Pergamon

Cement and Concrete Research, Vol. 25, No. 6, pp. 1360-1368, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00128-X

EFFECTS OF SODIUM SULFATE CONCENTRATION ON THE SULFATE RESISTANCE OF MORTARS WITH AND WITHOUT SILICA FUME

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(Refereed)
(Received December 20, 1994; in final form May 3, 1995)

ABSTRACT

An investigation was carried out on the effect of sodium sulfate concentration on the sulfate resistance of mortars. Experiments were carried out on the RILEM portland cement standard mortars and portland cement-silica fume mortars. Sulfate exposure of mortars were initiated after 28 days of lime saturated water curing. Some physical and mechanical properties were determined periodically up to 300 days of exposure. Low concentrations of sodium sulfate not exceeding 18000 mg/L had not any significant effect on the compressive and flexural strength of mortars. However, at a concentration of 18000 mg/L some of the properties, i.e. volume density, volumetric water absorption, indicated beginning of rapid deterioration of mortar structure at an exposure time which could be called critical time. Concentration of 72000 mg/L caused sharp strength reduction between 90 and 180 days for both compressive and flexural strengths. Silica fume replacement caused significant increase in sulfate resistance of mortar even at highest sulfate concentration.

Introduction

When concrete is subjected to sulfate attack new compounds are formed as a result of reactions of sulfate with cement hydration products. These reactions lead to volume expansion, softening and disintegration of concrete structure. Concrete structure can fail depending on the sulfate type, concentration and exposure time.

Sulfate concentration in water is an important factor governing the extent of damage. Concentration of 0-150 ppm, 150-1500 ppm, 1500-10000 ppm and above 10000 ppm can be classified as mild, moderate, severe and very severe respectively(1).

Reactions of sodium sulfate with $Ca(OH)_2$ and monosulfate produce gypsum and ettringite (1,2,3,4,5,6). Microcracks are formed and spalling is seen on the concrete surface as a result of these formations.

Table 1. Chemical analyses and physical properties of portland cement and silica fume

Chemical Composition (%)	Portland Cement	Silica Fume
Loss on ignition	1.51	2.37
SiO_2	20.40	90.54
Al_2O_3	6.33	0.89
Fe_2O_3	3.57	0.61
CaO	64.14	1.60
MgO	1.29	0.76
SO_3	2.33	1.16
Specific weight (g/cm^3)	3.18	2.11
Specific surface (cm^2/g)	3371	-
Setting time (min)		
- Initial	135	-
- Final	240	-
Mineralogical components (%)		
C_3S	46.94	
C_2S	22.35	
C_3A	10.74	
C_4AF	10.86	

Numerous authors have reported that partial replacement of cement with silica fume increases resistance of concrete to sodium sulfate attack (2,4,7,8,9,10). This beneficial effect is attributed to decrease in $Ca(OH)_2$ and alumina which are necessary for gypsum and ettringite and to refined pore structure(10).

To establish deteriorating effect of sulfate attack on concrete, some properties must be examined periodically. These are visual experience, change in mass, length, volume and bulk density, total porosity, compressive and flexural strengths and elastic modulus(4).

In the present work, changes of some physical and mechanical properties of portland cement (PC) and portland cement-silica fume (PC-SF) mortars exposed to sodium sulfate solutions were measured periodically and examined for different concentrations.

Experimental Procedure

An ordinary portland cement, a siliceous sand according to the RILEM guidelines and a silica fume were used for the mortar mixtures. Cement and silica fume properties are indicated in Table1. The sand/cement was 3, and water/cementitious material was 0.5. For the PC-SF mortars silica fume was replaced 10% of the cement by mass. After mixing, the mixtures were cast into 40x40x160 mm prismatic moulds. They were kept in laboratory conditions for 24 hours and then demoulded specimens were transferred into the lime saturated water at 20°C. After having 27 days cure time under this conditions, excepting control specimens all others were transferred into the sodium sulfate solutions at 20°C. This time is the beginning of exposure days.Sulfate (SO_4^{-2}) concentrations were 2700 mg/L (NK), 18000 mg/L (NL) and 72000 mg/L (NM). Solutions were renewed in periods of 14 days. Physical and mechanical tests were carried out for both the control and sulfate exposed specimens at different times. Mass changes were measured in periods of 14 days and capillary water absorption, volumetric water absorption, density, and compressive and flexural strengths were determined at the 28th, 90th, 180th and 300th.

