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Long term durability of Portland-limestone cement mortars exposed to magnesium sulfate attack

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Abstract

Mortar prisms made with Portland-limestone cement have been stored in air and in 1.8% magnesium sulfate solution at 5 °C and have been examined over a period of 5 years. This paper is primarily concerned with the results obtained at the end of this period. The limestone content in the samples varied from 0% to 35%, but the water to cement plus limestone powder ratio was kept constant. The status of the samples after storage for 5 years is reported based on visual examination and a thorough characterisation using X-ray diffraction, infra-red spectroscopy and scanning electron microscopy. The prisms stored in magnesium sulfate solution were all showing clear signs of deterioration, increasing in intensity with limestone content. The mortar prism with 5% limestone replacement was, however, seriously degraded in comparison with the ordinary Portland cement control prism, and it is shown that this was due to the thaumasite form of sulfate attack.

Keywords: Thaumasite; Portland-limestone cement; Infra-red spectroscopy; Scanning electron microscopy; X-ray diffraction

1. Introduction

Hartshorn et al. have reported the formation of thaumasite in Portland-limestone cement pastes [1,2] and mortars [3,4] stored in magnesium sulfate solutions at 5 °C for periods of up to 420 days. It was reported that the extent of thaumasite formation was greater with increasing replacement of cement by limestone. Furthermore, the mortar prisms containing 35% limestone, that were exposed to magnesium sulfate solution at 5 °C, suffered extensive damage and deterioration within 1 year. The prisms containing 15% limestone also gave clear signs of impending damage due to the thaumasite form of sulfate attack (TSA). The other prisms, containing either no limestone replacement or 5% replacement, showed fewer symptoms of deterioration and their engineering properties were generally superior to those containing 15% and 35% limestone [3]. At first sight these observations seem to concur with the conclusion of the UK Government's Thaumasite Expert Group [5] that, "this relatively low level of carbonate material (5%) will not adversely affect the Portland cement's performance in concretes containing either siliceous or carbonate aggregates". It should be noted, however, that the presence of thaumasite was consistently detected in the cement paste samples containing 5% limestone that had been stored at 5 °C in 1.8% $MgSO_4$ and 1.8% Na_2SO_4 solution for 280–364 days [1]. The amount of thaumasite detected was small, substantially less than that in the pastes containing 35% limestone. It was sufficient, however, to make us comment [2] that "in exposure conditions which are susceptible to sulfate attack, such as in foundations and sulfate-bearing soils, extreme care as to the amount of filler content needs to be exercised".

When the mortar prisms had reached an age of 5 years, it seemed timely to re-examine them. Attention is particularly directed in this paper to the mortar prisms made with 5% limestone replacement to determine their ability to resist sulfate attack when exposed to sulfate-containing groundwaters.

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2. Experimental programme

The samples used for the tests reported in this paper were obtained from test specimens prepared 5 years ago, and reported earlier [3,4]. The mortar prisms, 40×40×160 mm consisted of a cement:aggregate ratio of 1:2.5 with a water to cement plus limestone ratio of 0.5. The limestone powder additions replaced the Portland cement mass for mass at three levels of 5%, 15% and 35%. The Portland cement was of normal typical composition with 8.5% C_3A, and the limestone was a Carboniferous limestone with a calcium carbonate content greater than 98%, and a mean particle size of 0.21 μm. The test specimens were cured in water for 27 days after demoulding and then exposed to air at 5 °C or 20 °C, or completely submerged in 1.8% $MgSO_4$ solution at 5 °C. The solution was changed every 3 months. The test specimens were kept in this condition for a minimum of 4 years, after which the $MgSO_4$ solution was allowed to evaporate gradually, and the test specimens were exposed to a drying environment at 5 °C for about a year. The specimens were 5 years old at the time of the tests reported here.

