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Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar

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Abstract

Concrete made from limestone cement may exhibit a lack of durability due to the formation of thaumasite. The addition of minerals that improve the concrete durability is expected to slow down the formation of thaumasite. In this work the effect of natural pozzolana, fly ash, ground granulated blastfurnace slag (ggbs) and metakaolin on the thaumasite formation in limestone cement mortar is examined. A limestone cement containing 15% w/w limestone was used. Mortar specimens were prepared by replacing a varying part of the limestone cement with the above minerals. Siliceous and calcareous sand was used in order to study the effect of the sand type on the thaumasite formation. The specimens were immersed in a 1.8% $MgSO_4$ solution and cured at 5 and 25 °C. The formation of thaumasite was checked and confirmed by visual inspection, strength tests, ultrasonic pulse velocity measurements, XRD and TGA. It is concluded that the use of specific minerals, as partial replacement of cement, inhibits the thaumasite formation in limestone cement mortar.

Keywords: Portland limestone cement; Mineral admixtures; Sulfate attack; Thaumasite

1. Introduction

Limestone has been widely used as a filler or as a main cement constituent for many years. In addition, calcareous aggregates are extensively used in many countries. 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. Recent research [1–7] 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 [1–7].

Thaumasite formation requires the transportation of ions like Ca^{2+}, CO_3^{2-}, SO_4^{2-} and sufficient moisture through the hardened cement. The use of mineral admixtures that lower the permeability and refine the pore structure may, therefore, contribute to better performance of mortars and concretes containing limestone.

This paper reports results related to the effect of a second mineral addition on the sulfate resistance of limestone cement. Limestone cement mortars containing natural pozzolana, blastfurnace slag, fly ash or metakaolin were exposed to sulfate solution at low and room temperature and their performance was studied for over a year.

2. Experimental details

Ordinary 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 cement, containing 15% w/w limestone, was produced

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Table 1
Chemical and mineralogical composition of clinker

Chemical composition (%)		Mineralogical composition (%)	
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; F: Fe_2O_3.

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_2O_3	0.43	16.12	20.72	10.44	43.94
Fe_2O_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_2O	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

by intergrinding clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity (sample LC1 of Table 3). The specific surface of the cement was 3950 cm^2/g, according to the Blaine method.

The minerals 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, ggbs (S) is an imported mineral and is also used as a main cement constituent. The above minerals were ground and their mean particle size (d_{50}) was 10.5, 12.3 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.

The mixes of Table 3 have been prepared by replacing a given amount of the Portland limestone cement with the specific minerals. Depending on the mineral, a replacement of 10–50% per Portland limestone cement by mass was used. These percentages were selected in relation to their expected reactivity.

Table 3
Codes and composition of the produced mixes

Code	Composition of samples
LC1	Portland limestone cement (clinker: 85% w/w, limestone: 15% 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

Mortars have been prepared, using the mixes of Table 3, with a water to binder ratio of 0.5 and a binder:sand ratio of 1:2.50. Siliceous (s) and calcareous (c) sand have been used in order to study the effect of the sand type on 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 $40 \times 40 \times 53$ mm were prepared. The specimens were left in the mould for 24 h, then were water-cured for 6 days and finally they were air-cured for 21 days at laboratory temperature (approximately 25 ± 2 °C). This curing program is believed to be similar to the conditions in field constructions.

After the 28 days initial 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 changed every 3 months.

The visual examination of the samples was performed at regular intervals for 1 year. All significant modifications, such as changes in surface colour and texture, formation of any coatings, deterioration, expansion and cracking, were recorded.

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 nickel-filtered CuKα_1 radiation ($\lambda = 1.5405$ 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 (TG-DTG) was carried out in order to detect small amounts of compounds. A Mettler Toledo TGA/SDTA 851 instrument was used. The samples ($\sim$20 mg) were heated from 20 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.

