Investigation of the effects of different sulfate types found in seawater on concrete containing microfiber and silica fume

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Abstract
Sulfate salts which available in seawater with high concentrations cause the formation of ettringite in hydrated structures which formed as a result of the hydration of cement. On the other hand, ettringite causes excessive volume expansions and eventually leads to cracking of the concrete due to the internal stresses in concrete since it is a large volume mineral structure. In this study, ultrafine cement and silica fume as mineral additive were used together for binder design. Besides, microfiber has been added to the binder systems produced in different proportions. The produced specimens were kept separately in water, in solutions containing 2% Na_2SO_4 and 2% $MgSO_4$ by weight for 90 days. The compressive strength test was performed at 28th and 90th days on cured specimens. In addition to the compressive strength test, the solution samples were taken from the curing solutions every 10 days and the change of sulfate concentrations was followed in the solutions. According to the results, in Na_2SO_4 solution higher compressive strength values were observed up to 66 MPa while strength loss was observed in the specimens cured in the $MgSO_4$ solution. In parallel to this result, the remaining concentrations of SO_4^{2-} ions in the $MgSO_4$ solution were lower than those in the Na_2SO_4 solution. It was inferred that in Na_2SO_4 solution, the fibers could compensate for the internal stresses. This situation shows that especially the microfiber additive can compensate for the expansion that will occur as a result of ettringite formation, and thus it can help the mechanical stability of the concrete.

Keywords: sulfate attack, ultrafine cement, microfibers, sulfate concentration, concrete

INTRODUCTION

The sulfate (SO_4) effect is one of the most important durability problems in concrete. SO_4, especially in seawater, soil and groundwater, converts the phase from monosulfate (AFm) phase to the tri-sulfate (AFt) phase, which is formed as a result of the hydration process in cement [1-3]. This transformation continues after the hardening of concrete causes volume increase which results in cracking of concrete [4]. Among the aggressive chemicals, SO_4's are known to be the most aggressive ions affecting the durability of concrete structures [5]. Sodium sulfate (Na_2SO_4) is one of the main SO_4 types in reinforced concrete structures [6]. Although magnesium sulfate ($MgSO_4$) and potassium sulfate (K_2SO_4) are less common, they are more dangerous types of SO_4 in terms of their effects on concrete. It is known that $MgSO_4$ is the most aggressive type among SO_4 salts [1].

Reinforced concrete elements that are generally attacked by SO_4 are foundations, channel concretes, retaining wall concretes, marine pier concretes, and concrete pipes. The effect of SO_4 attack can be more destructive especially on pier concretes and concrete pipes because of exposure to many different types of SO_4's and their simultaneous physical and chemical effects.

The effect of SO_4 attack on concrete can be reduced in various ways. One of these measures is the use of low C_3A cement. In the ASTM C150 [7] standard, C_3A content is limited to a maximum 8% for moderately durable concretes and a maximum 5% for highly durable concretes for SO_4 attack. According to EN 197-1, this limit is a maximum 3% [8]. Also, the SO_4 resistance could be increased by reducing the porosity of concrete, using pozzolan (fly ash, silica fume, etc.), and isolating concrete with resistive coating products against SO_4 [9].

The purpose of this paper is to investigate the SO_4 resistance of the mixtures prepared with ultra-fine cement (DMFC-800), silica fume, and microfiber experimentally. While forming the mixtures, it is aimed to increase the impermeability by using ultra-fine cement and

silica fume. Moreover, microfibers were used to reduce micro-cracks during the expansion process.