Prior to examination by X-ray diffraction (XRD) and infra-red (IR) spectroscopy, all the test samples were thoroughly examined visually, and all significant physical changes in terms of surface damage and the formation of reaction products were carefully noted. XRD was carried out on a Siemens-D500 diffractometer using CuKα radiation to analyse the phases present in the mortars, including any deterioration products. In order to reduce the presence of quartz peaks, the material extracted from the surface of the prisms was gently ground in an agate pestle and mortar, and sieved through a series of 1200, 600 and 300 μm sieves. After this, they were further ground and sieved through a 44 μm sieve. The analyses were firstly performed between 5° and 50° 2θ at a speed of 2° 2θ/min. The diffraction pattern between 15° and 20° 2θ was then examined using a step size of 0.01° at 0.5°/min, on powder that had been ground in a ball mill using acetone for 30 min. This procedure was used to improve the quality of the data obtained. Backfilled aluminium holders were used for all experiments, which helped to diminish preferred orientation, but were responsible for the peaks at 38.3° and 44.5° 2θ observed in some of the XRD patterns.

The samples for IR spectroscopy were made as KBr discs, using 2 mg of sample to 198 mg of KBr. They were manually ground in an agate pestle and mortar until a fine homogeneous mixture was achieved. Each specific powder was placed in the appropriate die so that a 12 mm disc was prepared. The IR spectrum was determined using a Perkin–Elmer FT-IR 2000 spectrometer. The resolution of the instrument was ±1 cm^{-1}.

The microstructure of fractured surface samples was examined using a CamScan scanning electron microscope (SEM), with an accelerating voltage of 20 kV. Cubes were cut from the edges of each prism, dried in a desiccator and subsequently carbon coated. The chemical analysis was carried out using an energy dispersive X-ray (EDX) system and the appropriate Link software.

3. Results

3.1. Visual inspection

None of the prisms, with or without limestone additions and stored in air at 5 and 20 °C, had shown any visible deterioration after a year [3]. After exposure to air for 5 years, this was still the case, as can be seen from Figs. 1 and 2. Few signs of deterioration were detected even at the corners and edges of the prisms. Thus the test specimens made with Portland-limestone cements had good stability and remained undamaged in exposure conditions free from water-borne sulfate attack.

The prisms stored in 1.8% $MgSO_4$ solution for 1 year had, however, shown progressive deterioration, which increased with limestone content [3,4]. Damage was observed at the corners and edges of the prisms, generally worse at 5 °C than at 20 °C. Prisms with 35%

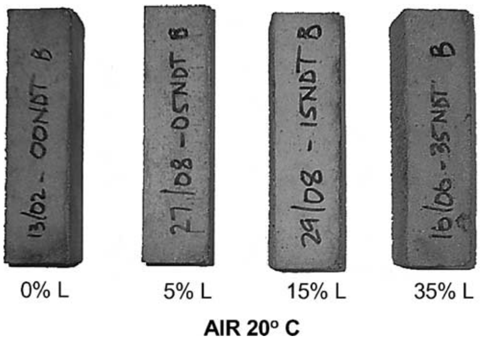

Fig. 1. Mortar prisms made with different Portland-limestone cements exposed to air at 20 °C for 5 years (L = limestone).

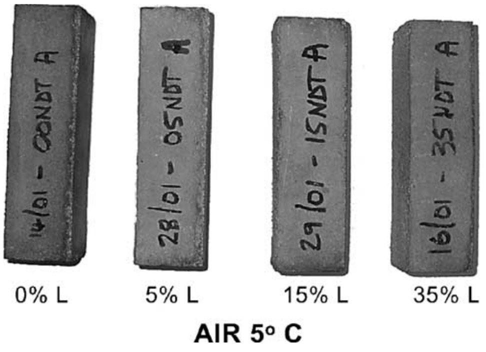

Fig. 2. Mortar prisms made with different Portland-limestone cements exposed to air at 5 °C for 5 years (L = limestone).

limestone stored at 5 °C had progressive cracking along the edges, peeling off of the surface layers, spalling, and loss of surface material from the ends. Blisters of soft white material had developed on the faces of the prisms [3].

This process had continued, and had extended to all the prisms stored at 5 °C, after 5 years, as shown in Fig. 3. The intensity of the corrosive attack was greater as the level of limestone replacement increased. The damage commenced at the corners and edges of the prisms, which were covered by a white deposit of expanded material, found by XRD to consist of thaumasite. In addition, epsomite ($MgSO_4 \cdot 7H_2O$) was found as a result of precipitation during the drying period. The depth of penetration of damage was random and highly irregular, but consistent with the level of limestone replacement. The spalling at the ends of the prisms was greater in the 5% limestone sample than in the 0% control mortar (Fig. 4). One important aspect arising from the visual examination was that the 5 year old mortars incorporating 5% limestone appeared to be even more distressed than those with 15% had been after 1 year [3]. Not only had material been lost from the edges, but aggregate was exposed on the surface, and a surface layer of skin had peeled off.

