Mechanical behavior of self compacting concrete equivalent mortar attacked by sodium sulfate solution

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Abstract. This article presents an experimental study of self compacting concrete equivalent mortar, and the effectiveness of microsilica and limestone fillers in minimization of the damage resulting from such attack. The test solution employed to provide the sulfate ion and cation was 4.5% sodium sulfate solution. 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 admixture. Compressive strength and flexural strength measured on (40x40x160) mm specimens were used to assess their mechanical properties after three months of exposure to sodium sulfate solution. Masses of mortar specimens were evaluated in time to determine the extent of deterioration. X-ray diffraction was used to evaluate the microstructural nature of the sulfate attack. The test results showed that the use of microsilica had a beneficial effect on the increase of durability and the mechanical resistance of mortars, as for limestone filler, its incorporation in the formulation of mortars generated a loss in their mechanicals properties caused by their expansions.

1 Introduction

External sulfate attack covers all phenomena of degradation of the concrete in which the aggressive agent is the SO_4^{2-} ion of sulfate. These sulfates can be of natural, biological origin or come from domestic and industrial pollution, which around a concrete structure constitute a threat for its durability. However, until nowadays, the exact definition of the mechanism of attack seems very difficult because its chemistry is complex and involves numerous overlapping reactions. Indeed, many factors such as the type of cement, the type of sulfate cation, the sulfate concentration and the period of exposure can affect resistance to sulfate. This attack has often been discussed in terms of the chemical reactions between the cement hydration products (C_3A and $Ca(OH)_2$) and dissolved compounds, such as sodium sulfate, in the attacking solution, by the reaction of ions SO_4^{2-} to form expansible products (ettringite and gypsum) [1, 2]. This attack is accompanied by a precipitation of sulfate products known as "secondary", by an expansion and chemico-mechanical deterioration: loss of strength, cohesion and porosity with cracking [1, 3]. That leads to the ruin of cementitious materials.

Several ideas were suggested to increase the resistance of concrete against the sulfate attack by decreasing porosity (high rate of cement, low water/cementitious ratio) or by improving resistance (cement resistant to sulfate, addition pozzolanas).

Researchers have reported on the sulfate resistance imparted by microsilica, which is generally incorporated in concrete to improve its mechanical proprieties and durability. This excellent resistance is related to the filler action of microsilica because of its fine particles size, and the pore refinement process occurring due to the conversion of portlandite into secondary C-S-H gel (Calcium silicates Hydrate), through pozzolanic reaction [4, 5].

The purpose of this work is to develop a comparison of the mechanical strength evolution of self-compacting concrete equivalent mortar containing microsilica and that containing limestone filler in 4.5% sodium sulfate solution.

2 Experimental procedures

2.1 Materials

2.1.1 Cement

Two cements, CEM II/A 42.5 and CEM I/42.5, were used throughout in this research. Their chemical and mineralogical compositions are as given in Table 1.

Table 1. Chemical and mineralogical compositions of cements.

Component (%)	CEM I 42.5	CEM II/A 42.5
SiO_2	22.30	21.26
Al_2O_3	5.10	3.83
Fe_2O_3	3.99	2.91
CaO	63.60	61.22
MgO	1.70	1.17
SO_3	1.90	2.05
Na_2O	0.34	0.20
K_2O	0.70	0.95
Loss on ignition	1.5	6.24
Insoluble residue	0.7	2.64
C_3S	57.00	61.34
C_2S	19.00	17.54
C_3A	3.00	5.59
C_4AF	14.00	11.93
Admixture (limestone)	0.00	15

2.1.2 Mineral admixtures

Two mineral admixtures were employed, a microsilica with a density of 2.15 g/cm^3 and a limestone filler with a density of 2.62 g/cm^3. Chemical compositions of these additions are illustrated in table 2.

Table 2. Chemical composition of mineral additions.

Component (%)	Limestone filler	Microsilica
SiO_2	0.5	92.1
Al_2O_3	0.0	0.25
Fe_2O_3	0.0	0.79
CaO	54.84	-
MgO	0.1	-
SO_3	0.6	0.36
Na_2O	0.02	0.17
K_2O	0.1	0.96

2.1.3 Aggregates

River sand, with a maximum size of 3 mm, was used as the fine aggregate in the mixture. The specific gravity and fineness modulus of the fine aggregate were 2.5% and 2.59% respectively.

