

Resistance to Sulfate Attack of Mixtures with Limestone-Portland Blended Cements

M. Collepari, S. Monosi, O. Favoni and J.J. Ogoumah Olagot

Synopsis: Blended binders based on limestone-Portland cements are very popular in Europe after the advent of the EN 197-1 European norm. However, according to some British researchers concretes with limestone-Portland blended cements would be more vulnerable to sulfate attack than the corresponding concretes with Portland cement when exposed to sulfate environment.

In order to assess this hypothesis, the performances of cement mixtures with portland cement and limestone-portland blended cements containing two different percentages of ground limestone (15% and 30%) were studied. Sound and cracked specimens of cement pastes, all at a given water/binder ratio of 0.40, were exposed to a sulfate-rich aqueous solution (10% by Na_2SO_4) at 20°C and 5°C. There was no evidence of ettringite or thaumasite formation related to the sulfate attack in the sound specimens independently of the temperature and cement type. On the other hand, in the cracked specimens some ettringite and/or thaumasite was found into the cracks of the specimens kept at 5°C, particularly when they were prepared with blended cement at 30% of ground limestone. This appears to be merely related to a higher water-cement ratio at a given water-binder ratio.

Keywords: blended cements, ettringite, limestone-portland cement, sulfate attack, thaumasite

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INTRODUCTION

Due to the shortage of energy resources and environmental problems, blended cements, instead of pure portland cements, are successfully being used all over the EU specially after the advent of the European Norm EN 197-1 (1) for the standards of cement. One of the most used blended cement is the limestone-portland cement with two ranges of limestone content: 6-20% for CEM II A-L and 21-35% for CEM II B-L.

Moreover, Barker and Hobbs (2) have found that mortar specimens with limestone-blended cements are more vulnerable than the corresponding mortars with normal portland cements when exposed to environments containing sulfate salts.

The aim of the present work is to confirm the above hypothesis in order to establish if the concrete structures made of limestone-portland blended cements really run a greater risk of deterioration due to sulfate attack, with respect to those manufactured with normal portland cements.

MATERIALS AND TECHNIQUES

Since the sulfate attack deals with the cement matrix, cement paste specimens rather than concrete specimens were studied in order to assess in a better way the changes related with the above type of chemical attack.

Prismatic specimens (40x40x160 mm in size) made of cement paste with a water-binder ratio of 0.40 were manufactured, where the term “binder” includes both pure portland cement and blended cements. The pastes differed in the type of cement used. The first mixture was manufactured with pure portland cement (CEM I 52.5 R according to the EN 197-1 European Norm), the second one with a blended cement containing 15% of limestone (CEM II A-L 42.5R) and the third one with blended cement containing 30% limestone (CEM II B-L 32.5R). Table 1 shows the chemical analysis of portland cement and limestone, the composition of the cement pastes, and the w/c as well as the water/binder (w/b), adopted for manufacturing the cement paste specimens.

In the mixture with portland cement the w/c coincides with the w/b ratio of 0.40 whereas for the other two mixes the w/c is significantly higher (0.47 or 0.57) for the presence of CaCO₃ (15% or 30%).

The specimens demoulded at 1 day were all cured for a week inside a thermostatic box at 20°C and R.H > 95%. Subsequently, the curing of the specimens was diversified in order to investigate the influence of the temperature. Two different curing temperatures (5° and 20°C) were chosen for the specimens kept under tap water. After this preliminary curing at 5° and 20°C for 28 days, the specimens were exposed to an aggressive environment represented by an aqueous Na₂SO₄ solution (10%) at 5°C or 20°C. Since no evidence of damage was detected after 3 months of continuous immersion under the sulfate aqueous solution, the specimens were submitted to wet/dry weekly cycles for four months. Each cycle consisted in drying at 40°C for 2 days and immersion in the sulfate solution for 5 days at 5°C or 20°C.

The investigation carried out consisted in visual inspection for detecting any sign of damage. Moreover X-Ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) observation and Energy Dispersive Analysis X-Ray (EDAX) technique were used to examine the material withdrawn from the surface inside the damaged surface. In addition, observations with the optical microscope were carried out to assess the presence of any crack widening during each cycle.

RESULTS AND DISCUSSION

At the end of the first step of exposure to the sulfate (continuous immersion under the sulfate aqueous solution) the specimens kept at both 5°C and 20°C showed no sign of damage. During the second step of exposure to sulfate, characterized by wet/dry cycles, the formation of a network of cracks appeared after the first week (Fig. 1). Subsequently, no particular change was observed up to 120 days of cyclic exposure at 5°C; during the drying period of each cycle the microcracks opened and during the wetting period they closed.

