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Thaumasite form of sulfate attack (TSA) in limestone cement pastes

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Abstract

The thaumasite form of sulphate attack (TSA) concerns cements and concretes containing limestone and is attributed to the formation of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$). During the last 10 years, the TSA has been found in field structures and buildings in many countries worldwide. In the present work the behavior of Portland limestone cements was studied in the presence of sulfate ions at low temperatures. Cement paste specimens were constructed using Portland cement, Portland cement with 15% (w/w) limestone content and Portland cement with 30% (w/w) limestone content. Twenty-eight days paste specimens were cured in 1.8% (w/w) magnesium sulfate solution of temperature 5 °C. Visual inspection, mass measurements and ultrasonic pulse velocity measurements were carried out for 1 year. Pastes containing limestone are susceptible to the thaumasite formation of sulfate attack and the deterioration is severer, the higher the limestone content.

Keyword: Thaumasite

1. Introduction

It is generally accepted that conventional sulfate attack of cementitious materials involves the formation and the expansive properties of ettringite. However, another kind of sulfate attack, concerning cements and concretes containing limestone and attributed to the formation of thaumasite has been widely discussed during the last years.[1–3] This kind of sulfate attack is of great importance, as the limestone is widely used as filler or as main cement constituent for many years due to its technical and economical advantages. In addition, the new European Standard EN 197-1 (2000) identifies Portland limestone cements that may contain limestone as main constituent, in percentages ranging from 6% to 35%.[4]

The formation of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) is the result of sulfate attack at low temperature. Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and low temperature. It may also be connected with the prior formation of ettringite or the presence of some reactive alumina. 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 resisting Portland cements.[5–14]

The problem of thaumasite form of sulfate attack (TSA) has been discussed during the last years because it has been identified in UK, USA, Canada, South Africa, France, Germany, Norway, Denmark, Switzerland, Italy and Slovenia and is particularly prevalent in buried concrete. This form of sulfate attack completely destroys the cementious binding ability of the concrete by transforming it into a mush. The mechanism and factors affecting thaumasite formation have not been yet fully clarified. Besides its similarities with other hydrated compounds, found in cement and concrete, hinder its safe identification.[3]

This work deals with the effect of limestone content on the thaumasite form of sulfate attack. The experiments have been carried out in Portland limestone cement pastes. Cement pastes have been chosen instead of mortars or concretes, in order to eliminate the parallel effect of the calcareous sand and/or aggregates on the thaumasite formation.

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

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Table 1
Chemical and mineralogical composition of clinker

Chemical composition (%)	
SiO_2	21.47
Al_2O_3	5.00
Fe_2O_3	3.89
CaO	65.67
MgO	1.89
K_2O	0.68
Na_2O	0.16
SO_3	1.04
Total	99.70
FCaO	1.15
Mineralogical composition (%)	
C_3S[a]	65.0
C_2S	12.6
C_3A	6.7
C_4AF	11.8
Moduli	
Lime saturation factor (LSF)	95.79
Silica ratio (SR)	2.42
Alumina ratio (AR)	1.29
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	0.54
Al_2O_3	0.43
Fe_2O_3	0.20
CaO	53.61
MgO	1.29
K_2O	0.06
LOI	43.73

5 kg capacity. The codes, the composition and the specific surface of the produced cements are given in Table 3.

Paste prisms of size 40 mm × 40 mm × (50–60) mm were prepared, using the cements of Table 3 (w/c = 0.40). The specimens were air cured for 24 h and then they were water-cured for 27 days at temperature 20 ± 2 °C. After the 28-day initial curing the specimens were immersed in a 1.8% $MgSO_4$ solution of temperature 5 °C.

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

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

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.

Changes in specimens' mass were recorded at regular intervals up to 1 year. Concerning the mass and ultrasonic pulse velocity, three prisms for each measurement were used and the presented results are the average value.

