

The Effect of Chloride on Performance of Cement Mortars Subjected to Sulfate Exposure at Low Temperature

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ABSTRACT

The effect of chloride on performance of cement mortars made with CEMI and CEMI blended with 10% limestone filler and subjected to sulfate attack was investigated. The performance of the specimens was assessed by means of visual inspection and loss of mass. In addition, the mineralogy of the deterioration products was determined by infra-red spectroscopy and X-ray diffraction. Mortar made with CEMI blended with 10%LF showed higher deterioration rate than that made with CEMI. It was also found that at the concentration used in this study, chloride accelerates the development of thaumasite resulting in marked deterioration to the specimens at 5°C. This is contrary to reported favorable effects of chloride in mitigating sulfate attack at higher temperatures.

Keywords. Sulfate attack; Chloride; Concrete durability; Thaumasite

INTRODUCTION

Studies by Zuquan et al. (2007) and Ekolu et al. (2006) have shown that the presence of chloride ions in association with sulfate delay or mitigate the conventional form of sulfate attack, where ettringite is the main deterioration product. However, Torres (2004) and Sotiriadis et al. (2012) note that there is very little information available about vulnerability to the thaumasite form of sulphate attack of concrete/mortar exposed to both chloride and sulfate solutions at low temperatures. According to an experimental study reported by Torres (2004), the rate of deterioration due to thaumasite formation depends on chloride level in solutions. Samples made with Portland cement blended with 15% limestone filler that were immersed in sulfate solution containing 2.0% Cl⁻ displayed damage similar to that for pure sulfate solution. Less damage occurred to samples immersed in sulfate and 0.5% Cl⁻ solution, whereas, the largest damage is observed in samples immersed in sulfate plus 1.0%Cl⁻. On the other hand, according to a recent study Sotiriadis et al. (2012) in which a 2.1% chloride concentration was used; the thaumasite form of sulfate attack was mitigated. This paper reports and discusses the results of an on-going experimental study into the effect of chloride ions on performance of CEMI and CEMI with 10% limestone filler cement mortars subjected to conditions favourable to thaumasite formation. The samples were subjected to combined action of sulfate and chloride solutions for 12 months at low

temperature during which they were monitored using visual observation, mass change, X-ray diffraction and infra - red spectroscopy.

EXPERIMENTAL PROGRAM

Specimen Preparation and Exposure

The mortar mixtures shown in Table 1 were used to prepare 50mm cubes. A fixed water to binder ratio of 0.6, binder to sand ratio of 1:2.5 and siliceous sand were used to prepare the specimens. This high w/b ratio was selected to accelerate chemical diffusion and interaction, thus allowing identification of any potential reactions within a shorter time frame. The chemical and mineralogical composition of the cement and limestone are given in Tables 2 and 3.

After casting, the cubes were left for 24 hours, de-moulded and then placed in curing water for 6 days at 20°C. They were then air-cured at 20±1°C for 21 days, after which all the cubes were weighed and then transferred to their designated exposure solutions (Table 4) in small tanks maintained at 5± 0.5°C. Exposure solutions were made by dissolving sodium chloride (NaCl) and epsom salt (MgSO₄.7H₂O) in deionised water. The solutions were renewed every three months.

Table 1. Mortar mixtures

Mix	Binder	Per weight cement			
		Cement	Limestone	Water	Sand
A	CEMI	1	0	0.6	2.50
B	CEMI/10%LF	0.9	0.1		

Table 2. Chemical and mineralogical composition of cement

Chemical composition		Mineralogical composition	
	[%]		[%]
SiO ₂	19.85	C ₃ S	68.28
CaO	64.61	C ₂ S	5.4
Al ₂ O ₃	4.67	C ₃ A	7.74
Fe ₂ O ₃	2.74	C ₄ AF	8.34
Na ₂ O	0.23		
K ₂ O	0.449		
MgO	1.09		
SO ₃	3.015		
LOI	2.52		

Table 3. Chemical composition [weight %] of limestone

SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	SO ₃	LOI	Total
0.63	55.2	0.28	0.15	0.054	0.003	0.47	0.002	42.89	99.68

Table 4. Test solutions

Test solutions	Salts in test solutions			
	[g/l]		[%]	
	SO ₄ ²⁻	Cl ⁻	SO ₄ ²⁻	Cl ⁻
W	0	0	0	0
S	6.0	0	0.6	0
SC	6.0	5	0.6	0.5

Visual inspection and mass loss

A visual assessment of the specimens was made every two weeks by removing the cubes from the solutions. Particular note was made of any changes in colour, spalling and precipitation of any materials. They were also weighed so that changes in specimens mass could also be recorded. Before weighing, specimen surfaces were wiped dry and any loose parts were removed by hand.