The compressive strength of the specimens was measured after 28 days and after 9 months exposure in $MgSO_4$ solution, in order to investigate the influence of the sulfate attack on the strength loss of the samples. The ultrasonic pulse velocity tests (apparatus: 58-E48 of Controls Testing Equipment Ltd.) were used as a measure of internal soundness of the specimens. The measurements were carried out at regular intervals for 1 year.

3. Results and discussion

3.1. Visual inspection

A visual inspection of the specimens was carried out monthly. The observations are summarised in Table 4. Photos of specimens stored in the sulfate solution for 11 months are presented in Figs. 1–4. The samples stored at 5 °C showed the first signs of deterioration after 7 months of exposure while the specimens stored at 25 °C did not show any clear evidence of sulfate attack up to 11 months. The discussion below concerns the samples stored at 5 °C.

Indications of the start of deterioration were first observed on the surfaces of the specimen with limestone cement and pozzolana addition (samples: LPC-s and LPC-c) after 7 months exposure. A longer time of 8 months was required for the limestone cement mortar (LC1-s and LC1-c), while after 11 months only a slight damage was observed in the specimens of limestone cement mortar with fly ash (LFC-s and LFC-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. No deterioration has been observed in limestone cement mortar containing blast-furnace slag (LSC-s and LSC-c) or metakaolin (LMC-s and LMC-c).

As it can be seen, ggbs and metakaolin improve the resistance of the limestone cements against sulfate attack at low temperatures. The use of fly ash seems to retard the sulfate attack, whereas the pozzolana addition increases the vulnerability to sulfate attack at 5 °C. It was not possible, based on the visual inspection of the specimens, to distinguish the effect of the sand type on the sulfate attack resistance at low temperatures.

3.2. Mineralogy

The identification of products formed as a result of sulfate attack was based on XRD and DTG measurements. 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 and ettringite.

In the specimens which suffered from cracking and expansion, 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 and traces of brucite. The XRD patterns of the samples LC1-c, LPC-c and LFC-c are presented in Fig. 5. In addition to the peaks corresponding to the calcareous sand, the characteristic peaks of thaumasite and gypsum can clearly be seen. It seems that a small amount of ettringite had been formed in sample LFC-c. It may be associated with the higher alumina content of the fly ash. The peaks of brucite were too weak to allow a safe identification but its formation was confirmed based on DTG curves, such as that shown in Fig. 6.

It must be noted that no calcium hydroxide was detected in the degradation products. Portlandite most

Table 4
Appearance of specimens, stored in 1.8% $MgSO_4$ solution at 5 °C

Age (months)	LC1-s, LC1-c	LPC-s, LPC-c	LFC-s, LFC-c	LMC-s, LMC-s, LSC-s, LSC-c
7	No visible deterioration	Some deterioration at corners	No visible deterioration	No visible deterioration
8	Deterioration at corners	Deterioration at corners and cracking along edges	No visible deterioration	No visible deterioration
9	Some cracking along the edges	Extensive cracking and expansion	No visible deterioration	No visible deterioration
10	Cracking and expansion	Extensive expansion and spalling	No visible deterioration	No visible deterioration
11	Cracking and expansion	Extensive expansion and spalling	Some cracking along the edges	No visible deterioration

