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Parameters affecting 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. This work deals with the factors affecting thaumasite formation in cement mortars and particularly the limestone content, the curing conditions and the type of sand used. Three types of cement were examined: (i) OPC, (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 formation of thaumasite was checked and confirmed by XRD and TGA. In addition visual inspection, strength tests and ultrasonic pulse velocity measurements were carried out for several months. 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 at low temperature. At room temperature, no sulfate attack was observed after a year of exposure.

Keywords: Portland limestone cement; Sulfate attack; Thaumasite

1. Introduction

It is generally accepted that conventional sulfate attack in mortars and concretes involves the formation and the expansive properties of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$). However, another kind of sulfate attack, concerning cements and concretes containing limestone and 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 [1–5] or its formation in laboratory scale experiments [6–9].

Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and low temperature [10,11]. It may also be connected with the prior formation of ettringite or the presence of some reactive alumina [12]. 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) or even in sulfate resistant Portland cements.

This work deals with the performance of Portland limestone cement mortars exposed to magnesium sulfate solution and especially with the effect of limestone content, type of sand and curing temperature on the formation of thaumasite.

2. Experimental details

Ordinary Portland cement clinker of industrial origin and limestone of high calcite content ($CaCO_3$:95.7%) were used (Tables 1 and 2). Portland limestone cements were produced by intergrinding of clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity. The codes, the composition and the specific surface of the produced cements are given in Table 3.

Mortars have been prepared, using the cements of Table 3, with a water to cement ratio of 0.5 and a

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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 limestone (%)

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

Table 3
Composition and fineness of the cements used

Code	Synthesis of cements	Specific surface (cm^2/g)
PC	Clinker: 100% w/w (gypsum: 5% of clinker by mass)	3030
LC1	Clinker: 85% w/w, limestone 15% w/w (gypsum: 5% of clinker by mass)	3950
LC2	Clinker: 70% w/w, limestone 30% w/w (gypsum: 5% of clinker by mass)	5170

cement: 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 the 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 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 close to the conditions in field construction.

After the 28-day 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 replaced every 3 months. The visual examination of the samples was performed at regural intervals up to 1 year and 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 $CuK\alpha_1$ radiation ($= 1.5405$ 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 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 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 of exposure in $MgSO_4$ solution in order to investigate the effect of the sulfate attack on the strength loss of the samples. 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 1 year.

3. Results and discussion

3.1. Visual inspection

A visual inspection of the specimens was carried out monthly. The remarks are summarised in Table 4. Photos of specimens stored in the sulfate solution for 11 months are presented in Figs. 1 and 2. The samples stored at 5 °C showed the first signs of deterioration after 8 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 initial deterioration were first observed on the surface of sample LC2 after 8 months of exposure. A longer time was required for samples LC1, PC-c and PC-s, in ascending order. 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.

As can be seen, from Fig. 1, the damage due to sulfate attack was greater the higher the limestone content in the cement. However, even the presence of calcareous sand caused visible damage in the Portland cement samples without any limestone additions, that was not evident in the PC-s control sample.

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

Age (months)	PC-s	PC-c	LC1-c LC1-s	LC2-c LC2-s
7	No visible deterioration	No visible deterioration	No visible deterioration	No visible deterioration
8	No visible deterioration	No visible deterioration	Deterioration at corners	Deterioration at corners and cracking along edges
9	No visible deterioration	Some deterioration at corners	Some cracking along the edges	Extensive cracking and expansion
10	Some deterioration at corners	Cracking along the edges	Cracking and expansion	Extensive cracking and expansion
11	Cracking along the edges	Cracking and expansion	Cracking and expansion	Spalling

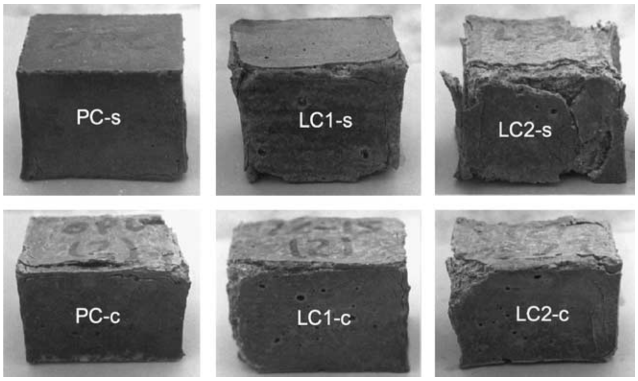

Fig. 1. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution, at 5 °C.

