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ARTICLE

Effect of the Addition of Microsilica on the Durability of Mortars Exposed To the Sodium Sulfate Attack

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Abstract: This article presents a detailed experimental study on the sulfate attack of mortars of self compacting concrete, and the effectiveness of employs microsilica and limestone fillers in the minimization of the damage resulting from such an attack. The test solution used to supply the sulfate ions and the cations was the sodium sulfate solution 4.5%. The solution saturated with lime was employed as the reference solution. The main variables investigated in the study were the type of cement and mineral addition. The expansion measured on prisms of mortar of (40x40x160) millimeters was employed to estimate their durability after exposure to the sodium sulfate solution attack during 91 days. Specimens of mortars were visually examined to assess the extent of deterioration due to the sulfate attack. The x-ray diffraction was used to evaluate the microstructural nature of the sulfate attack. The test results proved that the use of microsilica had a beneficial effect on the expansion due to the sodium sulfate attack. While mortars with limestone filler have undergoes degradation even with the use of cement resistant to sulfates.

Keywords: Microsilica; Limestone filler; Sodium sulfate attack; Mortars, Expansion.

Introduction

It has been recognized for a long time that the presence of sulfate ion in soils can cause severe damage to concrete structures. Until now, however, the exact definition of the mechanism of attack seems very difficult because of the complexity of its behavior. Indeed, many factors such as cement type, cation sulfate type, sulfate concentration and exposure period can affect the sulfate resistance [1, 2]. This attack was often been discussed in terms of chemical reaction between the hydrates in cement paste (C_3A and $Ca(OH)_2$) and the dissolved compounds, such as sodium sulfate in the attacking solution and by the reaction of SO_4^{2-} ions to form expansible products (ettringite and gypsum).

Several ideas were suggested to increase the resistance of concrete against the sulfate attack by decreasing porosity (contained high amount of cement or low water-cement ratio) or by

improving resistance (cement resistant to sulfate or addition of pozzolanas).

Researchers have reported on the sulfate resistance imparted by microsilica, which is generally incorporated in concrete to improve its technological proprieties and its durability. This excellent resistance is related to the filling action of microsilica because of its fine particles size, and pore refinement process occurring due to the conversion of portlandite into secondary C-S-H gel, through strong pozzolanic reaction [1, 2].

The aim of this work is to develop a comparative evolution of the sodium sulfate 4.5% resistance and durability of microsilica mortar and limestone fillers mortar, with two different cements. An experimental device was thus developed to obtain conclusive results about the effect of use of mineral additions of different reactivity.

Experimental

Materials

In the tests reported in this paper, studies of expansion of mortars samples (4x4x16 (cm)) were carried out. Two cements were used, an artificial Portland cement CPJ CEM II/A 42,5 produced by Ain El Kebira and cement resistant to sulfates CPA CEM I/42,5 produced by Lafarge. The chemical compositions of cements used in this investigation are shown in Table 1.

Two mineral additions were employed, a microsilica with a density of 2.15 g/cm³ and a limestone filler of density of 2.62 g/cm³. Chemical compositions of these additions are illustrated in Table 2.

TABLE 1. Chemical and mineralogical composition of cements

	CEM I	CEM II/A
	42,5	42,5
MgO (%)	1.7	0.17
SO ₃ (%)	1.9	1.00
Loss on ignition (%)	1.5	0.24
Insoluble residue (%)	0.7	2.64
C ₃ S (%)	57.00	61.34
C ₂ S (%)	19.00	17.00
C ₃ A (%)	3.00	5.59
C ₄ AF (%)	14.00	11.93

TABLE 2. Chemical composition of additions

	Limestone filler	Microsilica
SiO ₂ (%)	42.00	92.1
Al ₂ O ₃ (%)	0.0	0.25
Fe ₂ O ₃ (%)	0.0	0.79
CaO (%)	54.84	-
MgO (%)	0.1	-
SO ₃ (%)	0.6	0.36
Na ₂ O (%)	0.02	0.17
K ₂ O (%)	0.1	0.96

The water/cement ratio of all the mixtures of mortar examined in this study was 0.5 and the water /cementitious materials ratio was 0.45. In order to obtain adequate workability for a mortar of self-compacting concrete, the use of a superplasticizer was indispensable.

