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Sulfate resistance of limestone cement concrete exposed to combined chloride and sulfate environment at low temperature

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ABSTRACT

Concrete durability was investigated, taking under consideration the limestone content of the cement used, as well as the effect of chlorides on concrete's deterioration due to the thaumasite form of sulfate attack. A normal Portland cement and two Portland limestone cements (15% and 35% w/w limestone content) were used for concrete preparation. The specimens were immersed in two corrosive solutions (chloride-sulfate; sulfate) and stored at 5 ± 1 °C. Visual inspection of the specimens, mass measurements and compressive strength tests took place for 24 months. Concretes containing limestone, as cement constituent and/or as aggregate, suffered from the thaumasite form of sulfate attack, which was accompanied by brucite and secondary gypsum formation. Limestone cement concretes exhibited higher deterioration degree compared to the concrete made without limestone cement. The disintegration was more severe and rapid, the higher the limestone content of the cement used. Chlorides inhibit sulfate attack on concrete, thus delaying and mitigating its deterioration.

1. Introduction

Sulfate attack is a serious problem affecting concrete service life and several studies have investigated this problem. Conventional sulfate attack in mortar and concrete leads to the formation of expansive ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$). In this case, the calcium aluminate hydrate of the cement paste is mainly affected [1–3]. However, it has been widely discussed that the use of cementitious materials containing limestone may lead to the formation of thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$), as a result of the sulfate attack at low temperatures. This kind of sulfate attack is of great importance as limestone has been widely used as a filler or as a major cement constituent for many years due to its technical and environmental advantages [4–6]. In addition, calcareous sand is extensively used as fine aggregates in concrete production. The European Standard EN 197–1 (2000) identifies Portland limestone cements, which may contain limestone as a major constituent, in percentages ranging between 6% and 35% by mass [7].

Thaumasite is a complex hydrated compound, whose formation requires a source of calcium silicate hydrate, sulfate and carbonate ions, excess humidity and low temperatures (0–5 °C). Thaumasite formation is connected with the prior formation of ettringite or the presence of some reactive alumina [8–10]. It is mainly observed that thaumasite is formed in systems in which aluminate phases have already been consumed by the reaction with sulfate ions to form ettringite. Ettringite formation results in the expansion and cracking of the structure facilitating the ingress of external sulfates [11–13]. As calcium silicate hydrate is necessary for thaumasite formation, this form of sulfate attack gradually destroys the binding ability of the cement paste by transforming C–S–H gel into a mush [14]. Thaumasite can also be detected in normal Portland cement or sulfate resisting cements (cements with low C_3A content), since its formation affects calcium silicate hydrates [15,16]. In this case carbonate ions are derived from the calcareous sand which is used as fine aggregates or from extended atmospheric carbonation. Some authors consider that thaumasite formation is favoured at low temperatures independently of the type of cement used (high or low C_3A content) [12]. Other authors conclude that low C_3A cements produce higher amounts of thaumasite than high C_3A cements [17]. This is the case in one other study, where alumina-rich systems tend to be more resistant to the damage caused by thaumasite formation [18].

Besides sulfates that can enter into concrete and cause damage, chlorides are also often found in structures. Chloride ions enter the concrete either as contaminants derived from the materials used or during the construction's service life by transport from a chloride-bearing environment. In coastal areas, building constructions are found near the sea, where groundwater, mixed with seawater, contains significant amounts of chloride and sulfate ions. There are three considerations concerning the effect of chlorides on sulfate attack. The first suggests that chlorides intensify sulfate attack; the

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second considers that sulfate attack is mitigated by the presence of chlorides, while the third one assumes that the effect of chlorides on sulfate attack is insignificant [19]. However, literature references focus on the effect of chlorides on the deterioration caused by sulfates in concretes made with ordinary Portland cement at temperatures of about 20 °C, where ettringite, instead of thaumasite, is the main deterioration product [20–24]. Thus, it is of great interest to know how the presence of chlorides affects sulfate attack and thaumasite formation at low temperature.

This paper deals with the sulfate resistance of limestone cement concrete exposed to combined chloride and sulfate environment at low temperature (5 °C), taking under consideration the concomitant presence of chlorides, as well as the limestone content of the cements used.

2. Experimental

Portland cement clinker of industrial origin and limestone of high calcite content ($CaCO_3$: 97.5%) were used. The chemical composition of the above materials is presented in Tables 1 and 2, respectively. The used clinker has a moderate C_3A content. Portland limestone cements, containing 15% and 35% w/w limestone, were produced by intergrinding clinker, limestone and gypsum in a pilot plant ball mill of 5 kg capacity. Preliminary tests with varying grinding time have been done in order to produce cements of appropriate compressive strength. The composition of the produced cements, as well as their 28 days compressive strength and specific surface (Blaine method) are shown in Table 3.

