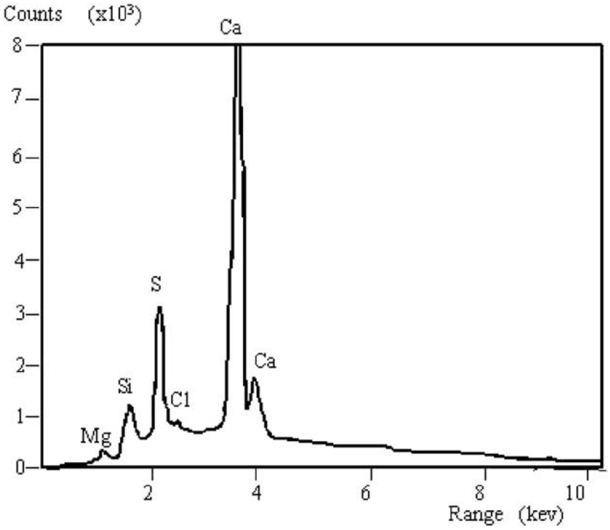

Fig. 9. EDS of thaumasite in Fig. 8.

aggregate and ferrite grains, and is also present within the C–S–H. The chemical analysis (Fig. 9) of this layer revealed $\bar{S}$, Si and Ca, which is indicative of thaumasite. Alongside some clinker grains, a mineral containing iron, silicon, potassium and chromium, but not calcium, was also found in the corroded area as shown in Fig. 8. This observation indicates that the ferrite phase had been attacked and was decalcified as a result. Crammond and Halliwell [12] also reported that the ferrite phase was attacked, but only in the most severe TSA-attacked regions. These observations, however, are in contrast to "conventional" sulfate attack at higher temperatures (≥20 °C), where Bonen and Cohen [13] reported that the ferrite phase remained unaffected even in concentrations as high as 4.2% SO_4, although it should be noted that this study reported results for up to 1 year of exposure.

3.3. Mortar with 15% limestone filler

The micrographs shown in Figs. 10 and 11 indicate that mortar containing 15% limestone filler suffered considerably greater damage when compared to those made with the 5% limestone filler and the control mortars. Although the entire surface was friable, the damage was more severe at the edges and corners, which turned the edges into a rounded shape [6,8]. The sub-surface parallel cracks extended along the whole surface, and were several times wider than those seen in the 5% limestone mortar. Additionally, the formation of cracks propagated to deeper sites as well. Thaumasite, as indicated by the EDS analysis shown in Fig. 12, thus became an all-pervasive phase in the material, as has also been observed elsewhere [2,12]. Although thaumasite has no binding properties, large areas of the cement surface were converted into this phase prior to the total disruption as can be seen in Fig. 11. This transformation is most likely due to the dry condition to which the samples were finally exposed, since thaumasite becomes mushy in wet concrete. It is noteworthy that thaumasite was more or less homogeneously distributed rather than intermixed with gypsum or C–S–H, which indicates that the greater the amount of limestone filler distributed in the matrix, the higher its susceptibility to TSA.

Closer investigation reveals a layer of thaumasite surrounding a clinker grain with clusters of ettringite (or