The original surface was totally disintegrated in the 5 year old prisms containing 15% and 35% replacement, as can be seen from the view of the sections of each prism shown in Fig. 4. The surface material in the 15% and 35% limestone samples was grey-white, soft and crumbly, and could easily be removed by hand.

Overall, it is concluded from the visual examination that all the mortars made with Portland-limestone cement and stored in $MgSO_4$ solution at 5 °C were displaying clear signs of serious deterioration after 5 years. The question now arose whether the deterioration in the case of the mortars containing 5% limestone replacement was due to TSA or due to conventional sulfate attack involving the formation of ettringite.

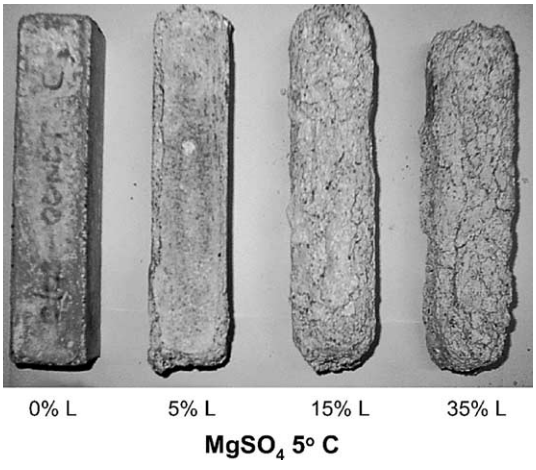

Fig. 3. Mortar prisms made with different Portland-limestone cements stored in $MgSO_4$ at 5 °C for 5 years (L = limestone).

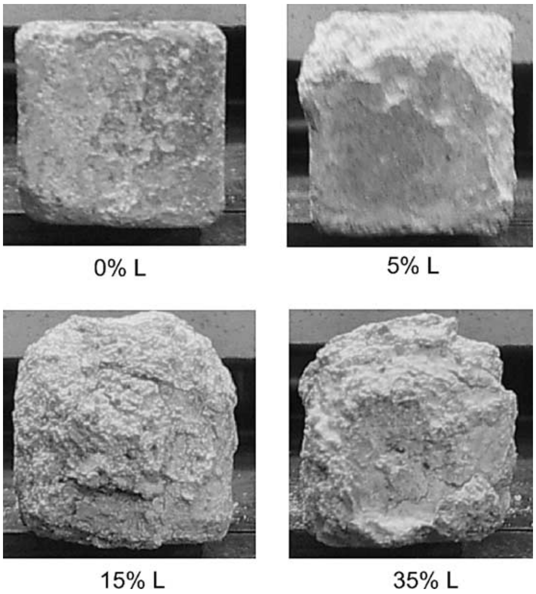

Fig. 4. The section view of prisms stored in 1.8% $MgSO_4$ at 5 °C for 5 years (L = limestone).

3.2. X-ray diffraction

XRD patterns of deteriorated portions of the mortar prisms are shown in Fig. 5 over the range from 5° to 50° 2θ. Although there are many similarities between these patterns, there are also apparent differences and trends can be observed with change in the limestone content of the mortar.

To distinguish between thaumasite and ettringite is not always easy, especially if there is the possibility of either both phases being present or of a solid solution being formed. Inspection of the XRD pattern of the mortar based on 35% limestone replacement clearly confirms the presence of thaumasite, based on the peaks observed at 9.2°, 15.9°, 18.5°, 19.3°, 23.3°, 25.1°, 26.0° and 28.0° 2θ. Note that the strongest peaks, the first two listed, taken alone, are not sufficient to distinguish thaumasite from ettringite. The separation of peaks attributable to thaumasite and ettringite is greater at 2θ values between 22° and 29°, as shown in Fig. 6. The peaks labelled T in the 35% limestone sample are clearly due to thaumasite and not to ettringite. The equivalent peaks, attributable to thaumasite, are probably also present in the other three XRD patterns, but there is a tendency for them to shift to slightly lower 2θ values (higher d-spacings). The pattern for the sample with no added limestone was somewhat different, emphasizing that the evidence for the presence of thaumasite is less certain.

