Pergamon

Cement and Concrete Research, Vol. 27, No. 2, pp. 205-214, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00009-4

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

Fikret Türker*, Fevziye Aköz, Sema Koral and Nabi Yüzer
*Akdeniz University, Technical Sciences, Campus, Antalya, Turkey
Yıldız Technical University,
Faculty of Civil Engineering Department of Construction Materials 80750, Istanbul, Turkey

(Refereed)
(Received November 10, 1995; in final form January 2, 1997)

ABSTRACT

An investigation was carried out on the resistance of mortars to magnesium sulfate attack. Experiments were carried out on portland cement (PC) and portland cement-silica fume (PC-SF) mortars. Mortars were immersed in magnesium sulfate solutions after 28 days of lime-saturated water curing. Concentrations were 1900, 13000 and 52000 mg/L as SO_4^{-2} solutions. A number of physical and mechanical properties were determined at different periods of exposure up to 300 days. For the first 28 days of exposure, some improvements of mortar properties in magnesium sulfate environment were observed. This is the early stage of sulfate attack. Thereafter, negative changes of the properties indicate a transition stage. Deterioration process of mortars was retarded by the presence of silica fume. After the transition stage, negative changes of physical properties accelerate, indicating the later stage. Compressive and flexural strength properties showed different response to magnesium sulfate attack at later stage. Only in 52000 mg/L concentration, all the measured properties showed clear negative changes. © *1997 Elsevier Science Ltd*

Introduction

Magnesium sulfate is generally accepted as the most detrimental of all the sulfates (1,2,3,4). Sulfate attack is a chemical process between sulfate solution and cement hydration products. Ettringite, gypsum and brucite can form depending on the sulfate concentration (2). The brucite film formed on the material surface hinders continued deleterious reaction with magnesium sulfate solution (5).

A different feature of magnesium sulfate attack is the disintegration of the CSH gel to MSH gel which is a non-cementitous product (2,3,4,6,7,8). This alteration results in the softening of material (6).

Reaction products produced by the sulfate attack fill the air and capillary voids (4) and may lead to improve the mechanical properties at early ages of exposure. On the other hand the same products result in expansion and formation of cracks (2). Finally a decrease in the performance of material and failure may be observed.

It will be accepted that, silica fume improves many properties of cement-based materials. Silica fume reacts with $Ca(OH)_2$, fills the micropores and the cement paste-aggregate interface (2,9). The depths of ingress of sulfate and amount of gypsum reduce because of silica fume effects against to sulfate attack (3,4). When the magnesium sulfate attack is considered, decalcification and alteration of CSH gel to MSH gel are increased by the presence of silica fume (4). So, some researchers have reported that the silica fume presence was detrimental in the case of magnesium sulfate attack (2,4,6). However, Lawrence reported good performance of portland cement-silica fume mortars which can be comparable with sulfate resisting portland cement. Mangat and El-Khatib (11) reported that sulfate resistance of concrete with silica fume in 7%Na_2SO_4 + 3%$MgSO_4$ solution increased.

Sulfate attack on concrete is a complex process as was reported by Cohen and Mather (2). Many factors such as cement type, sulfate concentration and exposure period may affect the results. Although different sulfate concentrations result in different reaction products in magnesium sulfate solution, much attention has not been paid to the effect of sulfate concentration on the performance of cement-based materials.

In this study, the effects of magnesium sulfate concentration on the properties of mortars were investigated. For this purpose, an experimental study was carried out on mortars with and without silica fume.

Experimental Procedure

An ordinary portland cement, a siliceous sand according to the RILEM guidelines and a silica fume was used for the mortar mixtures. Cement and silica fume properties are indicated in Table 1. The sand:cement was 3, and water:cementitious material was 0.5. Silica fume replaced 10% of the cement by mass for the PC-SF mortars. After mixing, the mixtures

TABLE 1

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	-
Mineralogica lcomponents (%)		
C_3S	46.94	
C_2S	22.35	
C_3A	10.74	
C_4AF	10.86	

were cast into 40 x 40 x 160 mm prismatic moulds. They were kept in laboratory conditions for 24 hours and then the demoulded specimens were transferred into the lime saturated water at 20°C. After having 27 days cure time under this conditions, with exception of the control specimens (PC-W, PC-SF-W) all others were transferred into magnesium sulfate solutions at 20°C. Sulfate (SO_4^{-2}) concentrations were 1900 mg/L (MK), 13000 mg/L (ML) and 52000 mg/L (MM). Solutions were renewed every 14 days. Capillary and volumetric water absorption, density, compressive and flexural strengths were determined at the 28th, 90th, 180th and 300th day.