Flexural strength test was carried out three 40x40x160 mm prismatic specimens and then compressive strength on six piece of prisms. Mass changes were calculated as the difference between the mass of saturated surface dry specimen at any time and just before the sulfate exposure. The other tests were performed on 40x40x75 mm prismatic specimens. For this purpose, 40x40x160 mm prismatic moulds were separated in two compartments by a metal sheet and then mortar mixture was cast into these compartments. This prisms were cured under the same conditions with the other specimens. Three prisms for the capillary water absorption and another three for the volumetric water absorption tests were used for each curing condition. Prior to testing, specimens were dried in the oven at 100±5°C until constant mass was achieved and then cooled in a desiccator. For the capillary water absorption test, lower face (parallel to the trowelled upper face) having 40x75 mm dimensions was brought in contact with water in a tray. Environment temperature was 20±1°C and relative humidity was 65±5% during the test. Absorbed water was measured at different intervals. Initial slope of the curve of absorbed water-square root of time was calculated representing the capillary water absorption coefficient. For the volumetric water absorption test, specimens were immersed in water and the mass was measured until constant value was achieved. Absorbed water was calculated as the difference between saturated surface dry and dry masses and the values are given as per cent by the volume of specimen. Density was calculated as dry mass/volume.

Results

Test results are the average of six value for the compressive strength test and three value for the other tests. The physical and mechanical test results of the specimens prior to sulfate exposure are presented in Table 2. The values of compressive and flexural strengths, capillary and volumetric water absorptions, and density are related to the results of control mortar (PC) and shown in Figures (1,2,4,5,6). Mass changes are shown in Figure 3.

Table 2. The physical and mechanical test results of the specimens prior to sulfate exposure

Mortar Type	Compressive Strength (MPa)	Flexural Strength (MPa)	Capillary Coefficient E-05(cm^2/sec)	Volumetric W.Absorption. (%)	Density (g/cm^3)
PC	39.79	7.89	3.09	19.53	2.05
PC-SF	45.83	8.84	1.96	20.59	2.00

Compressive strength

Compressive strength of PC mortars stored in sodium sulfate solutions did not show any significant difference in comparison with water stored control mortars (PC) at the 28th day (Figure 1). Compressive strengths of all the sulfate exposed series were significantly lower than that of control mortars at the 90th days. Then this time a strength gain was observed up to 180 days. After 180 days, series stored in solution of 18000 mg/L and 72000 mg/L showed strength loss while the mortars stored in solution of 2700 mg/L showed strength gain. Especially retained strength of 72000 mg/L series was very little at the end of 300 days. Higher sulfate concentration did not always caused lower strength. 18000 mg/L series had the highest compressive strength relative to the other sulfate exposed series up to 180 days, but then this time higher concentration resulted in lower strength.

10 percent replacement of portland cement with silica fume (PC-SF) resulted higher strength than that of PC mortars except for the 180th day (Figure 1). Changes in compressive strength of PC-SF mortars in sulfate solutions were more regular relative to PC mortars. It seems that sulfate attack had little effect on PC-SF series irrespective to sulfate concentrations. At 300

days of exposure a trend of strength reduction could be seen by increasing the sulfate concentration.