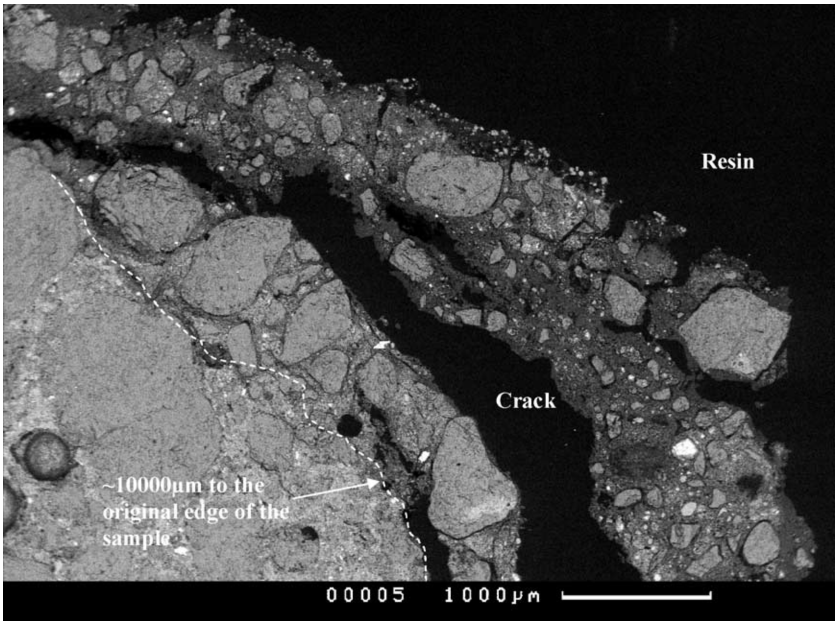

Fig. 10. SEM of microstructure at the corner of 15% limestone filler mortar specimen.

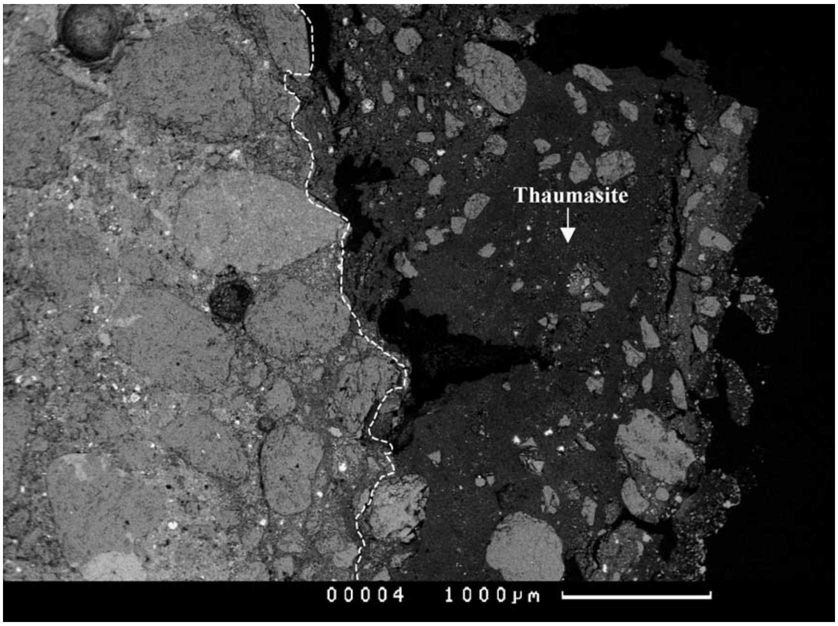

Fig. 11. SEM of microstructure of the edge of 15% limestone filler mortar specimen.

monosulfate) within its original boundaries as can be seen in Fig. 13. The grain, identified as belite (Fig. 14), has cracks penetrating inwards from the outside. It is believed that these cracks either offered sites for the occurrence of ettringite and thaumasite or they were caused by the formation of these reaction products. Interestingly, the chemical composition of the observed ettringite (Fig. 15) indicates that it may have contained some silicon. However, the chemical composition of the thaumasite region did not reveal any significant amount of aluminium. The precipitation of ettringite in belite grains has also been reported by Yang and Sharp [14] in samples exposed to an initial heat-curing regime. They concluded that the formation of a more porous inner product in belite allowed deposition of ettringite. Deterioration of a clinker grain of similar microstructural features to those presented here has also been reported by Crammond [2].

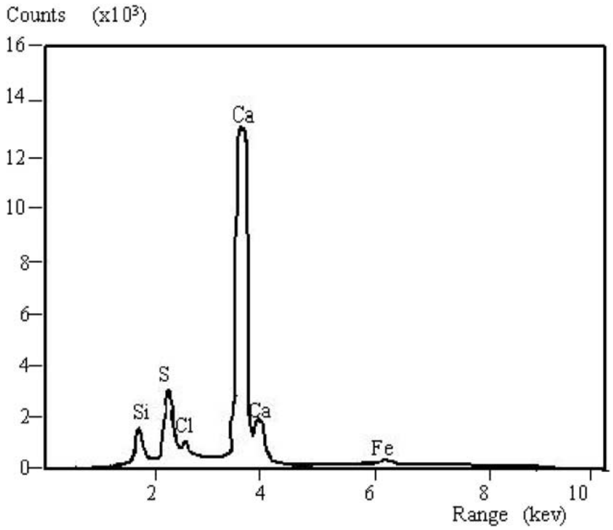

Fig. 12. EDS of thaumasite in Fig. 11.