Flexural strength tests were carried out on three 40 x 40 x 160 mm prismatic specimens and then compressive strength on six pieces of prisms. Mass changes were calculated as the difference of the mass of saturated surface dry specimen at any time and just before the sulfate exposure. The other tests were performed on 40 x 40 x 75 mm prismatic specimens. For this purpose, 40 x 40 x 160 mm prismatic moulds separated in two compartments by a metal sheet and then mortar mixture was cast into these compartments. These 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. Before the testing, specimens were dried in the oven at 105 ± 5°C until constant mass was achieved. For the capillary water absorption test, the lower face (parallel to the trowelled upper face) having 40 x 75 mm dimensions was brought in contact with water in a tray. During the test, environment temperature was 20 ± 1 °C and relative humidity was 65 ± 5%. Absorbed water was measured at different intervals. Capillary water absorption coefficient was calculated as the initial slope of the curve of absorbed water versus the square root of time. 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 percentage by the volume of specimen. Density was calculated by dividing dry mass to volume.

Results

The compressive and flexural strengths, the capillary coefficient, the volumetric water absorption, the density results of the PC and PC-SF mortar before the sulfate exposure are presented in Table 2. All the experimental results of these properties as rated in comparison of those of water cured PC control specimens (PC-W) and the mass changes are shown in Figs. 1-6.

Compressive Strength. PC control mortars (PC-W) gained strength up to 180 days and thereafter no further increase (Fig. 1). Specimens stored in sulfate solution of 13000 mg/L

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

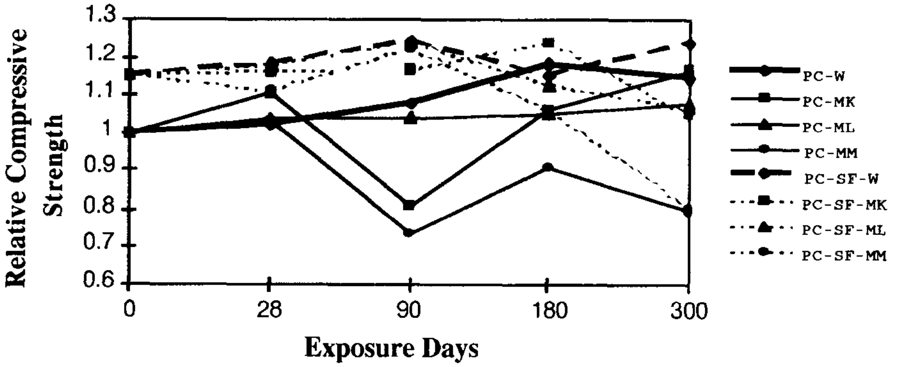

FIG. 1.
Relation between relative compressive strength and exposure days.

showed continuous increase in strength, but they had lower strength comparing to the control specimens after 28 days. Specimens stored in solution of 1900 mg/L exhibited irregular strength changes in time. The compressive strength of these specimens was not affected by the sulfate attack. Specimens in solution of 52000 mg/L showed continuous strength loss after 28 days. Strength of these specimens was lower 30.5% than the control specimens at the end of 300 days. Higher sulfate concentration resulted in lower compressive strength at 300 days.

For the PC-SF control mortars (PC-SF-W), silica fume replacement caused strength increase at 180 days (Fig. 1). The concentration of 13000 mg/L showed no significant effect on the compressive strength up to 90 days, while the other concentrations caused slight strength reductions. In contrast to PC-W specimens, the compressive strength of PC-SF-W did not increase at early days of sulfate exposure for all the concentrations. Rapid strength decrease was observed after 90 days in solution of 13000 and 52000 mg/L and 180 days in 1900 mg/L. Especially considerable strength reduction could be seen for the specimens in solution of 52000 mg/L.

