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Use of mineral admixtures to improve the resistance of limestone cement concrete against thaumasite form of sulfate attack

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ABSTRACT

In this work the effect of mineral admixtures on the thaumasite form of sulfate attack in limestone cement concrete is studied. Additionally, the effect of the type of sand (calcareous or siliceous) and the storage temperature is investigated. Limestone cement, containing 15% limestone, was used. Concrete specimens were prepared by replacing a part of cement with the studied minerals. The specimens were immersed in a 1.8% $MgSO_4$ solution and stored at 5 °C and 25 °C for 3 years. A well designed concrete made with limestone cement and fly ash, blastfurnace slag or metakaolin seems to have the ability to withstand thaumasite form of sulfate attack. The addition of natural pozzolana presented only a limited improvement of concrete's sulfate resistance. The type of the sand and its cohesion with the cement paste has a remarkable effect on the performance of concrete at low temperature. Finally, no damage was observed in the specimens exposed to sulfate solution at 25 °C.

1. Introduction

As it is well known, sulfate attack may cause severe damage to cementitious materials. The conventional sulfate reaction in mortars and concretes leads to the formation of expansive ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$). However, another kind of sulfate attack, attributed to the formation of thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$), has been widely discussed during the recent years. There are several reports concerning either the presence of thaumasite in damaged structures [1] or its formation in laboratory scale experiments [2–10].

Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and preferably low temperature. Portland limestone cement is susceptible to thaumasite sulfate attack (TSA) and this is a serious problem because limestone has been widely used as filler or as main cement constituent for many years [11]. Even the CEM I (pure Portland cement) can contain up to 5% limestone as minor cement constituent (EN 197-1). Thaumasite formation may also be connected with carbonation, prior formation of ettringite or the presence of some reactive alumina [12–15].

Since the formation of thaumasite involves the reaction of C–S–H with carbonate and sulfate ions, it may well take place in all Portland cement based binders (carbonate ions can be supplied from fine limestone aggregates or extended atmospheric carbonation) [14]. The use of sulfate resisting Portland cements with low C_3A content (types CEM I-SR 0, CEM I-SR 3 and CEM I-SR 5 of the EN 197-1:2011) is not an effective way to preserve cementitious materials against the thaumasite form of sulfate attack since, in this kind of attack, calcium silicate hydrates (and not calcium aluminate hydrates) are attacked [16–18].

The use of mineral admixtures improves the sulfate resistance of limestone cement, due to their beneficial effect on the permeability and pore structure. Besides, some authors suggest that the silicon rich C–S–H, which is formed in the presence of pozzolanic materials, shows higher resistance against thaumasite formation [19,20]. Most of the published work concerns the performance of pastes and mortars. Limited work has been done on concretes and especially on the effect of the kind of sand, which may be an additional source of carbonate ions. The role of sand type has been investigated in a previous paper and there were indications that the use of siliceous sand accelerates the deterioration, due to thaumasite formation, of pure limestone cement mortars [7].

In this work the effect of natural pozzolana, fly ash, ground granulated blastfurnace slag and metakaolin on the thaumasite formation in limestone cement concrete is studied. In addition, the effect of the type of sand (calcareous or siliceous) and the curing temperature is investigated.

2. Experimental

Portland cement clinker (K) of industrial origin and limestone (L) of high calcite content ($CaCO_3$: 95.7%) were used. Portland limestone cement, containing 15% (w/w) limestone, was produced by

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Table 1
Chemical composition (%) of the materials used.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	LOI
Clinker (K)[a]	21.47	5.00	3.89	65.67	1.89	0.68	0.89
Limestone (L)	0.54	0.43	0.20	53.61	1.29	0.06	43.73
Natural pozzolana (P)	59.18	16.12	6.14	4.92	1.96	2.15	4.78
Fly ash (F)	49.33	20.72	7.98	10.26	2.19	1.94	2.02
Blastfurnace slag (S)	36.74	10.44	1.20	40.32	7.60	0.31	0.44
Metakaolin (M)	54.41	43.94	0.35	0.37	–	0.31	–

[a] Mineralogical composition (Bogue): $C_3S = 65\%$, $C_2S = 12.6\%$, $C_3A = 6.7\%$, $C_4AF = 11.8\%$.

Table 2
Binder composition of concretes.

Code	Binder composition
LC1[a]	Clinker (K): 85% w/w, limestone (L): 15% w/w
LPC	LC1: 80% w/w, natural pozzolana (P): 20% w/w
LFC	LC1: 70% w/w, fly ash (F): 30% w/w
LSC	LC1: 50% w/w, blastfurnace slag (S): 50% w/w
LMC	LC1: 90% w/w, metakaolin (M): 10% w/w

[a] Gypsum: 5% of clinker by mass.

intergrinding clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity. This cement was used for the preparation of concrete specimens. In addition, concrete specimens were prepared by replacing a part of limestone cement with natural pozzolana (P), fly ash (F), blastfurnace slag (S) and metakaolin (M). The chemical composition of the materials used is given in Table 1, while the binder composition of the concretes is given in Table 2.

