

A Long Term Study on Thaumasite Form of Sulfate Attack (TSA) in Limestone Cement Pastes

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ABSTRACT

The thaumasite form of sulphate attack (TSA) concerns cements and concretes containing limestone and is attributed to the formation of thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$). In the present work the behavior of Portland limestone cements was studied in the presence of sulfate ions at low temperatures. Cement paste specimens were constructed using Portland cement and Portland limestone cement. In addition, cements were prepared by replacing a varying part of the Portland limestone cement with natural pozzolana, fly ash, ground granulated blastfurnace slag and metakaolin. The specimens were immersed in 1.8% w/w magnesium sulfate solution and cured at 5°C. Visual inspection, mass measurements, ultrasonic pulse velocity measurements and analytical techniques were carried out for a period of 30 months. Pastes containing limestone are susceptible to the thaumasite formation of sulfate attack and the deterioration is severer, the higher the limestone content. The use of specific minerals, as partial replacement of cement, inhibits the thaumasite formation in limestone cement pastes.

1. INTRODUCTION

One of the factors, which adversely influence the durability of concrete, is its ability to resist deterioration due to sulfate attack. It is generally accepted that conventional sulfate attack of cementitious materials involves the formation and the expansive properties of ettringite. However, another kind of sulfate attack, concerning cements and concretes containing limestone and attributed to the formation of thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$), has been widely discussed during the last years [1-3]. This kind of sulfate attack is of great importance as the limestone is widely used as filler or as main cement constituent for many years due to its technical and economical advantages.

The problem of Thaumasite form of Sulfate Attack (TSA) has been discussed during the last years because it has been identified in UK, USA, Canada, South Africa, France, Germany, Norway, Denmark, Switzerland, Italy and Slovenia and is particularly prevalent in buried concrete. This form of sulfate attack completely destroys the cementitious ability of the concrete by transforming hydrated cement into a mush.

The mechanism and the factors affecting thaumasite formation have not been yet fully clarified. Besides its similarities with other hydrated compounds, found in cement and concrete, hinder its safe identification [3]. Generally, the sulfate solutions penetrate the concrete and react with the hydration products of the cement paste leading to the formation of sulfate bearing phases like gypsum, ettringite or thaumasite causing profound changes in the microstructure and strength of the original cement paste [4].

Recent research shows that Portland limestone cement is susceptible to the thaumasite form of sulfate attack at 5°C after only a few months exposure to sulfate solutions. The extent of thaumasite formation is proportional to the limestone content. This type of attack is particularly deleterious when magnesium ions are also present. The thaumasite formation is accompanied by formation of brucite and secondary gypsum. There is always a delay before thaumasite is formed. During this initial period the usual cement hydration reactions take place, leading to the formation of ettringite, C-S-H gel and portlandite. Reduction of the pH of the system may be important in that it results in the chemical attack of the C-S-H gel [2, 5-9].

Thaumasite form of sulphate attack (TSA) requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and low temperature. The use of mineral admixtures that lowers the permeability and refines the pore structure may, therefore, contribute to better performance of pastes containing limestone [10-13].

In the present work the behavior of Portland limestone cements was studied in the presence of sulfate ions at low temperatures. In addition, this paper reports results related to the effect of a second mineral addition on the sulfate resistance of limestone cement. Limestone cement pastes containing natural pozzolana, fly ash, blastfurnace slag or metakaolin were exposed to sulfate solution at low temperature and their performance was studied for over 30 months.

2. EXPERIMENTAL

Portland cement clinker of industrial origin and limestone (L) of high calcite content (CaCO_3 : 95.7%) were used (Tables 1 and 2).

The mineral used and their chemical analysis are given in Table 2. Natural pozzolana (P) and Fly ash (F), with high Ca content (ASTM type C), are Greek minerals and are used by cement and construction industries for the production of composite cements. Ground granulated blastfurnace slag (S) is an imported mineral that is also used as a main cement constituent. The above minerals were ground and their mean particle size (d_{50}) was 10.5 μm , 12.3 μm and 10.9 μm for the pozzolana, fly ash and ggbs respectively. Metakaolin (M) is a commercial product (Metastar) of high purity with a mean particle size of 5.1 μm .