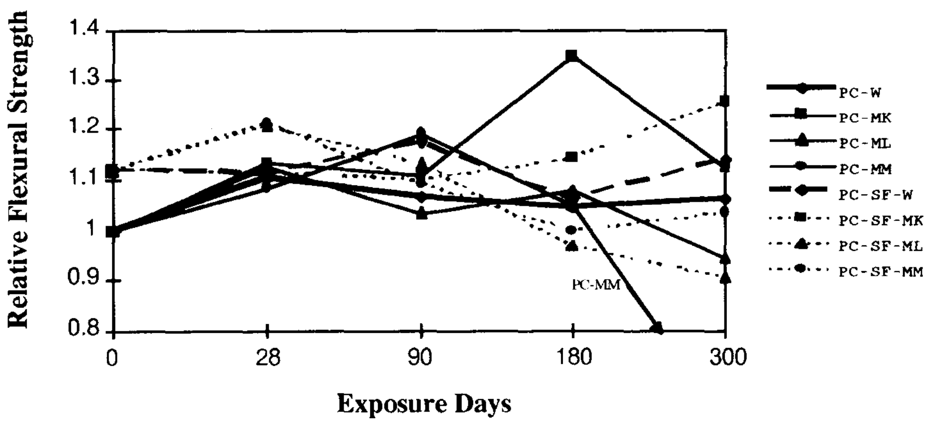

FIG. 2.
Relation between relative flexural strength and exposure days.

Flexural Strength. As is presented in Fig. 2, sulfate attack did not have a significant effect on the flexural strength up to 180 days for PC mortars at all concentrations. Moreover, relatively high flexural strengths were obtained at the 90th and 180th day for some concentrations. At later days, a considerable strength decrease was observed for all the sulfate exposed specimens. Especially, specimens immersed in 52000 mg/L solution exhibited 42.5% flexural strength loss among 180 and 300 days. At 300 days, higher sulfate concentration resulted in lower flexural strength as was observed for compressive strength.

Silica fume replacement had a beneficial affected on the flexural strength of mortars which in the solution of 13000 and 52000 mg/L at 28 days (Fig. 2). Thereafter, the specimens in 13000 mg/L solution showed continuous strength loss. After some reduction, strength increase was observed in 1900 mg/L solution. Flexural strength of the specimens immersed in 52000 mg/L showed up and down behavior.

Mass Change. There was a continuous increase in mass of the PC-W specimens (Fig. 3). At early age, the specimens immersed in 1900 and 13000 mg/L solutions lost weight. This lost was offset to some extent over time. The mass of the mortars placed in solution of 52000 mg/L showed a different trend. After a short period of decrease, the mass increased period up to 126 days. Thereafter mass loss was again observed up to 300 days.

In water and in solutions of 1900 and 13000 mg/L, mass changes of PC-SF mortars were very limited up to 300 days. For the specimens in solution of 52000 mg/L, three different periods can be identified similar to the companion PC specimens. First of all mass loss at early days, mass gains later, and finally mass loss up to 300 days.

Capillary Water Absorption. The results of the capillary water absorption are given as relative capillary coefficient in Figure 4. Capillary coefficient showed regular decrease in time for PC control mortars. All the specimens exposed to sulfate attack had lower capillary coefficient at the 28th day than the control specimens. For the specimens in solution of 1900 mg/L there was a slight change among 28 and 180 days. A sharp increase in capillarity was observed after 180 days for these specimens and 90 days for the other sulfate exposed specimens.

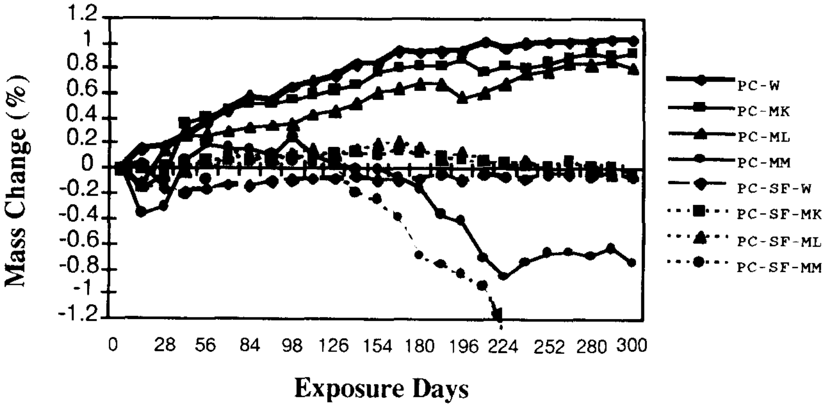

FIG. 3.
Relation between mass changes and exposure days.