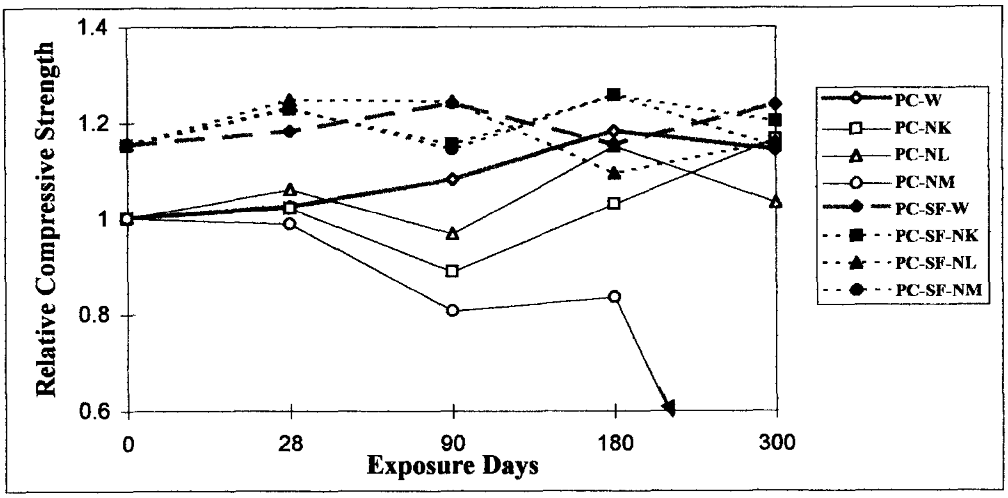

FIG 1. Relation between relative compressive strength and exposure days

Flexural strength

For the PC mortars, flexural strength of sulfate exposed specimens were lower than that of the control mortars at the 28th day (Figure 2). Than this time all the series exposed to sulfate solution gained strength until 90 days. 90-day strengths were the highest value for the sulfate exposed mortars up to 300 days. 2700 mg/L series had nearly equal values with control mortars between 90 and 300 days. After 90 days higher concentrations resulted more strength reductions. 18000 mg/L series had higher flexural strength than those of the other series between these days, but it had almost the same flexural strength with the 2700 mg/L series at the end of 300 days. 72000 mg/L series showed drastic strength drop after 90 days of exposure, as was observed for the compressive strength. These specimens had practically no resistance to flexure at the end of 300 days.

Silica fume replacement caused flexural strength increase relative to control mortar (PC) for all ages (Figure 2). In this series sulfate exposure caused beneficial effect on the flexural strength for all concentrations. Especially concentration of 2700 mg/L series resulted in significantly higher strength than that of control mortars (PC-SF) at 180 and 300 days of exposure. A flexural strength reduction trend was observed as the sulfate concentration increased at the end of 300 days as it was observed for the compressive strengths.

Mass Change

There was a continuously mass increase for the control mortars (PC) as shown in Figure 3. Sulfate exposed series showed mass loss at earlier ages. Later an increase was observed for all concentrations. Mass changes of 2700 and 18000 mg/L series were similar in the course of experience. 72000 mg/L series showed rapid mass increase after 140 days of exposure and this increase was eight fold of control mortars (PC) at the end of 300 days.

There was slight mass reduction in control mortars (PC-SF) and exposed to the solution of

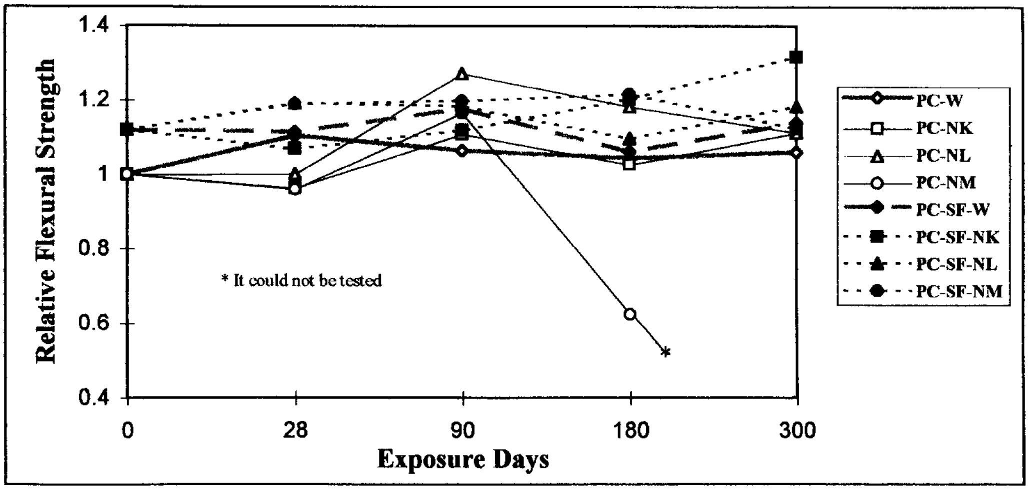

FIG 2. Relation between relative flexural strength and exposure days

2700 mg/L. Mass decrease at early ages and mass increase at later ages were observed in PC-SF mortars exposed to sulfate solutions of 18000 and 72000 mg/L series, but mass increases were less than those were observed for the PC mortars (Figure 3).