Table 1. Chemical and mineralogical composition of clinker

Chemical composition (%)		Mineralogical composition (%)	
SiO ₂	21.47	C ₃ S *	65.0
Al ₂ O ₃	5.00	C ₂ S	12.6
Fe ₂ O ₃	3.89	C ₃ A	6.7
CaO	65.67	C ₄ AF	11.8
MgO	1.89		
K ₂ O	0.68	Moduli	
Na ₂ O	0.16	Lime Saturation Factor (LSF)	95.79
SO ₃	1.04	Silica Ratio (SR)	2.42
Total	99.70	Alumina Ratio (AR)	1.29
FCaO	1.15	Hydraulic Modulus (HM)	2.18

* Cement chemistry notation: C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃

Table 2. Chemical analysis of minerals (%)

Oxide	Limestone (L)	Natural Pozzolana (P)	Fly ash (F)	Ggbs (S)	Metakaolin (M)
SiO ₂	0.54	59.18	49.33	36.74	54.41
Al ₂ O ₃	0.43	16.12	20.72	10.44	43.94
Fe ₂ O ₃	0.20	6.14	7.98	1.20	0.35
CaO	53.61	4.92	10.26	40.32	0.37
MgO	1.29	1.96	2.19	7.60	-
K ₂ O	0.06	2.15	1.94	0.31	0.31
LOI	43.73	4.78	2.02	0.44	-
TOTAL	99.86	95.25	94.44	97.05	99.38

Portland cement (PC) was produced by intergrinding clinker and gypsum in a pro-pilot plant ball mill of 5kg capacity. Portland limestone cements, containing 15% and 30% w/w limestone (LC1, LC2), were produced by intergrinding clinker, limestone and gypsum. The codes, the composition and the specific surface of the produced cements are given in Table 3. The rest mixes of Table 3 (LPC, LFC, LSC, LMC) have been prepared by replacing an amount (depended on expected mineral reactivity) of the Portland limestone cement LC1 with the minerals given in Table 2.

Table 3. Composition and fineness of the cements used

Code	Composition of samples
PC	Portland cement (clinker: 100% w/w) (gypsum: 5% of clinker by mass)
LC1	Portland limestone cement (clinker: 85% w/w, limestone: 15% w/w) (gypsum: 5% of clinker by mass)
LC2	Portland limestone cement (clinker: 70% w/w, limestone: 30% w/w) (gypsum: 5% of clinker by mass)
LPC	LC1 + 20% Natural Pozzolana of LC1 by mass
LFC	LC1 + 30% Fly ash of LC1 by mass
LSC	LC1 + 50% Ggbs of LC1 by mass
LMC	LC1 + 10% Metakaolin of LC1 by mass

Paste prisms of size 40x40x(50-60)mm were prepared, using the cements of Table 3, with a water to binder ratio of 0.4 ($w/c=0.40$). The specimens were air cured for 24h and then they were water-cured for 27 days at temperature 20°C ($\pm 2^\circ\text{C}$). After the 28-day initial curing the specimens were immersed in a 1.8% MgSO_4 solution at 5°C.

The visual examination of the samples was performed at regular intervals up to 30 months and all significant modifications, such as changes in surface color and texture, formation of any coatings, deterioration, expansion and cracking were recorded.

The ultrasonic pulse velocity test (apparatus: 58-E48, Controls Testing Equipments Ltd) was used as a measure of internal soundness of the samples. The measurements were carried out at regular intervals up to six months.

Changes in specimens' mass were recorded at regular intervals up to almost three years. Concerning the mass and ultrasonic pulse velocity, three prisms for each measurement were used and the presented results are the average value.

XRD measurements were performed on samples at regular intervals in order to identify any compounds formed during the curing. A Siemens D-5000 X-ray diffractometer, with $\text{Cu K}\alpha_1$ radiation ($\lambda=1.5405 \text{ \AA}$) was used. Measurements were carried out on samples coming from the deteriorated part of the specimens. In addition, thermogravimetric analysis (TG-DTG) was carried out in order to detect small amounts of compounds. A Mettler Toledo TGA/SDTA 851 instrument was used. The samples (~20 mg) were heated from 20°C to 600°C at a constant rate of 5°C/min, in an atmosphere of carbon dioxide free nitrogen, flowing at 50cm³/min. Finally, deteriorated surfaces of selected samples were examined using a JEOL JSM-5600 Scanning Microscope.