The cracks produced in order to favor the aggressive solution penetration, to accelerate the sulfate aggression and especially to highlight the different performances of the three cements, did not lead to the expected results.

Only moderate damage in the specimens, limited to a surface layer about one millimetre deep, was recorded in the worst situation after 4 months of cyclic wet/dry exposure to sulfate at 5°C (Fig. 2). Figure 3 shows the typical morphology of ettringite fibrous crystals deposited into a crack of a pre-cracked specimen cured at 5°C and immersed in the Na₂SO₄ solution at 5°C. The chemical analysis by EDAX (Fig. 4) shows the presence of Ca, Al and S with traces of Si corresponding to a mixture of ettringite (C₃A·3CaSO₄·32H₂O) with minor amounts of thaumasite (CaCO₃·CaSiO₃·Ca SO₄·15H₂O) rather than to pure ettringite (3,4).

The combined use of SEM and EDAX is very useful to distinguish the morphology of C-S-H and ettringite crystals (both of fibrous character). For instance Figs. 5 and 6 show the morphology by SEM, and the chemical analysis by EDAX, respectively, for a typical fibrous microstructure observed in some cracks.

Small fragments of material withdrawn from the cracks were analyzed by XRD. Figure 7 shows the typical peaks of ettringite (E), thaumasite (T), gypsum (G) and calcium hydroxyde (CH): there was negligible difference in the XRD patterns of materials withdrawn from cracks in specimens manufactured with pure portland cement or blended limestone-Portland cement. In the cracked specimens manufactured with blended cement containing 30% of ground limestone, there is some thaumasite accompanying the ettringite crystals, and therefore confirming the EDAX analysis shown in Fig. 5.

CONCLUSIONS

There is no significant difference in the sulfate resistance of cement pastes manufactured with Portland cement or blended limestone portland cement.

It appears that only in pre-cracked specimens, cured at 5°C and kept at 5°C in a cyclic wet/dry exposure to sulfate, there is slightly more evidence of ettringite/thaumasite formation when a blended portland cement with 30% of ground limestone was used instead of the other cements. This small difference in the behavior seems to be related with a higher w/c, at the same water/binder, for the blended cement with respect to a pure portland cement.

Since the actual w/c of the paste with the higher limestone content (30%) is 0.57 vs. 0.47 or 0.40 for the others cements (Table 1), we can conclude that there is no evidence of any damage caused by the presence itself of CaCO₃ even when it is relatively high as in the CEM II/B-L 32.5R according to the European Norm EN 197-1.

REFERENCES

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Table 1 - Mix proportions of the cement pastes at the same water/binder (w/b) ratio.

Portland Cement *	Limestone **	Cement Type (European Designation)	w/b	w/c
100	0	CEM I 52.5 R	0.40	0.40
85	15	CEM II/A-L 42.5 R	0.40	0.47
70	30	CEM II/B-L 32.5 R	0.40	0.57

* Chemical composition (%): CaO = 65.1% ; SiO₂ = 21.4% ; Al₂O₃ = 6.2% ; Fe₂O₃ = 2.4% ; SO₃ = 3.1% ; Na₂O = 0.1% ; K₂O = 1.1% ; Blaine fineness = 400 m²/kg