Capillary water absorption

Capillary water absorption results are indicated as relative capillary coefficient in Figure 4. Sulfate exposed (PC) series had lower capillary water absorption at 28 days than that of control mortar (PC). Capillarity increase was observed after 90 days for 2700 mg/L series and after 28 days for 18000 and 72000 mg/L series. This increase was moderate for 18000 mg/L series up to 180 days, then showed sharp increase. This sharp increase was observed at the 28th days for the 72000 mg/L series and capillary water absorption coefficient reached to a very high level at the end of 300 days.

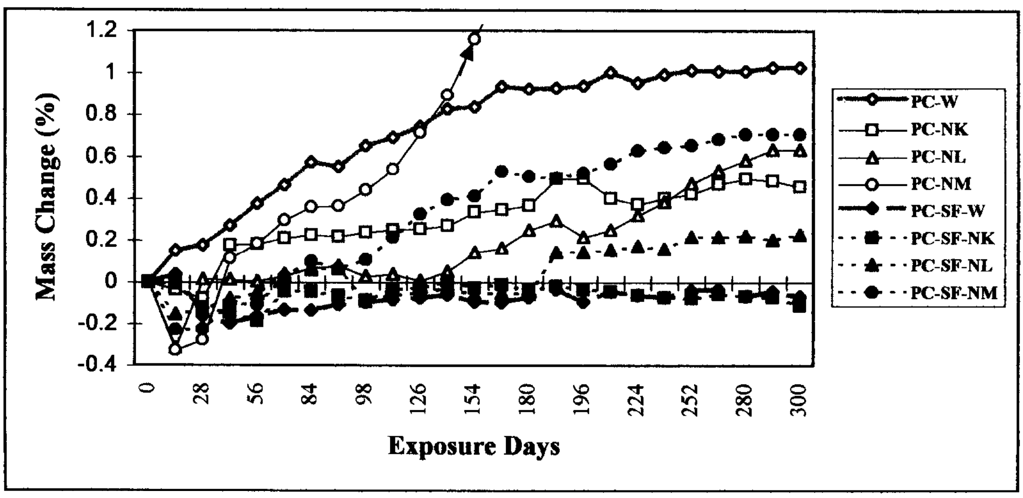

FIG 3. Relation between mass changes and exposure days

Silica fume replacement caused capillarity drop relative to the PC mortars stored in water at early ages (Figure 4). At later ages there was not much changes. From Figure 4, it can be seen that sulfate attack did not much affect the capillarity of PC-SF mortars up to 90 days. Thereafter 2700 and 18000 mg/L series did not show any significant difference relative to control series (PC-SF), however the 72000 mg/L series showed relatively high increase in capillarity. This increase was not sharp as compared with the PC mortars.