3.4. Mortar with 35% limestone filler

Various features of deterioration attributed to TSA in samples containing 35% limestone filler are shown in Fig. 16. The damage can be seen to be extensive, and is in fact more severe than that in samples with lower levels of limestone replacement. Some material had spalled away from the surface leaving the prism smaller than those with lower limestone contents [6]. The cement matrix was totally converted into thaumasite up to about 15 000 µm depth, rather than intermixed with gypsum as in conventional sulfate attack in the presence of magnesium sulfate solution at room temperature. The pervasive homogeneity of thaumasite distribution was very similar to that observed in the 15% limestone filler mortar samples, but as expected, more extensive since more carbonate was available. It is also important to emphasise that the porosity of this mix must be higher due to the dilution of the cement and the associated increase in water/OPC ratio, resulting from the high level of limestone filler used as a cement replacement.

Fig. 17 shows the modifications in the cement matrix arising from the chemical attack, and the following can be identified: the presence of C–S–H gel with inclusions of sulfate, chloride, iron, potassium and magnesium; C–S–H+Tss containing some aluminium and titanium; and thaumasite (outer dominant dark area). The thaumasite rich

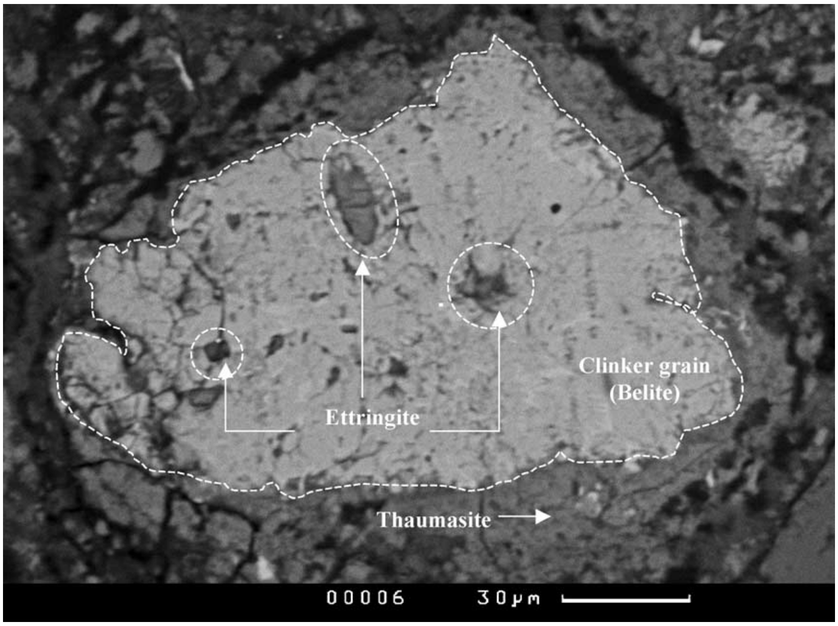

Fig. 13. SEM of clinker grain in 15% limestone filler mortar specimen.

region seems to be progressing inwards replacing C–S–H in the clinker grain (Fig. 18).

3.5. Progress of TSA as a function of limestone content and period of exposure

In comparison with our previous papers [4,5] reporting on the deterioration of the same mortar specimens at an earlier age, the present work reveals that the extent of the deterioration is greater now that the specimens have been exposed to the magnesium sulfate solution for 5 years. Whilst the OPC control sample with no limestone filler exhibited no thaumasite formation at the end of exposure for 1 year [7], now clear evidence of thaumasite is present. The level of deterioration, as evident from microstructural examination using SEM, is also greater, the greater the level of limestone filler. The trend found here between microstructural deterioration and limestone filler content agrees well with the deterioration and general appearance of the bulk samples, as reported elsewhere [6]. As mentioned earlier, the high level of deterioration found in the 35% limestone filler specimens may have been exacerbated by the dilution of the binding OPC, as the limestone replacement level was increased at a constant water/binder ratio. Nevertheless, a direct correlation between the availability of carbonates and the unit cell parameters has been found for these samples [8], in which the higher the level of carbonates, the closer were the unit cell parameters to those of the thaumasite end-member.