Concrete specimens, 40 × 40 × 53 mm, were prepared using a binder content (B) of 350 kg/m^3, a water to binder ratio (W/B) of 0.5 and aggregates with a maximum size of 8 mm (Table 3). A varying proportion of superplasticizer was used in order to have similar slump values in the tested concretes (Table 3). Natural siliceous sand (s) and crushed calcareous sand (c) were used in order to study the effect of the sand type on the thaumasite form of sulfate attack. Siliceous sand contains 98.5% SiO_2 (as quartz mineral), while calcareous sand contains 97.5% $CaCO_3$ (as calcite mineral). The used coarse aggregate was crushed limestone. The concrete specimens containing siliceous sand are referred as XXX-s (for example LC1-s) while the concretes containing calcareous sand are referred as XXX-c (for example LC1-c). The specimens were left in the molds for 24 h, then cured in water for 6 days and finally air-cured (average relative humidity: 60%) for 21 days at laboratory temperature (25 ± 2 °C). After the 28-days initial curing the specimens were stored in a 1.8% w/w $MgSO_4$ solution. The samples were stored at: (i) 5 °C (laboratory refrigerator, ±2 °C) and (ii) 25 °C (laboratory environment, ±2 °C). In both cases, the $MgSO_4$ solution was replaced every 3 months.

Table 3
Concrete composition and properties.

Sample	Concrete composition (kg/m^3)				Concrete properties	
	C	Aggregates[a]	*W*	SP[e]	Slump (mm)	28-Day compressive strength (MPa)
LC1-s	350	Fine[b]: 1190	175[c]	0.74	110	44.9
LPC-s		Coarse[b]: 740		0.90	110	34.2
LFC-s				1.33	100	42.9
LSC-s				1.10	110	35.9
LMC-s				1.50	100	51.7
LC1-c			175[d]	0.52	110	47.0
LPC-c				0.60	110	40.0
LFC-c				0.97	110	49.8
LSC-c				0.70	110	41.0
LMC-c				1.12	100	54.1

[a] Aggregate grading (passing, w/w): 8 mm 100%; 4 mm 63%; 2 mm 45%; 1 mm 29%; 0.25 mm 11%.

[b] Water absorption (w/w): calcareous sand 1.51%; siliceous sand 1.72%; coarse aggregates 0.81%.

[c] Total water content: 201 kg/m^3; water absorbed by the aggregates: 26 kg/m^3; effective water: 175 kg/m^3 (W/C = 0.50 according to EN 206-1).

[d] Total water content: 199 kg/m3; water absorbed by the aggregates: 24 kg/m^3; effective water: 175 kg/m^3 (W/C = 0.50 according to EN 206-1).

[e] Superplasticizer: CHEM SLP P by Domylco Ltd., type E and F of ASTM C494/C494 M-08a.

Visual inspection of the samples was performed monthly and all significant variations, such as changes of surface color and texture, formation of coatings, deterioration, expansion and cracking were recorded. Changes in specimens' mass (water-saturated specimens) were also recorded. The ultrasonic pulse velocity test (apparatus: 58-E48, Controls Testing Equipments Ltd.) was used as a measure of the internal soundness of the samples. The measurements were carried out at regular intervals (approximately every 4 weeks) up to 3 years. Concerning the mass and ultrasonic pulse velocity, three prisms for each measurement were used and the results presented in this paper are the average of the three values.

The compressive strength of the specimens was measured after 28 days (reference strength) and after 6, 12 and 24 months of exposure in $MgSO_4$ solution (at 5 and 25 °C).

XRD measurements were performed on samples at regular intervals in order to identify any compounds formed during the exposure to $MgSO_4$. A Siemens D-5000 X-ray diffractometer, with Cu Ka1 radiation ($\lambda = 1.5405$ Å) was used. Measurements were carried out on samples coming from 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 (~50 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 by SEM using a FEI Quanta 200 instrument operating at 30 keV and equipped with an EDX detector.

3. Results and discussion

3.1. Exposure in a 1.8% $MgSO_4$ solution at 5°C

3.1.1. Visual inspection

Visual inspection of the specimens was carried out monthly and the observations are summarized in Table 4 (exposure at 5 °C). Indications of the onset of deterioration were first observed on specimens with limestone cement (LC1-s) and natural pozzolana (LPC-s) with siliceous sand after 10–11 months. A longer time (13 months) was required for the beginning of deterioration in the samples with fly ash (LFC-s) and LC1-c. The specimens with natural pozzolana and calcareous sand (LPC-c) showed the first signs of deterioration after 15 months of exposure. Finally, a slight damage of specimens with blastfurnace slag (LSC-s) and metakaolin (LMC-s) with siliceous sand was observed after 17 months. 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 by a white soft substance. After 34 months of exposure (Table 4, Fig. 1), specimens with LC1-s presented the most severe deterioration, followed by LC1-c and LPC-s. Specimens LPC-c suffered a lesser degree of deterioration, while LFC-s, LSC-s and LMC-s showed the most limited deterioration. It must be noted

Table 4
Visual assessment[a] of specimens' deterioration (1.8% $MgSO_4$ solution at 5 °C).

Sample	Exposure duration (months)													
	9	10	11	13	15	17	19	21	22	24	28	30	32	34
LC1-s	0	1	2	2	2	3	4	5	6	6	7	7	7	7
LPC-s	0	0	1	1	2	3	3	3	3	3	4	4	4	5
LFC-s	0	0	0	1	1	1	2	2	2	2	2	2	2	2
LSC-s	0	0	0	0	0	1	1	2	2	2	2	2	2	2
LMC-s	0	0	0	0	0	1	1	2	2	2	2	2	2	2
LC1-c	0	0	0	1	2	2	3	3	4	4	4	5	5	5
LPC-c	0	0	0	0	1	1	1	1	1	2	2	2	3	3
LFC-c	0	0	0	0	0	0	0	0	0	0	0	0	0	0
LSC-c	0	0	0	0	0	0	0	0	0	0	0	0	0	0
LMC-c	0	0	0	0	0	0	0	0	0	0	0	0	0	0

[a] Deterioration scale
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.
9: Complete damage.