Concretes were produced, using the cements of Table 3; cement content (C) of 350 kg/m^3, water to cement ratio (W/C) of 0.52 and calcareous aggregates with a maximum size of 16 mm were used (Table 4). Concrete specimens (cubes of 100 mm) were prepared. The specimens were left in the moulds for 24 h, then cured in water for 6 days and finally air-cured for 21 days at laboratory temperature (25 ± 2 °C). This curing program is assumed to simulate the conditions found in field structures. The concrete properties are presented in Table 4. After the 28-days initial curing the specimens were immersed in the solutions of Table 5, and stored in an industrial refrigerator at 5 ± 1 °C. The two corrosive solutions were replaced every 2 months and were prepared using commercial NaCl and $MgSO_4{\cdot}7H_2O$ salts. The specimens stored in water were used as reference samples.

Visual inspection of the specimens was performed at regular intervals for 2 years and all significant modifications, such as changes in surface colour and texture, formation of coatings, deterioration, expansion and cracking, were recorded.

Changes in specimens mass were recorded at regular intervals for 2 years. The compressive strength of the specimens was measured after 28-days initial curing (Table 4), as well as after 9 and 18 months of exposure in corrosive solutions and water. Three cubes were used to measure mass and compressive strength. The results presented in this paper are the average of the three values.

Table 1
Chemical and mineralogical composition of clinker.

Chemical composition (% w/w)		Mineralogical composition (% w/w)	
SiO_2	21.92	C_3S[a]	48.4
Al_2O_3	5.68	C_2S	26.3
Fe_2O_3	3.29	C_3A	9.5
CaO	63.35	C_4AF	10.0
MgO	1.44		
K_2O	1.32	Moduli	
Na_2O	0.84	Lime Saturation Factor (LSF)	0.92
SO_3	1.25	Silica Ratio (SR)	2.44
LOI	0.91	Alumina Ratio (AR)	1.73
fCaO	1.15	Hydraulic Modulus (HM)	2.05

[a] Cement chemistry notation: C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3.

Table 2
Chemical analysis of limestone (% w/w).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	Total
0.57	0.33	0.19	54.60	1.64	0.04	–	0.02	42.76	100.15

Table 3
Composition, 28-days compressive strength and fineness of the cements used.

Code	Cement composition[a]	28-days compressive strength (MPa)	Specific surface (cm^2/g)
PC	Clinker: 100% w/w	43.0	3010
LC1	Clinker: 85% w/w, limestone: 15% w/w	41.3	3980
LC2	Clinker: 65% w/w, limestone: 35% w/w	32.4	5040

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

XRD measurements were performed on samples at regular intervals to identify any deterioration products (such as thaumasite) formed during the curing period. A Siemens D-5000 X-ray diffractometer, with Cu Ka1 (λ = 1.5405 Å) was used. Measurements were carried out on samples coming from the deteriorated parts of the specimens.

3. Results and discussion

3.1. Visual inspection

Visual inspection of the specimens was performed monthly. Table 6 presents the deterioration scale used to evaluate the damage observed. The observations are summarized in Table 7, while Figs. 1 and 2 show the evolution of specimens' deterioration in solutions CS and S, respectively. Photos of specimens stored in CS and S corrosive solutions for 4, 10, 18 and 24 months, are presented in Figs. 3 and 4, respectively.

All specimens showed indications of the onset of deterioration after 5 months of exposure in both corrosive solutions. As it is clearly shown in Figs. 3 and 4, the deterioration was increasing with time for the specimens stored in both corrosive solutions; however its evolution was more rapid for the limestone cement concretes (LC1 and LC2) compared to that of the samples containing normal cement (PC). After 24 months of exposure in both CS and S solutions, PC specimens were less severely deteriorated than LC1 or LC2 cubes. Deterioration was more intense in LC2 specimens, which had a higher limestone content. This observation indicates that when increasing the limestone content of the cement used, the deterioration caused by sulfates is more severe. In all cases, the first sign of attack was deterioration at the corners and along the edges followed by cracking. Progressively, expansion, spalling and loss of concrete pieces took place, while some specimens collapsed. Additionally, the inner surface of the cracks was covered by a white soft substance.

The degree of deterioration as well as its evolution was found to be dependent on the presence of chlorides in the corrosive solutions. As it is clearly shown in Figs. 1 and 2, the evolution of the deterioration of the specimens tested was slower in CS solution compared to that of S solution. It can also be observed that the final degree of deterioration (24 months) for all specimens was lower in CS solution than in S solution (Table 6, Figs. 3 and 4). The presence of chlorides appears to have delayed the deterioration caused by sulfate attack.

Table 4
Concrete composition and properties.