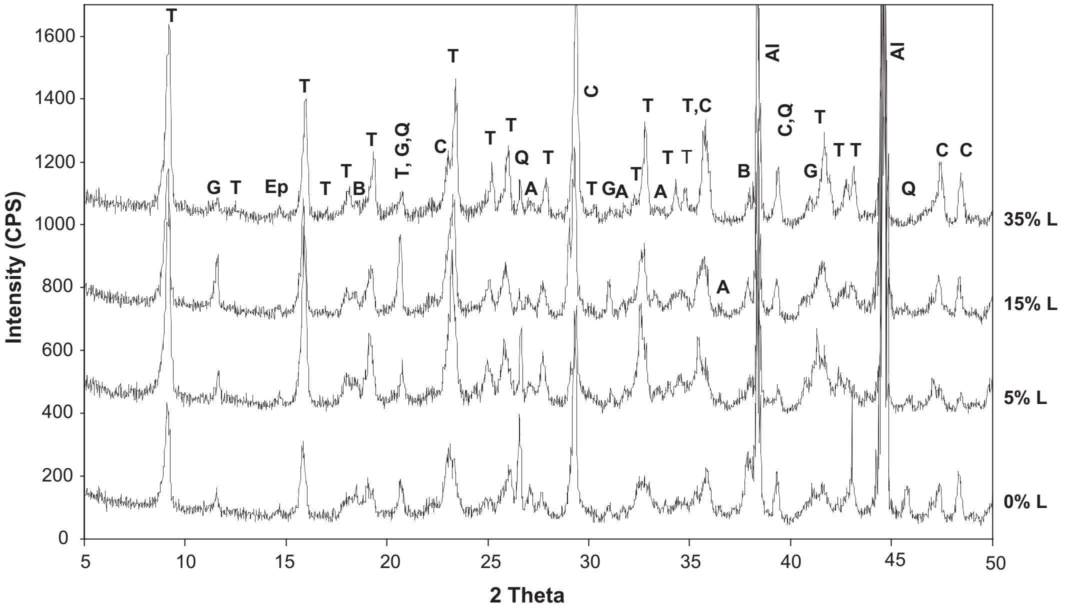

Fig. 5. XRD patterns of corroded parts of Portland cement mortars with and without added limestone stored in magnesium sulfate at 5 °C after 5 years. Key: see panel.

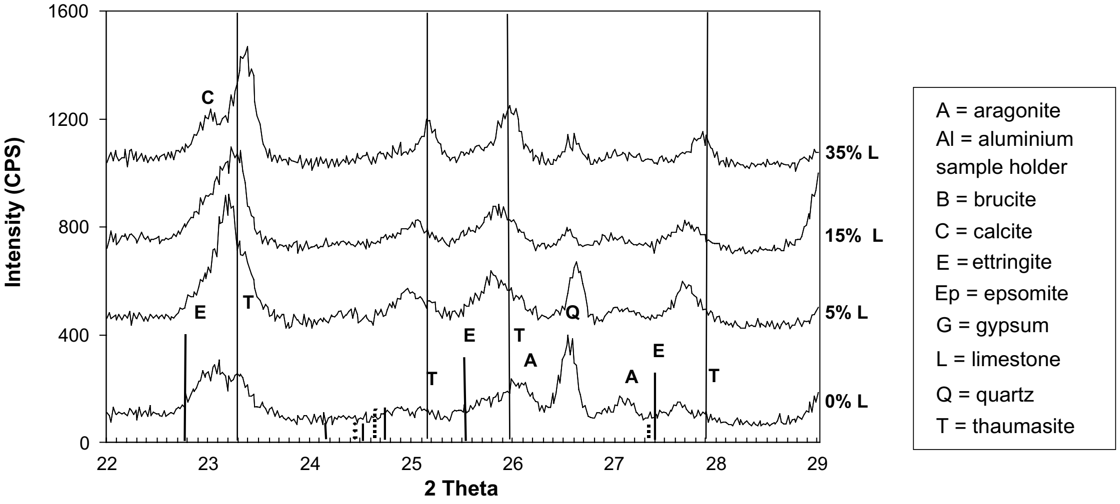

Fig. 6. XRD pattern between 22° and 29° of corroded parts in Portland cement mortars with and without limestone replacement stored in magnesium sulfate at 5 °C after 5 years. Key: see panel.