3. RESULTS AND DISCUSSION

3.1. Visual Inspection

A visual inspection of the specimens was carried out monthly. Photos of specimens stored in the sulfate solution for 3, 6, 13, 18, 24 and 30 months are presented in Fig. 1.

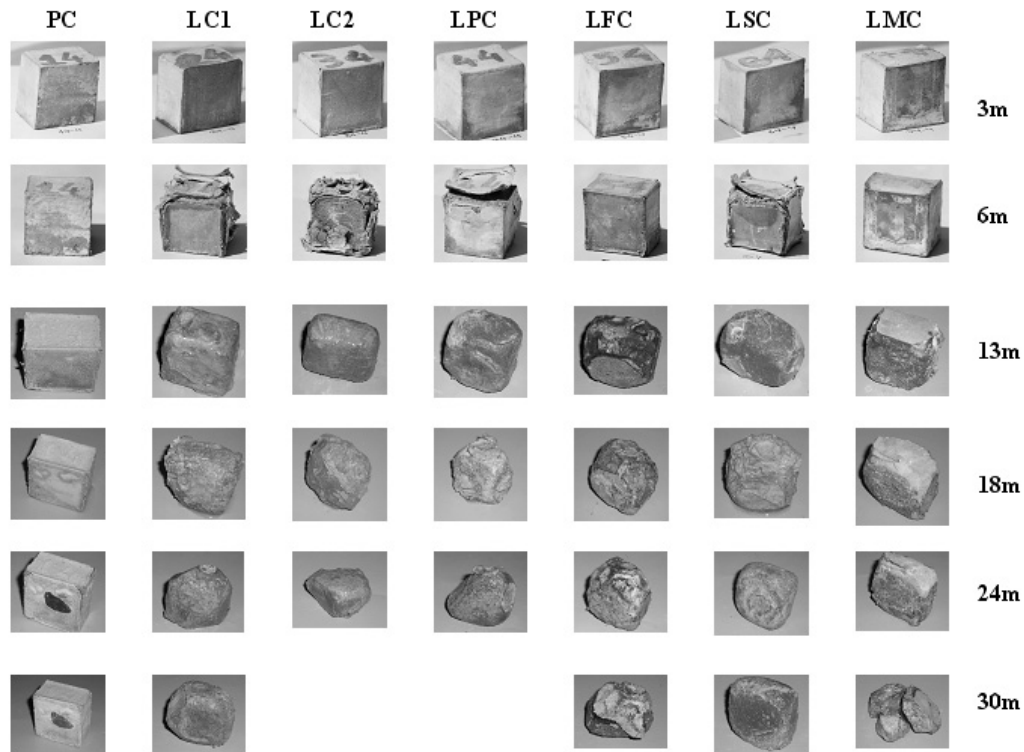


Fig.1 Specimens cured in a 1.8% $MgSO_4$ solution, at 5°C

In all cases, the first sign of attack was the deterioration of the corners followed by cracking along the edges. Progressively, expansion and spalling took place on the surface of the specimens. The surface of the cracks was covered with a white soft substance.

The first sign of attack was observed on LC2 after three months of exposure. A longer time was required for the samples LC1, LPC and LSC, while the specimens of limestone cement with fly ash (LFC) and metakaolin (LMC) showed the indications of a starting deterioration after 10 months. However, the rate of the deterioration, after 18 months, seems to be higher in LMC and LFC than in LSC. The specimen of Portland cement (PC) showed the best behaviour.