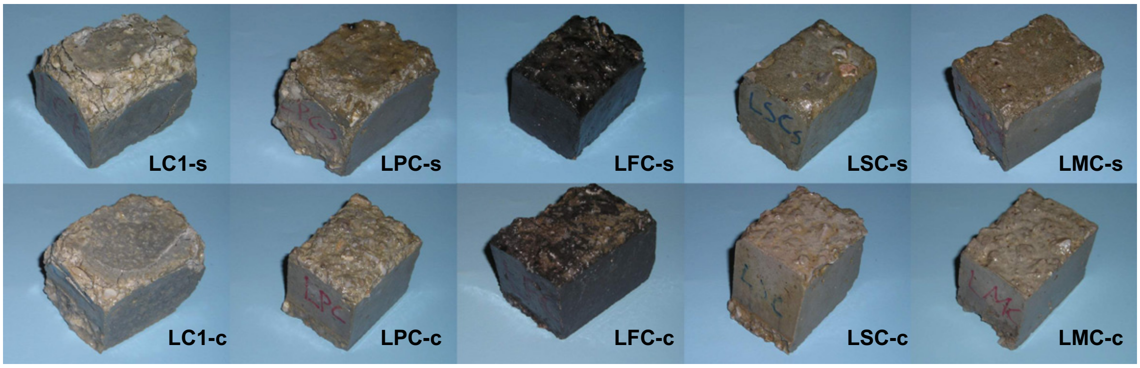

Fig. 1. Specimens stored for 34 months in a 1.8% $MgSO_4$ solution at 5 °C.

that no damage was observed in the concretes with fly ash, blastfurnace slag and metakaolin with calcareous sand (LFC-c, LSC-c, LMC-c).

It is obvious that the use of mineral admixtures improved the resistance of the limestone cement concrete against sulfate attack at low temperature. Fly ash, blastfurnace slag and metakaolin showed the best behavior, while natural pozzolana presented only a limited improvement of concrete's sulfate resistance. The specimens with calcareous sand performed better than those with siliceous sand.

3.1.2. Mass measurements

In the case of siliceous sand, the limestone cement concrete (LC1-s) presented the greatest mass loss (17%) after 35 months of exposure in the sulfate solution (Fig. 2). Concrete with natural pozzolana (LPC-s) showed a mass loss of 5.5% for the same period, while no mass loss was recorded in the specimens with fly ash (LFC-s), blastfurnace slag (LSC-s) and metakaolin (LMC-s) (Fig. 2).

In the case of calcareous sand, no mass loss was observed in the concrete specimens during the 35 months of storage in the 1.8% w/w $MgSO_4$ solution at 5 °C (Fig. 3).

Mass measurements verify that the use of mineral admixtures improved the resistance of limestone cement concrete against TSA, especially in the case of siliceous sand when concrete seems to be more susceptible τo TSA.

3.1.3. Ultrasonic pulse velocity

The test gives information about the interior of the specimen and provides evidence of internal micro-cracking and of the soundness of the material's microstructure. This method seems to be more sensitive than mass measurements (Section 3.1.2) as velocity decrease is recorded, although no mass loss is observed. The results for specimens with siliceous and calcareous sand are presented in Figs. 4 and 5, respectively. In the case of siliceous sand, the concrete with natural pozzolana (LPC-s) and the limestone cement concrete (LC1-s) showed the worst behavior. In the case of calcareous sand, the limestone cement concrete (LC1-c) showed the worst behavior. The addition of natural pozzolana (only in the case of calcareous sand, LPC-c), fly ash (samples: LFC-s, LFC-c), ggbs (samples: LSC-s, LSC-c) and metakaolin (samples: LMC-s, LMC-c) seems to improve the performance of limestone cement concrete against sulfate attack.

3.1.4. Compressive strength

In the case of siliceous sand, the compressive strength development of the specimens exposed in the $MgSO_4$ solution at 5 °C is shown in Fig. 6. The limestone cement concrete (LC1-s) presented

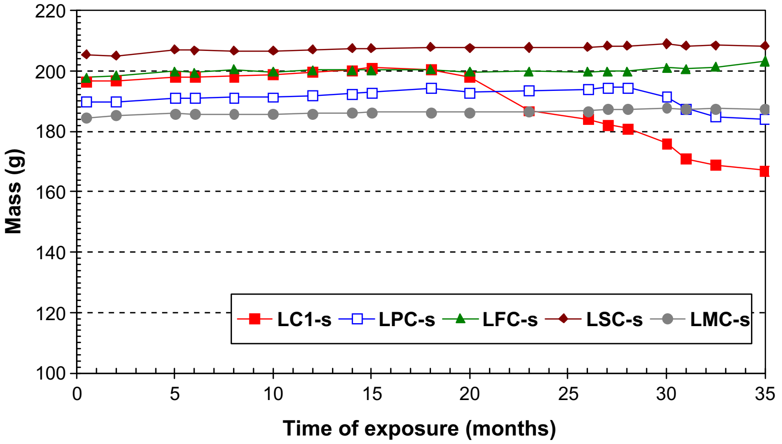

Fig. 2. Mass of specimens with siliceous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 5 °C.