X-ray diffraction and infra - red spectroscopy analysis

Samples of degraded surface deposits were dried at room temperature, ground by hand using a cleaned agate pestle and mortar to a fine powder of <63µm. The powder was examined by a Siemens-D500 diffractometer using monochromatic CuKα radiation operating at a voltage of 40 kV and current of 30 mA. The samples for IR spectroscopy were made as KBr discs, using 2 mg of sample to 200 mg of KBr that were manually ground in an agate mortar and pestle until a fine homogeneous mixture was achieved. Each specific powder was placed in the appropriate die so that a 12 mm disc was prepared. The IR spectrum was determined using a Perkin-Elmer FT-IR 2000 spectrometer.

RESULTS AND DISSCUSSION

Visual Observations

The first signs of deterioration were detected at corner and edges of the specimens after 100 days of immersion in pure sulfate and combined sulfate and chloride solutions. This was more evident in mix B specimens, containing limestone filler.

As time progressed, the degree of deterioration depended on the presence of chloride in the test solutions and carbonate content of cement. After 360 days of immersion (Figure 1), it can be clearly seen that the specimens stored in sulfate solution with 0.5% chloride suffered greater damage than in pure sulfate solution (S) and mix B specimens containing limestone were more seriously damaged. It was obvious that the presence of chloride in test solution accelerates the rate of deterioration.

Test solutions	CEMI	CEMI/10%LF
Water		
Sulfate		
Sulfate plus Chloride		

Figure 1. Specimens after 360 days of immersion in test solutions

Mass Loss

Figures 2 and 3 show the mass changes for the mortars after 360 days exposure to the test solutions. As shown, all specimens showed weight gain in all test solutions. However, whereas this increase in weight continued for specimens stored in pure water for the whole exposure period, specimens stored in combined sulfate and chloride (SC) solutions showed first loss in mass after 160 days, while those stored in pure sulfate (S) solutions began to lose mass after 270 days. Mass loss was greater for the limestone containing mortars mix B than for mix A, at 360 days in SC solution amounting to 4.56% and 1.44%, respectively (relative to mass at 28 days).

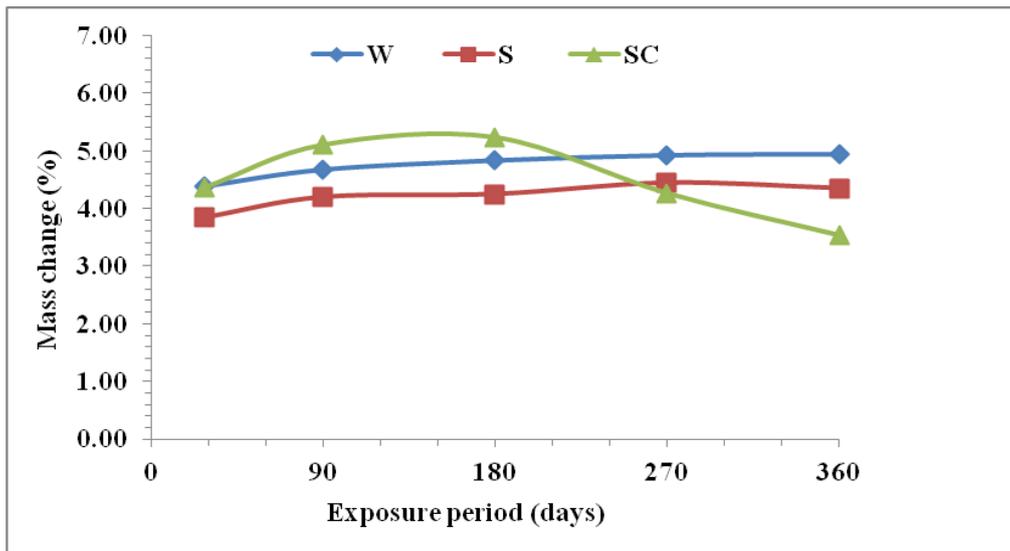


Figure 2. Mass change of mortar made from mix A stored for 360 days in test solutions