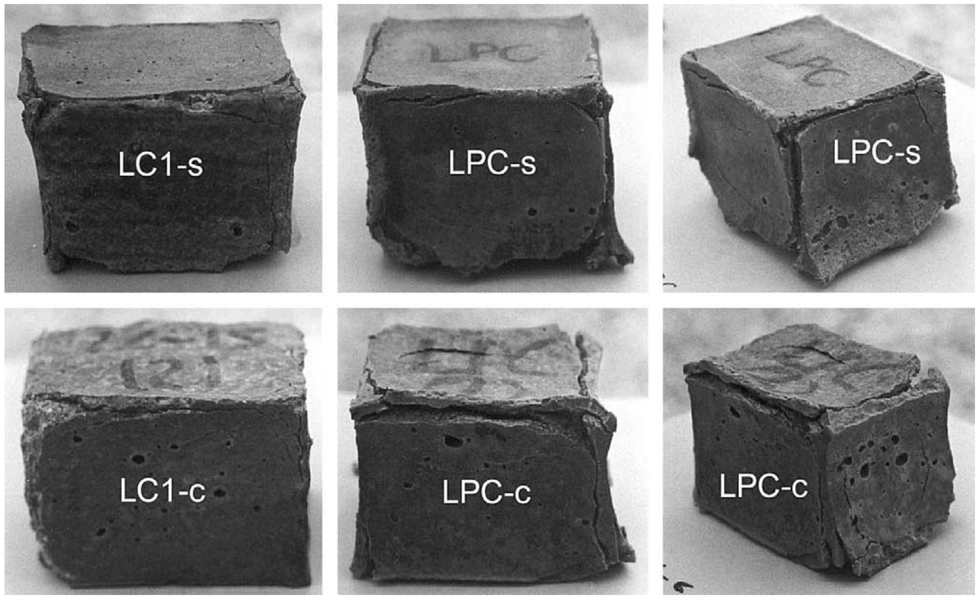

Fig. 1. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution at 5 °C (LC1 and LPC).

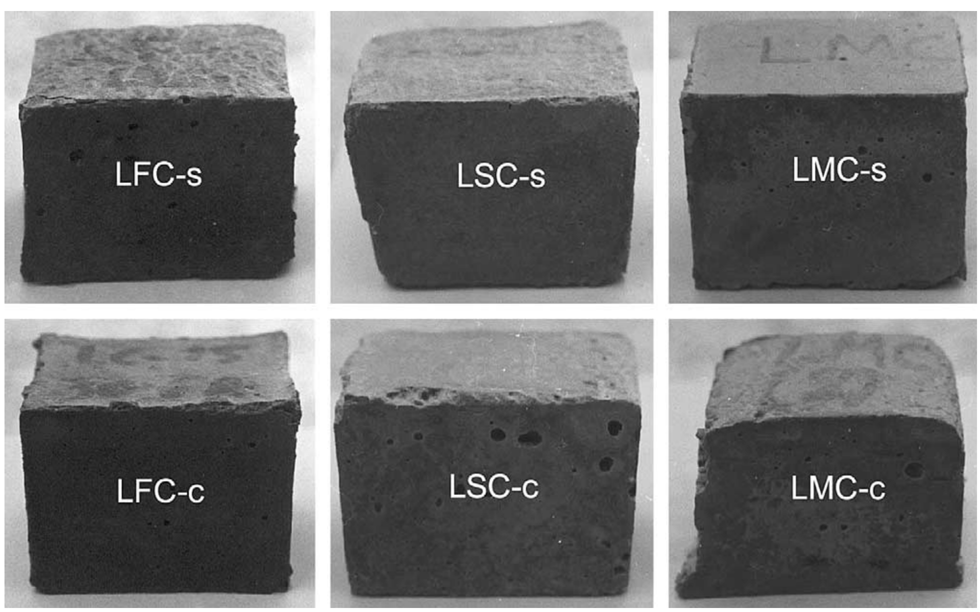

Fig. 2. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution at 5 °C (LFC, LSC and LMC).

probably had reacted with magnesium sulfate to form gypsum and brucite, both present in the degradation products. The low solubility of brucite 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 [5].

Fig. 6 presents the DTG curve of the degradation products from sample LPC-s. The double peak in the range 100–130 °C is associated with the dehydration of thaumasite and gypsum. The dehydration of ettringite and other hydrated products, unaffected by sulfate attack, takes place at lower temperature. It is clearly seen that the samples contain also small amounts of brucite (peak temperature approximately 350 °C) and no portlandite at all.

