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

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ABSTRACT

Concrete and mortar made from limestone cement may exhibit a lack of durability due to the formation of thaumasite. This work deals with the long term behavior of limestone cement mortars in relation to the limestone content, the curing conditions and the type of the sand. Three types of cement were examined: (i) Portland cement (PC), (ii) Portland limestone cement containing 15% w/w limestone and (iii) Portland limestone cement containing 30% w/w limestone. Mortar specimens were prepared using calcareous and siliceous sand. The specimens were immersed in a 1.8% $MgSO_4$ solution and cured at: (i) 5 °C and (ii) 25 °C. The status of the samples for a storage period of 5 years are reported, based on visual inspection, compressive strength, mass measurements, ultrasonic pulse velocity measurements and analytical techniques, including X-ray diffraction, thermal analysis and scanning electron microscopy. It is concluded that mortars containing limestone, either as sand or as a main constituent of the cement, suffer from the thaumasite form of sulfate attack (TSA) at low temperature. In some cases, the TSA leads to almost complete damage of the specimens after only 60 months of exposure. At 25 °C the specimens do not show any signs of conventional sulfate attack, even after 60 months of exposure to sulfate solution.

1. Introduction

Limestone has been widely used as a filler or as main cement constituent for many years due to its technical and economical advantages [1,2]. A serious problem associated with the use of limestone in cement and/or concrete is the formation of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) as a result of sulfate attack at low temperature. This problem has been discussed during recent years because the thaumasite form of sulfate attack (TSA) has been found in over 80 UK field structures and buildings and is particularly prevalent in buried concrete. Apart from UK, this problem of sulfate attack has been identified in a number of countries worldwide, including USA, Canada, South Africa, France, Germany, Norway, Denmark, Switzerland, Italy and Slovenia buildings [3]. In addition to that, there are many reports concerning the formation of thaumasite in laboratory scale experiments [4–13].

This form of sulfate attack completely destroys the binding ability of the cement by transforming C–S–H gel into a mush. Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and preferably low temperature [14,15]. It may also be connected with the prior formation of ettringite or the presence of some reactive alumina [14]. Since the formation of thaumasite involves the reaction of C–S–H with carbonate and sulfate ions, it may well take place in ordinary Portland cement (carbonate ions can be supplied from fine limestone aggregates or extended atmospheric carbonation) [16] or even in sulfate resistant Portland cements.

This work deals with the long term behavior of limestone cement mortars in relation to the limestone content, the curing conditions and the type of the sand.

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). Portland limestone cements, containing 15% and 30% w/w limestone, were produced by intergrinding clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity. The codes and the composition of the produced cements are given in Table 3. The specific surface of the cement was 3030, 3950 and 5170 cm^2/g (according to the Blaine method) for PC, LC1 and LC2, respectively.

Mortars were prepared, using the cements of Table 3 (w/c = 0.5, cement:sand = 1:2.50). Siliceous (s) and calcareous (c) sand have been used in order to study the effect of the sand type on the

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Table 1
Chemical and mineralogical composition of clinker.

Chemical composition (% w/w)		Mineralogical composition (% w/w)	
SiO_2	21.47	C_3S[a]	65.0
Al_2O_3	5.00	C_2S	12.6
Fe_2O_3	3.89	C_3A	6.7
CaO	65.67	C_4AF	11.8
MgO	1.89		
K_2O	0.68	*Moduli*	
Na_2O	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

[a] Cement chemistry notation – C: CaO, S: SiO_2, A: Al_2O_3, and F: Fe_2O_3.

Table 2
Chemical analysis of limestone (% w/w).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	LOI
0.54	0.43	0.20	53.61	1.29	0.06	43.73

thaumasite formation. The mortars containing siliceous sand are referred as XXX-s (for example LC1-s) while the mortars containing calcareous sand are referred as XXX-c (for example LC1-c). Mortar prisms of size 40 × 40 × 53 mm were prepared. The specimens were air-cured for 24 h, then they were water-cured for 6 days and finally they were air-cured for 21 days at laboratory temperature (25 ± 2 °C). After the 28-days curing the specimens were stored in 1.8% $MgSO_4$ solution. The samples were cured at: (i) 5 °C (laboratory refrigerator, ±2 °C) and (ii) 25 °C (laboratory environment, ±5 °C). In both cases, the $MgSO_4$ solution was replaced every 3 months.

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

The compressive strength of the specimens was measured after 28 days and after 9 months of exposure in $MgSO_4$ solution in order to investigate the effect of the sulfate attack on the strength loss of the samples.

Table 3
Codes and composition of the produced mixes.

PC	Clinker 100% (gypsum: 5% of clinker weight)
LC1	Clinker: 85% w/w, limestone: 15% w/w (gypsum: 5% w/w of clinker weight)
LC2	Clinker: 70% w/w, limestone: 30% w/w (gypsum: 5% w/w of clinker weight)

The ultrasonic pulse velocity test (apparatus: 58-E48, Controls Testing Equipments Ltd.) was used as a measure of the soundness of the samples. The measurements were carried out at regular intervals up to 1 year.