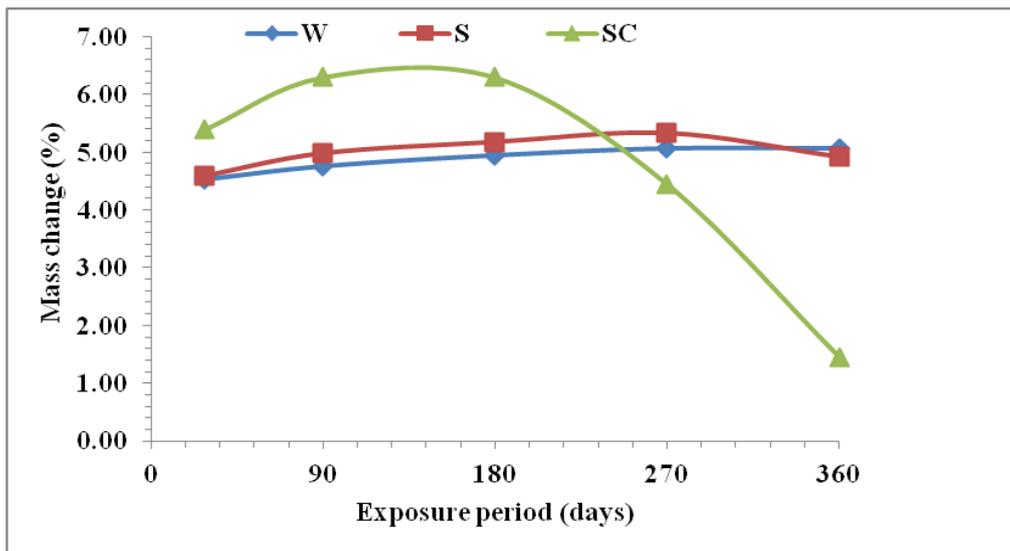


Figure 3. Mass change of mortar made from mix B stored for 360 days in test solutions

X-Ray Diffraction

In order to determine the composition of the deterioration products, materials from damaged areas were examined using X-ray diffraction (XRD) analysis, where the resulting XRD patterns are shown in Figures 4 and 5. It was found that the presence and intensity of some phases depended strongly on test solutions and cement composition. As expected, the relatively strong calcite peaks were detected in mortar made from mix B. Higher intensity of brucite [peaks at 18.52° and 37.98° 2θ]; gypsum [peaks at 11.6° and 20.72° 2θ] and the absence of portlandite [strong peaks at 18.08° and 34.17° 2θ] were detected in mix B

samples subjected to combined sulfate and chloride (SC) solutions. The chances of the dissolution of portlandite increases at lower temperature. This would result in a rapid reaction with sulfate ions to form gypsum and brucite, both of which were identified in the degradation products. The very low solubility of brucite would cause a reduction in pH so that ultimately C-S-H becomes more vulnerable to sulfate attack. This process appeared to occur more rapidly in mix (B) specimens immersed in combined sulfate and chloride (SC) solutions, which showed higher deterioration rate. Moreover, higher thaumasite intensity was detected in deteriorated products of the same mortar.