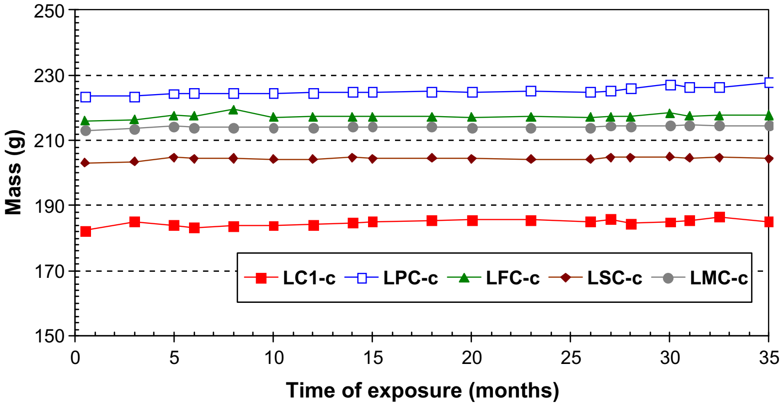

Fig. 3. Mass of specimens with calcareous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 5 °C.

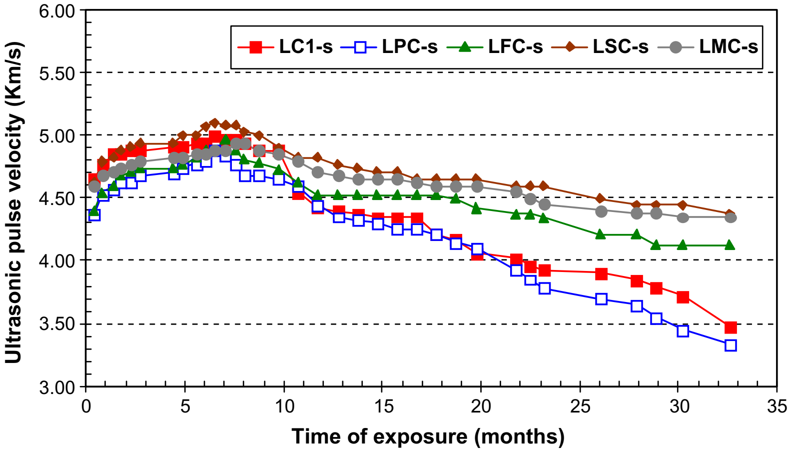

Fig. 4. Ultrasonic pulse velocity of specimens with siliceous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 5 °C.

a slight strength loss after 6 and 12 months and a complete strength loss after 24 months. Concrete with natural pozzolana (LPC-s) showed a slight strength loss after 12 months and a severe strength loss (about 40%) after 24 months. Specimens with fly ash (LFC-s), blastfurnace slag (LSC-s) and metakaolin (LMC-s) presented better performance with a 20–25% strength loss after 24 months.

In the case of calcareous sand, the compressive strength development of the specimens exposed in the $MgSO_4$ solution at 5 °C is shown in Fig. 7. The limestone cement concrete (LC1-c) presented a severe strength loss (about 50%) after 24 months of exposure. Concrete with natural pozzolana (LPC-c) showed a 20% strength loss after 24 months. No strength loss was observed for the specimens with fly ash (LFC-c), blastfurnace slag (LSC-c) and metakaolin

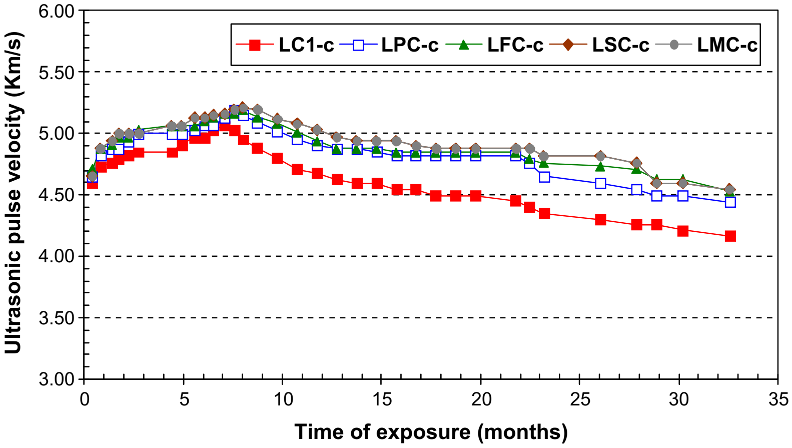

Fig. 5. Ultrasonic pulse velocity of specimens with calcareous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 5 °C.