Sample	Concrete composition (kg/m^3)				Concrete properties			
	C	Aggregates[a]	W[b]	SP[c]	Slump (mm)	Unit weight (kg/m^3)	Air content (%)	28-days compressive strength (MPa)
PC	350	Fine: 1100	210	0.83	110	2379.0	1.6	42.7
LC1		Medium: 800		0.83	110	2354.5	2.2	40.0
LC2				1.40	100	2347.3	1.9	31.7

[a] Fine aggregates: 100% w/w passing an 8 mm sieve, 95% w/w passing a 4 mm sieve. Medium aggregates: 100% w/w passing a 16 mm sieve, 1% w/w passing a 1 mm sieve.
[b] Total water content: 210 kg/m^3; water absorbed by the aggregates: 28 kg/m^3; effective water: 182 kg/m^3 (W/C = 0.52 according to EN 206–1).
[c] Superplasticizer: CHEM SLP P by Domylco Ltd., type E and F of ASTM C494/C494 M-08a.

Table 5
Storage solutions.

Code	Type	Cl^- (g/L)	SO_4^{2-} (g/L)
W	Water	–	–
CS	Cl^-/SO_4^{2-} solution	21.14	20.0
S	sulfate solution	–	20.0

Table 6
Deterioration scale and damage observed.

Deterioration scale	Damage observed
0	No visible deterioration
1	Some deterioration at corners and edges
2	Deterioration at corners, edges and bottom
3	Cracking at corners and along the edges
4	Serious cracking and expansion along the edges
5	Extensive cracking and specimen expansion
6	Further expansion of the specimen and sides' deterioration
7	Extensive expansion and spalling
8	Extensive deterioration, loss of whole pieces
9	Specimens collapse

Table 7
Visual inspection of specimens stored in CS and S solutions.

Code	Deterioration start (month)		Deterioration[a] after 24 months	
	CS	S	CS	S
PC	5	5	6	7
LC1	5	5	7	8
LC2	5	5	8	9

[a] Deterioration scale according to Table 6.

3.2. Mass measurements

The mass of the specimens was recorded monthly and it is presented in Figs. 5 and 6 (CS and S solutions, respectively). Initially, all specimens in both corrosive solutions showed a gradual rise in mass, attributed to water imbibition during the hydration process. This was followed by a decrease in their mass, which started at different times depending on concrete's composition and type of the corrosive solution. In both CS and S solutions, mass loss initiated after the 7th and 11th month of exposure for the LC2 and LC1 specimens, respectively, while for the PC specimens it was found to start after the 16th month. As it can be observed, in both solutions LC2 showed by far the greatest and the most rapid mass loss, compared to PC and LC1 specimens. On the contrary, PC specimens presented the best behaviour. This phenomenon indicates that limestone content strongly affects concrete's resistance against sulfate attack. Higher limestone contents in cement resulted in more severe deterioration.

In Fig. 7, mass loss is expressed as an m/m_0 ratio, where m is the specimen mass after 24 months of exposure in a corrosive environment, and m_0 corresponds to the maximum mass recorded in the same environment. It is clearly indicated that the presence of chlorides retarded sulfate induced deterioration. More specifically, mass loss for PC specimens was 1.1% and 2.1% in CS and S solutions, respectively. LC1 specimens lost 1.7% of their mass in CS solution and 5.2% in S solution. LC2 specimens showed a mass loss of 12.3% in CS solution and 16.5% in S solution. In addition, the above data confirm that concrete's damage caused by sulfates was more intensive the higher the limestone content of the cement used.

3.3. Compressive strength

The compressive strength values (reference strength) of the specimens stored in water for 9 and 18 months are shown in Figs. 8 and 9, respectively. In Fig. 8 the compressive strength values of all specimens after 9 months of exposure in CS and S solutions are also shown. The LC1 and LC2 specimens showed strength loss in both corrosive solutions compared to the reference strength values. The PC specimens presented strength loss when stored in CS solution, while compressive strength values remained steady when stored in S solution. In Fig. 9, the compressive strength values of all specimens after 18 months of exposure in CS and S solutions are presented. All specimens cured in corrosive solutions show lower strength values in comparison to the reference ones. The strength of the LC2 specimens stored in S solution is the lowest compared to those of the rest of the specimens. The higher compressive strength values recorded for all specimens immersed in CS solution, compared to these immersed in S solution, indicate the beneficial contribution of chlorides on inhibiting sulfate attack. In addition, compressive strength loss is greater, the higher the limestone content of the cements used.

According to Fig. 10, where s/s_0 values are presented (s: compressive strength after 18 months of exposure in corrosive environment; s_0: reference strength after 18 months of curing in water), the compressive strength loss of all specimens due to sulfate attack was mitigated when chlorides were present. More specifically, PC specimens presented 14% and 43% loss of their strength in CS and S solutions, respectively. Strength loss for the LC1 specimens was 31% in CS solution, while a 47% loss was recorded for the S solution. LC2 specimens presented significant compressive strength loss in both corrosive solutions, which was 46% for the specimens stored in CS solution and 59% for those stored in S solution. The above results confirm that a higher limestone content of the cements used leads to a greater degradation of concrete.