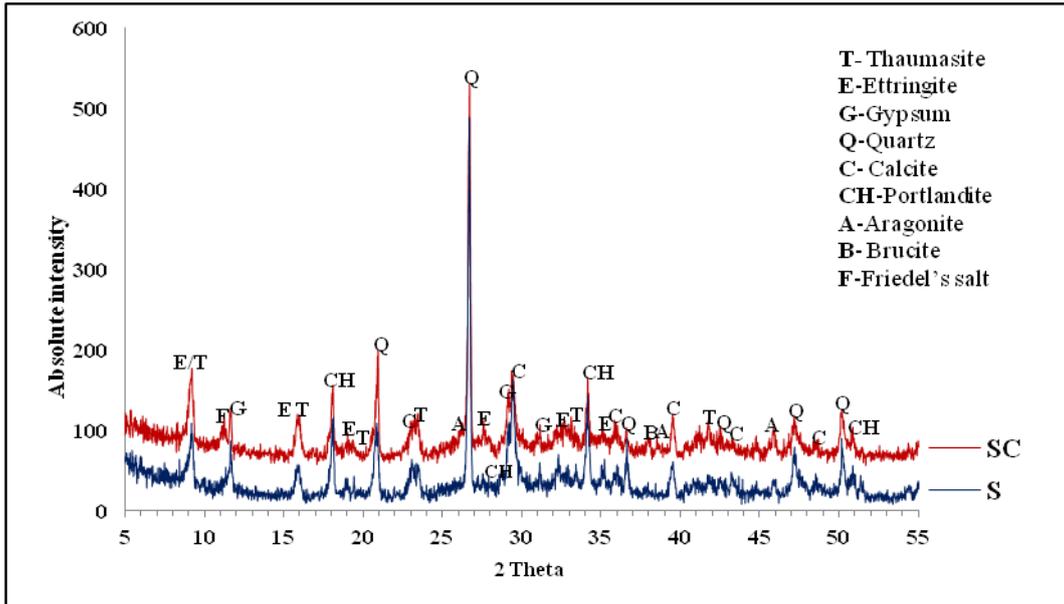


Figure 4. XRD patterns of the degraded surface of the mortars made from mix A

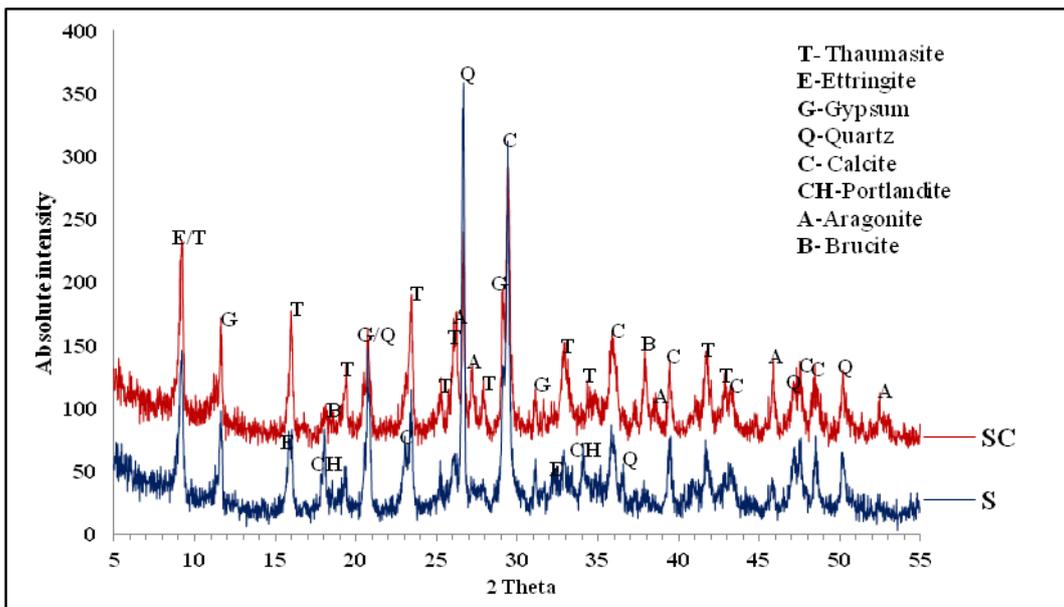


Figure 5. XRD patterns of the degraded surface of the mortars made from mix B

Infra-red Spectroscopy

In order to obtain further evidence about the deterioration process and to confirm the XRD identifications of thaumasite and ettringite and other minerals, IR spectroscopy was used. This technique enables a phase in which silicon is octahedral coordinated to be identified. The relevant infra-red spectra and peaks are shown in Figures 6, 7. All spectra show a peak at 500 cm^{-1} which is diagnostic for the presence of thaumasite, whereas the peak at 855 cm^{-1} is attributed to the $\text{Al}(\text{OH})_6^{3-}$ group (for peak identification see Zhou et al. 2006). This indicates that thaumasite was not present as the end member of the solid solution series with ettringite (Torres et al. 2004). It can be clearly seen from Figures 6 and 7 that the intensity of 855 cm^{-1} peak was increased by the presence of chloride in solution. This suggests that samples immersed in SC solutions contain mostly thaumasite in a thaumasite-ettringite solid solution.