MEDAFLUID SFR 122 chemical admixture was incorporated in the mortar mixture with a proportion. The superplasticizer was added to the mixing at a level of 1.5% by mass of total

cement. River bed sand of density 2.5 g/cm³, with a maximum size of 3 mm, was used as the fine aggregate in all mortar mixtures.

Exposure of mortar samples

The mortars were cast in prisms of (4x4x16 cm)). the mortar samples were cured in a saturated Ca(OH)₂ solution during 12 days. At the end of this period, some samples were remained in the preceding solution, employed as reference solution for control samples. Some samples were moved to sodium sulfate solution (Na₂SO₄) of 4.5 % concentration and kept continuously immersed for predetermined periods.

The sodium sulfate solution used for the immersion tests is renewed every 4 weeks to reduce the increase in pH due to the leaching of OH⁻ ions from the mortar specimens and cement paste (to avoid reaching the pH of saturated Ca (OH)₂ solution and to compensate for the loss of the concentration of the sulfate solution due to the process of degradation).

TABLE 3. Composition of mortars specimens

	MSCII (Kg/m ³)	MFCII (Kg/m ³)	MFCI (Kg/m ³)
CEM II	625	625	-
CEM I	-	-	625
Sand 0/3	1073	1073	1073
Limestone filler	-	69.5	69.5
Microsilica	69.5	-	-
Water	312.5	312.5	312.5
Superplasticizer	9.39	9.39	9.39

The deterioration of the mortar samples was studied by evaluating their expansions for predetermines periods (14, 21, 28, 56 and 90 days). At each age of test, three specimens of each type of mortar were placed on the comparator and their expansions were determined, and then their values were brought to an average. The morphological changes of the cement hydrates, due to the exposure to the sodium sulfate solution, were studied using the x-ray diffraction, which provides semi-quantitative information on the elementary composition of the mortar.

Results and discussions

Visual examination

A thorough visual examination was carried out every month on the mortars cured without

interruption in the sodium sulfate solution and saturated $\text{Ca}(\text{OH})_2$ solution to evaluate the visible signs of degradation (material damages) and spalling on surfaces of mortar specimens.

No surface sign deterioration was detected on the mortar samples after 90 days of immersion in the test solutions. No sign of spalling was observed and no layer of white material was found deposited on the faces of the mortars, as shown in figs. 1 and 2; that confirms the results obtained by Dehwah (2007) [3]. This result is in agreement with that found by Wee *et. al* (2000), which concluded that a replacement of cement by 5 to 10% of microsilica played a key role in resisting sodium sulfate attack, indicating no signs of spalling after about 1 year of exposure to 5% Na_2SO_4 [4].



Fig. 1. Mortars preserved in the 4.5% sodium sulfate solution during 90 days.



Fig. 2. Mortars preserved in the saturated lime solution during 90 days

Day and Ward (1988) observed expansions of 1% and more, accompanied by the significant reductions of the mechanical properties of the samples without any surface sign degradation

[5]. According to Hill *et. al* (2003), mortars preserved in the saturated $\text{Ca}(\text{OH})_2$ solution (control solution) were not faded and the visual examination did not show any sign of degradation, which is in agreement with the results of our study [6].

Figs 1 and 2 show the results of the visual examination of mortar specimens subjected to sulfate attack after 90 days of immersion in the test solutions.