3.4. XRD analysis

The identification of the degradation products formed as a result of sulfate attack was based on XRD measurements, which were carried out on the soft material obtained from the deteriorated part

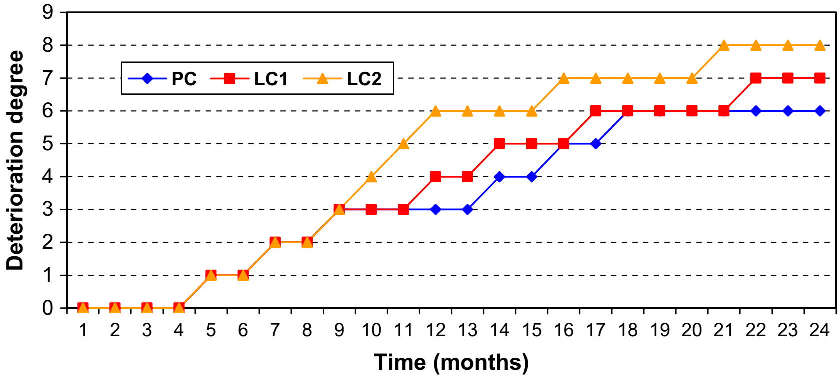

Fig. 1. Deterioration degree of the specimens exposed in CS solution in relation to time (deterioration scale according to Table 6).

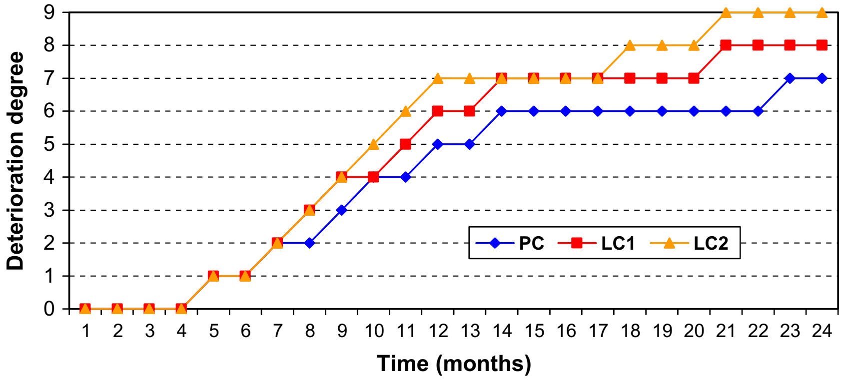

Fig. 2. Deterioration degree of the specimens exposed in S solution in relation to time (deterioration scale according to Table 6).

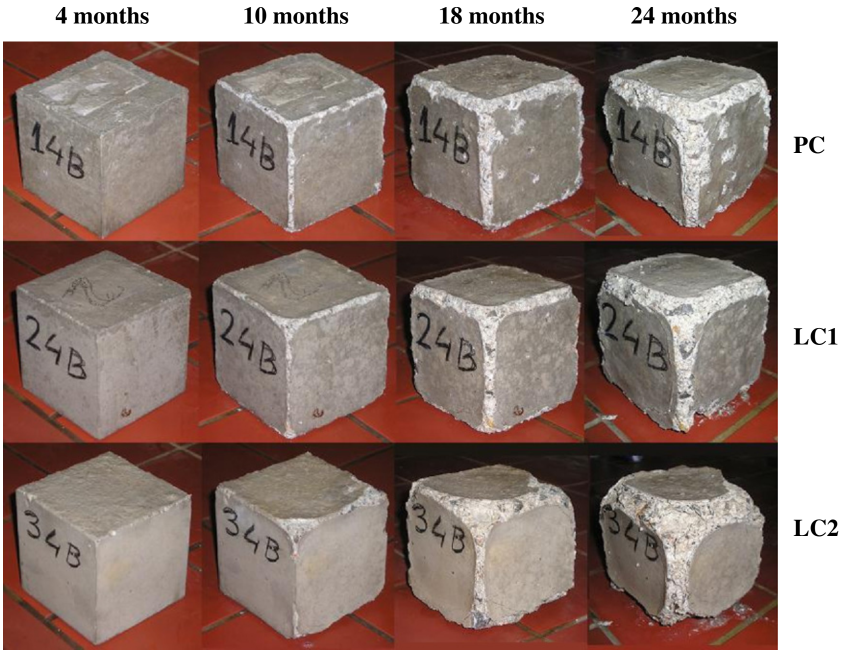

Fig. 3. Concrete specimens after 4, 10, 18 and 24 months of exposure in CS solution.

of the specimens. In all cases, the main phases detected include thaumasite, calcite and gypsum. The presence of calcite is due to the use of calcareous aggregates and limestone cements. In addition, traces of brucite were also found. Thaumasite, gypsum and brucite are the degradation products. It must be noted that no peaks of ettringite were detected on all XRD patterns.