Changes in specimens' mass were recorded at regular intervals. 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 Cu Ka1 radiation (λ = 1.5405 Å) was used. Measurements were carried out on samples coming from either the hard core or the deteriorated part of the specimens. In addition, thermogravimetric analysis (TGA) was applied 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 50 cm^3/min. Finally, deteriorated surfaces of selected samples were examined using a JEOL JSM-5600 Scanning Electron Microscope. An OXFORD LINK ISIS 300 Energy dispersive X-ray spectrometer (EDXS) was used in order to observe the composition of various phases (accelerating voltage: 20 kV, beam current: 0.5 nA).

3. Results and discussion

3.1. Visual inspection

Visual inspection of the specimens was carried out monthly. The observations are summarized in Table 4. Photos of specimens, stored in the sulfate solution for 11, 16, 35, 41, 53 and 60 months at 5 °C, are presented in Figs. 1 and 2.

Almost all samples showed indications of commencement of deterioration after 8 months of exposure at 5 °C. The deterioration rate was greater in LC2 specimens than in LC1, while the PC specimens showed very slight attack for both kinds of sand. 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 inner surface of the cracks was covered with a white soft substance.

As can be seen, the PC specimens with siliceous sand are less damaged than those with calcareous sand after 60 months of exposure. In the case of limestone cements (LC1, LC2), the specimens with calcareous sand are less damaged than those with siliceous sand. Apart from this, it is obvious that the damage due to sulfate attack was greater the higher the limestone content in the cement.

No damage whatsoever was observed in the specimens exposed to sulfate solution at 25 °C (Figs. 3 and 4), nor was there any evidence of thaumasite formation at the higher temperature. It can be stated that "conventional" sulfate attack of well made mortars, at ambient temperature, is very slow, much slower than TSA at low

Table 4
Visual inspection of specimens cured in a 1.8% $MgSO_4$ solution at 5 °C.

Sample	Exposure (months)														
	7	8	9	10	11	16	30	37	42	48	49	50	53	56	60
PC-s	0	0	0	1	1	2	2	3	4	5	5	5	5	5	5
LC1-s	0	1	2	2	2	3	5	5	5	6	6	7	8	8	9
LC2-s	0	1	3	3	3	5	6	6	7	9	9	9	–	–	–
PC-c	0	0	1	2	2	3	3	5	5	6	6	6	6	6	6
LC1-c	0	1	2	2	3	3	4	4	5	6	6	6	7	8	9
LC2-c	0	1	2	2	3	4	5	5	5	6	6	7	8	9	9

0: No visible deterioration, 1: some deterioration at corners, 2: deterioration at corners, 3: deterioration at corners and some cracking along the edges, 4: deterioration at corners and cracking along the edges, 5: cracking and expansion, 6: bulge of surfaces, 7: extensive cracking and expansion, 8: extensive spalling, and 9: complete damage.

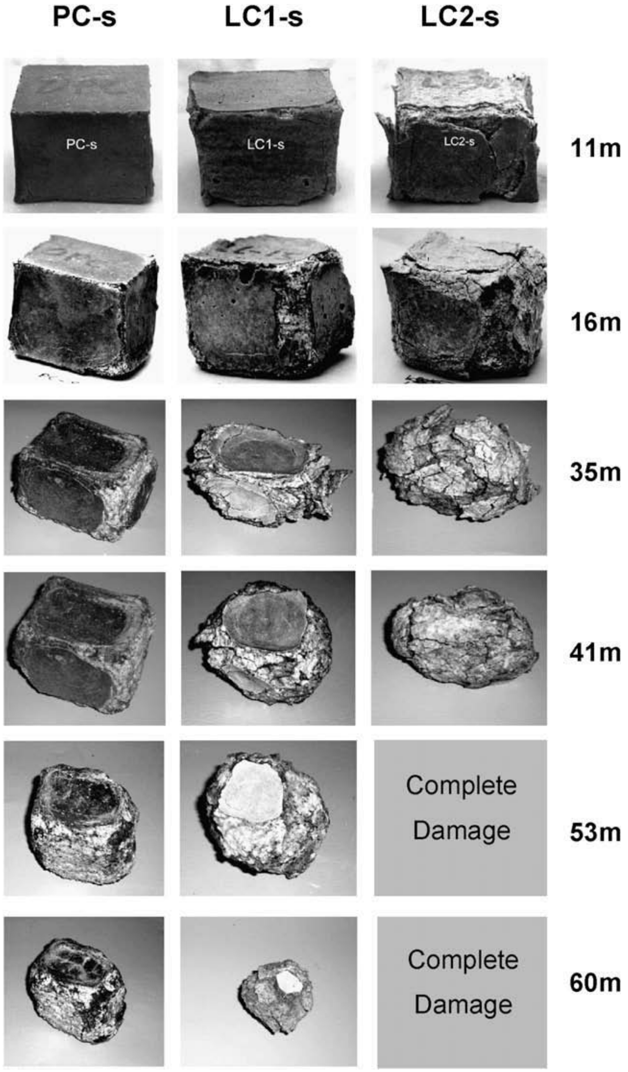

Fig. 1. Specimens with siliceous sand cured up to 60 months in a 1.8% $MgSO_4$ solution at 5 °C.