2.1.4 Chemical admixtures

In order to obtain adequate workability for a self-compacting concrete equivalent mortar, the use of a superplasticizer was necessary; the chemical admixture employed during this study was a superplasticizer high water reducing with density 1.22 and pH 6.5 at a level of 1.5% by weight of total cement.

2.2 Mixture proportions

The Formulate a self-compacting concrete is a complex operation that requires finding a good combination of compatible materials and the proper dosage of each of these components in order to obtain a formulation that meets their properties. Several methods of formulation have been developed and that which is focused in this paper is that originally proposed by the research team of professor Okamura, called Japanese method.

In this study, three mortars equivalent to a self-compacting concrete mixes were made, which had total powder content of 694,5 kg/m^3 (cement + mineral admixture). The mortar mixes (MSCII, MFCII, MFCI) were made by adding 11% of mineral admixture by weight of cement. Their mix proportions are given in Table 3. The water/cement ratio of the mortar mixtures proportions was 0.5 and the water/cementitious materials ratio was 0.45.

The mixing of all the mortar was carried out using the appropriate amounts of cementitious materials, sand and water with the added of superplasticizer. The sequence of mixing retained is that recommended for concrete with microsilica which is the following [6]: first, mixing 75% of water and microsilica during one minute and half. Then, adding to the mixture cement and mixing again during one minute and half. After that, mixing fine aggregates, superplasticizer (diluted in the remainder of mixing water) during five minutes, rest for three minutes. Lastly, mixing the unit during five minutes.

Table 3. Mix proportions of mortars.

Materials (Kg/m^3)	MSCII	MFCII	MFCI
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

2.3 Casting, curing and testing of specimens

Mortar samples were cast in prisms of (40x40x160) mm and demoulded after two days. After then, mortar samples were cured in a $Ca(OH)_2$ saturated solution during 12 days. At the end of this period, some samples were remained in the preceding solution, used as reference solution for control samples. Some of other were moved to sodium sulfate solution (Na_2SO_4) of concentration of 4.5 % and kept continuously immersed for predetermined periods.

The sodium sulfate solution used for the immersion tests was renewed every four weeks to reduce the increase in pH due to the leaching of OH^- ions from the mortar and paste specimens (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).

The deterioration of the mortar prismatic samples was investigated by evaluating their mechanical strength for predetermines periods (14, 21, 28, 56 and 91 days). At each test age, the flexural strength and the compressive strength of samples were measured. The morphological changes of cement hydrates, due to the exposure to the sodium sulfate solution, were studied by using the X-ray diffraction, which provides semi-quantitative information on the elementary composition of the mortar.

3 Results and discussion

3.1 Microstructural analysis

The surface parts of the test samples were selected for XRD analysis. They were grounds by hand to a fine powder of <63 µm, and the XRD test was conducted using monochromatic CuKα radiation.

Patterns shown in figure 1 indicate a veritable difference between the two samples coming from the test solutions. Especially in graph MSC II$_{(Na2SO4)}$, an abundant presence of ettringite was detected. Indeed, three peaks were detected at 35.9°, 42.4° and 47.63° 2θ. In addition to portlandite at weak peaks intensities and gypsum at 29.4° and 35.9° 2θ. On the other hand, as shown in figure 2, signs of mortars' degradation exposed to sodium sulfate solution (graph MFC II$_{(Na2SO4)}$) 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 shown. Figure 3 shows resemblances of diffractograms MFC I$_{(Na2SO4)}$ and MFC I$_{Ca(OH)2}$ on the level of portlandite peaks intensities and angles of their detections. This element was marked important intensities at 18.06°, 34.09° and 50.7° 2θ. In addition to portlandite, diffractogram MFC I$_{(Na2SO4)}$ showed a concomitant presence of ettringite at 32.1° 2θ, of thaumasite and gypsum. Indeed, three gypsum peaks were detected at 29.45°, 35.9° and 45.8° 2θ. Two peaks of thaumasite, one at 27.9° 2θ and another at 47.6° 2θ were noted.

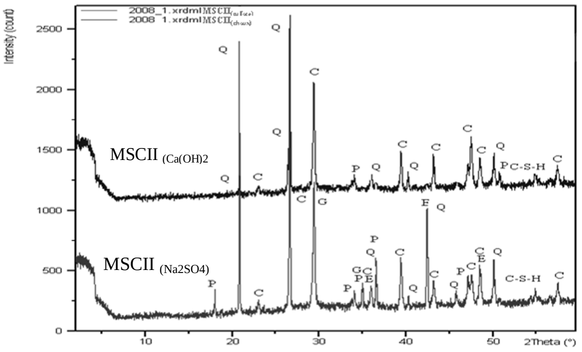

Fig. 1. XRD of MSCII mortars stored in Na_2SO_4 and $Ca(OH)_2$ solutions for 91 days. (P= portlandite, C= calcite, Q= quartz, E=ettringite, T= thaumasite, G= gypsum, C-S-H=calcium silicate hydrated).