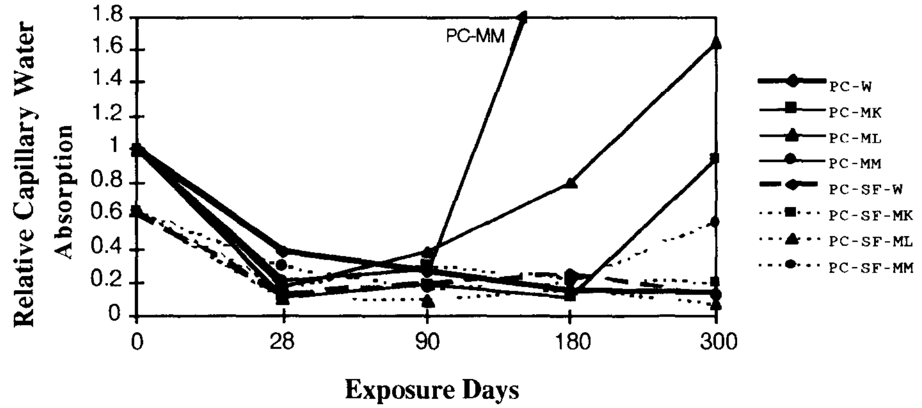

FIG. 4.
Relation between relative capillary water absorption and exposure days.

Silica fume replacement resulted in lower capillarity for the PC-SF control mortars at early days (Fig. 4). The effect of magnesium sulfate solution on the capillarity of PC-SF mortars was very small except for the mortars placed in the 52000 mg/L solution at 300 days.

Volumetric Water Absorption. Volumetric water absorption of PC control mortars showed a decrease at early days and a slight increase at later days (Fig.5). All the sulfate exposed specimens had lower volumetric water absorption than that of PC control mortars at the 28th day. They exhibited continuous increase in volumetric water absorption at later days and rapid increase depending on the sulfate concentration. At the end of 300 days, volumetric water absorption of mortars in solution of 13000 mg/L was higher than that in solution of 52000 mg/L.

Before the sulfate exposure, volumetric water absorption of PC-SF mortars was higher than that of PC mortars, probably because of the higher porosity of the former due to less

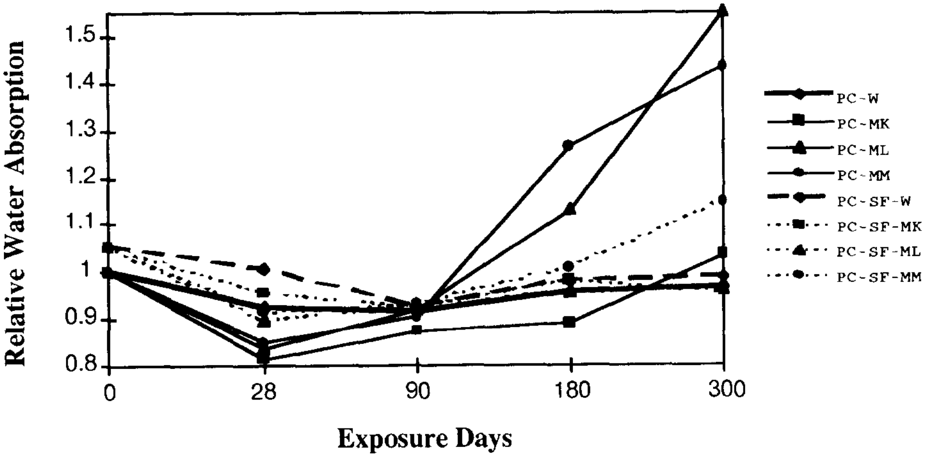

FIG. 5.
Relation between relative volumetric water absorption and exposure days.

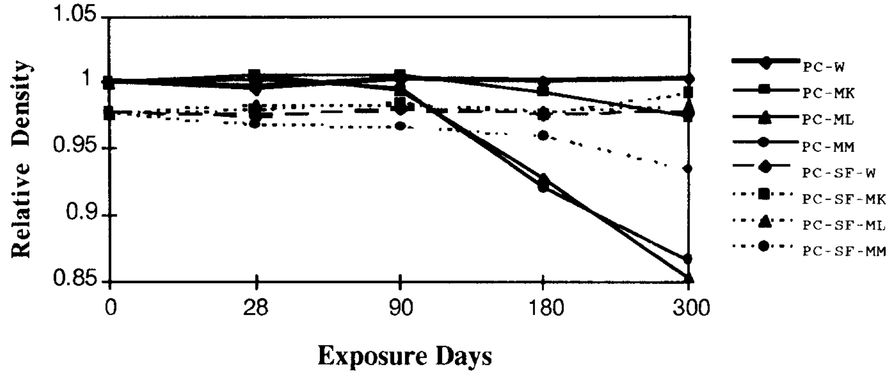

FIG. 6.
Relation between relative density and exposure days.

workability (Fig.5). PC-SF control specimens exhibited decrease at early days and increase at later days as was observed for the PC control specimens. While the mortars in solution of 52000 mg/L showed rapid increase in volumetric water absorption, change was very limited for the other concentrations. For the companion conditions, PC-SF mortars had lower volumetric water absorption than the PC mortars at the end of 300 days.