3. Results and discussion

The visual assessment of the specimens is summarized in Table 4. Photos of specimens stored in the sulfate solution for 5 and 8 months are presented in Fig. 1.

Indications of the start of the deterioration were first observed on almost all samples after 1-month exposure. The LC2 samples suffered a greater degree of attack than those of LC1 samples, while the PC samples showed very slight attack. 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.

After 12 months exposure the PC prisms indicate only deterioration at corners. The needed carbonates are produced by the carbonation of the calcium hydroxide. The LC1 prisms indicate cracking and expansion, while the LC2 prisms indicate expansion and spalling. It must be noted that the presence of thaumasite, in the white soft material covering the surface of the cracks, was confirmed by XRD, TG and SEM and this is reported elsewhere.

The changes in specimens' mass are shown in Fig. 2. Initially, specimens showed a gradual rise in mass, but after longer exposure in the sulfate solution they began to loss mass, due to the gradual disintegration of the specimens. Fig. 2 gives a clear indication about the time that a severe deterioration begins, as it is accompanied by a great mass loss. The LC2 prisms began to lose mass after 4 months exposure, while the LC1 prisms began to lose mass after 6 months. The PC prisms did not present any mass loss for the 12 months exposure. After 12 months exposure in the magnesium sulfate solution, LC2 shows a significantly greater mass loss than LC1.

The ultrasonic pulse velocity was measured periodically, until the deterioration led to a significant weathering of the parallel

Table 4
Visual assessment[a] of the specimens' deterioration

Sample	Exposure duration (months)						
	0	1	2	4	6	9	12
PC	0	0	1	2	2	2	2
LC1	0	0	2	2	4	5	5
LC2	0	0	1	3	5	6	7

[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: extensive cracking and expansion; 7: expansion and spalling.