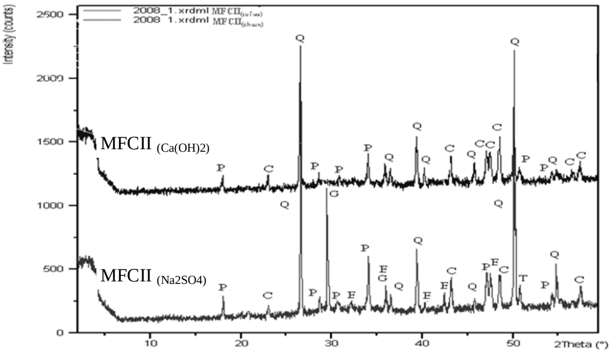

Fig. 2. XRD of MFCII mortars stored in Na_2SO_4 and $Ca(OH)_2$ solutions for 91 days. (P= portlandite, C=calcite, Q= quartz, E=ettringite, T=thaumasite, G=gypsum).

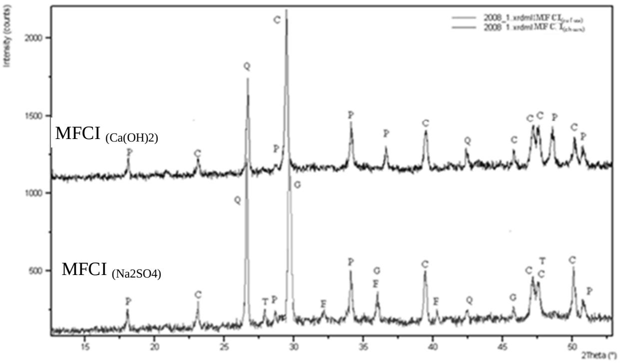

Fig. 3. XRD of MFCI mortars stored in Na_2SO_4 and $Ca(OH)_2$ solutions for 91 days (P= portlandite, C=calcite, Q= quartz, E=ettringite, T=thaumasite, G=gypsum).

3.2 Evaluation of the masses

Figure 4 shows the test results of mass change versus time for mortar specimens exposed to the test solutions for 91 days. The percentage gain in mass with time for MSC II(Na_2SO_4) and MSC II$_{Ca(OH)2}$ mortars was higher than that for MFC II$_{(Na2SO4)}$, MFC II$_{Ca(OH)2}$, MFC I$_{(Na2SO4)}$ and MFC I$_{Ca(OH)2}$.

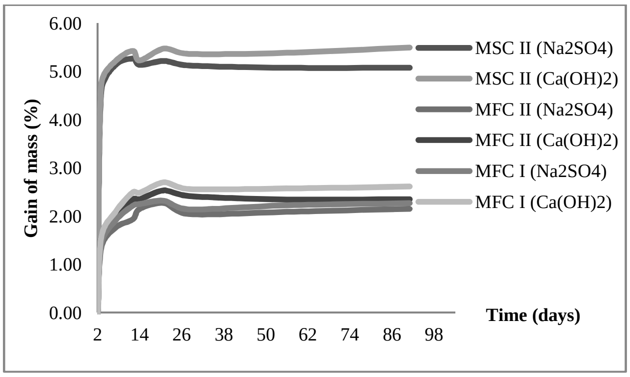

Fig. 4. Masses evolution of mortar samples versus time.

The mass increase of mortars stored in sulfate solution came from water absorption to fill the vacuums, products of cement paste hydration and water used to precipitate the phase of ettringite. As the degradation of microsilica mortar is not deleterious, the mass increase is relied to the formation of hydration products (C-S-H) which confer on material its density and compacity [7]. All mortars marked a catch of mass. Rozière et al. (2009) and El-Hachem et al. (2012) explained the mass increase by the swelling caused by gypsum and/or ettringite formation in damaged mortar specimens. [7, 8]. Girardi et al. (2010) have also showed a constant slow increase in mass in specimens exposed to a sulfate solution alone, which was due mainly to the formation of calcium sulfate [9].

3.3 Mechanical resistance of mortar samples

3.3.1 Flexural strength

As reported earlier, the flexural strengths of all the test specimens were determined from (40x40x160) mm prismatic specimens. Figure 5 summarizes theses results at the ages of 14, 21, 28, 65 and 91 days of immersion in the test solutions.

