The Effect of Mineral Admixtures on Long Term Durability of Limestone Cement Mortars Exposed to Sulfate Attack

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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 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 part of limestone cement with the above minerals. The specimens were immersed in a 1.8% $MgSO_4$ solution and cured at 5°C and 25°C. The status of the samples for a storage period of 5 years was reported based on visual inspection, mass measurements, ultrasonic pulse velocity measurements and analytical techniques. It is concluded that the use of specific minerals, as partial replacement of cement, inhibits the thaumasite formation in limestone cement mortar.

1. INTRODUCTION

As it is well known, sulfate attack may cause severe damage of cementious materials. Besides the conventional sulfate attack in mortars and concretes involving the formation and the expansive properties of ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$), 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 last years. There are several reports concerning either the presence of thaumasite in damaged structures [1] or its formation in laboratory scale experiments [2-10].

Portland limestone cement is susceptible to the thaumasite form of sulfate attack and that is a serious problem because limestone is widely used as a filler or as a main cement constituent for many years [11-12]. Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and low temperature. Recent research shows that carbonate ions can also derived from atmospheric carbonation [13]. Thaumasite formation may also be connected with the prior formation of ettringite or the presence of some reactive alumina [14-15]. According to a research, thaumasite uses ettringite as a template for its initial nucleation, due to the structural similarities of these compounds [16].

The most common way to improve the resistance to sulfate attack is to reduce the permeability of cementious material. Therefore, the use of specific mineral admixtures can contribute to the 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 5 years.

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

Table 1. Chemical and mineralogical composition of clinker

Chemical composition (%)		Mineralogical composition (%)	
SiO_2	21.47	C_3S *	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

* Cement chemistry notation: C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3

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.

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

The mixes of Table 3 were prepared by replacing a given amount of the Portland limestone cement with the specific minerals. Depending on the mineral, a replacement of 10-50% by mass was used. These percentages were selected on the basis of the minerals' reactivity. Mortars were prepared, using the mixes of Table 3 (w/c=0.5, binder/sand=1:2.50). Siliceous (s) and calcareous (c) sand were 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).

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
MC	LC1 + 10% Metakaolin of LC1 by mass

Mortar prisms of size 40x40x53 mm were prepared. The specimens were left in the mould for 24h, then were water cured for 6 days and finally they were air-cured for 21 days at laboratory temperature (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 % MgSO4 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 MgSO4 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 colour and

texture, formation of any coatings, deterioration, expansion and cracking were recorded.

Changes in specimens' mass were recorded at regular intervals. 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 one year. 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.

3. RESULTS AND DISCUSSION

3.1. Visual inspection

Visual inspection of the specimens was carried out monthly. Photos of specimens stored in the sulfate solution for 11, 16, 35, 41, 53 and 60 months are presented in Figures 1 and 2.

Indications of the beginning of the deterioration were first observed on specimens with 15% limestone (LC1-s, LC1-c) and natural pozzolana (LPC-s, LPC-c) for both kind of sand after 8 months of exposure at $5^{o}C$. A longer time (11 months) was required for the beginning of deterioration in samples with fly ash (LFC-s, LFC-c). The specimens with metakaolin and siliceous sand (LMC-s) showed the first signs of deterioration after 16 months of exposure. Finally, a slight damage of specimens with blastfurnace slag (LSC-s, LSC-c) and with metakaolin and calcareous sand (LMC-c) was observed after 30 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 with the white soft substance.