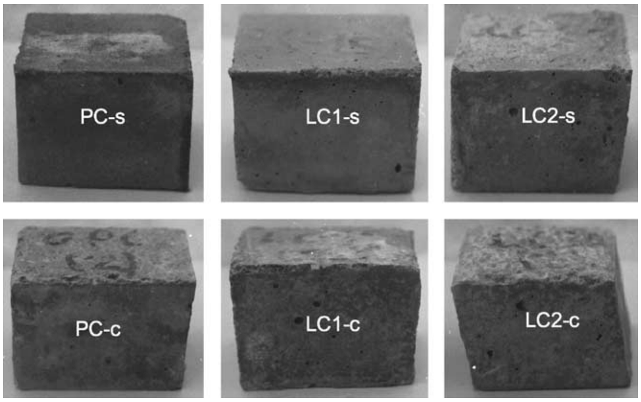

Fig. 2. Specimens cured for 11 months in a 1.8% $MgSO_4$ solution, at 25 °C.

In the presence of 15% and 30% limestone filler, there was no apparent difference in the extent of damage between samples with siliceous and calcareous sand.

3.2. Mineralogy

The identification of products formed as a result of the 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 suffering from extensive 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 PC-c, LC1-s and LC2-s are indicatively presented in Fig. 3. In addition to the peaks corresponding to the aggregates, the characteristic peaks of thaumasite and gypsum are clearly seen. Thaumasite belongs to the ettringite-like group of minerals and this results in very similar XRD patterns. The identification of thaumasite was mainly based on the peaks at around 16, 23.5 and 28° 2θ, which are absent from the ettringite pattern. The absence of ettringite was confirmed by the absence of its characteristic peaks at around 15.8, 18.9, 22.9 and 25.5° 2θ. The peaks attributable to brucite were too weak to allow a safe identification but its formation was confirmed based on DTG curves.

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, both found in the degradation products, according to the equation:

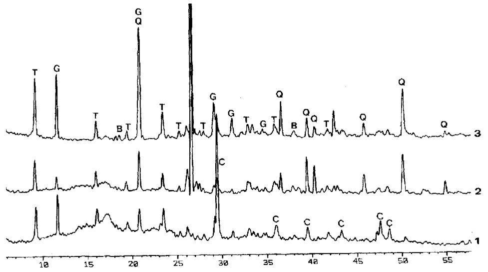

Fig. 3. XRD patterns of deterioration products at 5 °C: (1) PC-c, (2) LC1-s, (3) LC2-s; (T) thaumasite, (G) gypsum, (B) brucite, (Q) quartz, (C) calcite.

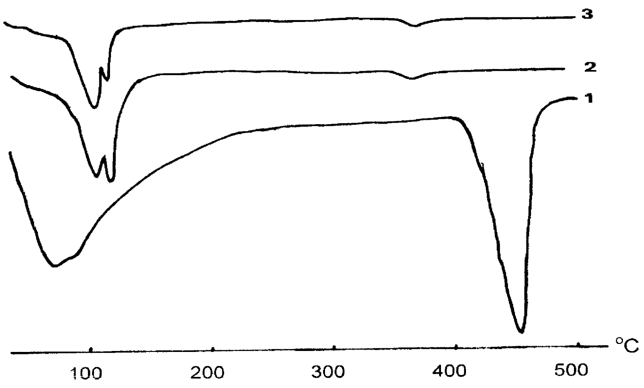

Fig. 4. DTG curves: (1) sound core of sample PC-c, (2) deterioration products of LC2-c, (3) deterioration products of PC-c.

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

The very low solubility of brucite favors the consumption of calcium hydroxide. This leads to a pH reduction 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. 4 presents the DTG curves of degradation products from samples PC-c and LC2-s in relation to the DTG curve of the hard core of the sample PC-c. The double peak in the range 100–130 °C must be associated with the dehydration of thaumasite and gypsum. The dehydration of ettringite and other hydration products, unaffected by sulfate attack, takes place at lower temperature as confirmed by the curve of the sound sample. It is clearly seen that degradated samples also contain small amounts of brucite and no portlandite at all.

3.3. Compressive strength

The 28 day compressive strength, prior to any exposure to sulfates, is shown in Fig. 5. It is seen that mortars made with calcareous sand show higher strength than the mortars made with siliceous sand. After 9 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 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 greater—27%, 21% and 36% of the 28 day strength for the samples PC, LC1 and LC2 respectively. These results show that the cementitous limestone content as well as the use of calcareous sand negatively affects the resistance of the cements against sulfate attack at low temperatures.

Concerning the specimens cured at 25 °C, their compressive strength has increased in most samples. There may be a slight strength loss in the sample PC-s. The long term curing of the specimens will provide more data concerning the effect of the sand on the sulfate resistance of the mortars at 25 °C.

3.4. Ultrasonic pulse velocity

The ultrasonic pulse velocity was measured periodically, after the first signs of damage were observed in our 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's. In general, the above results indicate that microcracking of the specimens is in progress.