3.2 Mass measurement

The changes in specimens' mass were measured periodically and the results are shown in Fig. 2. This figure shows the ratio m/m_0 , where m_0 is the initial mass (measured prior to the immersion in the sulfate solution) and m is the mass after the exposure in sulfate solution. Initially, specimens showed a gradual rise in mass, but after longer exposure in the sulfate solution they began to lose mass, due to the gradual disintegration of the specimens. Fig. 2 gives a clear indication about the time that the severe deterioration begins, as it is accompanied by a great mass loss. LC2 and LPC showed the worst behaviour, losing after 25 months of exposure 95% and 71% of their mass, respectively. The other samples, through this period (25 months), lost less than 50% of their mass. The Portland cement (PC) specimen showed the best behaviour with no mass loss.

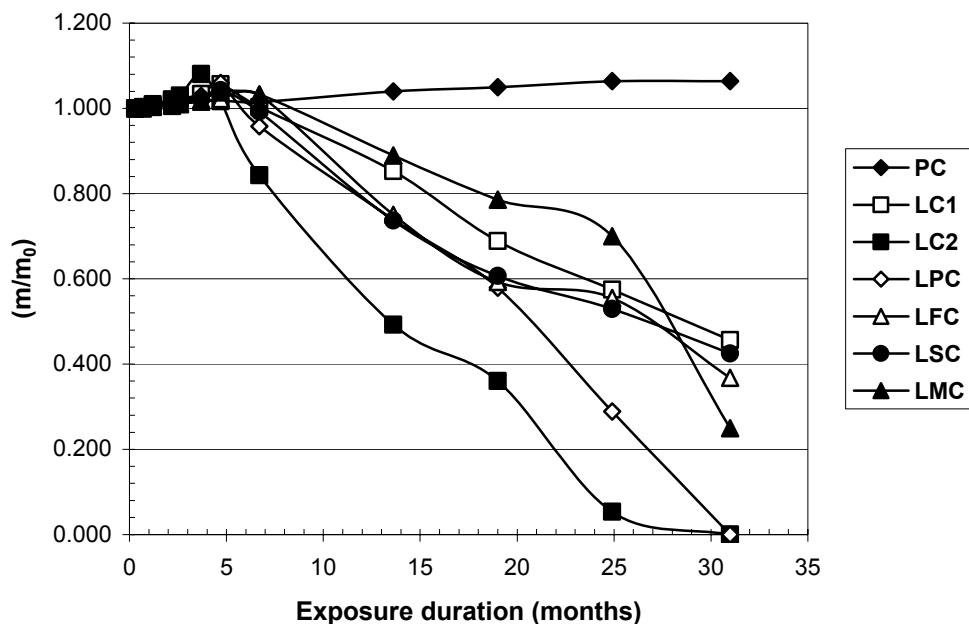


Fig. 2 Changes in mass of the specimens

3.3 Ultrasonic pulse velocity

The ultrasonic pulse velocity was measured periodically, until the deterioration led to a significant weathering of the parallel surfaces of the specimens. Due to the high deterioration rate of the studied samples, the test had to be discontinued after a short period of exposure. For an exposure period of 1.5 to 3 months, the ultrasonic pulse velocity increased, due to the continuous hydration of the cement. After this period

there is a low decrease of the ultrasonic pulse velocity. This low decrease cannot be attributed to the formation of microcracks within the body of the material. As the sulphate attack is a deteriorating process that begins from the outside, the low decrease in the pulse velocity is attributed to the weathering of the specimen's surface. When the surface damage became serious, the pulse velocity apparatus cannot give reliable or consistent information. Therefore, the inability to take sensible pulse velocity measurements is an indirect way that indicates the extensive surface damage and the beginning of an internal deterioration process. As it is shown from fig. 3, problems concerning the pulse velocity measurements begin after about 4, 4, 5, 5, 6, 7 and 8 months for the samples LC2, LPC, LC1, LSC, LFC, LMC and PC respectively. Thus, the pozzolana addition (LPC) has a negative effect on the behaviour of limestone cement that requires further investigation, while the addition of fly ash (LFC) and mainly of metakaolin (LMC) delays the onset of thaumasite formation. It must be noted that natural pozzolana (P) is a very good pozzolanic material, widely used in construction. The pozzolanic reaction of this material is slow, compared with the other minerals used in this study. The pozzolanic reaction in LPC specimens is further depressed when they are stored at low temperature. As a result the sulfate resistance of these pastes is impaired.