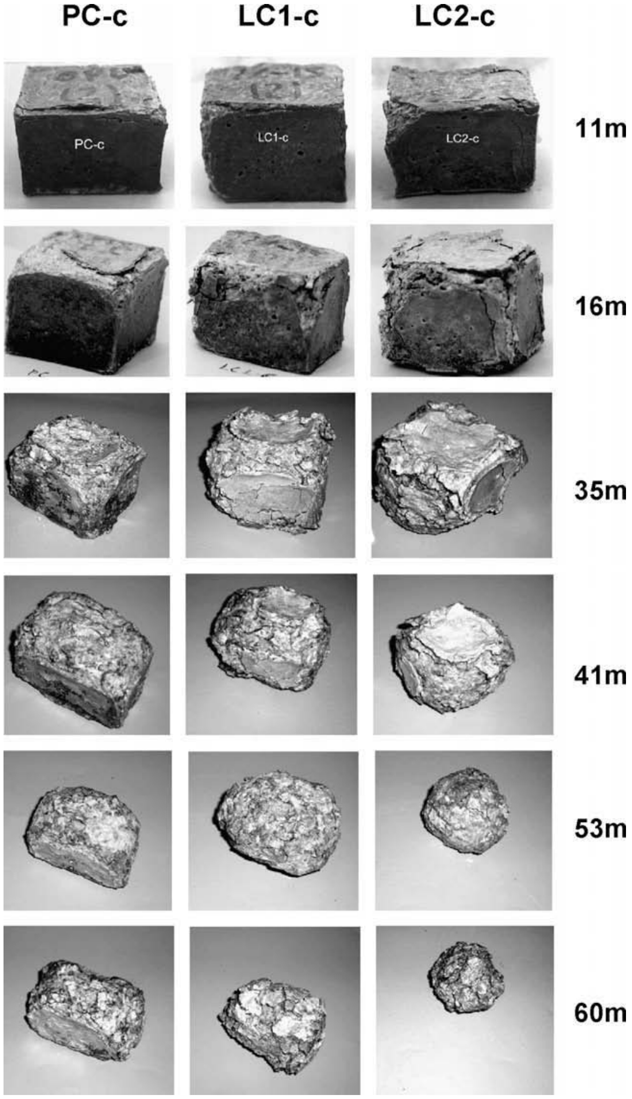

Fig. 2. Specimens with calcareous sand cured up to 60 months in a 1.8% $MgSO_4$ solution at 5 °C.

temperatures. Some researchers have reported the thaumasite formation at 20 °C [17–19]. Thermodynamic studies have also shown that the formation of small quantities of thaumasite may happen, at room temperature, only in systems where the Al present has already been consumed to form ettringite and the molar SO_3/Al_2O_3 ratio exceeded 3 [20]. It seems that, in some cases, thaumasite may be the end product of the conventional sulfate attack which is the main cause of samples' deterioration, at room temperature.

3.2. Compressive strength

The 28 day compressive strength, prior to any exposure to sulfates, is shown in Fig. 5. It is seen that mortars with calcareous sand show higher strength than those with siliceous sand. After nine months exposure to the $MgSO_4$ solution at 5 °C, a significant loss of strength was observed (Fig. 5). More specifically, in the case of

Fig. 3. Specimens with siliceous sand cured for 60 months in a 1.8% $MgSO_4$ solution at 25 °C.

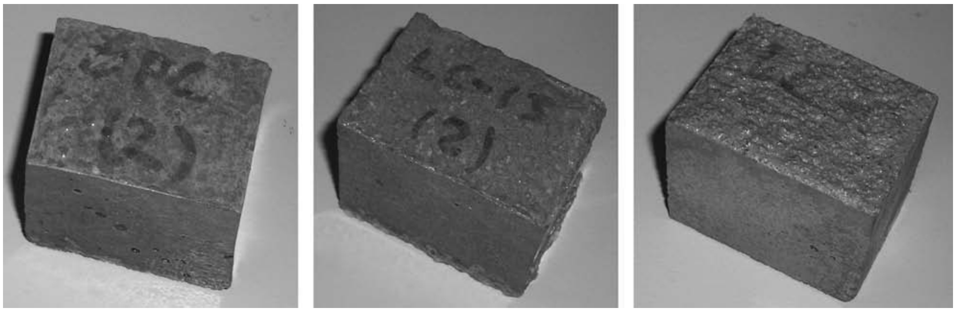

Fig. 4. Specimens with calcareous sand cured for 60 months in a 1.8% $MgSO_4$ solution at 25 °C.