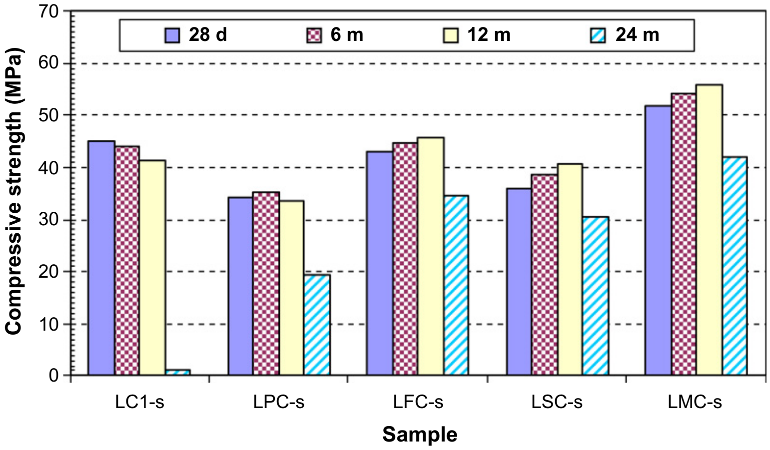

Fig. 6. Compressive strength of the specimens with siliceous sand after 28 days (reference strength) and after 6, 12 and 24 months of exposure in a 1.8% $MgSO_4$ solution at 5 °C.

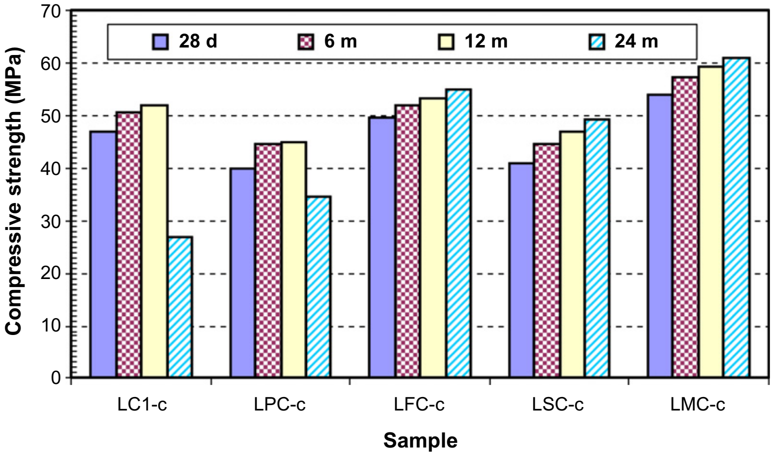

Fig. 7. Compressive strength of the specimens with calcareous sand after 28 days (reference strength) and after 6, 12 and 24 months of exposure in a 1.8% $MgSO_4$ solution at 5 °C.

(LMC-c), which showed normal strength development (strength increases with age) during the 24 months storage in the 1.8% w/w $MgSO_4$ solution at 5 °C.

The compressive strength results verify that the use of mineral admixtures improved the resistance of limestone cement concrete against sulfate attack at low temperature. The results are in accordance with the deterioration degree of the specimens (Table 4), mass measurements (Figs. 2 and 3) and ultrasonic pulse velocity measurements (Figs. 4 and 5) and confirm the better performance of concrete with calcareous sand compared to the concrete with

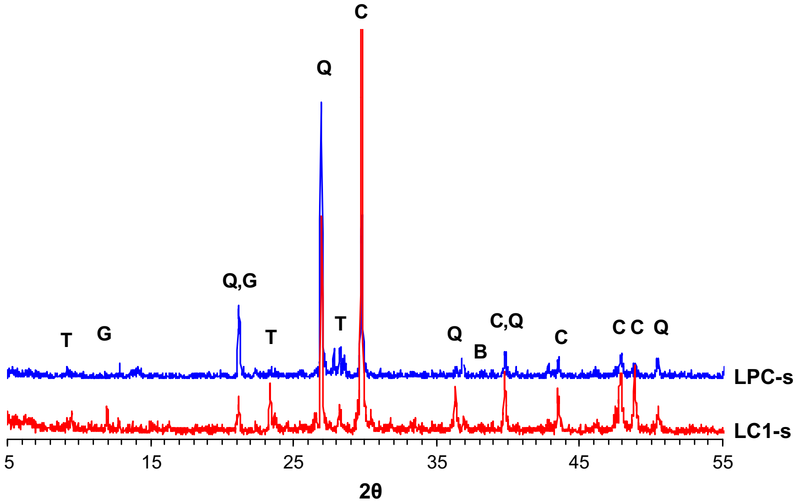

Fig. 8. XRD patterns of LC1-s and LPC-s specimens after 18 months of exposure in a 1.8% $MgSO_4$ solution at 5 °C (T: thaumasite; C: calcite; Q: quartz; G: gypsum; B: brucite).

siliceous sand. Concerning the role of sand type, these results strengthen, elucidate and expand the findings of a previous paper [7] that were based on mass measurements of mortar specimens.

3.1.5. Analytical techniques

XRD measurements were carried out on the soft white material covering the surface of the cracks. The XRD patterns of the samples LC1-s and LPC-s, after 18 months of exposure at 5 °C, are presented in Fig. 8. The degradation material was found to consist mostly of thaumasite, gypsum, calcite, quartz (due mainly to the siliceous sand) and traces of brucite. It must be noted that no calcium hydroxide was detected in the degradation products. Portlandite most probably has reacted with magnesium sulfate to form gypsum and brucite, both found in the degradation products. The very low solubility of brucite shifts the reaction [$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2$] to the right (Le Chatelier's principle) 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. As it has already been discussed, the deterioration of the specimens containing fly ash, blastfurnace slag and metakaolin (Table 4) was rather limited (siliceous sand) or none (calcareous sand). Thus, it was not possible to take the necessary samples from the deteriorated part of the specimens, in order to carry out XRD analysis.