3.3. Compressive strength

The 28 days compressive strength of the specimens with siliceous sand, prior to any exposure to sulfates, is shown in Fig. 7. The addition of ggbs (sample LSC) and metakaolin (sample LMC) led to an increase in the

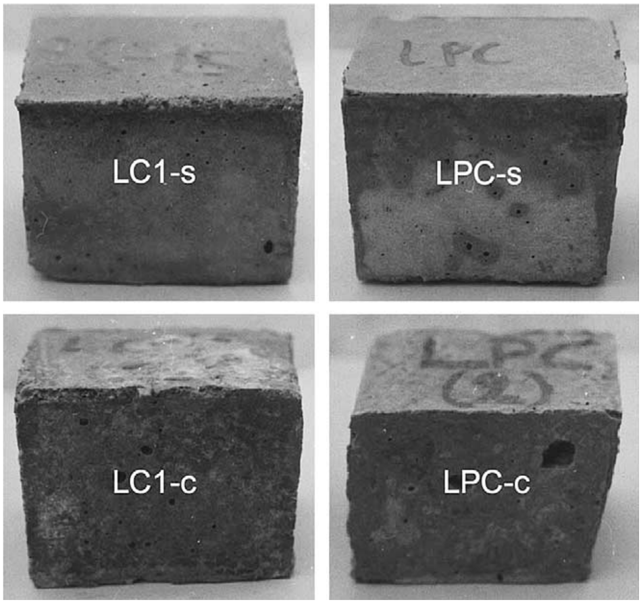

Fig. 3. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution at 25 °C (LC1 and LPC).

strength while the addition of fly ash (sample LFC) had no detectable effect on the strength. The pozzolana addition (sample LPC) decreased the strength measured after 28 days. After nine months exposure in the $MgSO_4$ solution at 5 °C, a significant loss of strength has been measured in limestone cement mortar and in the mortar containing pozzolana (Fig. 7). The mortar containing fly ash showed a lower strength loss. More specifically, the loss of strength was 18% of the 28 days strength for the Portland limestone cement (LC1), 34% for the limestone cement mortar containing 20% pozzolana (LPC) and 9% for the limestone cement mortar containing 30% fly ash (LFC). The strength of the mortar containing metakaolin was found to be the same as the 28 days strength. On the contrary, the addition of ggbs led to a strength increase. Based on the strength results, it is concluded that ggbs and metakaolin improve the resistance of the limestone cements against sulfate attack at low temperatures. The use of fly ash seems to retard the sulfate attack, whereas the presence of pozzolana impairs the resistance of limestone cement against sulfate attack. Concerning the specimens cured at 25 °C, their compressive strength increased with storage time in all samples. This fact was expected as no visual damage of the specimens had been observed.

The 28 days compressive strength of the specimens with calcareous sand, prior to any exposure to sulfates, is shown in Fig. 8. The addition of ggbs (sample LSC) and metakaolin (sample LMC) led to an increase of the strength, the addition of fly ash (sample LFC) had no effect on the strength, while the pozzolana addition (sample LPC) decreased the 28 days strength. After 9 months exposure in the $MgSO_4$ solution at 5 °C, a significant loss of strength has been measured in limestone cement mortar and in the mortar containing pozzolana (Fig. 8). More specifically, the loss of strength was 21% of the 28 days strength for the Portland limestone cement (LC1) and the same for the limestone cement mortar containing 20% pozzolana (LPC). The 9 months strength of the mortar containing metakaolin was found to be the same as the 28 days strength. On the contrary, the addition of ggbs and fly ash led to a strength increase. Based on the strength results, it is shown that fly