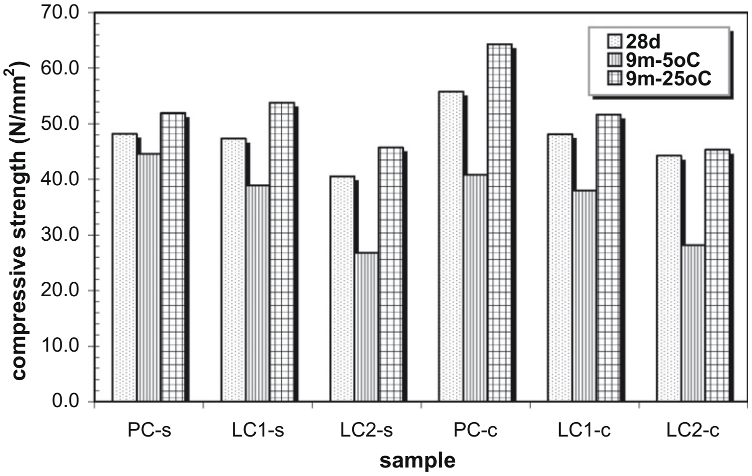

Fig. 5. Effect of curing temperature on the compressive strength of the specimens.

siliceous sand, the loss of strength was 8% of the 28 day strength for the Portland cement (PC), 18% for the limestone cement containing 15% limestone (LC1) and 34% for the limestone cement containing 30% limestone (LC2). In the case of calcareous sand the loss of strength is 27%, 21% and 36% of the 28 day strength for the samples PC, LC1 and LC2, respectively. These results show that the limestone content has a negative effect on the resistance of the cements against thaumasite sulfate attack at low temperatures.

Concerning the specimens cured at 25 °C, their compressive strength increased with storage time in all samples.

3.3. Ultrasonic pulse velocity

The ultrasonic pulse velocity was measured periodically, after the first signs of damage were observed in the samples. The results for specimens cured at 5 °C are presented in Figs. 6 and 7 for siliceous and calcareous sand, respectively. In the case of siliceous sand (Fig. 6) although the decrease in velocity is small, it is clearly observed that LC2-s shows the worst behavior. In the case of calcareous sand (Fig. 7), samples LC1-c and LC2-c seem to have an almost similar behavior, worse than PC. After 13 months the specimens were too damaged to continue the measurement of ultrasonic pulse velocity.

In specimens cured at 25 °C, there was no significant decrease of pulse velocity which remained almost stable.

3.4. Mass measurements

The mass loss of specimens is presented in Figs. 8 and 9 for siliceous and calcareous sand, respectively. LC2 showed the worst behavior. In case of siliceous sand (Fig. 8), LC2-s lost 92% of its mass after 46 months of exposure in the sulfate solution. In case of calcareous sand (Fig. 9), LC2-c lost 80% of its mass after 60 months of exposure in the sulfate solution.

3.5. Analytical techniques

The identification of products formed as a result of the sulfate attack was based on XRD, TGA measurements and SEM observations. In all cases, the composition of the sound core of the specimens corresponded to that of a normal hydrated cement containing mainly calcite and/or quartz (depending on the composition of the mortar) as well as calcium hydroxide. There was no sign of sulfate attack at the sound core of the specimens, since no degradation products were observed. The XRD patterns of the sound core of the samples PC-c and LC1-c are presented in Fig. 10. At the sound core of the specimens no gypsum was observed, which indicates that there is no or almost no diffusion of sulfates into the sound core.

Measurements were also 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) and traces of calcite. The XRD patterns of the surface material (samples PC-c and LC1-c) are presented in Fig. 11.

TGA measurements confirmed the XRD observations. Figs. 12 and 13 present the TG/DTG curves of the sound core and the degradation products of the sample LC1-c, respectively. The relative curves of the other tested samples are very similar. As can be seen, the curves of the sound core (Fig. 12) are typical of hydrated cement. The broad peak in the range 100–120 °C is associated with

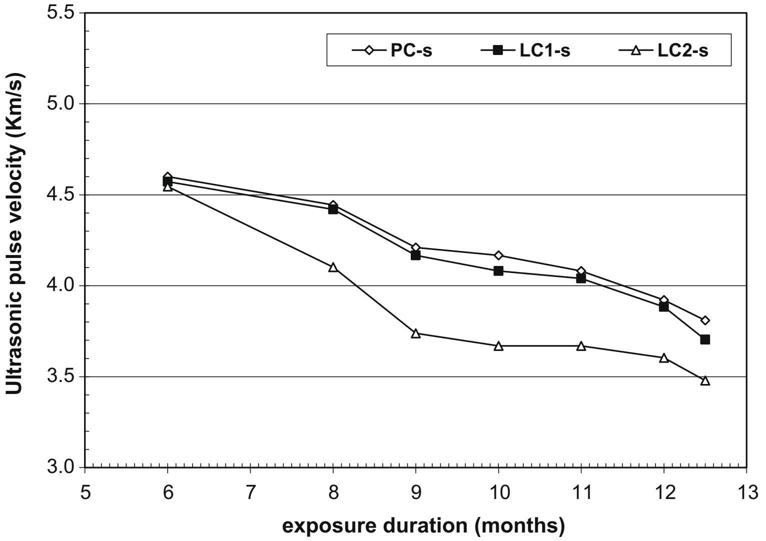

Fig. 6. Ultrasonic pulse velocity of specimens with siliceous sand (5 °C, 1.8% $MgSO_4$ solution).