A PC specimen stored in water for a 9 month period was used as a reference. The sample was obtained using a destructive tech-

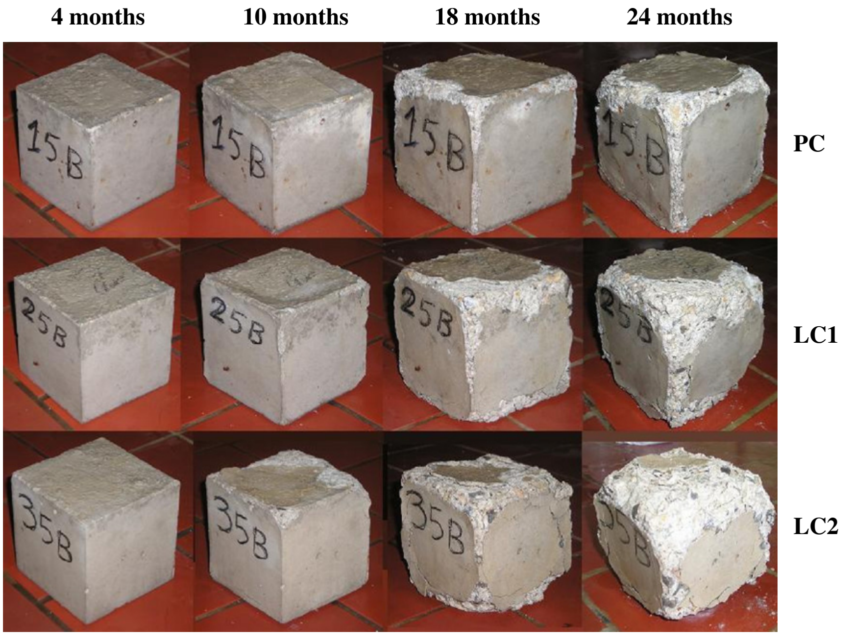

Fig. 4. Concrete specimens after 4, 10, 18 and 24 months of exposure in S solution.

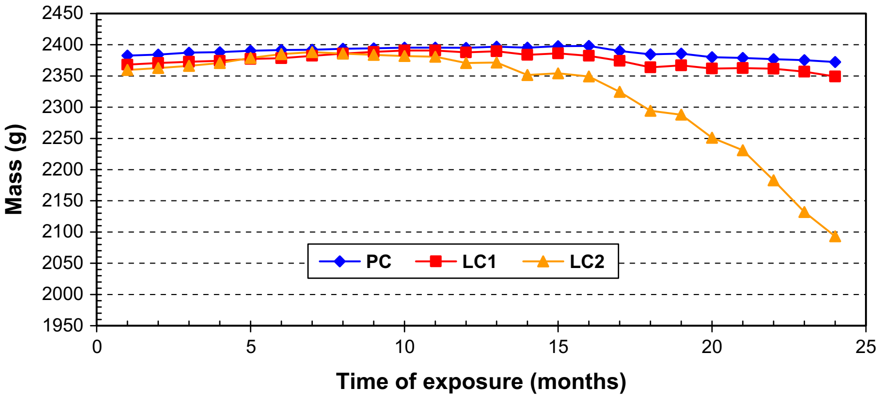

Fig. 5. Mass of concrete specimens related to exposure duration in CS solution.

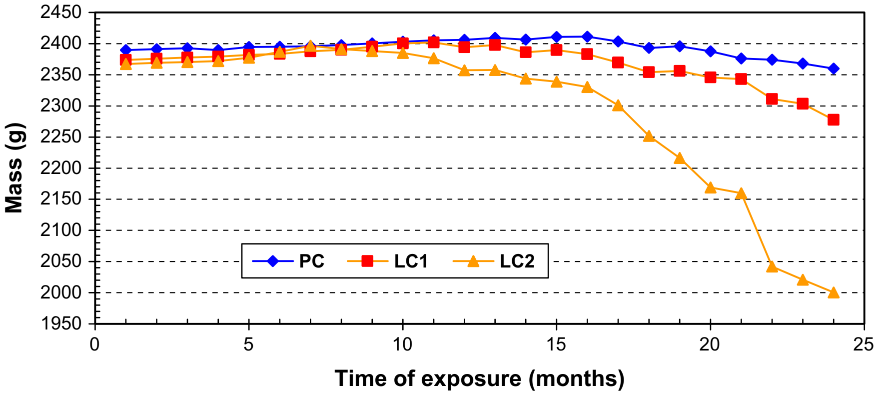

Fig. 6. Mass of concrete specimens related to exposure duration in S solution.

nique since no damage was observed for this specimen. Fig. 11 shows that no thaumasite was detected. However, portlandite was present in the sample, produced during cement's hydration process, due to the absence of sulfates which would transform it into gypsum. Evidence of thaumasite formation was observed in the LC1 and LC2 specimens as early as 9 months after their immer-