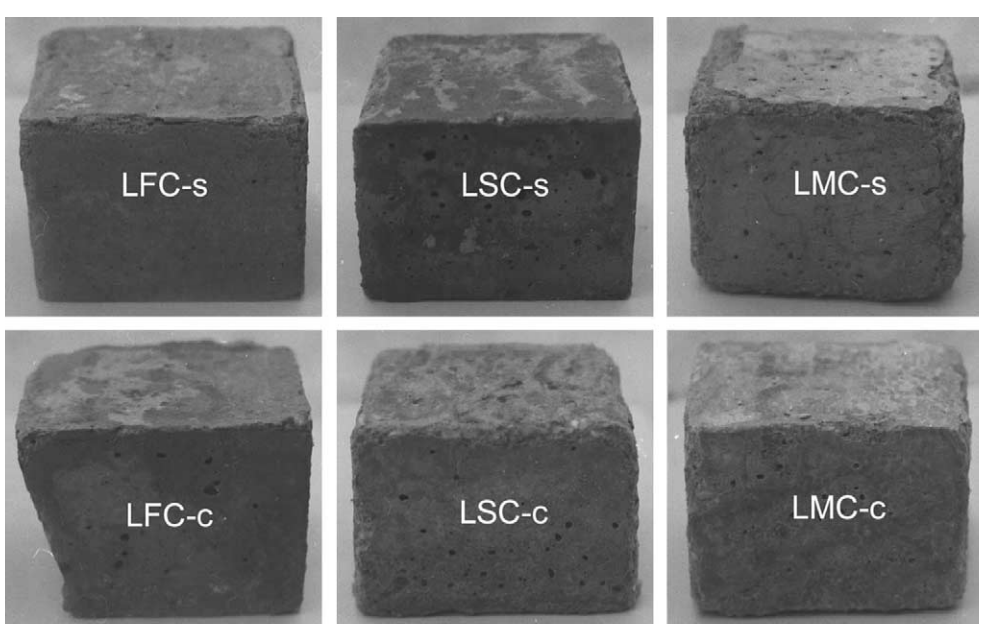

Fig. 4. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution at 25 °C (LFC, LSC and LMC).

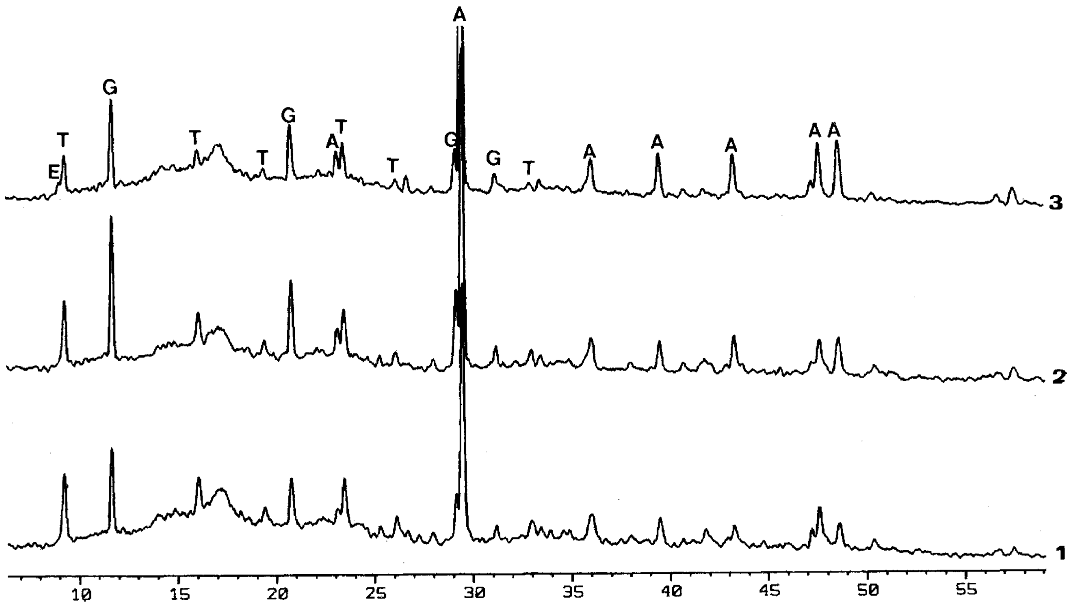

Fig. 5. XRD patterns of deterioration products at 5 °C: (1) LC1-c; (2) LPC-c; (3) LFC-c; (T) thaumasite; (E) ettringite; (G) gypsum and (A) sand.