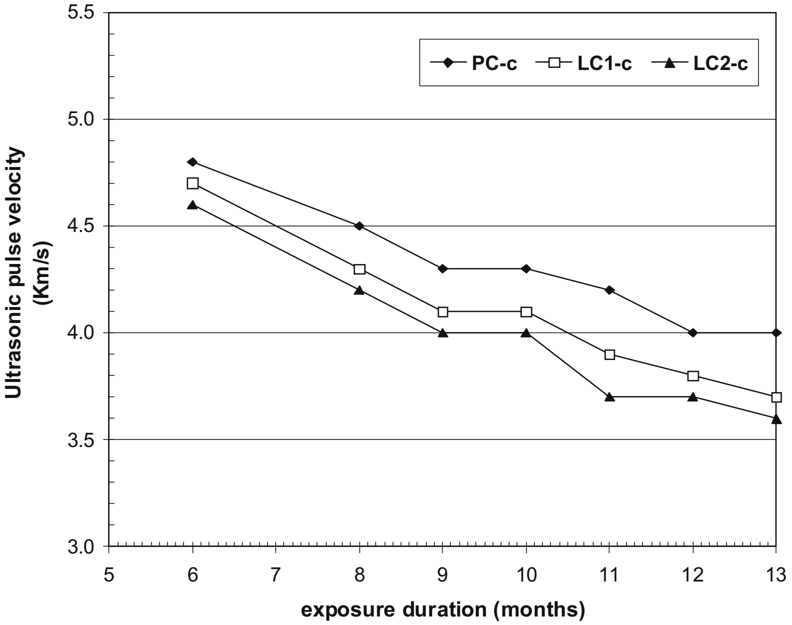

Fig. 7. Ultrasonic pulse velocity of specimens with calcareous sand (5 °C, 1.8% $MgSO_4$ solution).

the dehydration of hydrated compounds and especially C–S–H, while the endothermic peak at ca. 450 °C is connected with the dehydroxylation of $Ca(OH)_2$.

In the case of the degradation products (Fig. 13), 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 found in the degradation products. The small peak at around 400 °C is attributed to the dehydroxylation of brucite ($Mg(OH)_2$). Portlandite most probably has reacted with magnesium sulfate to form gypsum and brucite, both found in the degradation products, according to the reaction:

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \qquad (1)$$

The very low solubility of brucite shifts the reaction to the right and favors the consumption of calcium hydroxide. This leads to a reduction in pH and as a result C–S–H becomes more susceptible to sulfate attack. Other researchers have also reported that portlandite is a reactant rather than a product of thaumasite formation [7].

Fig. 14 present two SEM micrographs of sample LC1-c cured in $MgSO_4$ solution at 5 °C for 35 months. In Fig. 14a cubic grains of gypsum, limestone and hydrated phases of cement are observed (deterioration products), while Fig. 14b shows the white soft material that covers the damaged area of the sample. This material with the needle-like texture is thaumasite. This observation is in good accordance with XRD and thermogravimetric analysis.

Based on all the above measurements but mainly on long term tests (visual inspection and mass loss), it is concluded that in the case of Portland cement (PC), the specimens with siliceous sand showed better behavior than those with calcareous sand. It is obvious that the formation of thaumasite proceeds more readily through the reaction of the fine sand particles (in specimens with calcareous sand) than through carbonation (in specimens with siliceous sand). On the other hand, in the case of limestone cements, the specimens with calcareous sand showed better performance

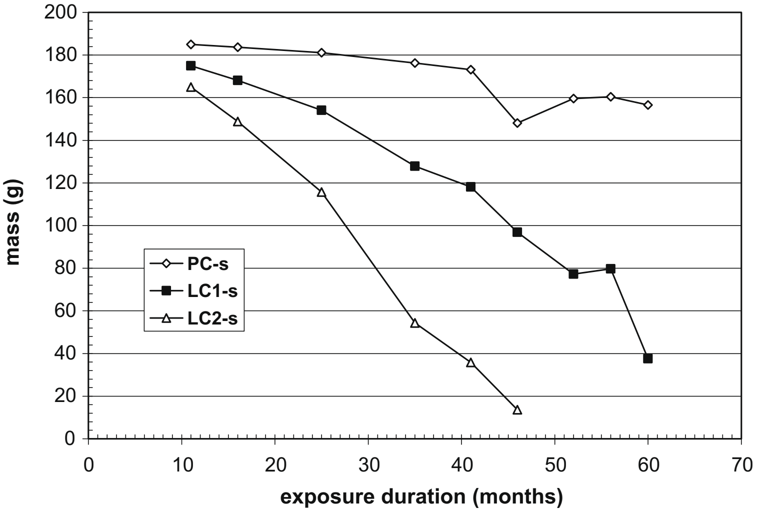

Fig. 8. Changes in mass of specimens with siliceous sand (5 °C, 1.8% $MgSO_4$ solution).