Density. PC control specimens did not exhibit significant density change in time (Fig.6). At early days, sulfate exposed specimens had slightly higher density relative to PC control mortars. Density of the specimens in sulfate solutions decreased at later days. Decrease began after the 28th day and acceleration of it was after then the 90th day. Density decrease was sharp for the mortars in solution of 13000 and 52000 mg/L.

PC-SF mortars had lower density relative to PC mortars before the sulfate exposure (Fig.6). Density of PC-SF control specimens was nearly constant in the course of the experiment. In solution of 1900 and 13000 mg/L, density of PC-SF mortars was slightly higher than that of PC-SF control mortars during the experiment. In solution of 52000 mg/L, density of mortars continuously was lower than that of the other specimens and accelerating density drop was observed after 180 days. However this drop took place sooner and was rapid in the case of PC mortars.

Discussion

For the PC mortars, magnesium sulfate attack can be examined in three different stages. These stages can be defined as early, transition and later. At early stage of sulfate attack, decrease in capillary and volumetric water absorption, and slight increase in density can be observed. Pore filling process of reaction products of sulfate attack is effective at this stage. On the other hand, magnesium sulfate attack produces an outer brucite film on the surface of material (3). Brucite has low solubility (6,8) and is relatively impermeable (7). Probably these two phenomena result in the reduction of water absorption. There was no significant difference among the specimens due to sulfate concentration at early days. This implies that, at the early stage of magnesium sulfate attack, the pore filling process is the dominant factor. At this stage, some improvements in mechanical strengths were observed. It seems that early stage ended at about 28 days of exposure. After the 28th day, capillary and volumetric water absorption increase and density decrease indicate effectiveness of deterioration processes. However these negative changes were not rapid for a period. This period can be called the transition stage and ends at about 90 days for 13000 and 52000 mg/L and 180 days for 1900 mg/L. Mechanical strengths did not show a clear trend. Decreasing and increasing cycles could be seen at this stage.

After the transition stage, negative changes of physical properties accelerate indicating the later stage. Beginning of this stage is the critical time. After this time, deterioration processes due to magnesium sulfate attack become clearly dominant.

When the capillary water absorption is considered, there were clear differences among the specimens depending on the sulfate concentration. While the changes of volumetric water absorption and density in 13000 and 52000 mg/L solution were almost at the same rate, they were at a lower rate in 1900 mg/L solution. On the other hand, when regarding mass changes, specimens in 1900 and 13000 mg/L showed almost the same trend. Rapid mass loss was observed in 52000 mg/L solution after 90 days. Complicated nature of response of the material properties to the magnesium sulfate attack can be attributed to the formation of different reaction products at different stages and dependence of product formation to the sulfate concentration. As mentioned above, brucite retards deleterious effect of sulfate attack at early stage. At later stage, sulfate solution can diffuse more easily into the material due to the decomposition of CSH gel to MSH gel. This alteration is the major process at high concentrations as was reported by Cohen and Mather (2).

Compressive and flexural strengths showed different response to magnesium sulfate attack at later stage. As flexural strength of the specimens showed rapid losses at every concentration after 180 days and compressive strength showed decrease only in 52000 mg/L concentration. Changes in mechanical and physical properties are not simultaneous. Sulfate attack stages can be identified best by the physical property changes for the PC mortars. Only in 52000 mg/L concentration, all the measured properties showed clear negative changes. Capillary water absorption is the most proper parameter to show the effect of magnesium sulfate attack on PC mortars. Capillary water absorption is sensitive to the formation of microcracks at the surface and to the changes in diameter of micropores which in the interior part of material (12).

Response of PC-SF mortars to magnesium sulfate attack was quite different from that of PC mortars. A significant difference was more regular changes of properties of the former. To identify clearly definable stages of sulfate attack is difficult. However, regarding capillary and volumetric water absorption, and density some improvements took place in early days of exposure. This period is the early stage. Thereafter, change of these properties was very limited for a long time. It seems that the transition stage was prolonged. This can be attributed to the beneficial effects of silica fume before the sulfate attack. Permeability reduced by the presence of silica fume so penetration of sulfate into the material reduced (5).