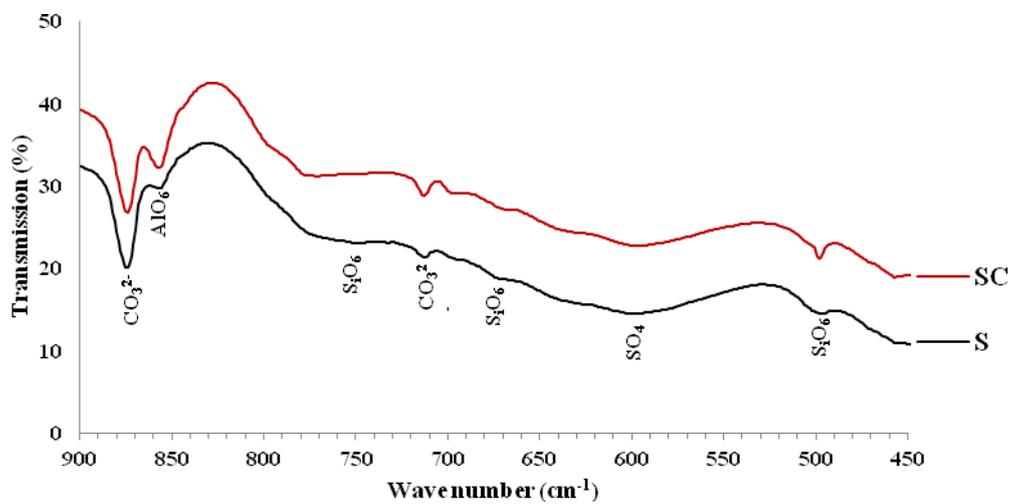


Figure 6. FT-IR spectra of the degraded surface after 360 days of storage for mix A

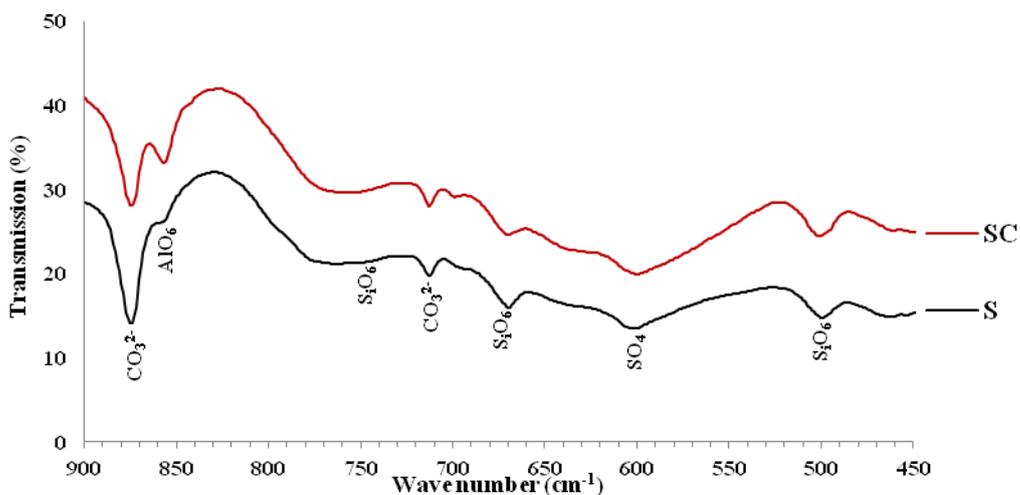


Figure 7. FT-IR spectra of the degraded surface after 360 days of storage for mix B

These results agree with the XRD findings in showing that thaumasite or thaumasite-ettringite solid solution result from the attack in both pure sulfate and sulphate -chloride solutions and for both CEMI and CEMI/10% limestone mixes.

CONCLUSIONS

The conclusions from this study are summarised as follows:

- 1- Sulfate attack is more severe in specimens immersed in combined sulfate and chloride solutions, compared to those stored in the pure sulfate solution. It appears that the presence of low chloride concentration accelerates mortar damage caused by thaumasite formation.
- 2- The deterioration degree of mortars increased as the carbonate content increased. Mortars with 10% limestone replacement showed three times higher deterioration compared to that of the mortar made without replacement, as determined by mass loss.
- 3- Both XRD and IRS confirm that in these experiments carried out at 5°C thaumasite formation (thaumasite- ettringite solid solutions) is responsible for the deterioration observed due to sulfate attack

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