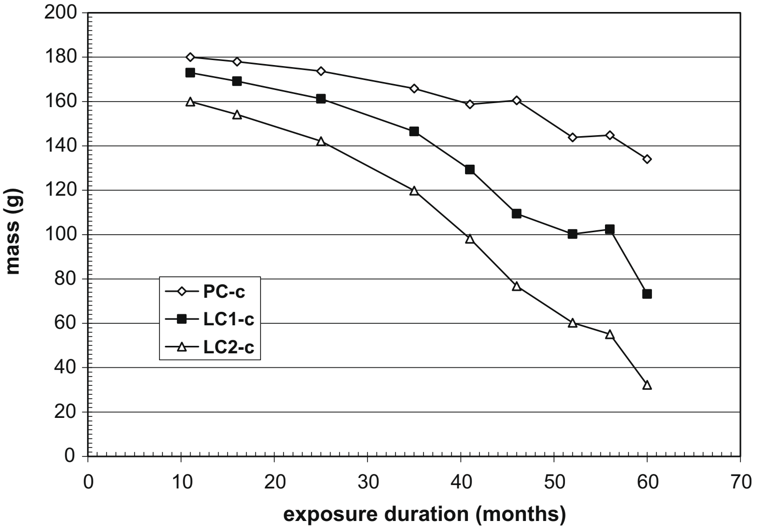

Fig. 9. Changes in mass of specimens with calcareous sand (5 °C, 1.8% $MgSO_4$ solution).

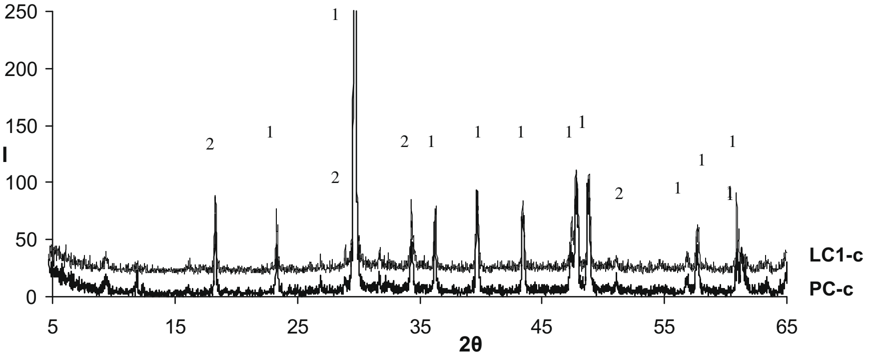

Fig. 10. XRD patterns of sound core of specimens cured for 60 months at 5 °C, 1.8% $MgSO_4$: (1) Calcite and (2) Portlandite.

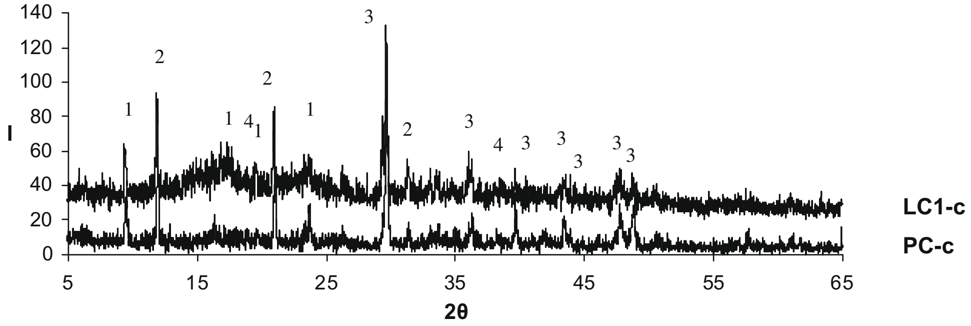

Fig. 11. XRD patterns of surface material (degradation products) of specimens cured for 60 months at 5 °C, 1.8% $MgSO_4$: (1) Thaumasite; (2) Gypsum; (3) Calcite and (4) Brucite.