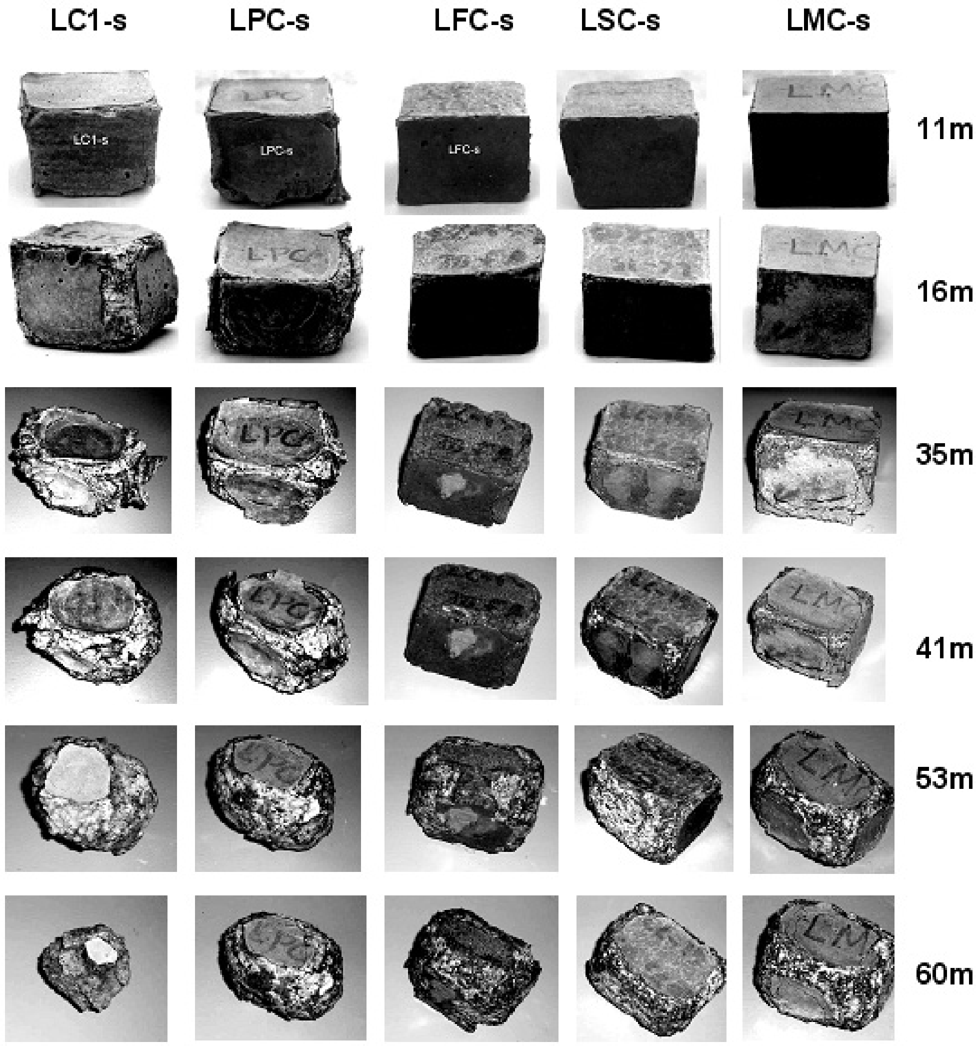

Fig. 1. Specimens with siliceous sand, cured for 11,16, 35, 41, 53, 60 months in a 1.8% $MgSO_4$ solution at 5° C