It is noticed, according to the figure 5, that flexural strength of mortar samples increases with the time of immersion on the level of the two solutions, for all the period of the test (three months). The strength of specimens exposed to sodium sulfate solution is greater than those cured in $Ca(OH)_2$ saturated solution for the same period.

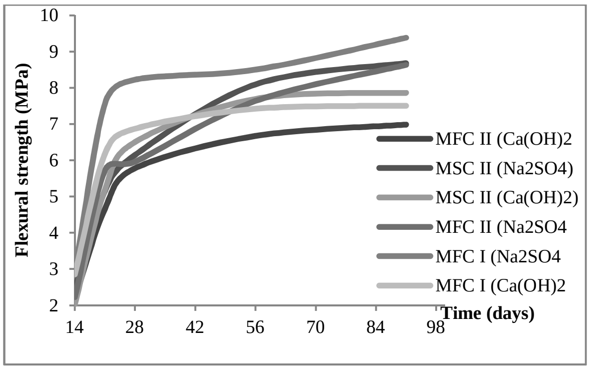

Fig. 5. Flexural strength versus time in the test solutions.

The increase in flexural strength of mortar samples, stored in the test solutions, was a macroscopic response of the absence of the cracks within materials even after three months of immersion. This result is also due to the strong compacity of mortar samples coming from the evolution of hydration of cement and formation of hydration products. Uysal and Sumer (2011) have concluded, based on the strength results, that mineral admixtures improve the resistance of Self compacting concrete's against sulfate attack [10]. According to Zhang MH et al. (2008), this increase was due to the effect of the nucleation and growth of delayed ettringite crystal. The ettringite crystal may penetrate cross the surface and get into cement mortar matrix. In this case, the ettringite crystal can reinforce the cement mortar just like short fiber. Therefore, the flexural strength of the material will be slightly increased [11].

3.3.2 Compressive strength loss

The loss of compressive strength was given by comparing the pressure resistance test of mortar samples stored in sodium sulfate solution with that of similar specimens stored in $Ca(OH)_2$ saturated solution. Measurements were made on half-prisms (40x40x80) mm, each value given in figure 6 is the average of six results of six half prisms.

In figure 6, we notice an increase in strengths of the three mortars up to two months of immersion, then a light decrease in strength of MFC II$_{(Na2SO4)}$ and MFC I$_{(Na2SO4)}$ mortars.

In the Ca(OH)2 saturated solution, an increase in strength for all samples is noted. The curves traced on this figure enable us to note the following remarks:

Strengths of mortars with microsilica at early age was much lower than those with limestone fillers, this is the result of the slow pozzolanic reaction of microsilica. After then, the increase in strength took a remarkable speed to reach 53.06 MPa and 52.12 MPa in Na_2SO_4 and $Ca(OH)_2$ solution respectively.

Mortars with limestone filler and CEM II cement had an important strength at 14 days. The increase of strength was relatively fast for the period of the hydration until the maturity age. Thereafter, the progression speed became slow until the end of the test. After 91 days of immersion, a loss of strength of 3.23 MPa of MFC II$_{(Na2SO4)}$ compared to MFC II$_{(Ca(OH)2}$ was noted.

Mortars with limestone filler and cement CEM I had a very important strength at 14 days. The progression of this strength is relatively slow for all the period of the test. After 91 days of immersion, a loss of strength of 2.41 MPa of MFC I$_{(Na2SO4)}$ compared to MFC I$_{(Ca(OH)2}$ was noted.

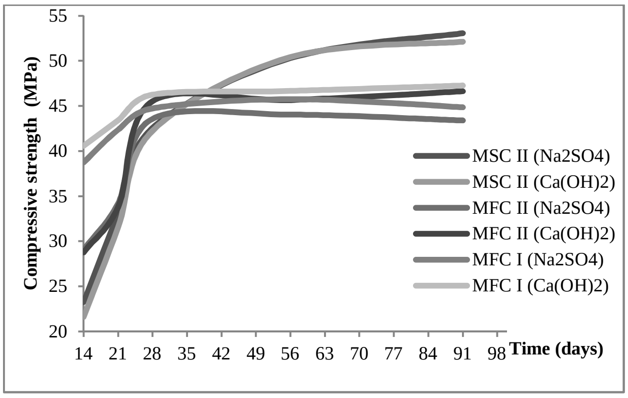

Fig. 6. Compressive strength versus time in the test solutions.