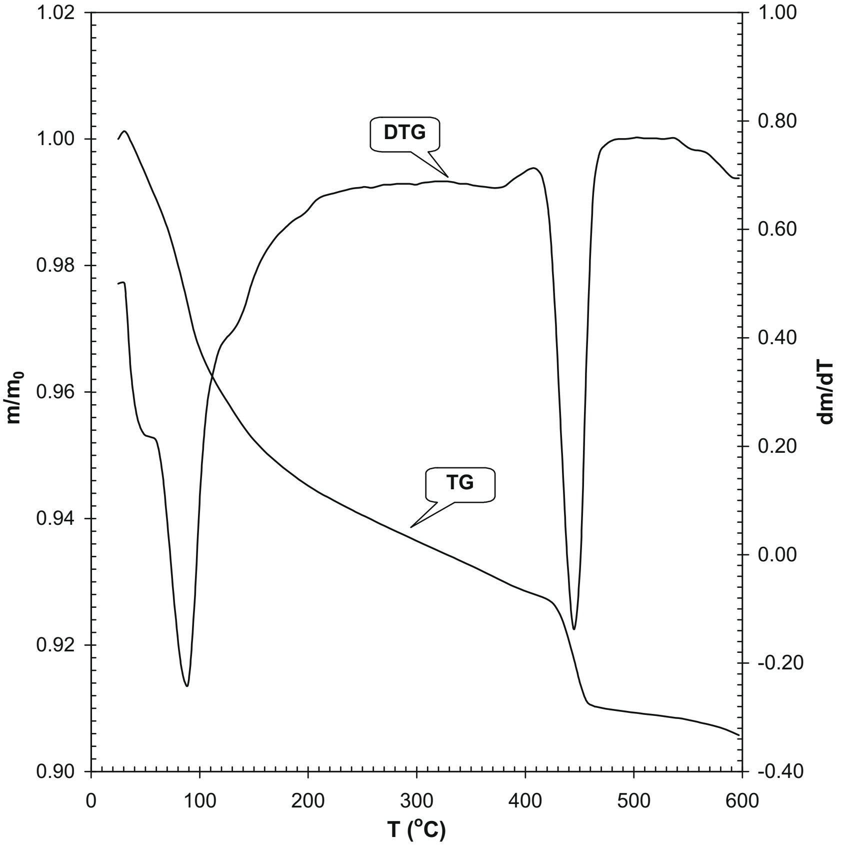

Fig. 12. TG–DTG curve of the sound core of LC1-c after 60 months of exposure in 1.8% $MgSO_4$ at 5 °C.

than those with siliceous sand. In this case, there is an overabundance of carbonate ions coming from the limestone of cement and probably the determinative factor is the cohesion between the cement paste and the sand, which is better in the case of calcareous sand.

All the measurements showed that mortars containing limestone, either as sand or as a main cementitous constituent, are susceptible to the thaumasite form of sulfate attack at low temperature. Surprisingly, the mortars with the Portland cement and siliceous sand which do not contain any calcite at all, also suffer from the thaumasite form of attack at low temperature. This must be associated with atmospheric carbonation, perhaps involving intermediate formation of bicarbonate ions [16].

4. Conclusions

- Mortars containing limestone, either as sand or as a major cementitous constituent, are susceptible to the thaumasite form 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 $MgSO_4$.
- No damage was observed in the specimens exposed to sulfate solution at 25 °C for 60 months. It seems that "conventional" sulfate attack, at ambient temperature, is much slower than

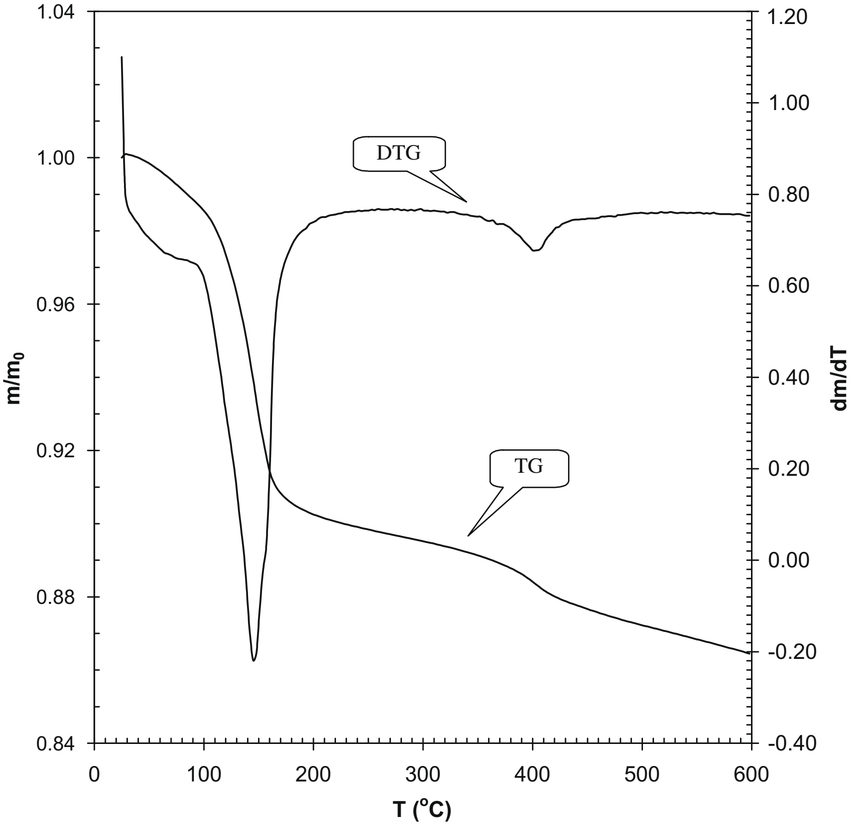

Fig. 13. TG–DTG curves of deterioration products of LC1-c after 35 months of exposure to sulfate solution.