One possibility is that a thaumasite–ettringite solid solution [6,7] is being formed, particularly in the mortar with no added limestone. To investigate this possibility more closely, the XRD pattern between 15° and 20° 2θ was examined at a slower scanning rate (0.05° 2θ/min) and with steps of 0.01° 2θ. The results are shown in Fig. 7. The XRD pattern of the mortar containing 35% limestone was attributable to a sample of almost pure thaumasite, with little if any evidence of solid solution. As the level of limestone replacement is reduced, the peaks due to thaumasite (observed at this slow scanning speed at 16.0° and 19.4° 2θ in the 35% limestone mortar) are (a) reduced in intensity and (b) shifted to lower angles. Observation (a) suggests that less thaumasite is present as the level of limestone replacement decreases, although there seems to be as much in the 5% sample as in the 15% sample. Observation (b) indicates that the composition of the phase changes, suggesting that it involves a solid solution of the type investigated by Barnett et al. [6,7]. A thorough examination of these samples is to be made using a Stoe diffractometer.

The presence of several other phases, including gypsum, calcite and quartz, can be confirmed in the XRD patterns shown in Fig. 5. Ettringite could not be posi-

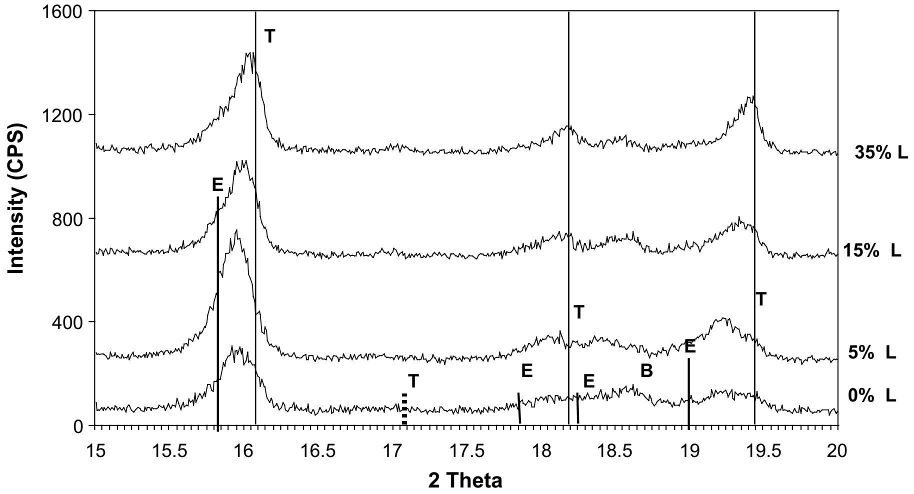

Fig. 7. XRD pattern between 15° and 20° of corroded parts in Portland cement mortars with and without limestone replacement stored in magnesium sulfate at 5 °C after 5 years. Key: see panel.

tively identified, although it may be present in the mortar with no added limestone, perhaps in the form of a solid solution. Some evidence was also found for the presence of aragonite (peaks labelled A in Fig. 5) and for brucite (peaks marked B in Figs. 5 and 7).

It is not surprising that the XRD data indicate the presence of considerable amounts of thaumasite in the mortars made with 15% and 35% limestone replacement. What is surprising is that

(a) the 5% limestone mortar seems to contain as large an amount of thaumasite (or a thaumasite-dominated solid solution) as the 15% sample, and
(b) even the mortar with no added limestone seems to contain a thaumasite–ettringite solid solution rather than ettringite.

3.3. Infra-red spectroscopy

To obtain further evidence to corroborate (or contradict) these observations from XRD, further investigation was made using IR spectroscopy, because it can identify a phase in which silicon is octahedrally coordinated.