In specimens cured at 25 °C, there is no significant decrease of pulse velocity and it remains almost stable.

The results drawn from each one of the above monitoring techniques are in good accordance with each other. It was confirmed that limestone cements suffer from the thaumasite form of attack at low temperature to an extent proportional to the limestone content. The interesting point is that the use of calcareous aggregates

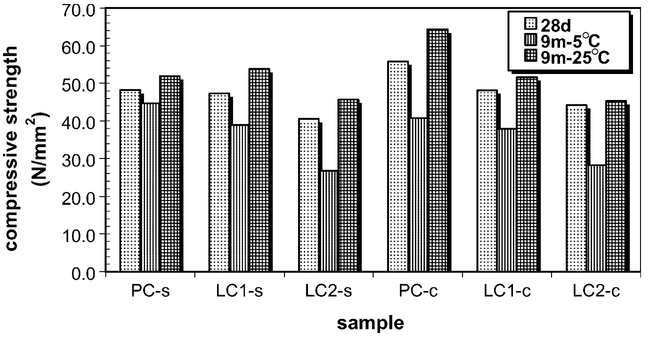

Fig. 5. Effect of curing temperature on the compressive strength of the specimens.

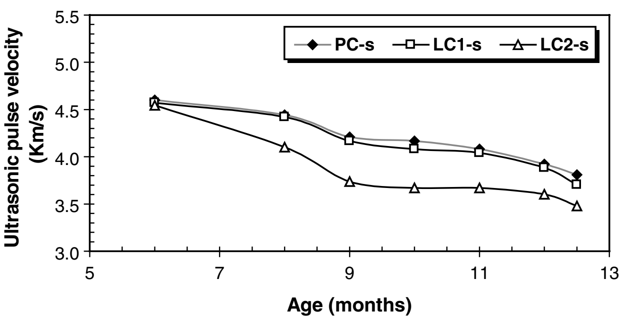

Fig. 6. Ultrasonic pulse velocity of specimens, with siliceous sand (5 °C).

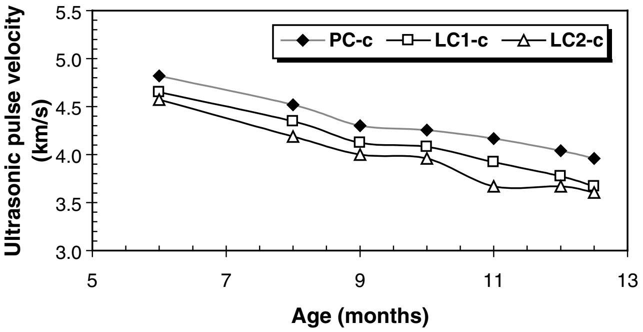

Fig. 7. Ultrasonic pulse velocity of specimens, with calcareous sand (5 °C).

results in thaumasite formation even in OPC mortars, when the appropriate conditions prevail.

4. Conclusions

From the present study the following conclusion can be drawn:

- Mortars containing limestone, either as sand or as main 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.
- Calcium hydroxide is a reactant, rather than a product of reaction, during sulfate attack of cement at 5 °C. Thaumasite formation is accompanied by the formation of brucite and secondary gypsum.

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References

[1] Crammond NJ, Nixon PJ. Deterioration of concrete foundation piles as a result of thaumasite formation. In: Nagataki S, editor. Proceedings 6th Int. Conc. Durability Building Materials and Components. London: E. & F.N. Spon, 1993, vol. 1, pp. 295–305.
[2] Hobbs DW, Taylor MG. Nature of thaumasite sulfate attack mechanism in field concrete. Cement Concr Res 2000;30:529–33.
[3] Collepardi M. Thaumasite formation and deterioration in historic buildings. Cement Concr Compos 1999;21:147–54.
[4] Bickley JA. The repair of arctic structures damaged by thaumasite. Cement Concr Compos 1999;21:155–8.
[5] Sarkar SL, Little DN. Microstructural investigation of severe distress in a crushed concrete base. Cement Concr Res 1998; 28:401–10.
[6] Barker AP, Hobbs DW. Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5 °C. Cement Concr Compos 1999;21:129–37.
[7] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland-limestone cement pastes. Cement 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. Cement Concr Compos 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. Cement Concr Res 1997;27:259–65.
[10] Bensted J. Thaumasite—background and nature in deterioration of cements, mortars and concretes. Cement Concr Compos 1999;21:117–21.
[11] Aguilera J, Blanco Varela MT, Vazquez T. Procedure of synthesis of thaumasite. Cement Concr Res 2001;31:1163–8.
[12] Taylor HFW. Cement chemistry. 2nd ed. London: Academic Press; 1997.