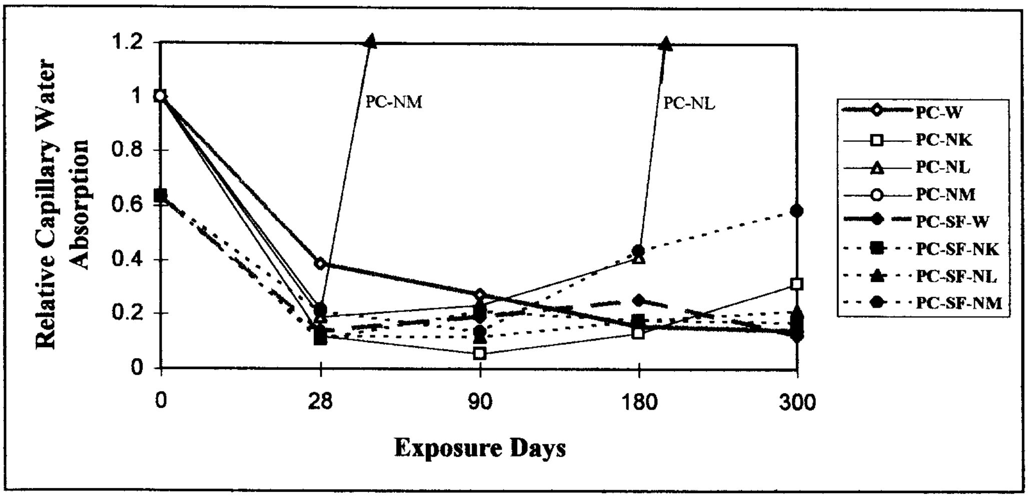

FIG 4. Relation between relative capillary water absorption and exposure days

Volumetric water absorption

Volumetric water absorption results are indicated in Figure 5. After a slight decrease in volumetric water absorption up to 90 days, a slight increase was observed up to 300 days for the PC control mortars. All the sulfate exposed series had significantly lower volumetric water absorption than that of control mortars up to 28 days and their volumetric water absorption were nearly equal. Water absorption of 2700 mg/L series increased slightly after 28 days, but it was not higher than that of the control mortars at the end of 300 days. 18000 and 72000 mg/L series showed continuously significant increase in volumetric water absorption after 28 days. Higher concentrations resulted higher volumetric water absorption for the sulfate exposed mortars.

PC-SF control mortars had more volumetric water absorption than that of the PC control mortars at the beginning of experience (Figure 5). Exposure of sulfate solution of 2700 mg/L did not cause any significant change even at the end of 300 days. Higher concentrations resulted in drop during the first 28 days of exposure. Thereafter volumetric water absorption increase was observed for the 18000 and 72000 mg/L series, but all the series whether sulfate exposed or not had almost the same volumetric water absorption from 90 days up to 300 days.

Density

Density of PC mortars stored in water and sulfate solution of 2700 mg/L were nearly equal and did not show any significant change during the experience (Figure 6). 18000 and 72000 mg/L

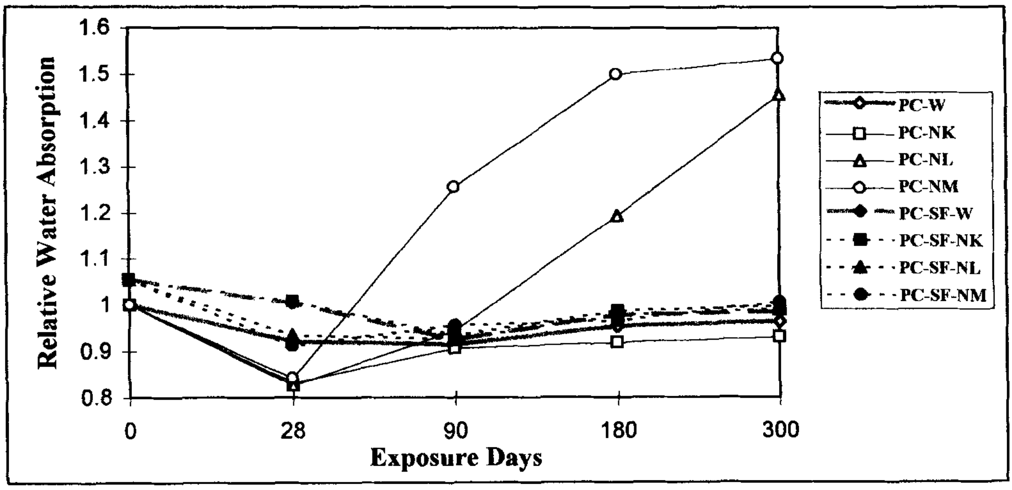

FIG 5. Relation between relative volumetric water absorption and exposure days

series showed a slight increase at first 28 days and thereafter rapid decrease up to 300 days. 72000 mg/L series had lower density than that of 18000 mg/L series, but the difference was in closing trend at later ages. The similar trend was observed for the volumetric water absorption.

PC-SF mortars had lower density than that of PC mortars at the beginning of experience (Figure 6). It can be seen from Figure that sulfate attack did not affect significantly density of mortars in the course of experience. Whether sulfate exposed or not all the series had nearly equal volume density up to 300 days.