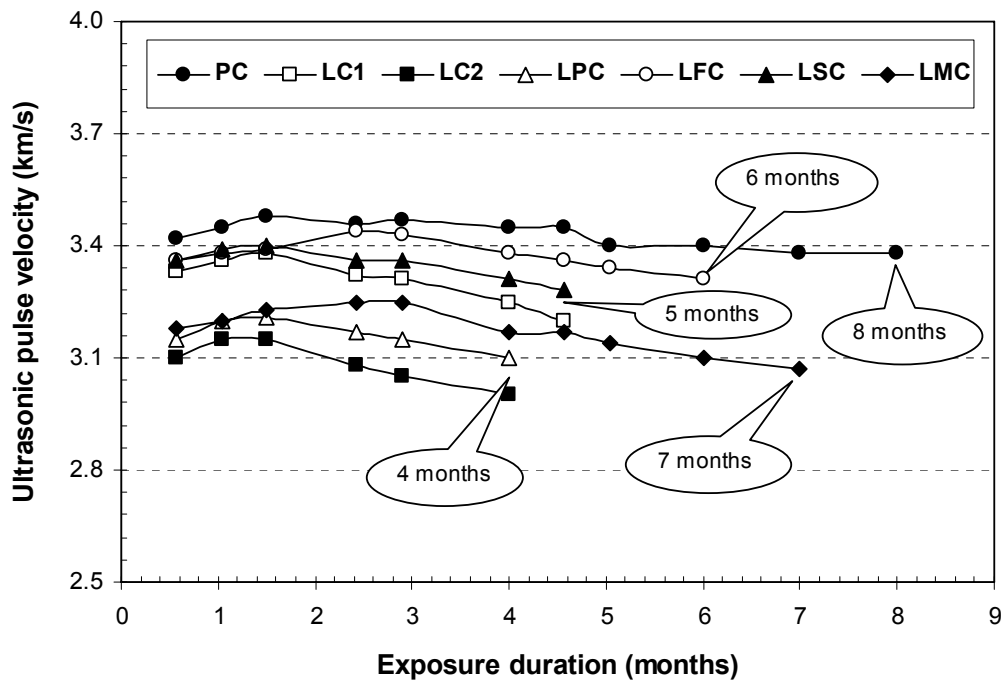
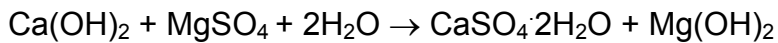


Fig. 3 Ultrasonic pulse velocity of the specimens

3.4 Analytical Techniques

The identification of products formed as a result of the sulfate attack was based on XRD, DTG measurements and SEM observations. Measurements were carried out on the soft, white material covering the surface of the cracks. In all cases, this material was found to contain mainly thaumasite, gypsum (instead of portlandite), calcite and traces of brucite.

Figure 4 presents the XRD pattern of the surface material of the sample LC1. The characteristic peaks of thaumasite and gypsum are clearly seen. It must be noted that no calcium hydroxide was found in the degradation products. Portlandite most probably has reacted with magnesium sulfate to form gypsum and brucite (according to the following reaction), both found in the degradation product. The low solubility of brucite favours the consumption of calcium hydroxide. This leads to a pH reduction and as a result C-S-H becomes more susceptible to sulfate attack.



Magnesium ions may also attack calcium silicate hydrates to form magnesium silicate hydrates, which lack cohesive properties. This can explain why only traces of brucite are found in the samples.