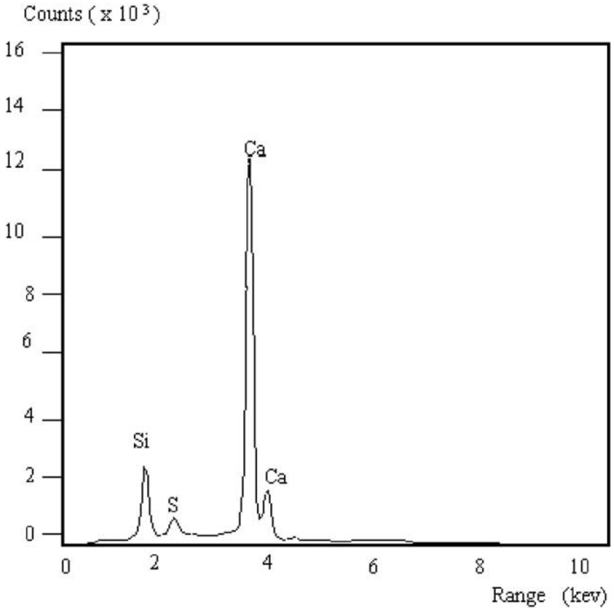

Fig. 14. EDS of clinker grain (belite) attacked by thaumasite, as shown in Fig. 13.

The disruption to the mortar prisms occurred due to the crystallisation of Tss phases within the cement matrix as well as at the aggregate–matrix transition zone. Although Hartshorn et al. [7] showed the formation of thaumasite, ettringite XRD peaks dominated the pattern of paste containing 5% LF after 1-year exposure. The fact that ettringite was not found in any analysis carried out after 4 years [6,8] indicates that ettringite is not a stable phase in the presence of carbonates, sulfates and silicate ions in the pore solution at low temperature. This has relevance to interpretation of site investigation data, in situations where conditions are favourable for thaumasite

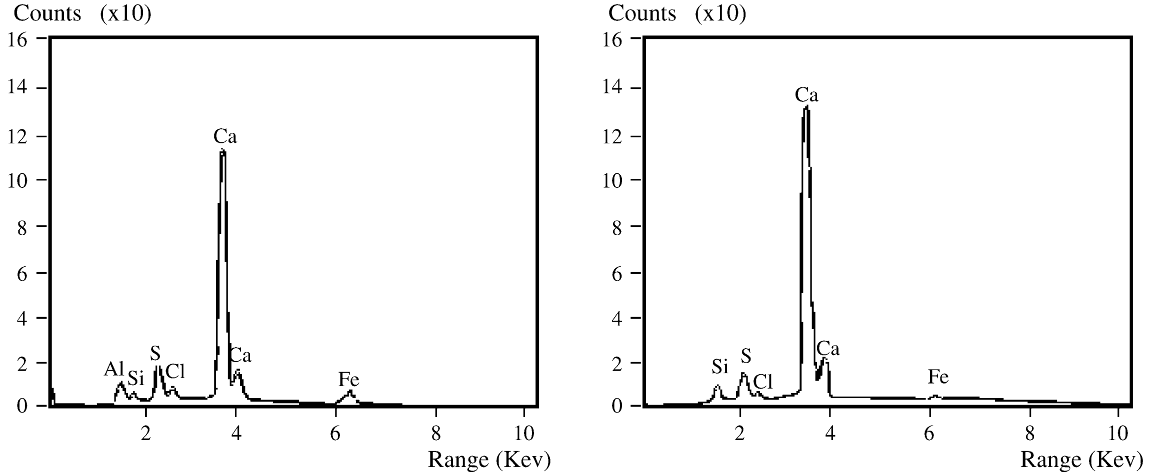

Fig. 15. EDS of ettringite (left) and thaumasite (right) in the clinker grain shown in Fig. 13.

formation but only ettringite was found, as this should not be interpreted that thaumasite would not develop at a later age.