MATERIALS AND METHODS

In the mixtures, the limestone aggregates of 0-4 mm (Type 1), 4-11.2 mm (Type 2), and 11.2-22.4 mm (Type 3) were used. The granulometry curves of the aggregates were presented in Figure 1. The ultra-fine cement (DMFC-800) and silica fume (SF) were used as binders. The microfibers (MFs) from KORDSA co. were added to the mixtures in 600 gr/m^3 dosage to reduce the expansion cracks. The polycarboxylate-ether-based high range water-reducing and retarding admixture (WRA) was used at 1% by mass of the binder. The water/binder ratio in all mixtures was kept constant at 0.65. The specifications of the used materials are given in Table 1-3, and the mixture proportions are given in Table 4.
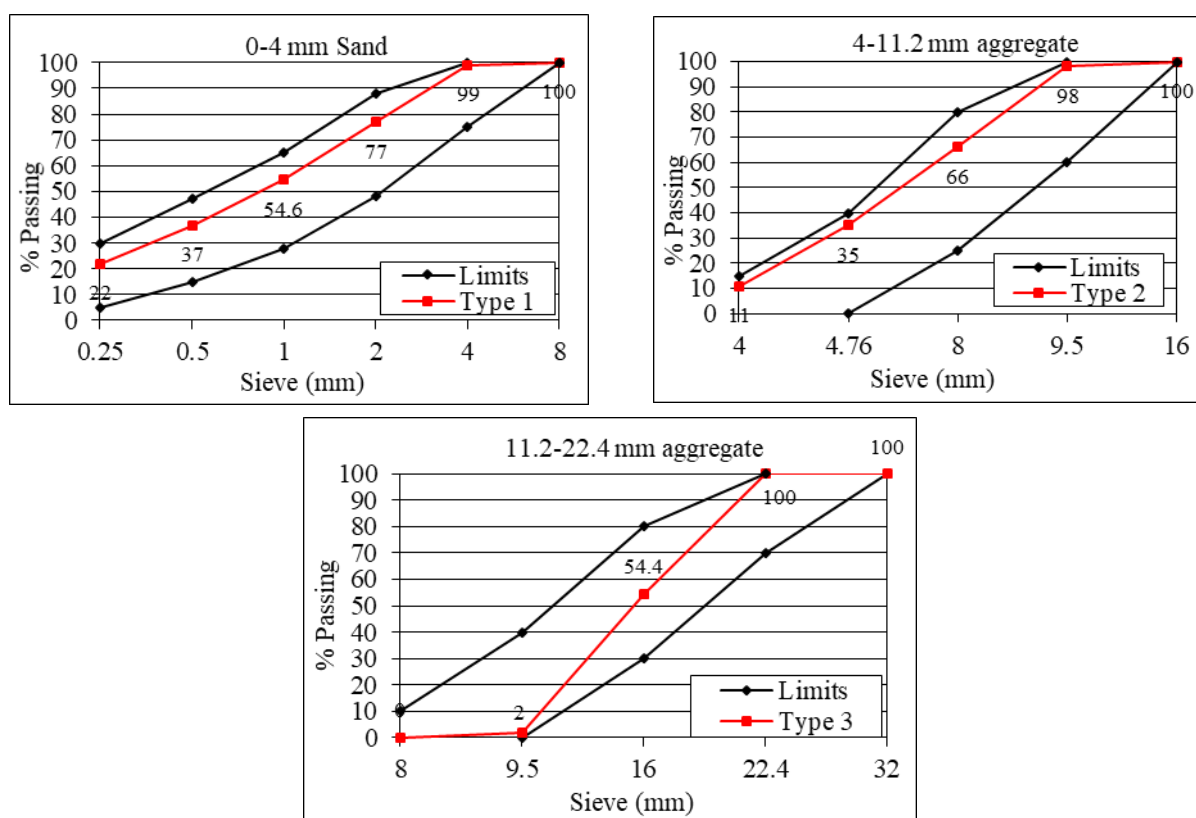

Fig. 1. Granulometry Curves of the Aggregates (Limits are taken from TS 802)

Table 1. Physical and mechanical properties of DMFC-800 ultra-fine cement

Analysis	Tests	Value
Physical	Density (g/cm^3)	3.12
	Blaine (m^2/kg)	≥ 600
	Color	Grey
	Initial setting time (min)	120
	Final setting time (min)	150
Compressive Strength	3 Days (MPa)	26
	7 Days (MPa)	47
	28 Days (MPa)	61

Table 2. XRF analysis results and physical specifications of silica fume.

XRF Analysis (%)		Physical Specifications	
SiO_2	89.94	Density	5.21 g/cm^3
Cr_2O_3	0.38	Blaine (m^2/kg)	14200
Fe_2O_3	0.41	Color	Dark Grey
Al_2O_3	0.83		
CaO	2.53		
MgO	7.68		
C	1.22		
S	0.923		
Loss of Ign.	2.96		

Table 3. Specifications of Kratos microfibers.