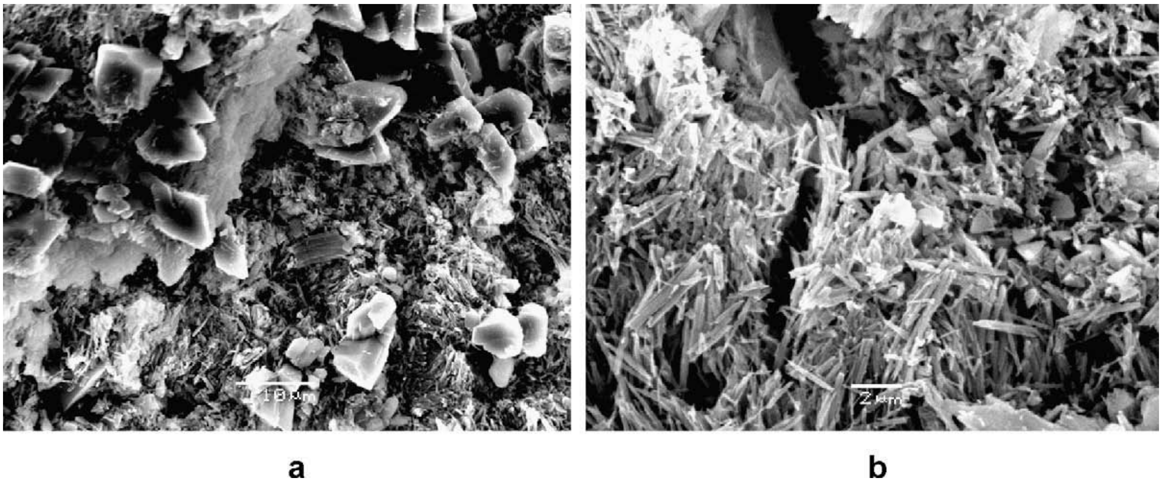

Fig. 14. SEM micrographs of sample LC1-c cured in $MgSO_4$ 1.8% w/w at 5 °C for 35 months.

thaumasite sulfate attack, at low temperature. Furthermore TSA was very slow or even non-existent in the samples stored at 25 °C.

- Even the mortars with no limestone addition suffer from thaumasite sulfate attack at low temperature.

References

[1] Tsivilis S, Chaniotakis E, Badogiannis E, Pahoulas G, Ilias A. A study on the parameters affecting the properties of Portland limestone cements. Cem Concr Comp 1999;21:107–16.
[2] Tsivilis S, Chaniotakis E, Kakali G, Batis G. An analysis of the properties of Portland limestone cements and concrete. Cem Concr Comp 2002;24: 371–8.
[3] Crammond NJ. The thaumasite form of sulfate attack in the UK. Cem Concr Comp 2003;25:809–18.
[4] Barker AP, Hobbs DW. Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5 °C. Cem Concr Comp 1999;21: 129–37.
[5] Tsivilis S, Kakali G, Skaropoulou A, Sharp JH, Swamy RN. Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar. Cem Concr Comp 2003;25:969–76.
[6] Kakali G, Tsivilis S, Skaropoulou A, Sharp JH, Swamy RN. Parameters affecting thaumasite formation in limestone cement mortar. Cem Concr Comp 2003;25:977–81.
[7] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland-limestone cement pastes. Cem Concr Res 1999;29:1331–40.
[8] Gaze ME, Crammond NJ. The formation of thaumasite in cement:lime:sand mortar exposed to cold magnesium and potassium sulfate solutions. Cem Concr Comp 2000;22:209–22.

[9] Gaze ME. The effect of varying gypsum content on thaumasite formation in a cement:lime:sand mortar at 5 °C. Cem Concr Res 1997;27:259–65.

[10] Torres SM, Lynsdale CJ, Swamy RN, Sharp JH. Microstructure of 5-year-old mortars containing limestone filler damaged by thaumasite. Cem Concr Res 2006;36:384–94.

[11] Lee ST, Moon HY, Swamy RN. Sulfate attack and role of silica fume in resisting strength loss. Cem Concr Comp 2005;27:65–76.

[12] Torres SM, Kirk CA, Lynsdale CJ, Swamy RN, Sharp JH. Thaumasite–ettringite solid solutions in degraded mortars. Cem Concr Res 2004;34:1297–305.

[13] Skaropoulou A, Tsivilis S, Kakali G, Sharp JH, Swamy RN. Thaumasite form of sulfate attack in limestone cement mortars: a study on long term efficiency of mineral admixtures. Constr Build Mater 2009;23:2338–45.

[14] Bensted J. Thaumasite-background and nature in deterioration of cements mortars, and concretes. Cem Concr Comp 1999;21:117–21.

[15] Aguilera J, Blanco Varela MT, Vazquez T. Procedure of synthesis of thaumasite. Cem Concr Res 2001;31:1163–8.

[16] Collett G, Crammond NJ, Swamy RN, Sharp JH. The role of carbon dioxide in the formation of thaumasite. Cem Concr Res 2004;34:1599–612.

[17] Hartshorn SA, Sharp JH, Swamy RN. The thaumasite form of sulfate attack in Portland-limestone cement mortars stored in magnesium sulfate solution. Cem Concr Comp 2002;24:351–9.

[18] Lee Seung Tae, Hooton Robert Doug, Jung Ho-Seop, Park Du-Hee, Choi Chang Sik. Effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature. Cem Concr Res 2008;38:68–76.

[19] Irassar EF, Bonavetti VL, Trezza MA, González MA. Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20 °C. Cem Concr Comp 2005;27:77–84.

[20] Schmidt T, Lothenbach B, Romer M, Scrivener K, Rentsch D, Figi R. A thermodynamic and experimental study of the conditions of thaumasite formation. Cem Concr Res 2008;38:337–49.