TGA measurements confirmed the XRD observations. Fig. 9 presents the TG/DTG curve of the degradation product of the concrete LC1-s after 18 months of exposure in the 1.8% $MgSO_4$ solution at 5 °C. The characteristic double peak at 150 °C is related to the dehydration of thaumasite and gypsum. The small endothermic peak at around 400 °C is attributed to the dehydroxylation of brucite ($Mg(OH)_2$). The TG/DTG curve confirms that no calcium hydroxide is found in the degradation products.

Fig. 10 presents the SEM photos of the deteriorated part of concrete LC1-s stored in $MgSO_4$ solution at 5 °C for 18 months. In Fig. 10a one may identify type II C–S–H (reticular or honeycomb morphology), while type III C–S–H (sponge-like morphology) is observed in Fig. 10b. In the same photo one can see needle-like grains. The magnification of these needle-like grains (Fig. 10c) as well as the EDS analysis, which detected the elements Ca, Si, S, C and Mg (Fig. 10d), identifies the presence of thaumasite. The presence of Mg is due to the precipitation of the used $MgSO_4$ salt or to the brucite (product of the reaction of portlandite with $MgSO_4$).

3.2. Exposure in a 1.8% $MgSO_4$ solution at 25°C

According to visual inspection, no damage was observed in the specimens exposed to sulfate solution for 36 months at 25 °C. No mass loss was recorded in concrete specimens during their storage

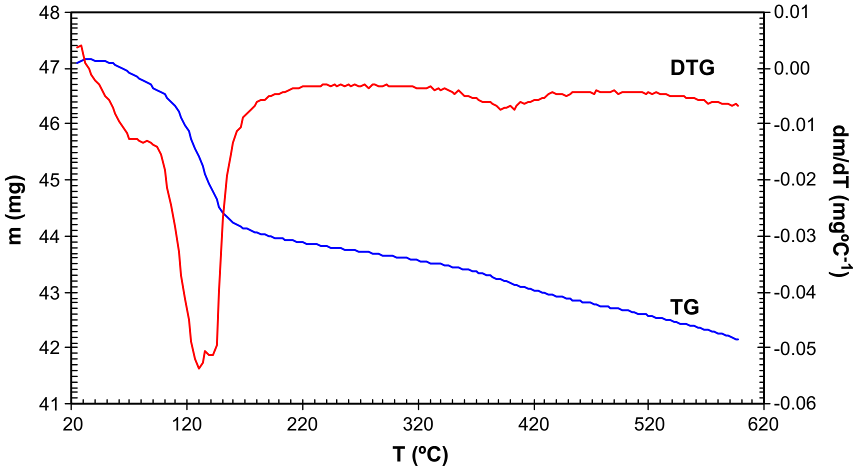

Fig. 9. TG-DTG curves of deterioration products of LC1-s after 18 months of exposure in a 1.8% $MgSO_4$ solution at 5 °C.