Physical Properties	Specifications and Values
Fiber class	EN 14889-2 class 1
Material	Polyamide 6.6
Density (g/cm^3)	1.14
Length (mm)	12
Tensile Strength (MPa)	970
Melting Temperature (^{0}C)	260

Table 4. Mixing proportions according to TS 802

Specimen No	Aggregate (kg/m^3)			DMFC-800 (kg/m^3)	Silica Fume		Water (L/m^3)	Micro-fiber (kg/m^3)	WRA %
	Type 1	Type 2	Type 3		(kg/m^3)	%			
SD0-B	858	429	429	265	0	0	170	0	0.8
SD5-B	860	430	430	252	13	5	170	0	0.8
SD10-B	863	431	431	238	26	10	170	0	0.8
SD15-B	865	432	432	225	40	15	170	0	0.8
SD0-kmB	858	429	429	265	0	0	170	0.6	1
SD5-kmB	860	430	430	252	13	5	170	0.6	1
SD10-kmB	863	431	431	238	26	10	170	0.6	1
SD15-kmB	865	432	432	225	40	15	170	0.6	1

The mixing ratios for concrete samples were calculated according to TS 802 [10] standard for C25/30 Class. According to the mixing ratios given in Table 4, the fresh concrete samples were prepared with PAN type mixer (Fig. 2a) and three cube specimens were prepared in molds in 150*150*150 dimensions for each group and age (Fig. 2b). Nine specimens were produced from each group to expose the tap water (reference test), Na$_2$SO$_4$ solution, and MgSO$_4$ solutions cures.

Fig. 2. a) Pan type mixer, b) Molding of specimens

For the SO₄ attack test, the magnesium-sulfate-heptahydrate ($MgSO_4 \cdot 7H_2O$) and sodium-sulfate-anhydrate (Na_2SO_4) from Merck co. were used to prepare the solution. The prepared concrete specimens were separately immersed in Na_2SO_4 and $MgSO_4$ solutions of 2% concentrations for 28 and 90 days (Fig. 3). The 50 mL solution samples were taken per 10 days to analyze the SO₄ concentrations while the specimens were being immersed in solutions. The concentration analyses were carried out according to Standard Methods, Method no 8051 [11] using a turbidimetric technique. In the experiment, Ba^{2+} ion was added to the sample and mixed with a magnetic stirrer. The concentration of SO₄ ions was read in 5 minutes after the experiment started on the HACH DR/4000U spectrophotometer.

Lastly, the CS test was conducted on cured and reference specimens to determine the mechanical strength of the concrete samples.

Fig. 3. a) Concrete curing in SO_4^{2-} solutions, b) Sampling from SO₄ solutions, c, d) HACH DR/4000U spectrophotometer

RESULTS AND DISCUSSION

Compressive strength results

The physical appearances of the specimens were examined at the end of the 28-day and 90-day curing periods (Fig. 4a). When looking at the specimens, neither color change nor crack was observed on the surfaces of the specimens cured in Na_2SO_4 solution (Fig. 4b). On the contrary, white spots and foams occurred on the surface of the specimens cured in $MgSO_4$ solution (Fig. 4c, 4d). After visual inspections, the CS test was performed on the specimens. The test results are given in Figures 5 and 6.

As the dosage of SF admixture increased, CS of the reference samples increased both in the presence and absence of MFs. In the reference samples, MFs caused a further increase in CS only up to 10%. The highest CS, 64.2 MPa, was observed in SD15-kmB specimen containing both MFs and SF, whereas, the lowest CS, 53.7 MPa, was observed for the reference specimens without admixtures. In the literature, McCarthy and Dyer [12] indicated that SF admixtures resulted in 29.1-46.8 MPa CS for various types of concrete samples and they reported that the performance is very much more dependent on the type of pozzolanic material used. The CS values of both the reference concrete and the specimens with SF admixture obtained in this study were much higher than the levels reported by McCarthy and Dyer [12].

Fig. 4. The cured specimens: a, b) Na_2SO_4 curing specimens; c, d) $MgSO_4$ curing specimens
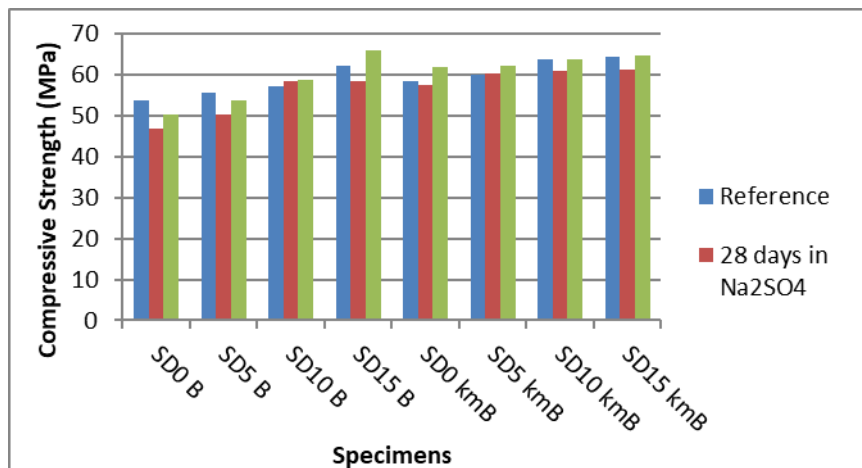