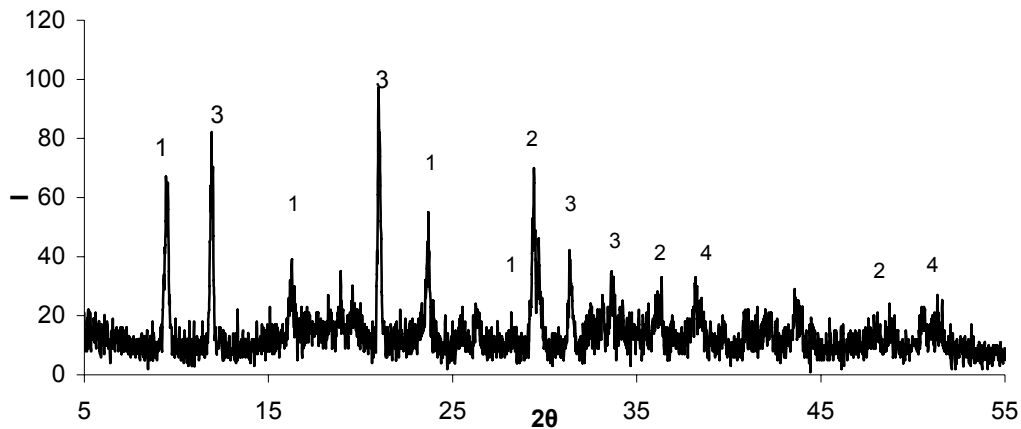


Fig. 4. XRD pattern of deterioration products of LC1 (1: Thaumasite, 2: Calcite, 3: Gypsum, 4: Brucite).

Figure 5 presents the TG/DTG curves of degradation products of LC1 sample. The curves of the other tested samples are very similar. A TG/DTG curve of a hydrated cement shows a peak in the range 100-120°C, which is associated with the dehydration of hydrated compounds and especially C-S-H. In the case of the degradation products (Fig. 5), the first peak is shifted to higher temperature, indicating the replacement of C-

S-H by thaumasite and gypsum. The characteristic double peak of gypsum is not clear due to the overlapping of the reactions. The TG/DTG curve confirms that no calcium hydroxide is present in the degradation products. The small peak at around 400°C is attributed to the dehydroxylation of brucite ($\text{Mg}(\text{OH})_2$).

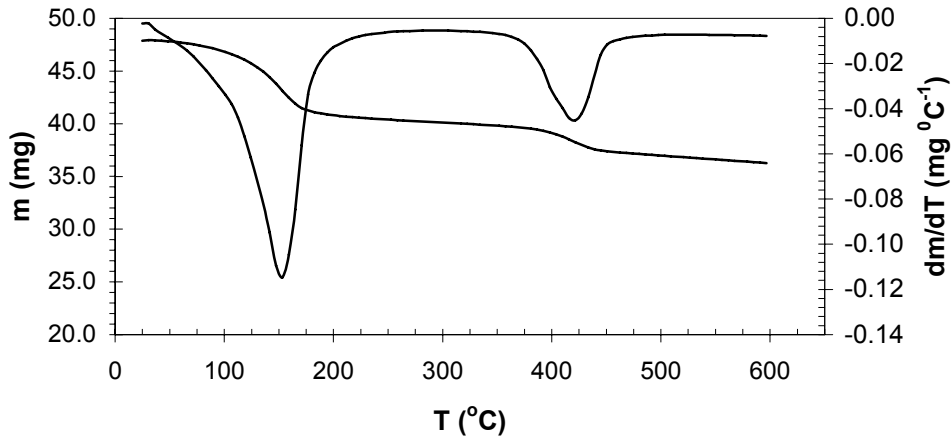


Fig. 5. TG/DTG curve of deterioration product of LC1

Figure 6 presents two SEM photos of the sample LC1 cured in MgSO_4 solution at 5°C, for 6 months.

In figure 6a, the elongated particles radiating outwards consist mainly of Ca, Si and O therefore they belong to C-S-H phase of hydrated cement. The microanalysis of these particles indicated also the presence of Mg, probably due to the diffusion of these ions through the pore solution. Characteristic cubic particles of gypsum are evident in the right corner of the photo. As it was mentioned gypsum is the product of the reaction between portlandite and MgSO_4 .

Figure 6b shows an agglomeration of needle like grains. The needles are approximately 2 microns long and 0.5 microns wide. The microanalysis showed that the needles consist mainly of Ca, S, Si and O. There are traces of Mg and no detectable amount of Al. The atomic ratio Ca:S:Si is close to 3:1:1. These observations, along with the XRD pattern, strongly suggest that this needle-like material is thaumasite. The results drawn from each one of the above measurements are in good accordance with each other.