The IR spectra of samples taken from the corroded parts of the mortar prisms are shown in Fig. 8. These

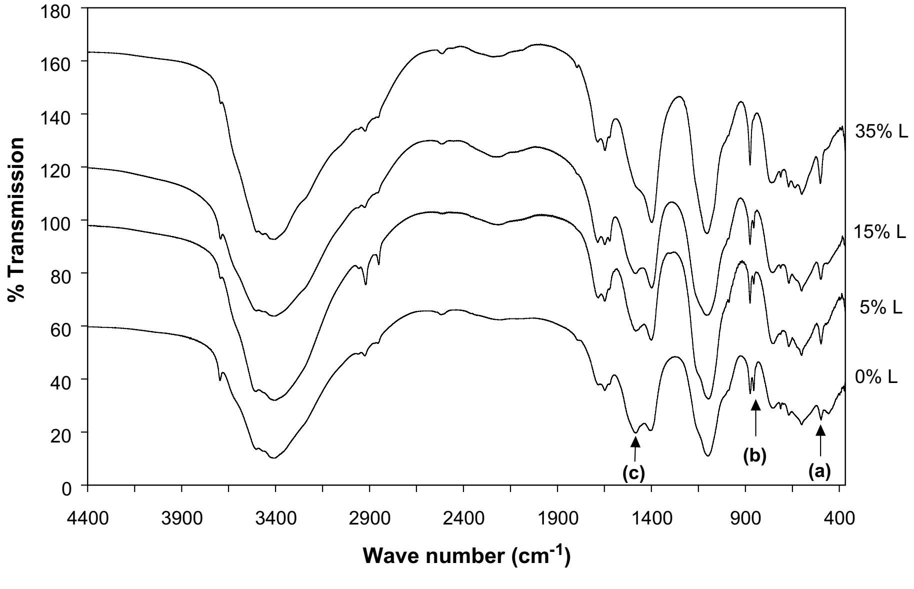

Fig. 8. IR spectra of mortars containing different amounts of limestone filler replacement stored in magnesium sulfate solution at 5 °C for 5 years (L = limestone).

four spectra are mostly very similar, but, as in the case of the XRD data, the most interesting features are the small differences between them. Firstly, peak (a) at 499.7 cm^{-1}, which was detected in all four samples but was strongest in that containing 35% limestone replacement, is assigned to the presence of SiO_6 bonds [8]. Octahedral Si is so rare in mineral silicates that the presence of this peak is indicative that either thaumasite or a thaumasite-containing solid solution must be present. All four samples contained this phase, but the amount present probably decreases with decreased limestone content, although caution has to be exercised in interpreting IR spectra quantitatively. Conversely, peak (b) at 852.7 cm^{-1}, most evident in the 0% limestone mortar, can be assigned to the Al–O–H stretching mode and hence is attributable to the presence of ettringite. This peak decreased in intensity with increasing limestone content and virtually disappeared in the 35% limestone mortar. These observations, taken together with the XRD data presented in Section 3.2, strongly suggest that the 35% limestone mortar contains thaumasite, *sensu strictu*, while the other samples, including that with no limestone replacement, contain a thaumasite–ettringite solid solution.

The remaining IR peaks are much as expected, although that labelled (c) at 1486 cm^{-1}, observed in all four samples, but most prominent in the mortar without limestone replacement, may be attributable to the presence of aragonite [9].

3.4. Scanning electron microscopy

Because of the conclusion from the XRD patterns and IR spectra that the 5-year old prisms containing only 5% limestone replacement indicate the presence of thaumasite (or a thaumasite-containing solid solution), it was decided to examine the microstructure of this prism by SEM. A secondary electron image of a fracture surface of this prism is shown in Fig. 9 at a relatively low magnification. The corroded surface of the sample can be seen on the right-hand side. Adjacent to the surface zone, at right angles to it, can be seen a crack filled with material that appears white in the micrograph. At higher magnifications this material can be seen to consist of needle-like crystals with lengths ranging between 2 and 6 µm length.

To determine whether these needles are composed primarily of ettringite or thaumasite, EDX analysis was carried out on a backscattered electron image of the same cluster of crystals. The results are shown in Fig. 10. The analysis shows the presence of Ca, Si and S, whereas Al is almost absent, hence confirming the presence of thaumasite in the mortar based on 5% replacement of cement by limestone.