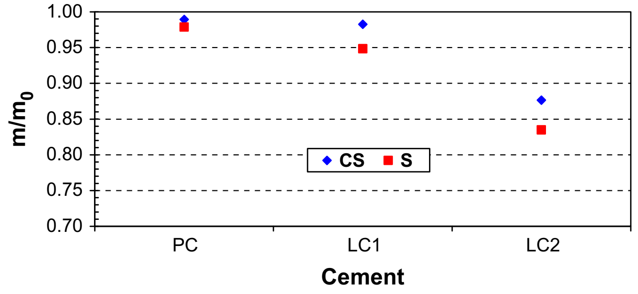

Fig. 7. m/m_0 ratio of concrete specimens exposed in CS and S solutions (m: mass after 24 months of exposure; m_0: maximum mass recorded).

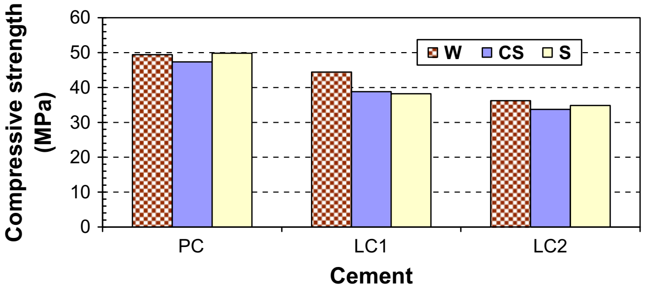

Fig. 8. Compressive strength of concrete specimens after 9 months of exposure in water and in corrosive solutions.

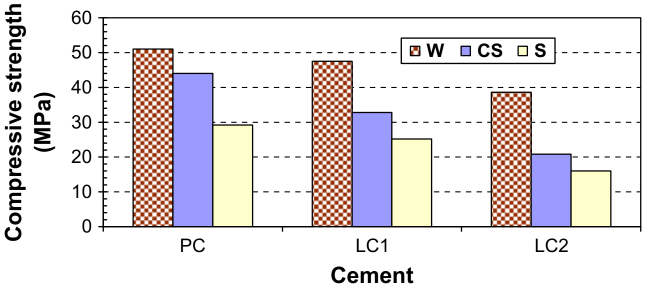

Fig. 9. Compressive strength of concrete specimens after 18 months of exposure in water and in corrosive solutions.

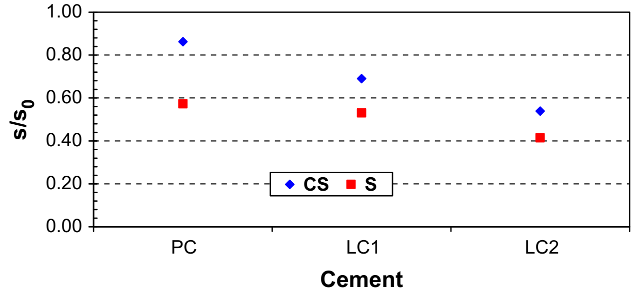

Fig. 10. s/s_0 ratio of concrete specimens exposed in CS and S solutions (s: compressive strength after 18 months of exposure in corrosive environment; s_0: reference strength after 18 months of curing in water).

sion in S solution (Fig. 11). It can be noted that the peaks of thaumasite are slightly more intense for the sample obtained from LC2 specimen compared to that from the LC1 specimen.

After 18 months of curing, thaumasite was detected in all concrete specimens (PC, LC1 and LC2) stored in both CS and S environments. Thaumasite peaks in XRD patterns (Figs. 12–14) are more intensive for the specimens stored in S solution in comparison to those cured in CS solution. Thaumasite formation in LC1 and LC2 specimens can be attributed, among other factors (sulfates, low temperature, humidity), to the high limestone content of the cements used. In the case of PC specimens, the source of CO_3^{2-} required for the thaumasite formation is the fine particles of the calcareous aggregates.

The above findings confirm visual inspection, as well as mass and compressive strength measurements. Thaumasite formation due to sulfate attack started earlier in the case of Portland limestone cement concretes in comparison to the concrete produced with ordinary Portland cement. Furthermore, deterioration caused by thaumasite formation was more severe when specimens were stored in the solution containing only sulfates.

It must also be noted that no calcium hydroxide was detected in the deterioration products. Most likely, portlandite had reacted with magnesium sulfate to form gypsum and brucite, both found in the degradation products, according to the reaction:

$$\mathrm{Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2} \tag{1}$$

The very low solubility of brucite shifts the above reaction to the right and favours 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 [11].