Fig. 5. CS test results for the specimens cured in Na_2SO_4 solution
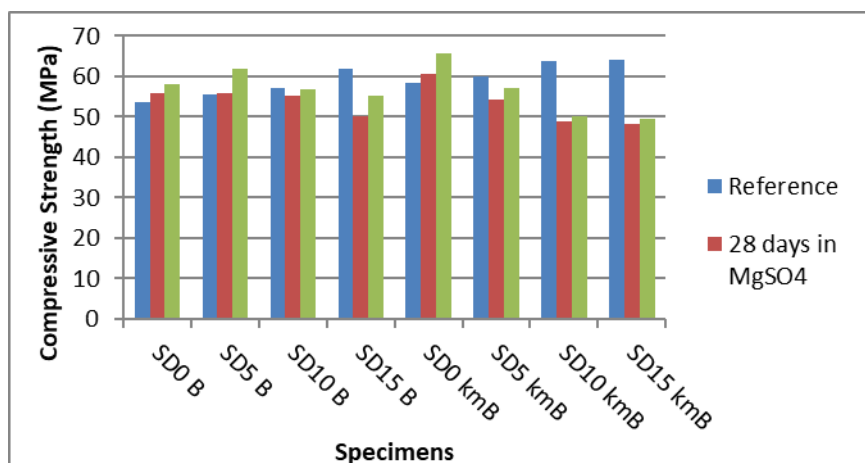

Fig. 6. CS test results for the specimens cured in $MgSO_4$ solution

The specimens cured in Na_2SO_4 solutions and tap water (reference) for 28 days presented similar CS results. At SF dosages greater than or equal to 10%, 90 days CS was higher than the reference samples in Na_2SO_4 curing solutions (Fig. 5). Similarly, when MFs were

used together with SF, the resultant 90 days CS of the samples cured in Na_2SO_4 were approximately equal or slightly higher than CS of the reference samples which were cured in tap water without SO_4. 15% SF admixture in the Na_2SO_4 without MF resulted in the highest CS as 66 MPa which was 50 MPa for the reference. Whereas, CS values of the samples including MFs increased from 61.6 MPa to 64.4 MPa. These indicated that MF is buffering the SO_4 reaction and cause all types of concrete specimens (i.e., reference, 28 days and 90-days concrete) to have CS levels close to each other in Na_2SO_4. However, the effect of SF dosage on CS with SF admixture alone is more belligerent without MFs (Figure 5). Na_2SO_4 is known to react with SiO_2 to form sodium silicate which is the mixture of the metasilicate and has a wide variety of uses, including the formulation of cement. Basic pH ranges and the presence of carbon may enhance these reactions and helps to obtain higher CS [13, 14]

On the other hand, white spots and deteriorations seen on the surface of the concrete specimens were indicated the formation of ettringite. The ettringite forms by the reaction of SO_4 ions which coming from the external environment (seawater, groundwater, etc.) with the products formed as a result of cement hydration and in the presence of a high amount of water. This reaction causes large volume increases. Sims, et al. reported that tests alternatively using Na_2SO_4 or $MgSO_4$ produce different results for each concrete mix, and $MgSO_4$ is usually considered to be more aggressive, although exceptions have been reported [4]. Being consistent with this inference, in this study, when the SO_4 in the curing medium is in the form of $MgSO_4$, the findings were completely different as compared to the results of Na_2SO_4 curing medium (Fig. 6). For example, 28-days and 90-days CS values were decreasing with SF dosage, both with MFs and without MFs in case of $MgSO_4$ curing. The CS of the specimens without MF were higher than those of the MF reinforced specimens. However, when MF admixture was used alone, without SF, high CS was achieved as 65.6 MPa in $MgSO_4$ in 90 days. This value can be considered as approximately equal to the highest CS achieved in Na_2SO_4 curing solution (Fig. 5 and 6). $MgSO_4$ has a more far-reaching action than other SO_4's and decomposes the hydrated calcium silicates in addition to reacting with the aluminates and calcium hydroxide [15].