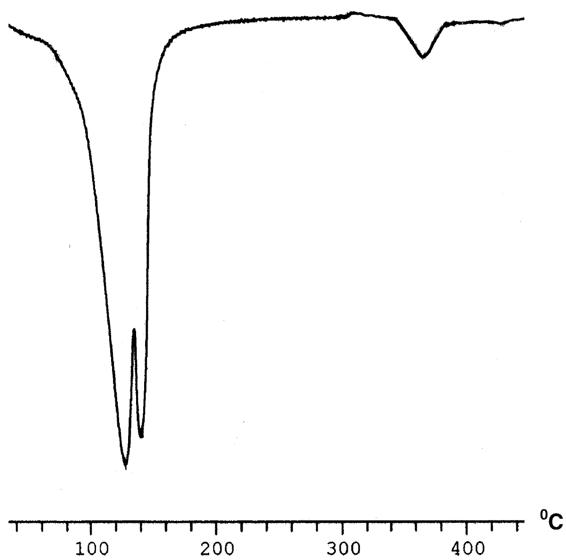

Fig. 6. DTG curve of the deterioration products in sample LPC-s.

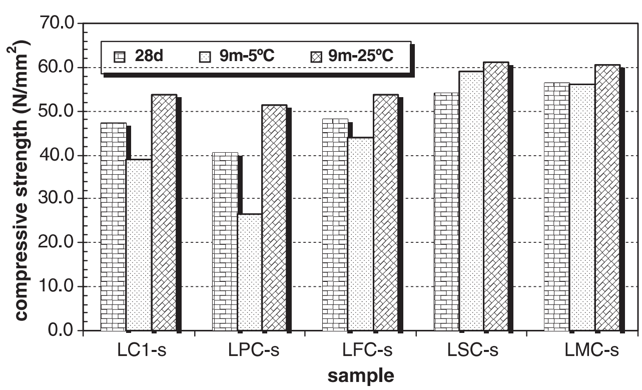

Fig. 7. Effect of the curing temperature conditions on the compressive strength of specimens made with *siliceous sand*.

ash, ggbs and metakaolin improve the resistance of the limestone cements against sulfate attack at low temperatures. The pozzolana addition impairs the resistance of the limestone cement against sulfate attack. Concerning the specimens cured at 25 °C, their compressive strength increased with storage time in all samples. This fact was expected as no visual damage of the specimens has been observed.

3.4. 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. 9 and 10 concerning the siliceous and calcareous sand, respectively. In both cases it is clearly observed that the limestone cement with the pozzolana addition (LPC-s and LPC-c) shows the worst behaviour while the addition of ggbs (samples: LSC-s and LSC-c), metakaolin (samples: LMC-s and LMC-c) and fly ash (samples: LFC-s and LFC-c) improved the behaviour of limestone cement mortar.

In specimens cured at 25 °C, there is no significant decrease in the pulse velocity, which remains almost stable.

The results drawn from each one of the above mentioned techniques are in good accordance with each other. It was confirmed that limestone cement is susceptible to the thaumasite-kind of sulfate attack at low temperatures. In some cases, the addition of a second mineral (fly ash, ggbs and metakaolin) improves the