4. Conclusions

The main conclusions derived from this study are summarised below:

- In deteriorated mortar, thaumasite solid solutions of different texture developed in the matrix and at the interface around aggregate grains. The Tss may vary in composition from one region of the sample to another according to the local conditions pertaining at the time of its precipitation.
- Thaumasite was observed in the corroded parts of 0, 5%, 15% and 35% limestone filler mortars. The extent of deterioration of the mortar prisms was greater as the level of limestone increased. The damage commenced at the surface of the prisms and proceeded inwards. Its extent increased with the period of exposure.
- In OPC prisms, the mode of attack changed with time, from being ettringite based at early age to the thaumasite form of sulfate attack at later ages. The source of carbonate in the control OPC mortar, where the damage was relatively slight, was most probably due to atmospheric carbon dioxide.

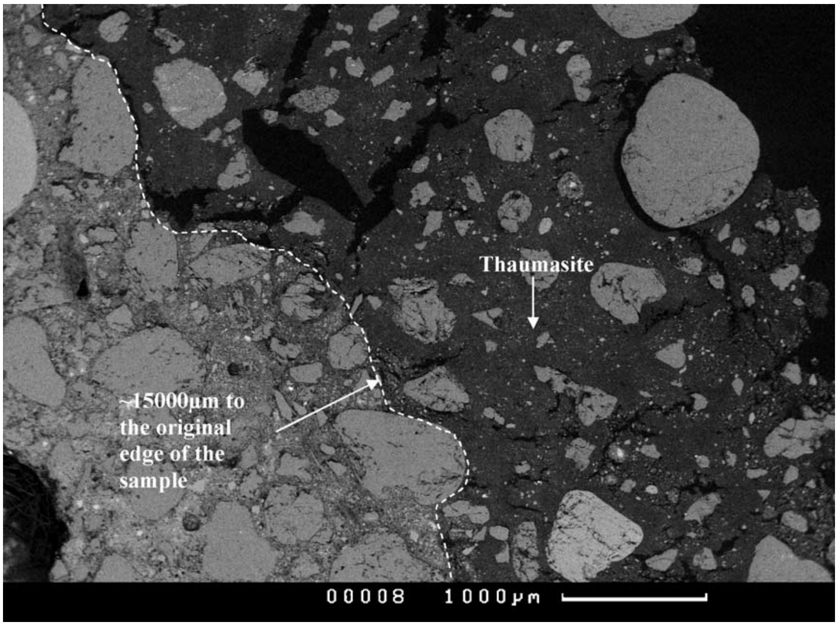

Fig. 16. SEM of pervasive thaumasite in 35% limestone filler mortar matrix.

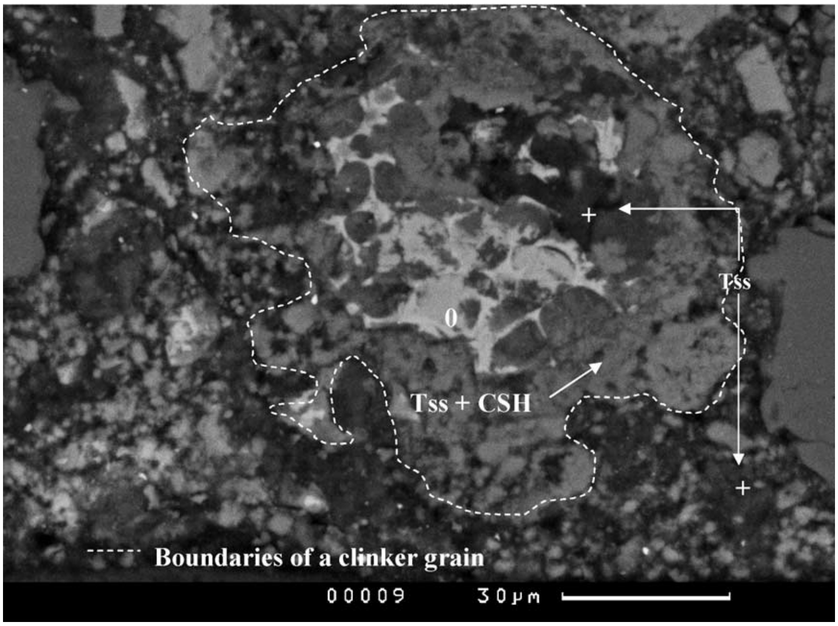

Fig. 17. SEM of cement matrix in 35% limestone filler: (+) TSS, (0) belite, and attacked CSH.