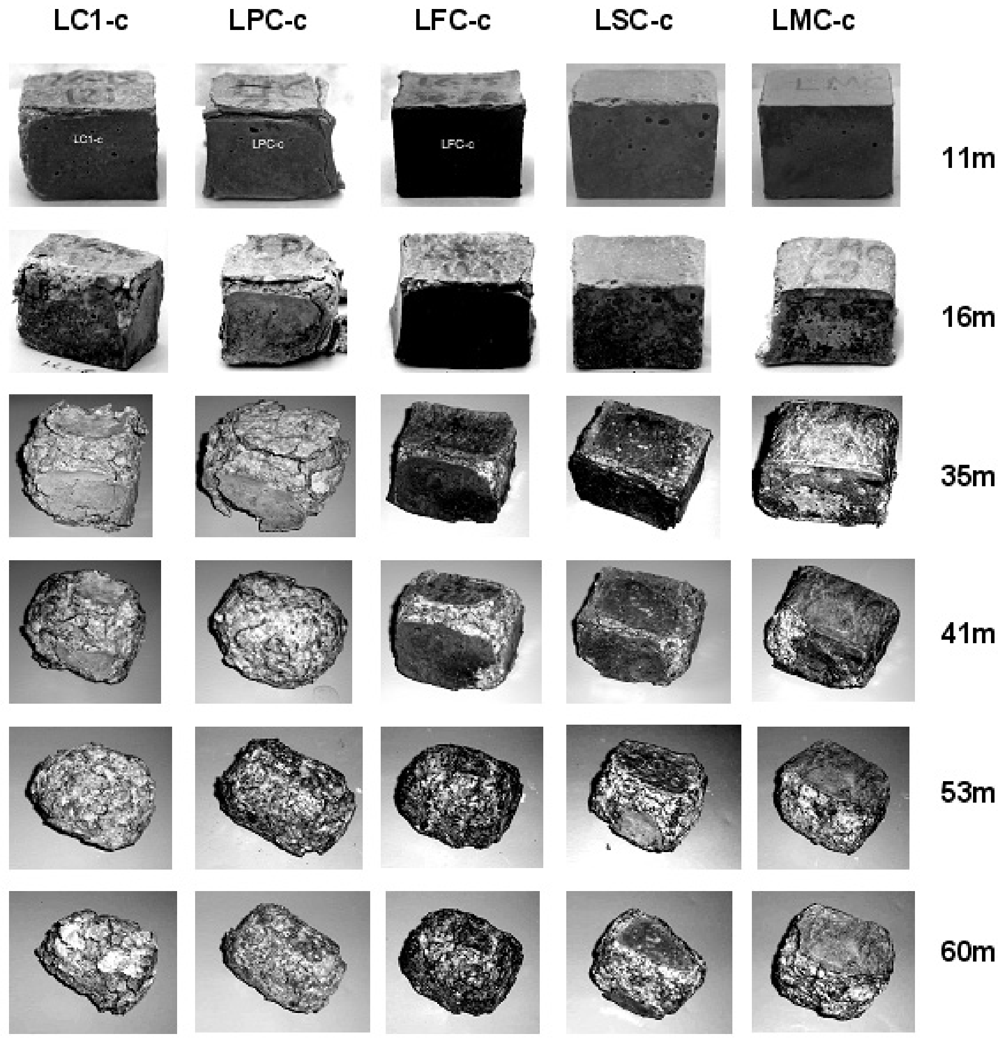

Fig. 2. Specimens with calcareous sand, cured for 11,16, 35, 41, 53, 60 months in a 1.8% $MgSO_4$ solution at 5^oC

It is obvious that the use of 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^oC.

No damage was observed in the specimens exposed to sulfate solution at 25^oC. It can be stated that “conventional” sulfate attack of well made mortars is very slow, much slower than TSA at low temperatures.

3.2 Ultrasonic pulse velocity

The ultrasonic pulse velocity was measured periodically, after the first signs of damage were observed. The experiments were carried out for 13 months. After this time, the condition of specimens’ surfaces did not permit to take any reliable measurements. The results for specimens with siliceous and calcareous sand are presented in Figs. 3 and 4 respectively. As it can be seen, the limestone cement with natural pozzolana (LPC-s, LPC-c) shows the worst behavior while the addition of fly ash (samples: LFC-s, LFC-c), ggbs (samples: LSC-s, LSC-c) and metakaolin (samples: LMC-s, LMC-c) seems to improve the behavior of limestone cement mortar.