** Chemical composition (%): CaCO₃ = 98.7% ; SiO₂ = 0.8% ; Fe₂O₃ = 0.1% ; Al₂O₃ = 0.1% ; Blaine fineness = 395 m²/kg.

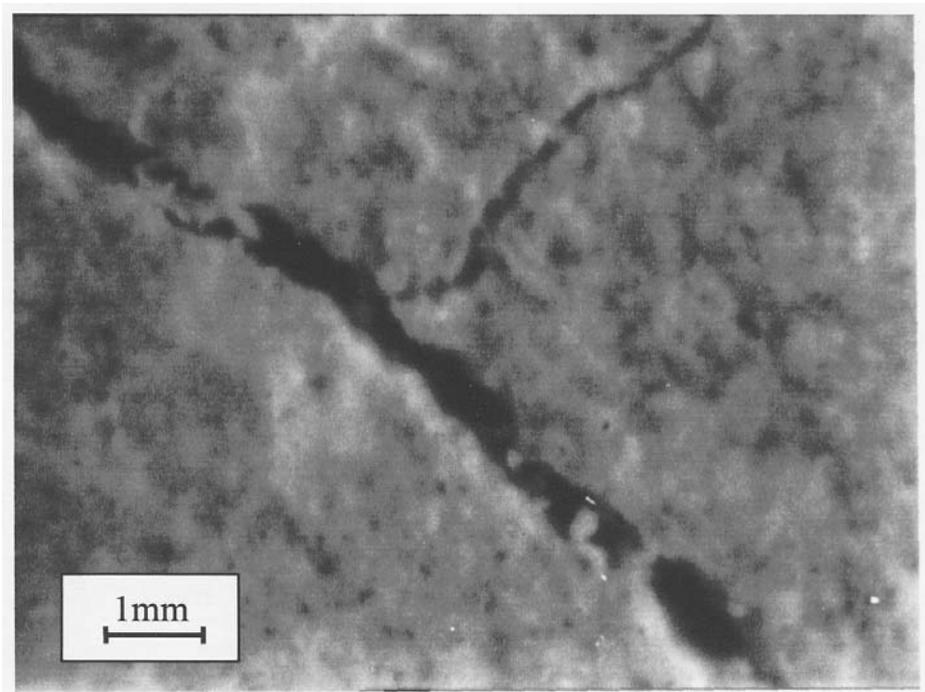


Figure 1 – Typical cracks observed by optical microscope after the first wet/dry cycle.

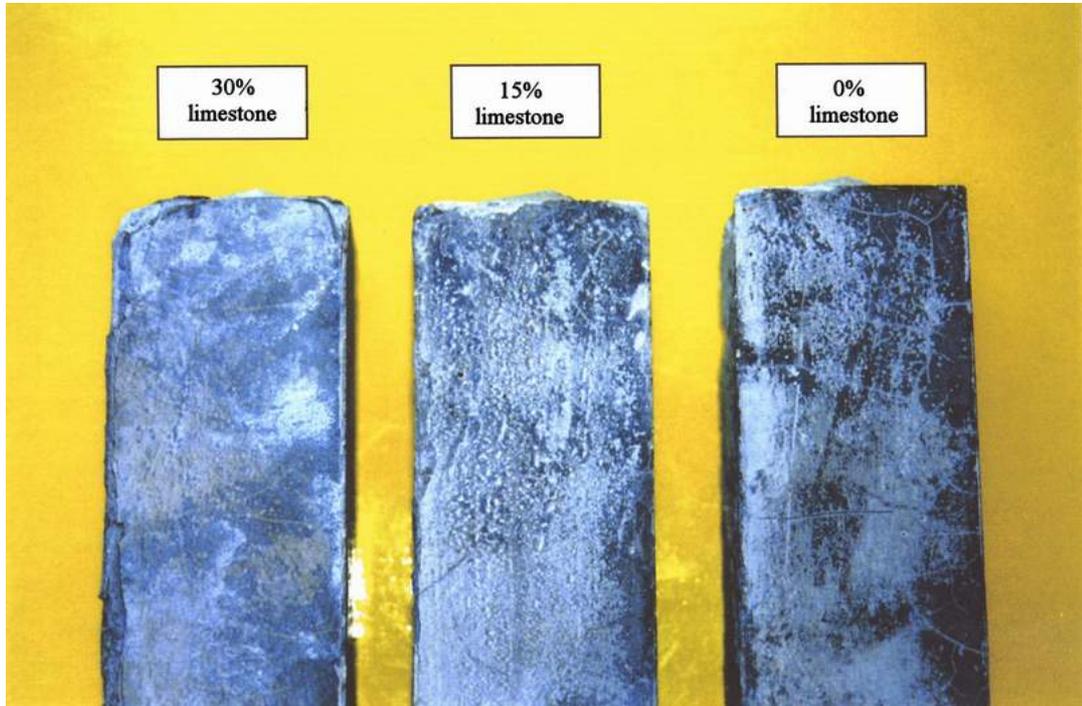


Figure 2 – Visual observation of cracked paste specimens with different limestone percentage in the cement after cyclic wet/dry exposure to sulfate at 5°C.



Figure 3 – Morphology of ettringite and/or thaumasite crystals grown into a crack formed by immersion in sulfate solution (2 days at 5°C) alternated with a drying period of 5 days at 40°C.