Discussion

The effect of sulfate concentration on the compressive and flexural strength is variable with time. Consecutive increasing and decreasing cycles could be seen. It seems that, reaction products of sulfate with hydrated cement reactions caused microcracks because of expansion while they fill

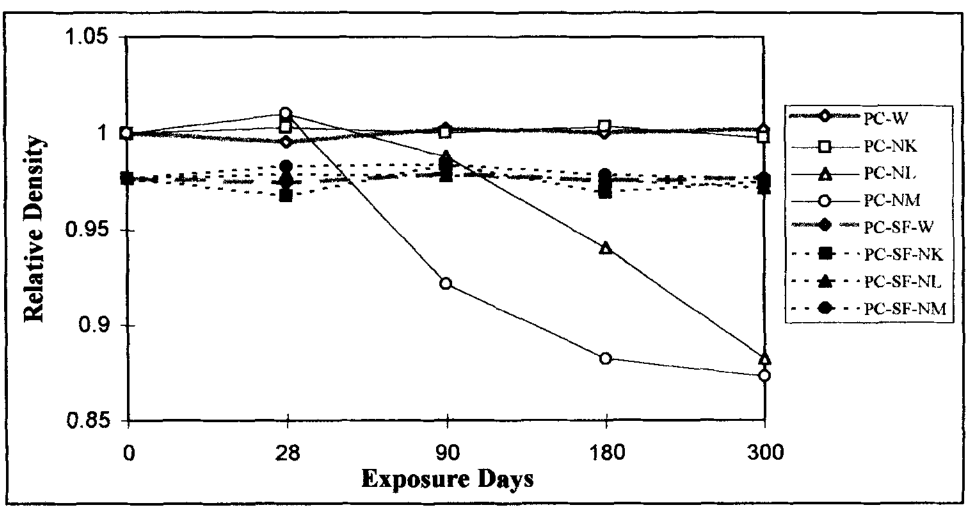

FIG 6. Relation between relative density and exposure days

the pores. If the latter is dominant an increase in strength can be observed.

Higher concentration did not always cause lower strength in the relatively low concentration region. For example compressive strength of mortars exposed sulfate solution of 18000 mg/L could be higher than that of stored in solution of 2700 mg/L. Similarly Kayyali (11) have reported that to increase sulfate concentration from 3300 mg/L to 16500 mg/L had little effect on compressive strength of cement pastes. More exposure time is needed to see any deteriorating effect of sulfate solution as the concentration decreases.

For PC mortars, 72000 mg/L series had always lower compressive strength than those of control and the other sulfate exposed series and were almost destroyed at the end of 300 days. It was not reported such an extreme damage in the literature for sodium sulfate solution. In this study, renewing of solution in periods of 14 days might have possibly accelerated of sulfate attack.

Concentrations of 2700 and 18000 mg/L did not affect negatively the flexural strength of PC mortars at longer ages. Only flexural strength of 72000 mg/L series decreased at earlier and more rapidly according to the compressive strength.

Beneficial effects of silica fume replacement on the compressive and flexural strengths can be seen from the results clearly, even at such a high concentration of 72000 mg/L. Although sulfate concentration varied at a wide range, strength changes limited during the experience. Improvement in flexural strength of the sulfate exposed series was more clear relative to compressive strength. This finding did not confirm Irassar (12) who have reported that flexural strength was a very good parameter to evaluate the phases of sulfate attack.

For PC mortars, capillary and volumetric water absorption decreased by the sulfate attack at early days of exposure. Decrease in the former was higher than the latter. Capillary water absorption is affected by the capillary pores. Volumetric water absorption represents total porosity (capillary pores + air voids). It seems that, pore filling process of sulfate attack affected mainly capillarity. Kayyali (11) reported that gypsum and ettringite formation by the sulfate attack caused increase in pore volume in the range of pores below 150 nm diameter while the volume of larger pores did not change. On the other hand, microcracks formed by the sulfate attack at the surface of the specimen would increase capillary rise. Probably these two phenomena are the reasons of very sharp increase in capillarity at high concentrations.