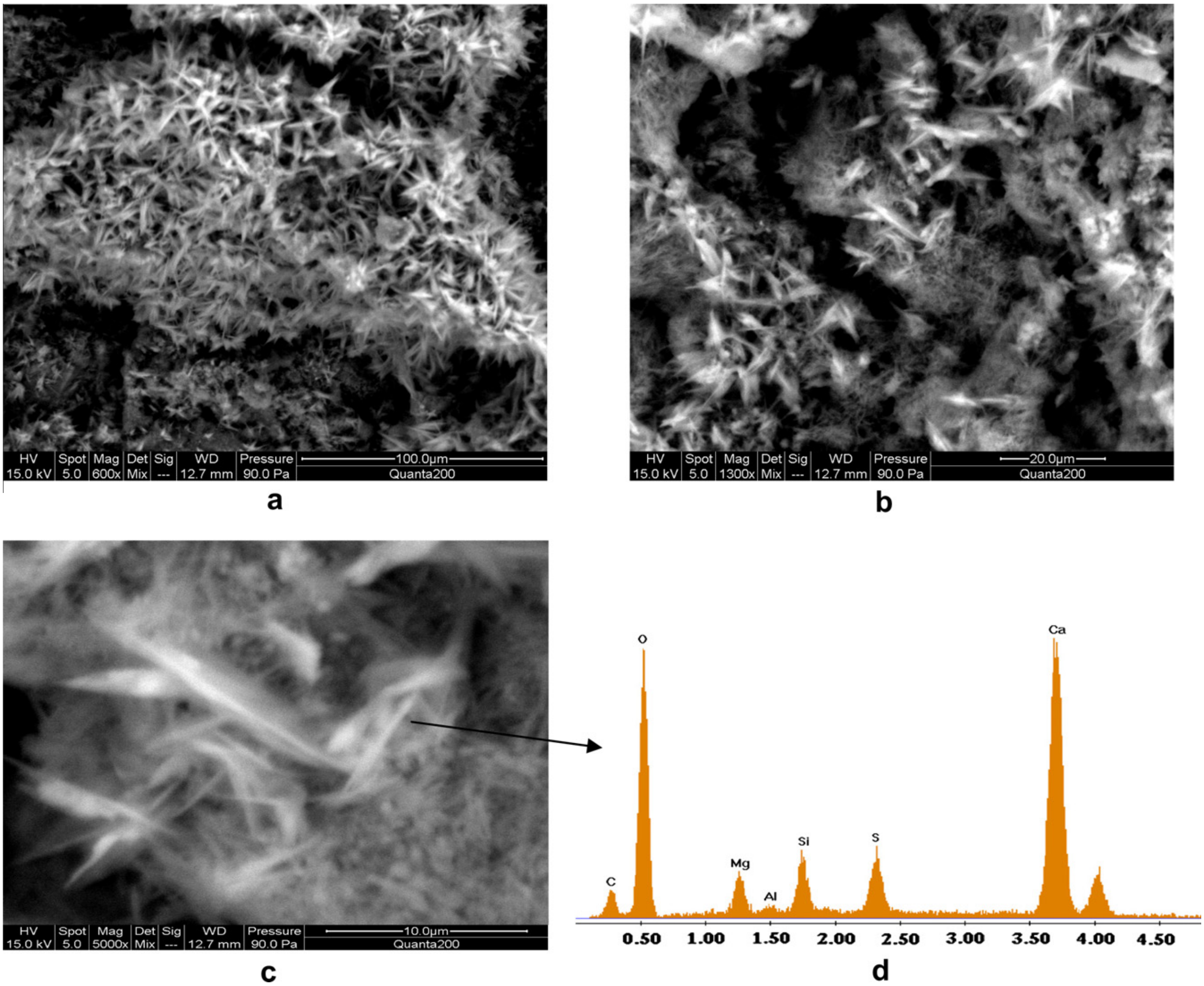

Fig. 10. SEM photos of LC1-s, stored for 18 months in a 1.8% MgSO4 solution at 5 °C (a, b, c: SEM, d: EDS).

in the 1.8% w/w $MgSO_4$ solution at 25 °C (siliceous sand: Fig. 11; calcareous sand: Fig. 12).

The compressive strength development of the specimens is presented in Fig. 13 (siliceous sand) and Fig. 14 (calcareous sand). All concretes showed normal strength development (strength increases with age) during the 24 months curing. The results confirm that no deterioration happened after 24 months exposure in the $MgSO_4$ solution at 25 °C.

It can be stated that "conventional" sulfate attack of well made concretes is very slow, much slower than thaumasite sulfate attack (TSA) at low temperatures. Some researchers have reported the formation of small quantities of thaumasite (in pastes and mortars), even at room temperature [2,4,17,21]. It is generally accepted that extensive thaumasite formation is related with low temperature. However, other factors (cement type and composition, specimen composition, degree of carbonation, type and concentration of sulfate solutions, pH of the pore solution) may also affect thaumasite formation.

3.3. Final remarks

The above measurements confirmed that the specimens with calcareous sand showed better behavior against thaumasite form of sulfate attack than those with siliceous sand. In our tests there is an overabundance of carbonate ions coming from the limestone of the cement used (thus the presence of the fine particles coming from calcareous sand is of minor importance) and probably the determinative factor is the cohesion between the cement paste and the sand, which is better in the case of calcareous sand (compare 28 days compressive strength values in Figs. 6 and 7).

The experiments also showed that concrete containing exclusively limestone cement is susceptible to the thaumasite form of sulfate attack at low temperature. Deterioration is less severe when a certain amount of the Portland limestone cement is replaced by the studied mineral admixtures. Such minerals act chemically by reacting with calcium hydroxide (pozzolanic reaction) and forming C–S–H, which is the main cohesive phase in the cement paste [22,23]. Some authors suggest that this silicon rich C–S–H, shows higher resistance against thaumasite formation [19,20].

In addition, pozzolanic materials act also physically, especially those that have a strong effect on pore structure refinement, reducing concrete's permeability, which inhibits the ingress of the deleterious sulfate ions. Fly ash, ggbs and metakaolin greatly improved the resistance of limestone cement concretes against TSA at low temperature. It is also of great importance that in the case of concrete with the above minerals and calcareous sand no deterioration was observed. Natural pozzolana presented only a limited

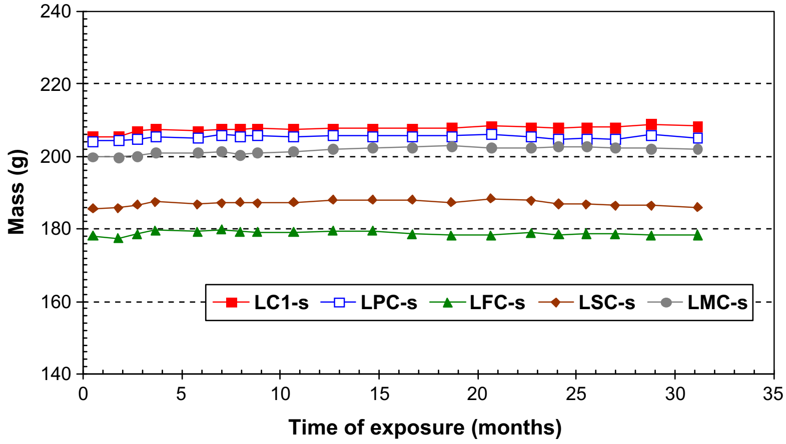

Fig. 11. Mass of specimens with siliceous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 25 °C.