All experimental results obtained, confirm that concrete's deterioration is more severe, the higher the limestone content of the cement used. This fact can be attributed to the hydration process, which differs between Portland limestone cements and normal Portland cement. Specifically, the incorporation of limestone accelerates the cement hydration process increasing the calcium hydroxide formation. The reaction between sulfates and calcium hydroxide in the paste results in an alteration of the predominant mechanism of sulfate attack. Additionally, the initial capillary porosity is increased leading to more rapid sulfate induced deterioration [13,25,26]. In our case, the use of cement with a high limestone content (LC2, 35% w/w) leads to concrete of lower compressive strength and resistance against sulfate attack. Furthermore, higher limestone contents of the cements provide increased amounts of calcium and carbonate ions, which are necessary for thaumasite formation during sulfate attack.

The experimental results showed that all concrete specimens exhibited better resistance against sulfate attack when immersed in the chloride-sulfate solution (CS) in comparison to the immersion in the solution containing only sulfates (S). The literature related to cementitious materials cured in combined chloride-sulfate solutions is mainly focused on deterioration caused by ettringite formation at ambient temperatures. Some studies [19–24] suggest that the better performance of specimens stored in chloride-sulfate solution compared to those stored in sulfate solution can be attributed to the following reasons:

(a) The rate of chloride ions diffusion is higher compared to that of the sulfate ions. This leads to a faster penetration of chlorides into concrete, allowing them to react first with the C_3A hydrated phases. The result is that chloroaluminate phases such as Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) are produced, which do not cause any expansion. Thus, the lower availability of susceptible C_3A hydrates can reduce the conventional sulfate attack.

(b) The increased solubility of ettringite in chloride solutions (three times higher than that in water) results in reduced ettringite formation.

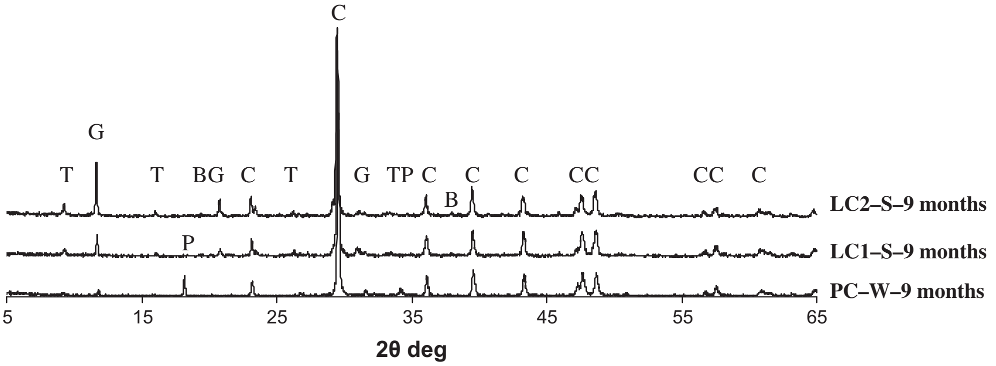

Fig. 11. XRD patterns of PC specimen stored for 9 months in water (W) and of LC1 and LC2 specimens exposed for 9 months in S solution (T: thaumasite, C: calcite, G: gypsum, B: brucite, P: portlandite).

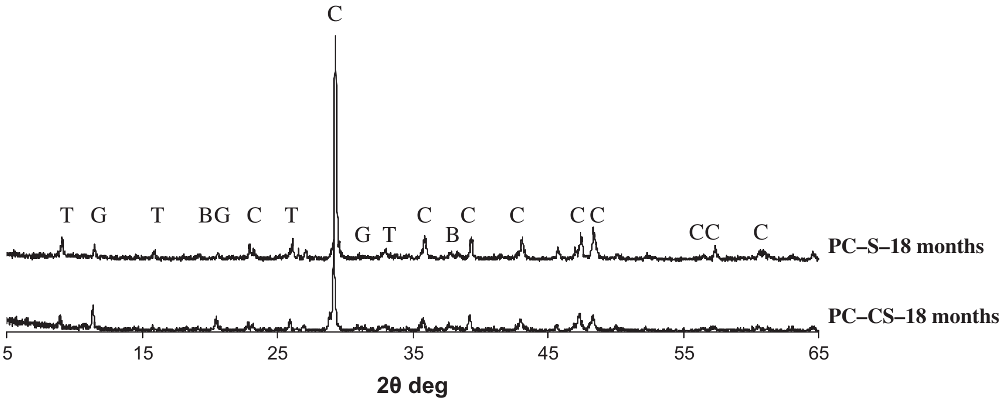

Fig. 12. XRD patterns of PC specimens exposed for 18 months in CS and S solutions (T: thaumasite, C: calcite, G: gypsum, B: brucite).