Density of PC-SF mortars were lower than that of PC mortars at the beginning of experience. This showed that PC-SF mortars were more porous. Higher volumetric water absorption of PC-SF mortars can be attributed to the higher porosity. However, PC-SF mortars had lower capillary water absorption than the PC mortars. Probably pozzolanic reaction of silica fume prior to sulfate sulfate exposure resulted in blocking of capillary pores. Test results showed that deteriorating effect of sulfate attack is affected mainly by the capillary pores of material. Although higher volumetric water absorption of PC-SF mortars relative to PC mortars, effect of sulfate attack on the former is very limited comparison with the latter. For the highest concentration, relatively high capillary water absorption increase at later ages indicated considerable crack formation in PC-SF mortars. Although there was not any significant change in mechanical strengths, capillarity increase indicates a possible reduction in mechanical strengths at a later age.

Density of control mortar (PC) and 2700 mg/L series were almost constant during the experiment. Rapid decrease in density of the series in higher concentrations can be attributed to the large expansion strains as stated by Lobo and Cohen (13). Sulfate solutions did not affect the density of PC-SF mortars. Torii and Kawamura (14) reported that, silica fume replacement caused a great reduction in the expansion of mortars. It seems that, density is affected mainly by the expansion of material.

Mass changes in sulfate solution were not a good parameter to evaluate the damage of mortar. Only, significant mass increase in 72000 mg/L series showed formation of too much reaction products which resulted to deterioration of mortar structure.

Very little mass increase of PC-SF mortars exposed to 2700 and 18000 mg/L sulfate solution showed limited reactions due to sulfate attack. This is probably resulted from reduced permeability of mortars by the presence of silica fume. Relatively high increase in mass for 72000 mg/L of concentration after 90 days can be attributed to the considerable increase capillarity.

Conclusions

Low concentration of sodium sulfate such as 2700 mg/L has not any significant effect on the mortar properties at 300 days of exposure.

To see a deteriorating effect of sodium sulfate on the mortars, more exposure time is needed as the concentration decreases.

300 days of exposure time is not enough to have meaningful conclusions in the concentration region not exceeding 18000 mg/L.

10% replacement of cement by silica fume improved sulfate attack resistance of mortars even at high concentrations.

Capillary water absorption is a good parameter to evaluate deterioration of mortar in the sodium sulfate solution.

Results imply that there is a critical exposure time for the acceleration of deteriorating of mortar structure. Properties change slowly until this time, but then this time rapid negative change of them is seen and the structure goes to failure. This critical time depends on sulfate concentration.

To understand if there is a critical time under low sulfate concentration, more exposure time is needed.

References

1. Committee Report, ACI Committee 201, ACI Materials Journal, 98, 544, (1991).
2. M. D. Cohen and A. Bentur, ACI Materials Journal, 85, 148, (1988).
3. A. M. Neville, Properties of Concrete 3rd Edition, Pitman Publishing Co., Marshfield, 779.
4. M. D. Cohen and B. Mather, ACI Materials Journal, 88, 62, (1991).
5. W.G. Piasta and L. Hebda, Magazine of Concrete Research, 43, 81, (1991).
6. R. S. Gollop and H.F.W. Taylor, Cement and Concrete Research, 22, 1027, (1992).
7. T. Yamato, M. Soeda, Y. Emoto, Trondheim Conference, ACI SP114-44, 897, (1989).
8. K, Kohno, F, Aihara, and K, Ohno, Trondheim Conference, ACI SP114-39, 815, (1989).
9. I, R, Almedia, Concrete durability Conference, ACI SP126-57,1073, (1991)
10. V.M. Malhotra, G.G. Carette and V. Sivasundaram, Symposium on Advances in Concrete Technology, Athens, (1992).
11. O.A. Kayyali, Cement and Concrete Research, 19, 423, (1989).
12. E. F. Irasser, Cement and Concrete Research, 20, 209, (1990).
13. C. Lobo and M.D. Cohen, CANMET and ACI 2nd. Intern. Workshop on Silica Fume in Concrete, Washington, (1991).
14. K. Torii and M. Kawamura, Cement and Concrete Research, 24, 361, (1994).