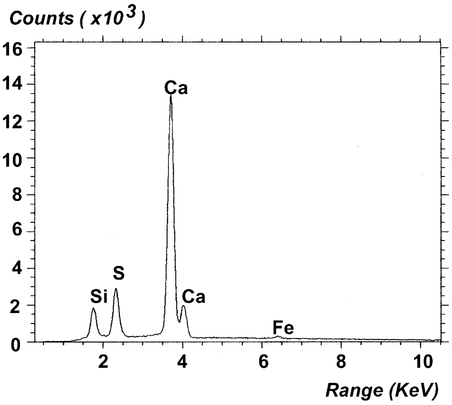

Fig. 10. (BEI–EDX) chemical analysis of thaumasite in a fracture surface of mortar containing 5% limestone filler replacement.

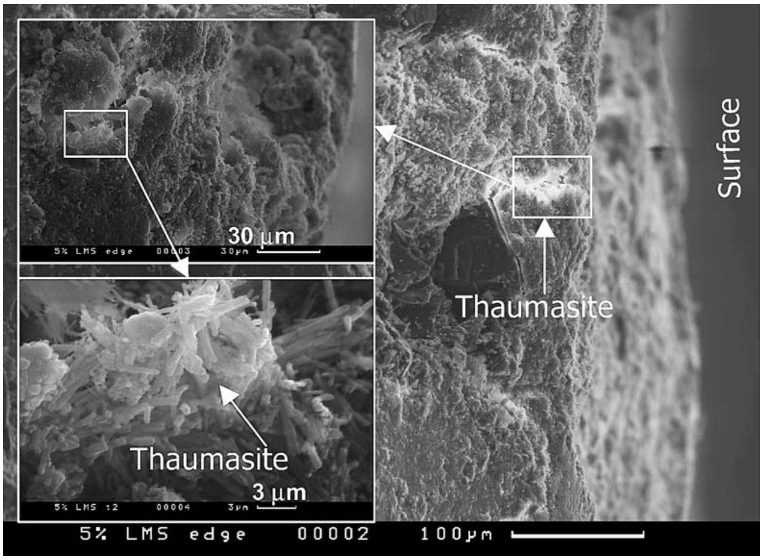

Fig. 9. (SEM–SEI) morphology of thaumasite in a fracture surface of mortar containing 5% limestone filler replacement.

A thorough examination of the microstructure of all four mortar prisms is now being undertaken.

4. Discussion

From the visual observations reported in Section 3.1, it is clear that the prisms that had been maintained in air, at either 5 °C or 20 °C, were still in excellent condition, whereas all the mortar prisms incorporating limestone filler had deteriorated badly after storage in 1.8% $MgSO_4$ solution for 5 years. The extent of the deterioration increased with increasing limestone content of the mortar. In particular, the mortar specimens with 5% limestone replacement were in a worse state after 5 years than the 15% samples had been after 1 year [3]. It is worth emphasising that the test specimens were made using a high quality German quartz sand, and ground limestone was used effectively as a filler, as is now permitted in the UK [10] and in most of Europe [11]. Thaumasite (or a thaumasite–ettringite solid solution) was observed in all the prisms made with limestone replacement.

The very poor condition and the extensive damage suffered by all the prisms stored in $MgSO_4$ solution at 5 °C were such that it was not possible to carry out satisfactorily any mechanical tests to ascertain the residual strength of these specimens. Nevertheless, the very friable nature of the 5% limestone test specimens gave a clear impression that their performance was significantly poorer that that of the ordinary Portland cement (OPC) control specimens. This conclusion, based on results obtained after 5 years immersion, differs from that drawn by Barker and Hobbs [12], who reported that mortars made from OPC were broadly similar in their vulnerability to sulfate attack at 5 °C as PLC mortars containing 15% limestone replacement after immersion in class 4A and 4B sulfate solutions at 5 °C for 12 months. Although Barker and Hobbs [12] noted that the mode of attack was different with substantial amounts of thaumasite being present in the surface layers of the deteriorated PLC mortars, but not in the OPC mortars, the Expert Group [5, p. 24] concluded that up to 5% replacement of cement by finely divided limestone should not adversely affect the performance of the Portland cement. The observations presented here, that the prisms based on 5% level of replacement were so badly corroded that their material and structural integrity were extensively affected, put this statement into dispute.