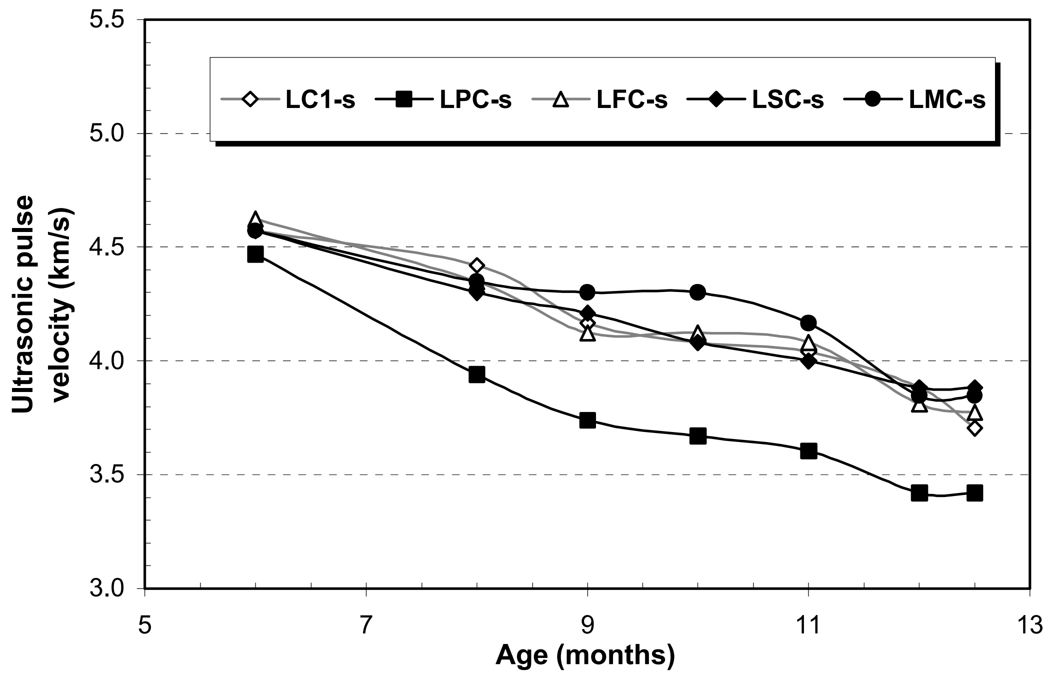

Fig. 3. Ultrasonic pulse velocity of specimens with siliceous sand (5^oC, 1.8% $MgSO_4$ solution)

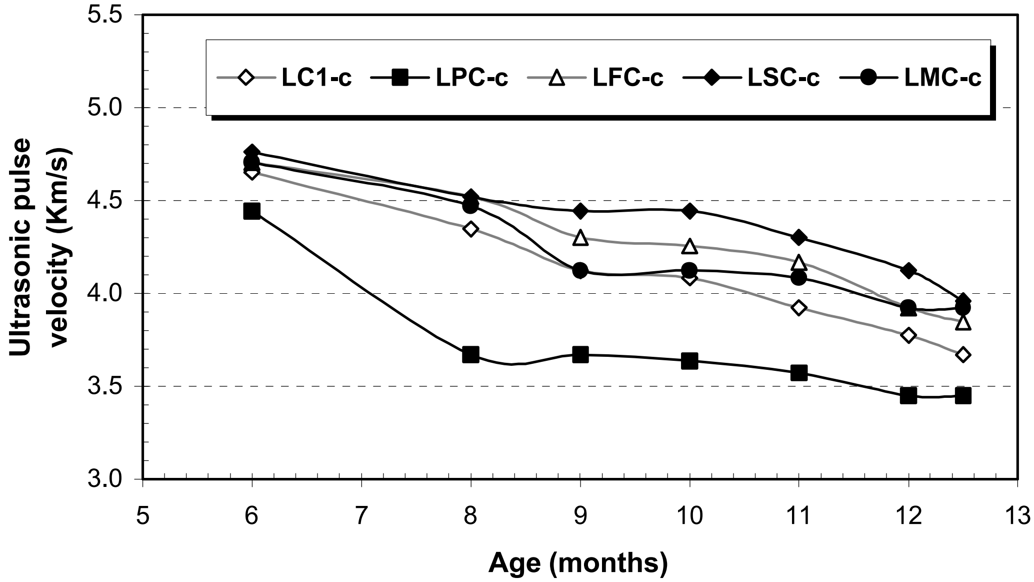

Fig. 4. Ultrasonic pulse velocity of specimens with calcareous sand (5^oC, 1.8% $MgSO_4$ solution)

3.3 Mass measurements

The changes in specimens' mass were also measured periodically, and the results are shown in Figs. 5 and 6, for siliceous and calcareous sand respectively. The mass loss is expressed as the ratio m/m_0, where m_0 is the initial mass and m is the mass after the exposure in sulfate solution.

In the case of siliceous sand, LC1 showed the worst behaviour, loosing after 60 months of exposure 79% of its mass. The specimens containing natural pozzolana (LPC), fly ash (LFC) and metakaolin (LMC) lost 54%, 33% and 31% of their mass respectively. The specimen with ground granulated blastfurnace slag showed the best behaviour, loosing 18% of its mass.

In the case of calcareous sand, LC1 and LPC showed the worst behaviour, loosing after 60 months of exposure 59% and 57% of their mass, respectively. The specimens containing fly ash (LFC) lost 44% of its mass. The specimens with ground granulated blastfurnace slag (LSC) and metakaolin (LMC) showed the best behaviour, loosing 32% and 34% of their mass respectively.

As it is seen, the use of the added minerals, especially ggbs and metakaolin, improves the sulfate resistance of the mortars.

It is not easy to evaluate the effect of the sand type on the low-temperature sulfate resistance of mortar, based on the mass measurements. It seems that, in the case of limestone cements with fly ash, pozzolana, ggbs or metakaolin, the type of the sand (calcareous or siliceous) does not affect the thaumasite form of sulphate attack. Further investigation is needed in the case of pure limestone cement where the use of siliceous sand seems to accelerate the deterioration of the mortar specimens.