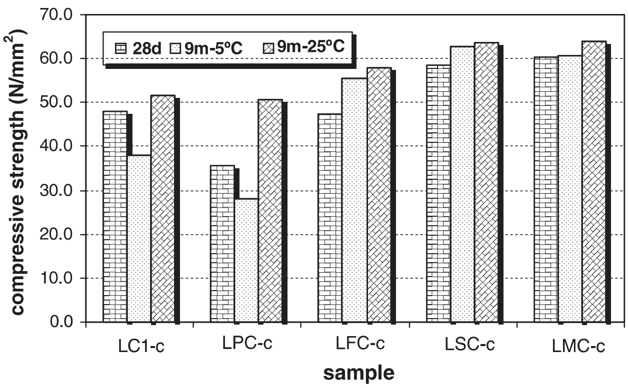

Fig. 8. Effect of the curing temperature on the compressive strength of specimens made with *calcareous sand.*

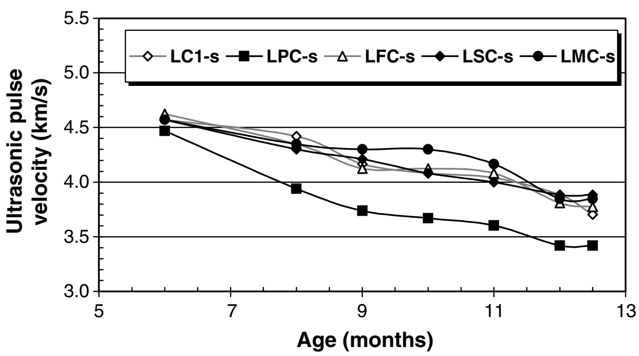

Fig. 9. Ultrasonic pulse velocity of specimens with *siliceous sand* (5 °C, 1.8% $MgSO_4$ solution).

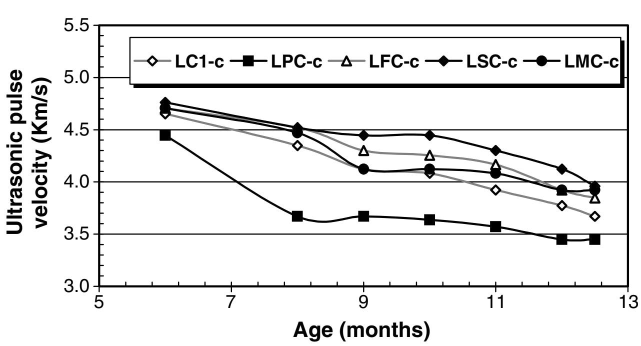

Fig. 10. Ultrasonic pulse velocity of specimens with *calcareous sand* (5 °C, 1.8% $MgSO_4$ solution).

sulfate resistance of the mortar. Blastfurnace slag and metakaolin prevent the sulfate attack of limestone cement mortars at least for ages up to 1 year. This positive effect is most probably attributed to the lower permeability and pore refinement of the composite cements. The incorporation of fly ash delays the onset of thaumasite formation. Natural pozzolana has a negative effect on the behaviour of limestone cement that requires further investigation. It must be noted that the specific mineral is a very good pozzolanic material, widely used in construction. According to our measurements, the pozzolanic reaction of this material is slow, compared with the other minerals used in this study. The slow pozzolanic reaction is also confirmed from Fig. 8. As it is seen, LPC specimens have the lowest 28 days compressive strength but they show a notable strength increase between 28 days and 9 months (curing at 25 °C). The pozzolanic reaction in LPC specimens is further depressed when they are stored at low temperature. As a result the sulfate resistance of these mortars is impaired.

Measurements are still in progress in order to evaluate the longer term behaviour of all samples.

4. Conclusions

From the present study the following conclusions can be drawn:

- Limestone cement mortar is susceptible to the thaumasite-kind of sulfate attack at low temperature.
- The use of specific mineral replacements retards the thaumasite formation in limestone cement mortar.
- Incorporation of metakaolin and ggbs substantially improve the resistance of the limestone cements against sulfate attack. The use of fly ash seems to retard sulfate attack. The effectiveness of natural pozzolans against sulfate attack very much depends on their rate of reaction. Slowly reacting pozzolans appear to be unable to provide effective resistance against sulfate attack if the concrete is exposed to sulfates before the pozzolanic reaction begins to act.

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