Obe, et al. has stated that the contact of Na_2SO_4 and $MgSO_4$ with concrete structures can be a matter of some concern, as the reactions between SO_4's and hydrated cement compounds result in volume increase and build-up of internal stresses, leading to the breakdown of structures [16]. McCarthy and Dyer revealed that $MgSO_4$ attack is considered to be more severe than that of Na_2SO_4 [12]. One feature of this form of attack is the deposition of a double layer composed of brucite and gypsum, followed by several internal layers of gypsum. The formation of the double layer is not necessarily detrimental, since it protects the surface of concrete and mortar from further ingress of SO_4, potentially limiting deterioration.

Concentration changes in the SO_4 solutions

The changes of curing solution SO_4 concentrations with curing time were indicated in Figure 7 for both $MgSO_4$ and Na_2SO_4 solutions. For both solutions, SO_4^{2-} ion was absorbed more rapidly in the first 30 days of curing, and after 40 days, SO_4 absorption almost finished. The SO_4^{2-} ion of $MgSO_4$ solution was absorbed by the specimens about 70%, which was more than SO4 absorption from Na_2SO_4, which was around 40%. Depending on the positions of Na and Mg elements in the periodic table, there are some differences in their chemical structures and compound properties. Mg has a larger nuclear charge and smaller atoms than Na, therefore, ionization and electrode potential as well as hydration energy of Mg are higher than Na. Na_2SO_4 is unreactive toward most oxidizing or reducing agents. It is a typical electrostatically bonded ionic salt with a solubility of 13.9 g/100 mL whereas the solubility of $MgSO_4 \cdot 7H_2O$ is 113 g/100 mL, therefore, it is clear that as the water solubility increases, the SO_4 ion in the solution become more available to the concrete to absorb under the alkaline conditions in the first days of the hydration. When the concrete

specimen gaining strength, SO_4 absorption of concrete stops. Consequently, no more SO_4 absorption into the structure occurs. This is the reason that SO_4 concentration in curing water remained almost constant after 40 days.
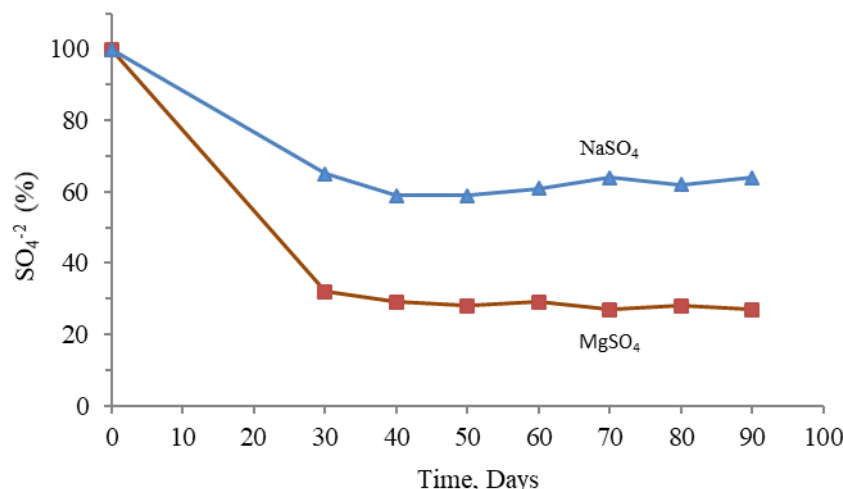

Fig. 7. Change of SO_4 concentration with time in curing solutions

CONCLUSIONS

In this study, the SO_4 effect in concrete was investigated on the produced specimens by using fine-grained cement with SF and MF additives in different proportions. According to the results obtained, SF additive the combination of silica fume and microfiber additives increased the CS values of specimens cured in Na_2SO_4.

It can be seen from the results that $MgSO_4$ has a greater negative effect on the CS value than that of Na_2SO_4. This situation is compatible with the literature. At the same time, the decrease in the concentration of SO_4 ions in MgSO4 solution confirms this situation.

Moreover, the concentration of SO_4 ions initially increased rapidly in concrete for the first 30 days, and then the rate of increase gradually decreased.

The formation of ettringite in pores increased significantly which reduced the permeability of the concrete and caused less solution to enter in it.

The most important result indicated by this study is the successful bearing capacity of microfiber additives against the internal stresses formed as a result of the expansions and ettringite formation due to Na_2SO_4. However, these additives cannot meet the internal stresses caused by $MgSO_4$. This situation shows that $MgSO_4$ causes much more ettringite formation and expansion in concrete than Na_2SO_4. Therefore, it can be concluded that SO_4 is an effective ion as an environmental effect on the concrete, but the type of cation bonded to SO_4 anion is determining whether that effect is positively or negatively.

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