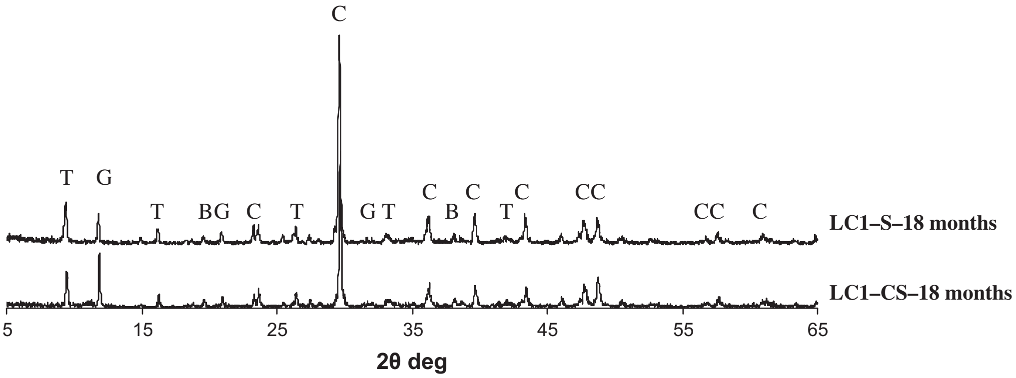

Fig. 13. XRD patterns of LC1 specimens exposed for 18 months in CS and S solutions (T: thaumasite, C: calcite, G: gypsum, B: brucite).

Concerning the present work, concrete specimens were stored in sulfate and chloride-sulfate solutions at the temperature of 5 °C. The deterioration observed, was due to the formation of thaumasite, as was proved by the XRD analysis. Calcium silicate hydrates are affected by sulfate attack and this phenomenon is in agreement with studies showing that thaumasite is formed at this temperature [8,10,11,14,27]. The better performance of the concrete specimens stored in combined chloride-sulfate environment can be mainly attributed to the more rapid penetration of chloride ions into concrete, in comparison to sulfate ones, inhibiting the attack of the latter on the calcium silicate hydrates. It is also considered that the presence of chlorides limits sulfate attack, due to the increased dissolution of portlandite ($Ca(OH)_2$), which is typically solubilized by chlorides, and the formation of hydrated $CaCl_2$ compounds [28]. This results in a substantial reduction of the pH of the pore solution [29], which does not promote thaumasite formation [30]. Furthermore, due to the similar structure of thaumasite and ettringite [1,4,31,32], it can be assumed that thaumasite is also more soluble in the chloride-bearing solution, as ettringite is, resulting in a slower thaumasite formation. When limestone additions are used, monocarbonate (instead of monosulfate) is formed as the stable AFm phase in the hydration products [12,33]. Chloride ions entering the concrete displace carbonates from the monocarbonate phase (instead of displacing and liberating sulfates in the presence of monosulfate) and form Friedel's salt. This reaction does not lead to the formation of expansive compounds [34].

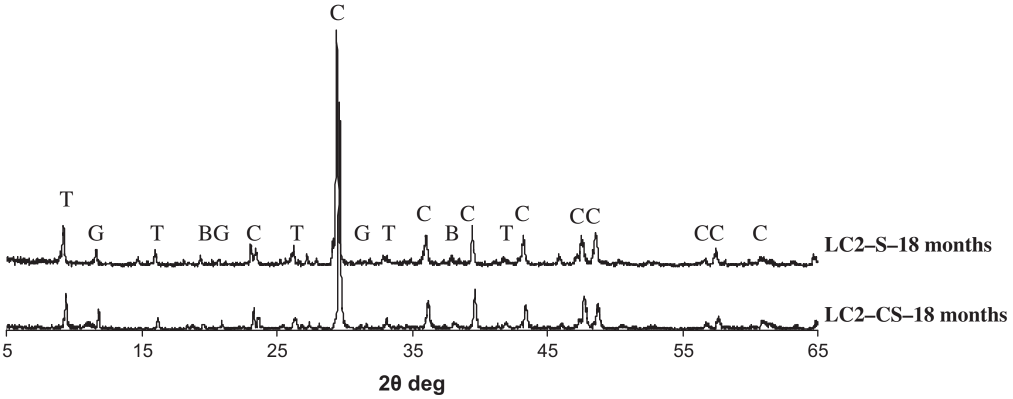

Fig. 14. XRD patterns of LC2 specimens exposed for 18 months in CS and S solutions (T: thaumasite, C: calcite, G: gypsum, B: brucite).

4. Conclusions

From the present study the following conclusions can be drawn:

- Concrete containing limestone, as cement constituent and/or as aggregate, suffers from the thaumasite form of sulfate attack at 5 °C.
- Thaumasite formation is accompanied by the formation of brucite and secondary gypsum, while no ettringite and/or portlandite were detected in the deteriorated zone.
- The deterioration degree of limestone cement concrete was higher compared to that of the concrete made without limestone cement. The damage of the latter concrete was also severe.
- The disintegration of limestone cement concrete is more severe and rapid, the higher the limestone content of the cement used.
- Concrete deterioration due to sulfate attack is more intensive for the specimens stored in sulfate environment, compared to those stored in the combined chloride-sulfate one. The concomitant presence of chlorides mitigates concrete damage caused by sulfates.

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