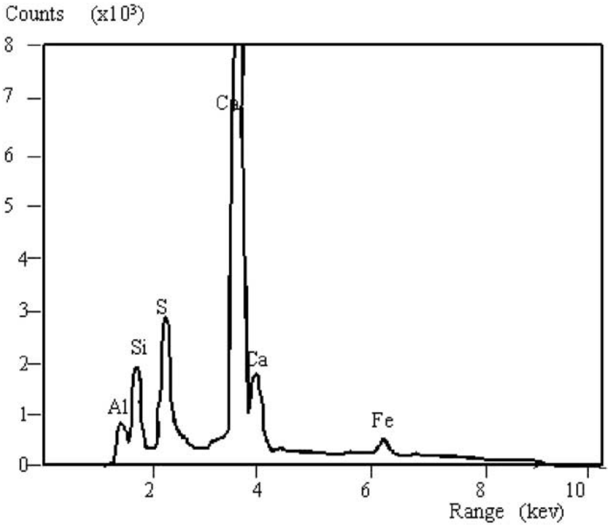

Fig. 18. EDS of TSS in Fig. 17.

- TSA gradually becomes all pervasive and is potentially very damaging because the consumption of CSH gel destroys the binding properties of the cement matrix.
- Ettringite is not a stable phase in the presence of carbonates, sulfates and silica in the pore solution at 5 °C.

Acknowledgements

The authors wish to acknowledge the award of a scholarship from CAPES–Brazil to the first author. They also wish to record their appreciation of the support of Paul Downs with sample maintenance and Dawn Bussey with SEM.

References

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

[2] N.J. Crammond, The thaumasite form of sulfate attack in the UK, Cem. Concr. Compos. 25 (8) (2003) 809–818.

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

[4] S.A. Hartshorn, R.N Swamy, J.H. Sharp, Engineering properties and structural implications of Portland–limestone cement mortar exposed to magnesium sulfate attack, Adv. Cem. Res 13 (2001) 31–46.

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

[6] S.M. Torres, J.H. Sharp, R.N. Swamy, C.J. Lynsdale, S.A. Huntley, Long term durability of Portland limestone cement mortars exposed to magnesium sulfate attack, Cem. Concr. Compos. 25 (2003) 947–954.

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

[8] S.M. Torres, C.A. Kirk, C.J. Lynsdale, R.N Swamy, J.H. Sharp, Thaumasite–ettringite solid solutions in degraded mortars, Cem. Concr. Res. 34 (2004) 1297–1305.

[9] S.J. Barnett, C.D. Adam, A.R.W. Jackson, P.D. Hywel-Evans, Identification and characterization of thaumasite by XRPD techniques, Cem. Concr. Compos. 21 (1999) 123–127.

[10] S.J. Barnett, C.D. Adam, A.R.W. Jackson, Solid solution between ettringite and thaumasite, J. Mater. Sci. 35 (2000) 4109–4114.

[11] G. Collett, N.J. Crammond, R.N. Swamy, J.H. Sharp, The role of carbon dioxide in the formation of thaumasite, Cem. Concr. Res. 34 (2004) 1599–1612.
[12] N.J. Crammond, M.A. Halliwell, The thaumasite form of sulfate attack in concretes containing a source of carbonate ions—a microstructural review, ACI SP 157-19, 2nd CANMET/ACI International Symposium for Advances in Concrete Technology, Las Vegas, Nevada, June 12, 1995, pp. 357–380.
[13] D. Bonen, M.D. Cohen, Magnesium sulfate attack on Portland cement paste: II. Chemical and mineralogical analysis, Cem. Concr. Res. 22 (1992) 707–718.
[14] R. Yang, J.H. Sharp, Hydration characteristics of Portland cement after heat curing: I. Degree of hydration of the anhydrous cement phases, J. Am. Ceram. Soc. 84 (2001) 608–614.