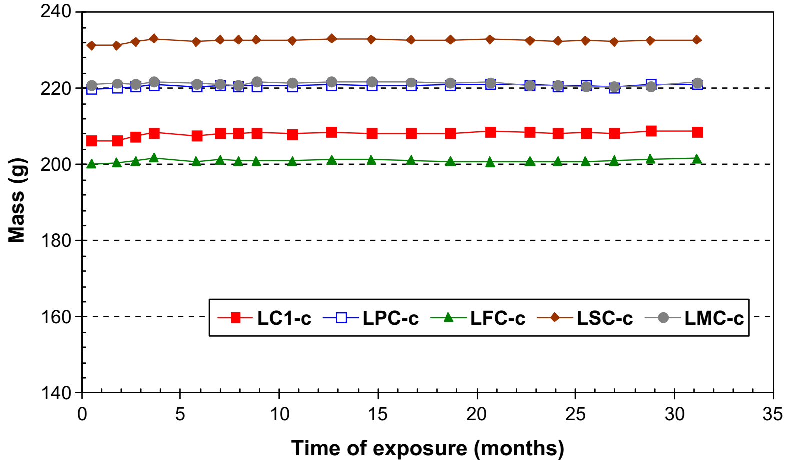

Fig. 12. Mass of specimens with calcareous sand related to exposure duration in a 1.8% $MgSO_4$ solution at 25 °C.

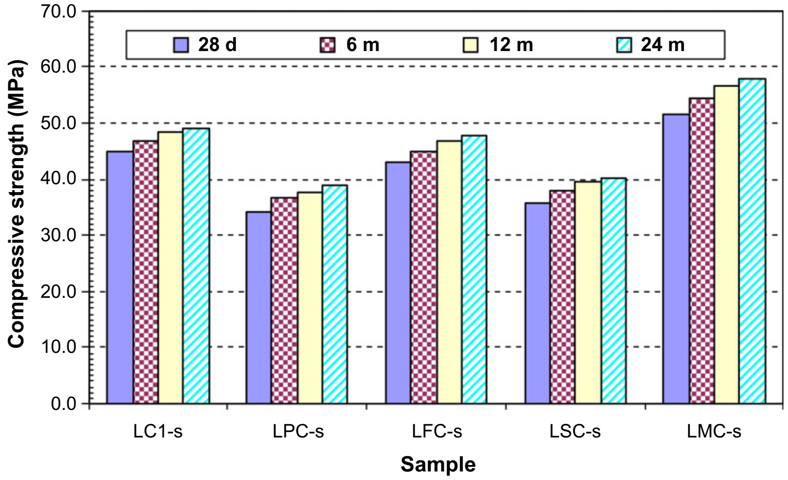

Fig. 13. Compressive strength of the specimens with siliceous sand after 28 days (reference strength) and after 6, 12 and 24 months of exposure in a 1.8% $MgSO_4$ solution at 25 °C.

improvement of concrete sulfate resistance. The pozzolanic reaction of this mineral is initially slow (the low temperature storage further depressed the pozzolanic reaction) and is accelerated mainly after the first 28 days. Finally, no damage was observed in the specimens exposed to sulfate solution at 25 °C for 36 months confirming that in $MgSO_4$ solutions the "conventional" sulfate attack, at ambient temperature, is much slower than the thaumasite form of sulfate attack, at low temperature.

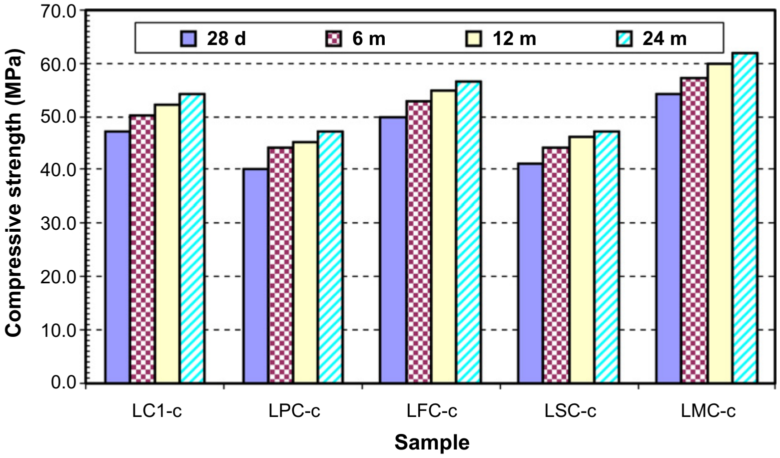

Fig. 14. Compressive strength of the specimens with calcareous sand after 28 days (reference strength) and after 6, 12 and 24 months of exposure in a 1.8% $MgSO_4$ solution at 25 °C.

4. Conclusions

The following conclusions can be drawn from the present study:

- The use of specific mineral admixtures improved the resistance of the limestone cement concrete against sulfate attack. Fly ash, blastfurnace slag and metakaolin showed the best behavior, while natural pozzolana presented only a limited improvement of concrete's sulfate resistance.
- The type of the sand and its cohesion with the cement paste has a remarkable effect on the performance of concrete at low temperature. Limestone cement concrete with calcareous sand showed better performance than concrete containing siliceous sand.
- No deterioration was observed at low temperature in limestone cement concrete made with calcareous sand and containing fly ash, blastfurnace slag and metakaolin.
- A well designed concrete made with limestone cement and appropriate mineral admixtures seems to have the ability to withstand thaumasite form of sulfate attack.
- No damage was observed in the specimens exposed to sulfate solution at 25 °C for 36 months. It seems that in $MgSO_4$ solutions the "conventional" sulfate attack, at ambient temperature, is much slower than the thaumasite form of sulfate attack, at low temperature.

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