Morphological changes

The XRD patterns, shown in Figures 3, 4 and 5, were obtained for samples scraped from the surface of the mortar specimens conserved in the test solutions. The diffractogram, shown in figure 3, indicate a veritable difference between the two samples from the two solutions. Especially in MSC II (Na_2SO_4), an abundant presence of ettringite was detected. Indeed, three peaks were detected at 35.9° , 42.4° and 47.63° 2θ for ettringite, in addition to portlandite with weak peaks intensities and gypsum at 29.4° and 35.9° 2θ . On the other hand, as shown in figure 4, signs of degradation of mortars exposed to the sodium sulfate solution (graph MFCII(Na_2SO_4)) were observed, and this according to the concomitant presence of ettringite, thaumasite, portlandite and gypsum. Indeed, gypsum peaks were detected at 29.3° and 35.9° 2θ . A thaumasite peak at 50.6° 2θ was observed in figure 3. Ettringite and portlandite were present as several weak and average intensity peaks. Figure 5 shows resemblances of diffractograms MFCI(sulfate) and MFCI(lime) on the level of the portlandite peaks intensities and angles of their detections. This element showed important intensities at 18.06° , 34.09° and 50.7° 2θ . In addition to the portlandite, diffractogram MFCI(Na_2SO_4) shows a concomitant presence of ettringite at 32.1° 2θ , gypsum and thaumasite. Indeed, three gypsum peaks were detected at 2θ of 29.45° , 35.9° and 45.8° . Two peaks of thaumasite, one at 27.9° 2θ and another at 47.6° 2θ , were noted. The decrease in CSH during the reaction with the gypsum and limestone promotes the appearance of thaumasite. The XRD Data shows that the peaks of CSH are very low in sulfate solutions. In other XRD Data is not the case.

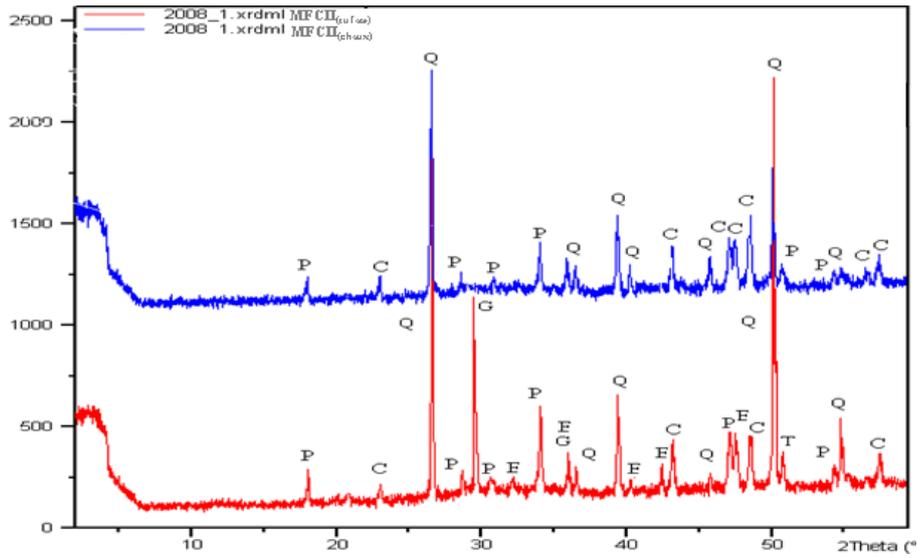


Fig. 3. XRD of mortars MSCII preserved in the solutions Na₂SO₄ and Ca(OH)₂ during 90 days. (P = portlandite, C = calcite, Q = quartz, E = ettringite, T = thaumasite, G = gypsum).