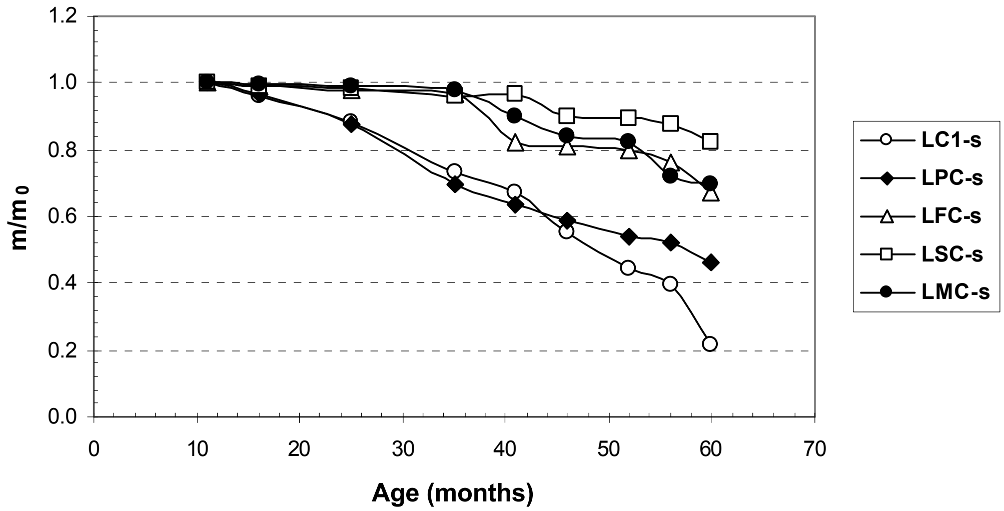

Fig. 5. Changes in mass of specimens with siliceous sand (5^oC, 1.8% $MgSO_4$ solution)

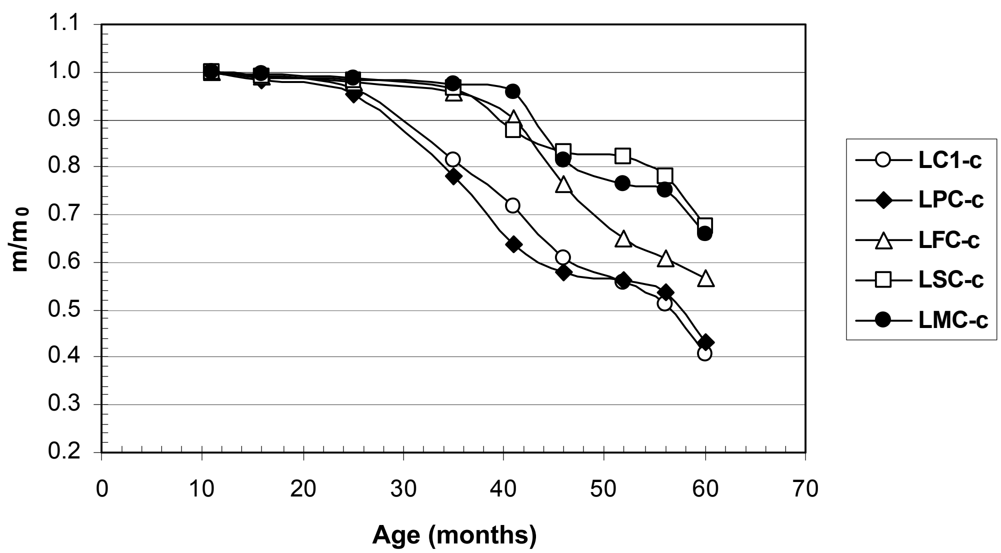

Fig. 6. Changes in mass of specimens with calcareous sand (5^oC, 1.8% $MgSO_4$ solution)

3.5 Analytical Techniques

The identification of products formed as a result of the sulfate attack was based on XRD. 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.

The XRD patterns of the sound core of the samples LC1-c and LMC-c is presented in Fig 7. Calcite and portlandite are the main constituents. The absence of gypsum indicates that the diffusion of sulfates in the sample is very slow.