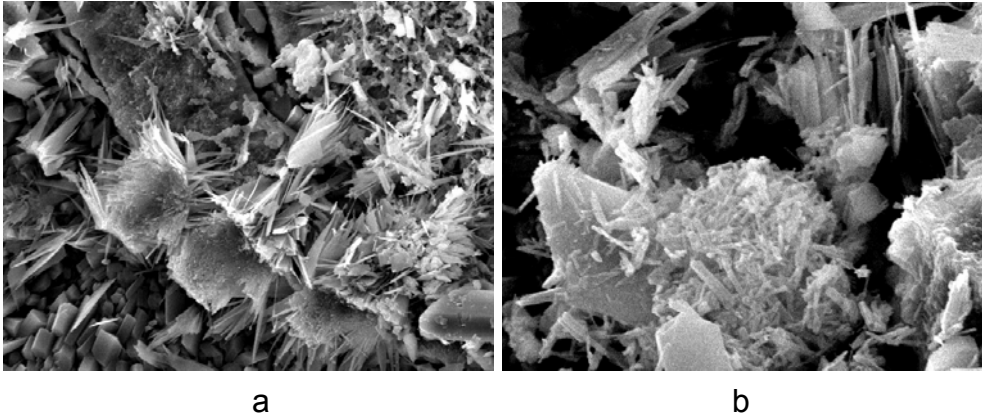


Figure 6 a, b. SEM photos of LC1 cured for 6 months in MgSO₄ 1,8% w/w

4. CONCLUSIONS

From the present study the following conclusions can be drawn:

- Limestone cement paste is susceptible to the thaumasite-kind of sulfate attack at low temperature. The rate of thaumasite formation is greater, the higher the limestone content.
- Thaumasite formation is accompanied by the formation of brucite and secondary gypsum through the reaction of Ca(OH)₂ with MgSO₄.
- The use of specific mineral replacements retards the thaumasite formation in limestone cement paste. The addition of fly ash and metakaolin in Portland limestone cement delays the onset of thaumasite formation.
- Slowly reacting pozzolana appears to be unable to provide effective resistance against sulfate attack.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- [1.] P. W. Brown, Thaumasite formation and other forms of sulfate attack, *Cem Concr Comp*, 24 (2002) 301-303.
- [2.] J. Bensted, Thaumasite-background and nature in deterioration of cements, mortars and concretes, *Cem Concr Comp*, 21 (1999) 117-121.
- [3.] R.N. Swamy, Editorial, *Cem Concr Comp*, 21 (1999), iii-iv.
- [4.] Thaumasite Expert Group: The Thaumasite form of sulfate attack: Risk, diagnosis, remedial works and guidance on new constructions, Report of the Thaumasite Expert Group, Dptm. of the Environment, Transport and the Regions, London, 1999.

- [5.] N.J. Crammond, P.J. Nixon, Deterioration of concrete foundation piles as a result of thaumasite formation, in: S Nagataki (Ed), Proceedings 6th Int. Conc. Durability Building Materials and Components, E. &F.N. Spon, London, 1993, pp. 295-305.
- [6.] NJ Crammond, MA Halliwell. The thaumasite form of sulfate attack in concretes containing a source of carbonate ions – A microstructural overview. In: Advances in Concrete Technology, 2d CANMET/ACI Symp. Adv. Concr. Technol. Las Vegas: (1995), p. 357-380
- [7.] A.P. Barker, Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5°C, Cem Concr Comp 2 (1999) 129-137.
- [8.] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, Thaumasite formation in Portland-limestone cement pastes, Cem Concr Res 29 (1999) 1331-1340.
- [9.] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, Engineering properties and structural implications of Portland limestone cement mortar exposed to magnesium sulphate attack, Advances in Cement Research 13 (1) (2001) 31-46.
- [10.] G. Kakali, S. Tsvilis, A. Skaropoulou J.H. Sharp, R.N. Swamy, Parameters affecting thaumasite formation in limestone cement mortar, Cem Concr Comp 25 (2003) 987-991.
- [11.] S. Tsvilis, G. Kakali, A. Skaropoulou J.H. Sharp, R.N. Swamy, Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar, Cem Concr Comp 25 (2003) 979-986.
- [12.] 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.
- [13.] 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.