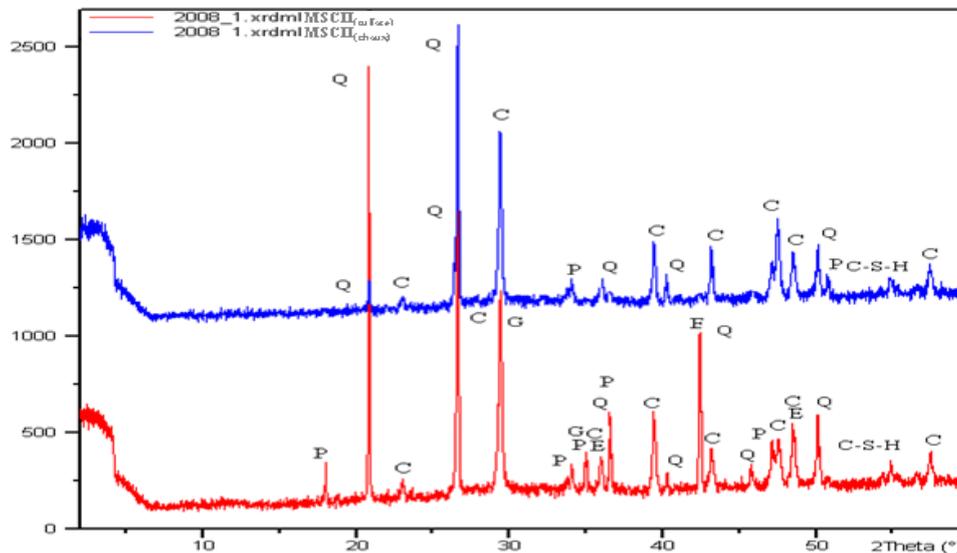


Fig. 4. XRD of mortars MFCII preserved in the solutions Na₂SO₄ and Ca(OH)₂ during 90 J. (P = portlandite, C = calcite, Q = quartz, E = ettringite, T = thaumasite, G = gypsum, C-S-H = calcium silicate hydrated).

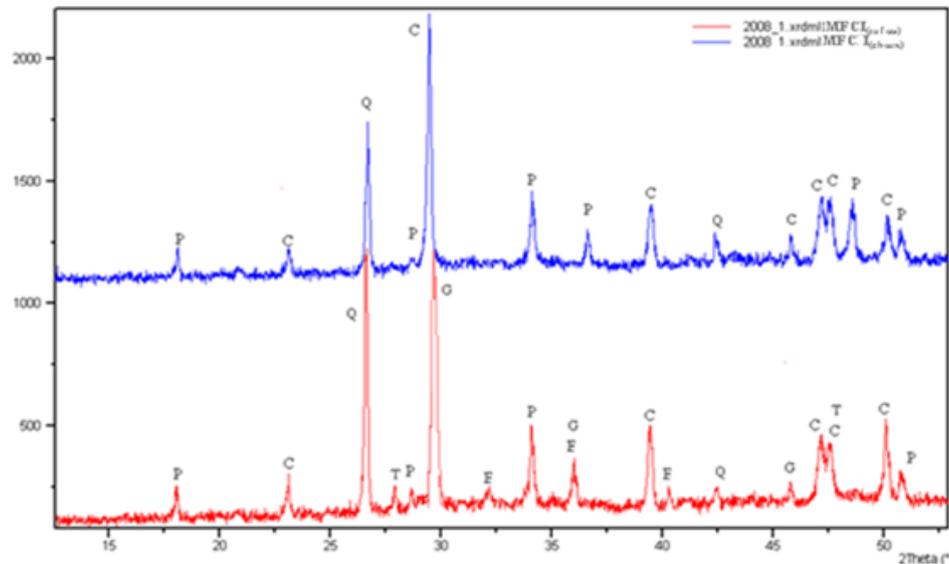


Figure 5: XRD of mortars MFCI preserved in solutions of Na₂SO₄ and Ca(OH)₂ during 90 J (P= portlandite, C=calcite, Q= quartz, E=ettringite, T=thaumasite, G=gypsum).

Expansion

Fig. 6 shows the test results of expansion of the mortar specimens conserved in the sodium sulfate solution. The expansion of mortars MFCII (mortars with limestone filler and cement CEMII) is much more important. It is approximately 940 $\mu\text{m}/\text{m}$ at 90 days, compared to mortars MSCII (mortars with microsilica) and MFCI (mortars with limestone filler and cement CEMI) which have expansions of 788 and 511 $\mu\text{m}/\text{m}$ at 90 days respectively. According to these curves, we see well that mortar MFCI is most resistant to sodium sulfate.

This is due to the small quantity of the phase of calcium aluminate hydrates (C_3A) with the predominance of the clinker (the only component of this cement) which generates more

calcium silicate hydrates. This result forms a compact concrete with a high resistance and durability. Mortar MSCII seems to be of important resistance to sodium sulfate, which is ensured by the fine particle size of microsilica which makes the unit very compact and impermeable to the aggressive solutions.