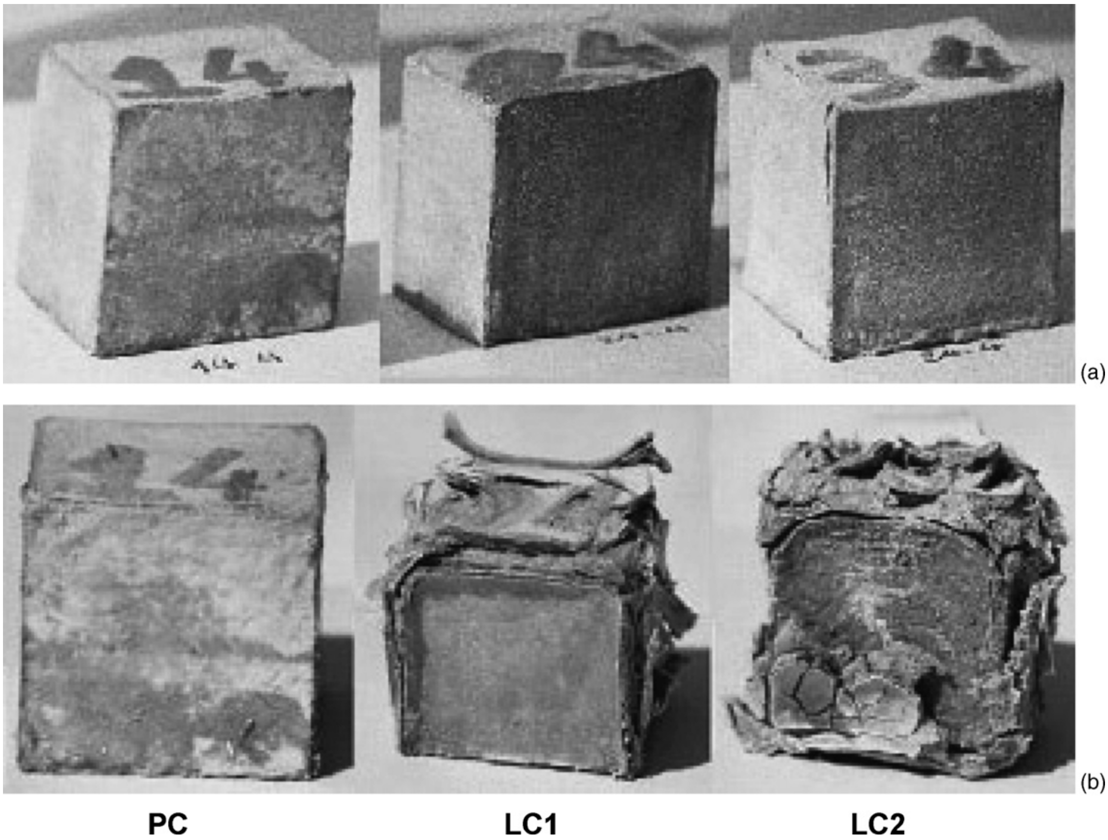

Fig. 1. Specimens cured in a 1.8% $MgSO_4$ solution at 5 °C: (a) 5 months and (b) 8 months.

surfaces of the specimens. Due to the high deterioration rate of the studied samples, the test had to be discontinued after a short period of exposure. Fig. 3 presents the ultrasonic pulse velocity of the studied samples. It is observed that the ultrasonic pulse velocity increased up to about 45 days, due to the continued hydration of the cement. After the 45 days exposure in sulfate environment the pulse velocity began to fall in LC1 and LC2 samples, while the PC sample did not show any significant change. The pulse velocity decrease is greater in LC2 samples.

The results of the above tests are in good accordance and confirm that limestone cements suffer from the thaumasite form of sulfate attack. It must be noted that Portland cements may also be susceptible in sulfate environment and low temperatures, depended on the depth of the carbonation.

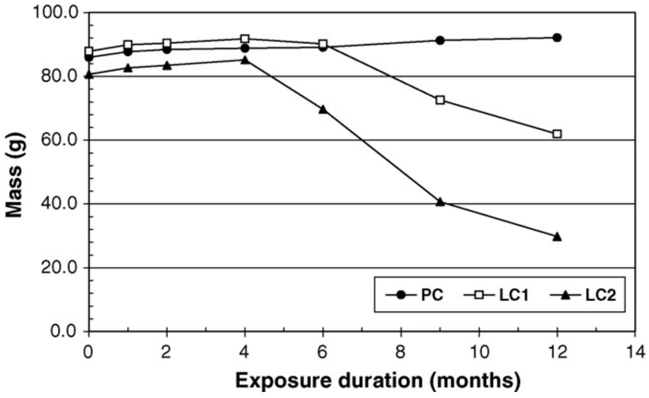

Fig. 2. Changes in mass of the specimens.

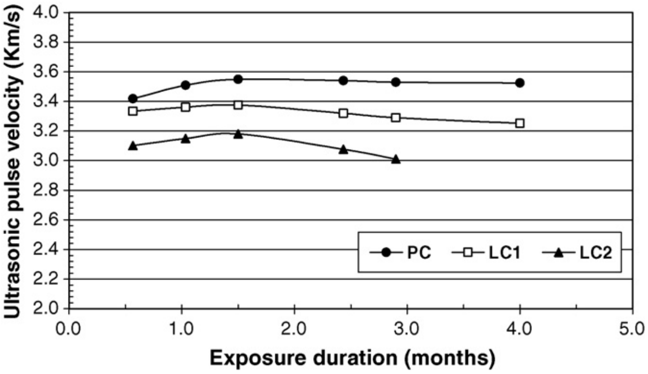

Fig. 3. Ultrasonic pulse velocity of the specimens.

4. Conclusions

From the present study the following conclusions can be drawn:

- Pastes containing Portland limestone cement are susceptible to the thaumasite form of sulfate attack at low temperatures.
- Portland cement pastes are also susceptible – in a lower degree – to the thaumasite form of sulfate attack, due to the carbonates derived from the carbonation of calcium hydroxide.
- The deterioration is severer, the higher the limestone content.

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