The increase in the compressive strength of all the mortars samples up to 28 days of age was the result of the continuation of the process of cement hydration and the progressive formation of C-S-H gel which was the first responsible of mechanical strength. This result coincides with those obtained by Zelié et al. (2007) [5]. According to Lee et al. (2005), the gain of strength in the first times is attributed to the evolution of the process of cement hydration and to the filling up of the pore space by the expansive products. The loss which is followed is caused by expansion and the beginning of the microcracking of the material [4].

The decrease in the strength of the MFC II$_{(Na2SO4)}$ and MFC II$_{(Ca(OH)2}$ after 28 days of exposure in the sodium sulfate solution is relied to the formation of ettringite expansive compounds; result justified by Skalny et al. (2002) [12]. In the MSC II$_{(Na2SO4)}$, those products gave rise to a containment of the cementitious matrix, consequently, the increase in compactness and compressive strength during all the time of immersion [13].

According to Lee et al. (2008), Tae Lee et al. (2008) and Pipilikaki et al. (2009), the incorporation of limestone filler in concrete reduces the compressive strength when it is attacked by sodium sulfate solutions. This result determined the negative effect of the use of limestone filler in concretes in sulfate environments [2, 4, 14].

The XRD test, conducted in this study, noted a presence of a little quantity of gypsum in MSC $II_{(Na2SO4)}$, by comparing this value with those marked by MFC $II_{(Na2SO4)}$ and MFC $I_{(Na2SO4)}$. According to Lee et al. (2008), that explains the absence of the loss of strength in this mortar samples [4]. The weak contents of portlandite in the MSC $II_{(Na2SO4)}$, which is caused by the pozzolanic reaction, played a key role in compressive strength increasing [15].

According to Tea Lee et al. (2008), the high quantity of portlandite in MFC $II_{(Na2SO4)}$ and MFC $I_{(Na2SO4)}$ mortars is due to the limestone excess in cement paste which comes from limestone filler [14].

Although the rate of ettringite is important in MSC $II_{(Na2SO4)}$ mortar, its expansion was not significant and its mechanical strength increased with the period of immersion; that can be explained by the containment of the pores by the expansive compounds and also by the weak gypsum contents. Kurtis et al. (1998) explain that by the equilibrium produced between ettringite and gypsum, which stabilize this mortar [16].

The compressive strength loss of MFC $II_{(Na2SO4)}$ and MFC $I_{(Na2SO4)}$ after 28 days of age is also due to the presence of gypsum. Mehta (1979) stated that the gypsum formation causes expansion based on his experimental study on alite paste. Indeed, in his testing alite mortar prisms were exposed to a 10% sulfate solution (5% Na2SO4 + 5% MgSO4) and short-term (75 days) expansion data were provided [17]. Gonzalez and Irassar (1997) investigated the sulfate attack mechanism on cements. Their XRD analysis showed that gypsum had formed in those specimens after 90 days of sulfate immersion. And they concluded that the expansive formation of ettringite was attributable to localized gypsum formation [18].

This loss is also due to the presence of thaumasite. According to Skanly et al. (2002), Richardson (2002) and Irassar (2009), damages due to the formation of thaumasite are probably more destructive than those caused by ettringite, because thaumasite is formed from C-S-H gel which is supposed to increase mechanical strength [12, 19, 20]. Irassar (2009) announced the presence of thaumasite in samples having a quantity of limestone filler higher than 5% preserved in sodium sulfate solution at 20±2 °C for 12 months of test [20].

The mortar with CEM I cement marked a simultaneous formation of ettringite and thaumasite. The presence of thaumasite in this mortar generates losses of strength. That explains why the use of sulfate resistant cement does not offer an improvement of strength for this kind of attack, the fact that it does not imply C_3A in its development.

4 Conclusions

This document carried out a detailed study of the process of degradation of mortar samples in an environment of sodium sulfate, and evaluated the potential consequences with the use of mineral admixtures of different reactivities on the durability of mortars of self compacting concrete. In the same way, our study made it possible to check if the differences in composition of mortars had a major influence on their mechanical strength and their durability. On this subject, tests on mortars proved that they have behaviors different concerning resistance to sodium sulfate. The use of microsilica in the mortar exposed to the external sulfate attack increased these mechanical performances and its durability because of its strong pozzolanic reaction and consumption of the calcium hydroxide. However, addition of limestone filler, presented a degradation of mortars even with the use of cement resistant to sulfates (CEM I / 42.5), result of the formation of thaumasite.

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