The prolonged hydration of the free lime which is in excess in mortars MFCII(sulfate) and MFCI(sulfate) (mortar with limestone filler) formed the portlandite which caused constraints by its crystalline growth, thereafter, an increase in volume. The low content of portlandite in MSCII(sulfate)

The introduction of microsilica in mortars can block the pores [7].

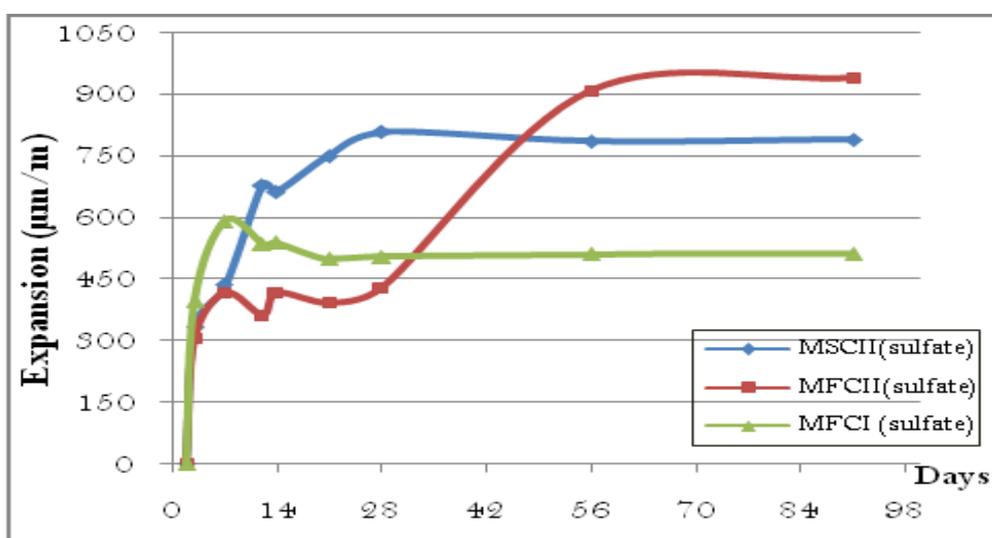


Fig. 6: Expansion of the mortars in the sodium sulfate solution.

According to Lachaud (1979), the portlandite is hydrated in MSCII(sulfate) and forms ettringite which does not cause an important expansion because of its weak specific surface and its weak adsorption capacity with respect to water [8].

Based on the small quantity of the portlandite (which is consumed by microsilica to form the C-S-H) in MSCII(sulfate), the ettringite formed is not expansible in spite of its high rate, this result agrees well with the results of Mehta (1973 a, b) which was observed, when the portlandite is in small quantity, the ettringite formed as coarse crystals of about 60 μm check labeling inside the figures with caption that have a weak specific surface and thus a weak adsorption and expansion capacity [9, 10].

Tian and Cohen (2000) showed in their study, that the formation of the gypsum by the external sulfate attack can cause a significant expansion even when the formation of the ettringite is excluded [11].

Even the mortar of cement CEMI (MFCI(sulfate)), which is supposed to be resistant to sulfates, marked a light swelling in the sodium sulfate solution. This expansion is appreciably slower and less severe than in MFCII(sulfate) mortar (cement CEMII). According to Eglinton (1998) and Lota (1995), the principal reason of the mortar resistance with respect to sulfates is due to the low quantity of calcium aluminate hydrates (C_3A) [12, 13].

Conclusions

This manuscript presented a detailed study of the process of degradation of the prisms of mortars in the environment of sodium sulfate, and evaluated the potential consequences of the use of mineral additions of different reactivity's, on the durability of the three compositions of mortar of self- compacting concrete.

The use of microsilica has a beneficial effect on the reduction of the expansion of the mortars in the aggressive solution, because of its strong

pozzolanic reaction and the consumption of the calcium hydroxide.

However, the addition of limestone filler did not prevent the expansion, and the formation of thaumasite. Even the use of cement resistant to sulfates (CPA-CEM I / 42.5) did not eliminate the expansion; consequently, the addition of limestone filler is to be avoided in the sodium sulfate environments.

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