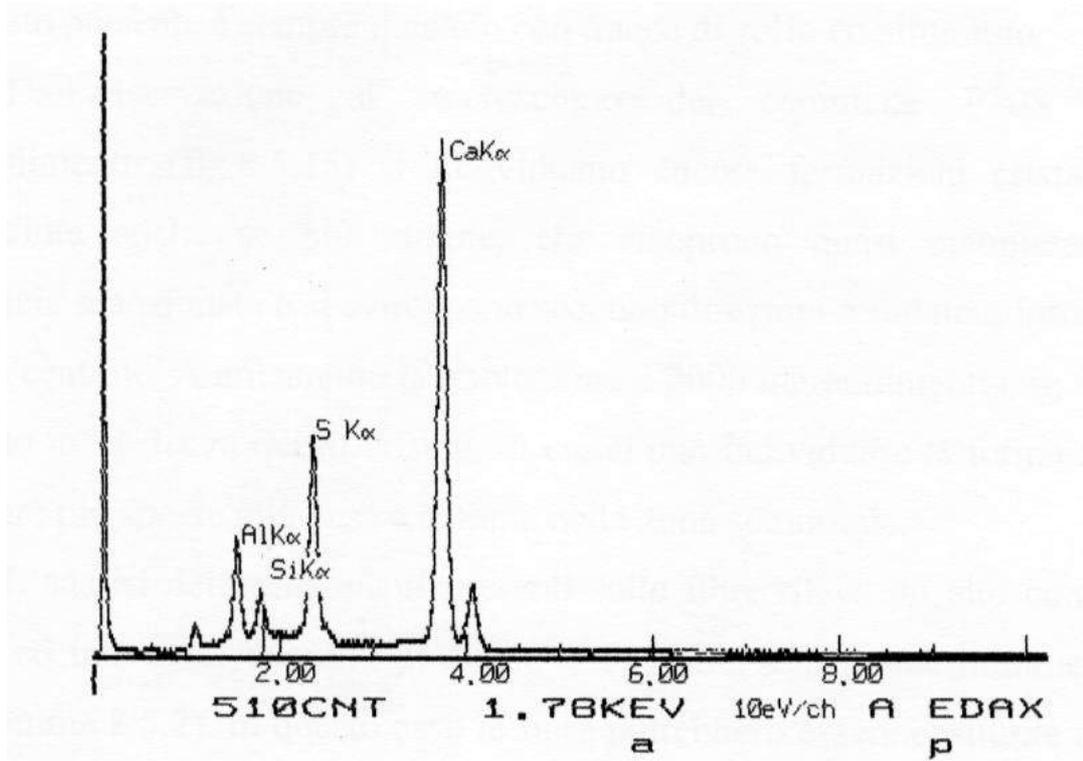


Figure 4 – EDAX analysis of crystals (shown in Fig. 3) deposited into a crack. The presence of Ca, S, Al with traces of Si correspond to a mixture of ettringite and thaumasite.

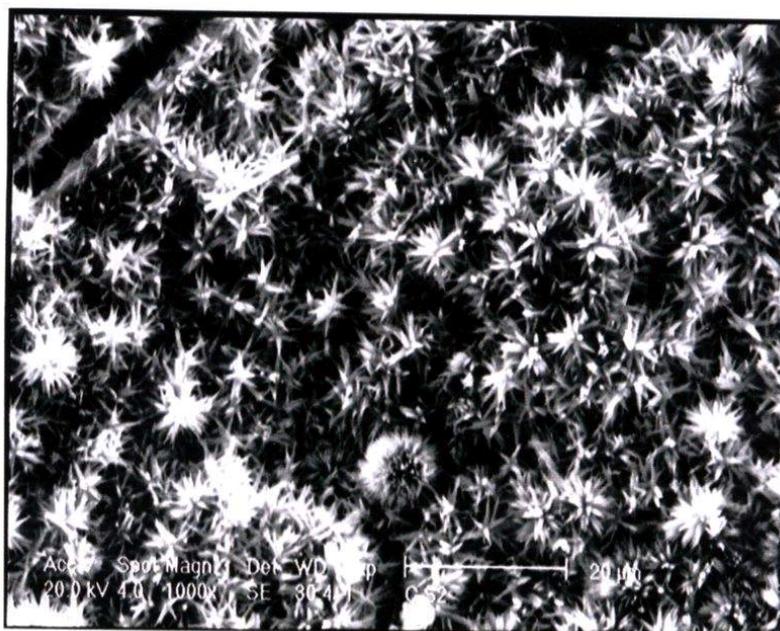


Figure 5 – Morphology of fibrous crystals of C-S-H as confirmed by EDAX analysis in Fig. 6.