For 300 days of exposure, there was no significant change of the physical properties in 1900 and 13000 mg/L solution. At the same period, mass changes were very limited. Lobo and Cohen (5) reported those silica fume pastes and mortars showed less expansion than portland cement pastes and mortars. Probably for this reason, less surface crack formed on the surface of silica fume mortars. Specimens in 52000 mg/L solution showed serious performance loss, especially after 90 days. An increasing rate of capillary and volumetric water absorption rise and density drop could be observed. Although, change rate of these properties was lower compared to PC mortars, indicates a serious deterioration process.

Mechanical strengths of PC-SF mortars showed a different trend in time. Flexural strength showed significant reduction after 28 days except for the lowest concentration.

Compressive strength reduced for all the concentrations at later days. Lobo and Cohen (5) mentioned a significant reduction related to cross sectional area of PC mortars. Probably for this reason mechanical strengths, especially compressive strength, reduced rapidly at later days. It can be suggested that mechanical strength tests are more proper parameters to evaluate the effects of magnesium sulfate on PC-SF mortars.

Test results showed that main deterioration process is the decomposition of CSH gel as reported by Cohen and Bentur (6). These alteration results loosen and powdering of surface. Cracking due to the formation of ettringite or gypsum affects the properties at a lesser degree. Hindering factor of the progress of magnesium sulfate attack is the brucite formation on the material surface for PC mortars, and the reduced permeability by the presence of silica fume. If the physical properties are considered, serious deterioration could not be realized in the case of PC-SF mortars during 300 days. Contrary to some researchers, silica fume seems to improve performance of mortar in magnesium sulfate solution. However, rapid drop in mechanical strengths indicates a more serious deterioration of PC-SF mortars at later days comparing to PC mortars. So, SF has beneficial effect in magnesium sulfate environment for a limited period.

Conclusions

The effect of magnesium sulfate on mortars can be examined in three stages. In the early stage, any detrimental effect of magnesium sulfate is not clear. Moreover some improvements in properties can be observed. Concentration increase does not cause acceleration of damage process at this stage. In the transition stage, changes in the physical properties indicate the beginning of damage process. At the later stage, most of the physical and mechanical properties indicate a rapid deterioration. These stages can be clearly defined for PC mortars. For PC-SF mortars different trends were observed. The transition stage is prolonged by the presence of silica fume.

The beginning of later stage is the critical time of sulfate attack. It depends on the sulfate concentration. Presence of silica fume retards critical time.

Contrary to expectation, silica fume replacement did not cause more performance loss for 300 days of exposure. However, mechanical strength drops indicate a possible rapid deterioration at later days. To have more reliable information about the effect of silica fume, sulfate exposure period must be longer.

Dependence of mortar properties on the magnesium sulfate concentration is complicated. For different stages of sulfate attack and different types of mortar, different material properties show different response to increase in sulfate concentration.

A very high sulfate concentration must be used to get information about the performance of cement based materials in magnesium sulfate solution quickly. However, it should be noted that high concentrations cause change in the damaging effects of magnesium sulfate.

References

1. A.M. Neville, Properties of Concrete 3rd Edition, Pitman Publishing Co., Marshfield, 779, (1981).
2. M.D. Cohen and B. Mather, ACI Materials Journal, 88, 62, (1992).
3. D. Bonen and M.D. Cohen, Cement and Concrete Research, 22, 169, (1992).
4. D. Bonen, Cement and Concrete Research, 23, 541, (1993).

5. C. Lobo and M.D. Cohen, CANMET and ACI 2nd. Intern. Workshop on Silica Fume in Concrete, Washington, (1991).
6. M.D. Cohen and A. Bentur, ACI Materials Journal, 85, 148, (1988).
7. R.S. Gollop and H.F.W. Taylor, Cement and Concrete Research, 22, 1027, (1992).
8. O.S.B. Al-Amoudi, M. Maslehuddin and M.M. Saadi, ACI Materials Journal, 92, 15, (1995).
9. V.M. Malhotra, G.G. Carette and V. Sivasundaram, Symposium on Advances in Concrete Technology, Athens, (1992).
10. C.D. Lawrence, Cement and Concrete Research, 22, 1047, (1992).
11. P.C. Mangat and J.M. El-Khatib, Cement and Concrete Research, 22, 1089, (1992).
12. F. Aköz, F. Türker, S. Koral and N. Yüzer, Cement and Concrete Research, 25, 1360, (1995).