The solution of magnesium sulfate used in this study may be considered to be quite strong (class 5), but recent experience in the UK has demonstrated the danger of higher than expected sulfate concentrations arising from oxidation of pyrites in the ground [5]. Additional problems may be caused by flood water carrying agricultural sulfate ions, or by combined attack of sulfate and chloride anions as when de-icing salts are used or in a marine environment. There is also evidence [13,14] that under certain circumstances, lower concentrations of sulfate ions can sometimes be as, or even more, effective than higher concentrations in promoting sulfate attack. All these possibilities emphasise the need to exercise careful control in the use of limestone as a cement replacement in situations where unpredictable changes in ground conditions combined with the presence of aggressive ions, as in buried concrete, can seriously damage cementitious-based material and the structural integrity of concrete containing limestone.

The concentration of sulfate ions is probably less important than the chemical composition of the salt. Although we often speak about “sulfate attack”, we are actually dealing with attack by a metal sulfate, and the intensity of this attack varies according to whether the cation is magnesium, calcium, ammonium or an alkali metal. Magnesium sulfate is known to be particularly corrosive in both conventional sulfate attack [14] and in TSA [1]. But magnesium ions are not uncommon in groundwaters and can also be introduced into concrete through the use of dolomitic limestone aggregate. These considerations suggest that complacency must be avoided and that caution should be exercised; hence, any level of limestone replacement must be regarded as potentially hazardous in the presence of sulfate ions.

The major thrust of the research presented in this paper was to determine whether the deterioration of the prism containing 5% limestone replacement was due to conventional sulfate attack associated with ettringite formation or to the thaumasite form of sulfate attack. In fact, thaumasite (or a thaumasite-dominated solid solution) was positively identified by XRD; octahedral silicon (present in thaumasite but not in any other silicate phase likely to be formed from Portland cement) was detected by IR spectroscopy; and needle-like crystals based on Ca, Si and S have been observed by SEM and analysed by EDX. The evidence is, therefore, overwhelming that the thaumasite form of sulfate attack was primarily responsible for the deterioration of the 5% limestone-Portland cement mortar prism.

The mortar prisms containing higher limestone replacement levels were also clearly suffering from TSA. Even that containing Portland cement without any limestone filler had deteriorated somewhat and there was evidence of formation of some thaumasite (or thaumasite–ettringite solid solution). This raises, not for the first time, the possibility of thaumasite formation involving atmospheric carbon dioxide.

Thaumasite formation in the presence of magnesium sulfate solution has been discussed previously [1], leading to the conclusion that the reaction followed the equation:

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

Evidence was obtained in the present study for the formation of brucite, $Mg(OH)_2$, while portlandite, $Ca(OH)_2$, a normal product of the hydration of Portland cement was not observed in the corroded products by XRD. Gypsum, which was also observed, is formed by the reaction between portlandite and magnesium sulfate:

$$CH + M\overline{S} + 2H \rightarrow CSH_2 + MH$$

5. Conclusions

Thaumasite (or a solid solution dominated by thaumasite) was formed in Portland cement mortars containing 5% limestone replacement, as well as in those containing 15% and 35% replacement, after exposure to a 1.8% solution of magnesium sulfate at 5 °C for more than 5 years. The formation of thaumasite in the presence of magnesium sulfate solution follows the chemical equations reported previously by Hartshorn et al. [1].

Extensive damage to the prisms made from Portland-limestone cement was observed and is attributed to the TSA. These observations emphasise that the conclusion of the UK Government's Thaumasite Expert Group [5] that "5% replacement of Portland cement by limestone will not adversely affect the performance of Portland cement in concrete containing either siliceous or carbonate aggregates" requires qualification, because it is evident that this sample had deteriorated more extensively than the OPC control mortar after exposure to magnesium sulfate at 5 °C.

The UK and European standards [10,11] that allow the incorporation of 5% fine limestone (or indeed any other filler material) should also be reconsidered. The authors consider that the nature of any such replacement should be declared. In addition, extreme care should be exercised in the use of Portland-limestone cements in exposure conditions susceptible to sulfate attack at low temperature, such as in below ground structures and in marine exposure conditions. Recent experience has demonstrated that sulfate ground conditions can be unpredictable in the long term, leading to uncertainty about the application of cements containing even as little as 5% limestone filler.

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