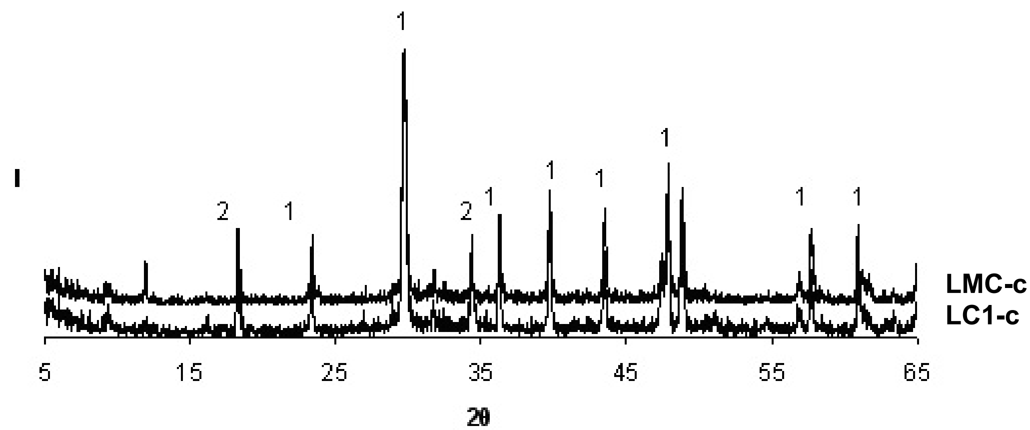

Fig. 7. XRD patterns of the sound core
(LC1-c, LMC-c) (1: Calcite, 2: Portlandite)

XRD measurements were also carried out on the soft, white material covering the surface of the cracks. The XRD patterns of surface materials of the samples LC1-c, LPC-c and LMC-c, after 60 months of exposure, are presented in Fig 8. In all cases, the degradation material was found to consist mainly of thaumasite, gypsum, sand (calcite or quartz) 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, according to the reaction:

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

The low solubility of brucite favors the consumption of calcium hydroxide. This leads to a reduction of pH and as a result C-S-H becomes more susceptible to sulfate attack.

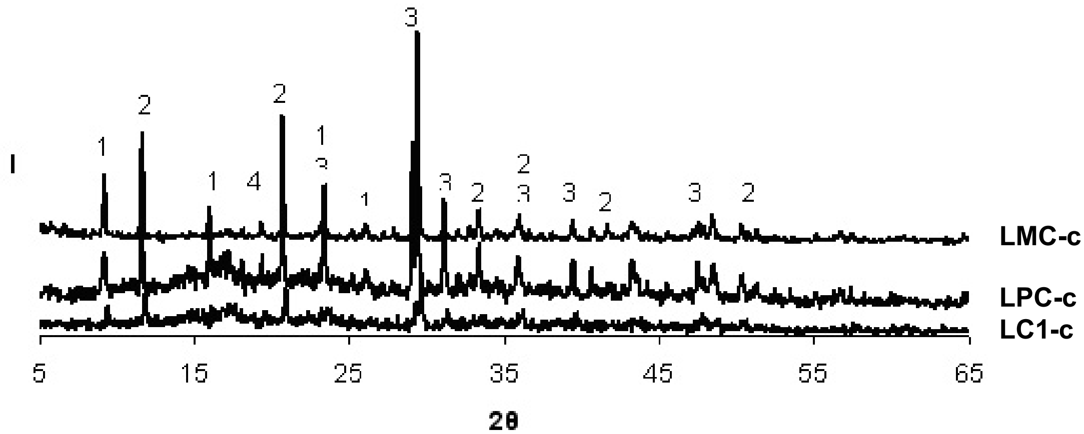

Fig. 8. XRD patterns of deterioration products
(LC1-c, LPC-c, LMC-c) (1: Thaumasite, 2: Gypsum, 3: Calcite, 4: Brucite)

4. CONCLUSIONS

The following conclusions can be drawn from the present study:

- 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 improves the resistance of the limestone cements against sulfate attack. The use of fly ash seems to retard the sulfate attack. Natural pozzolana is not very effective against sulphate attack, probably because the pozzolanic reaction of this material is slow, compared with the other minerals.
- No damage was observed in the specimens exposed to sulfate solution at 25^oC for 60 months. It seems that “conventional” sulfate attack, at ambient temperature, is much slower than thaumasite-kind of sulfate attack, at low temperature.

5. REFERENCES

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