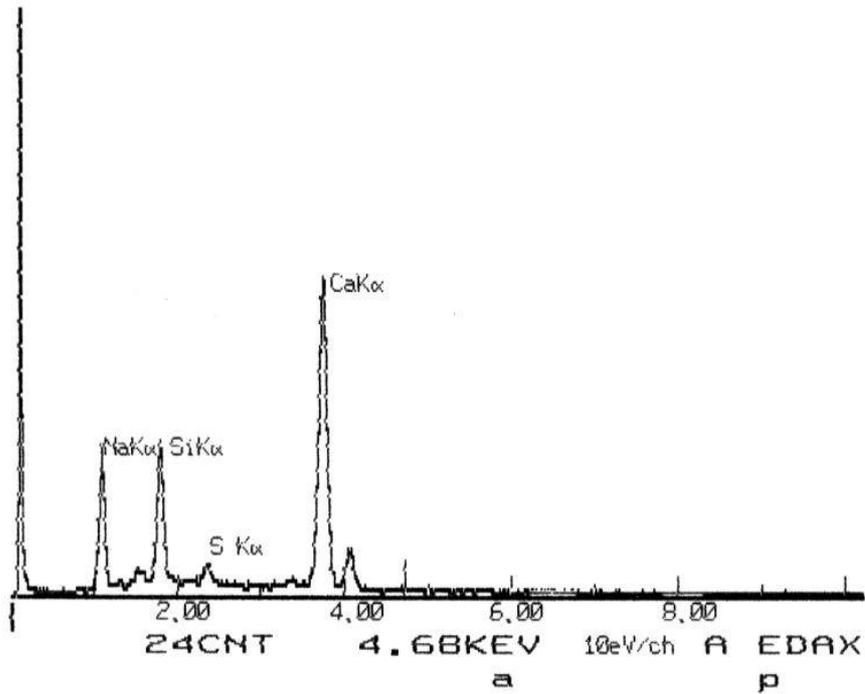


Figure 6 – EDAX analysis indicating the presence of Ca and Si (inquinated by Na_2SO_4) corresponding to the C-S-H crystals of Fig. 5.

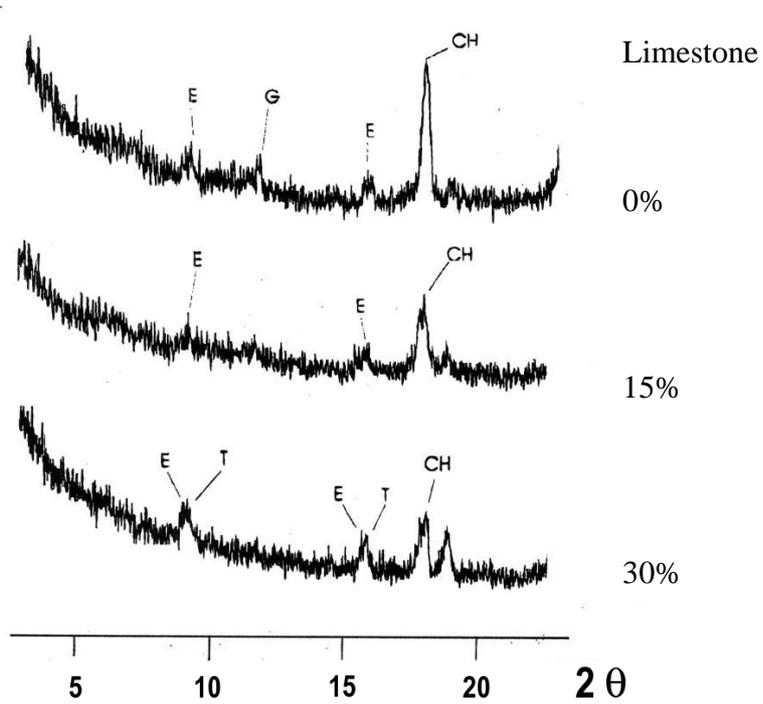


Figure 7 – XRD patterns of three types of pastes kept in sulfate solution, at the end of the experimentation. (E: Ettringite; T: Thaumassite; G: Gypsum; CH: Calcium Hydroxide).