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Effects of raised temperature of sulfate solutions on the sulfate resistance of mortars with and without silica fume

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Abstract

Effect of raised temperature of sodium sulfate and magnesium sulfate solutions on the resistance of mortars was investigated. Experimental study was carried out on mortars with and without silica fume. Sulfate concentration was 18000 mg/L as SO_4^{2-} for the sodium sulfate and 13000 mg/L magnesium sulfate solutions. Temperatures of solutions were 20 and 40°C. Some physical and mechanical properties were tested during the 300 days of sulfate exposure. Test results showed that raised solution temperature did not accelerate the deterioration of mortars under the conditions used in this research. Moreover, raised temperature improved many properties of the specimens. It can be suggested that there are some problems with raising the temperature of sulfate solution as an accelerated test method.

Keywords: Acceleration; Durability; Silica fume; Sulfate attack; Temperature

Sulfate attack on cement-based materials is a slowly progressing process. Some properties of material may be improved by the sulfate attack at early stage [1–3]. To have reliable information about the deteriorating effect of sulfate attack, a longer test duration may be needed. Some rapid test methods were suggested [3]. One of these methods is raising the temperature of solution. There is not much information in the literature about the effect of raised solution temperature on the performance of cement-based materials in sulfate environments.

Raising the solution temperature may have some difficulties because of the effects on the mixture composition, specimen size, chemistry, and microstructure of the material [3]. High curing temperature results in a coarser microstructure and formation of microcracks [4]. Mangat and El-Khatib [5] studied two different temperatures (20 and 45°C) for 7% Na_2SO_4 + 3% $MgSO_4$ solution. However, curing temperature was the same for the water curing for the first 28 days and the sulfate solution curing at later days. It is clear that their results depended on the initial curing temperature in water but not on the temperature of sulfate solution. Lawrence [6] studied magnesium sulfate resistance of mortars with different types of binder for two curing temperatures. However, curing temperatures in his study were 10 and 20°C but no higher temperatures. His results showed that the performance of mortars depended not only on the temperature of sulfate solution, but at the same time, the binder type.

In this study, the effect of temperature of sodium and magnesium sulfate solutions on the portland cement (PC) and portland cement-silica fume (PC-SF) mortars was studied. In this manner it was intended to reach a conclusion on the usability of raising solution temperature as a rapid test method.

1. Experimental procedure

Experimental study was carried out on mortars with and without silica fume. An ordinary PC, 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 Table 1. The sand/cement ratio was 3 and water/cementitious material ratio was 0.5. Silica fume replaced 10% of the cement by mass for the PC-SF mortars. Mortar specimens were cured in lime-saturated water during the first 27 days. Thereafter some of the specimens were transferred to the sulfate solutions. The solution and water temperatures chosen were 20 and 40°C. Sulfate concentrations were 18000 mg/L for the sodium sulfate solution and 13000 mg/L magnesium sulfate solution as SO_4^{2-}. Solu-

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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_2O3	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		

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 water 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

tions and water were renewed in periods of 14 days and mass changes were determined at the same periods. Compressive and flexural strengths, capillary and volumetric water absorptions, and density were measured on days 28, 90, 180, and 300 of the exposure.

A flexural strength test was carried out on three 40 × 40 × 160-mm prismatic specimens and then a compressive strength test was conducted on six pieces 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 40 × 40 × 75-mm prismatic 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 40 × 75-mm dimensions was brought in contact with water in a tray. Environment temperature was 20 ± 1°C and relative humidity was 65 ± 5°C 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 were given as percent by the volume of specimen. Density was calculated as dry mass/volume.

2. Results

2.1. Sodium sulfate solution

The compressive and flexural strength, capillary coefficient, volumetric water absorption, and density results of the PC and PC-SF mortars prior to sulfate exposure are presented in Table 2. The results of the properties at any time (except mass changes) are related to the results of PC control mortar and shown in Figs. 1, 2, 3, 4 and 5. Mass changes are shown in Fig. 6.

Flexural strength of the PC mortars in water at 40°C was continuously lower compared to those at 20°C (Fig. 1). The change of compressive strength due to raised temperature

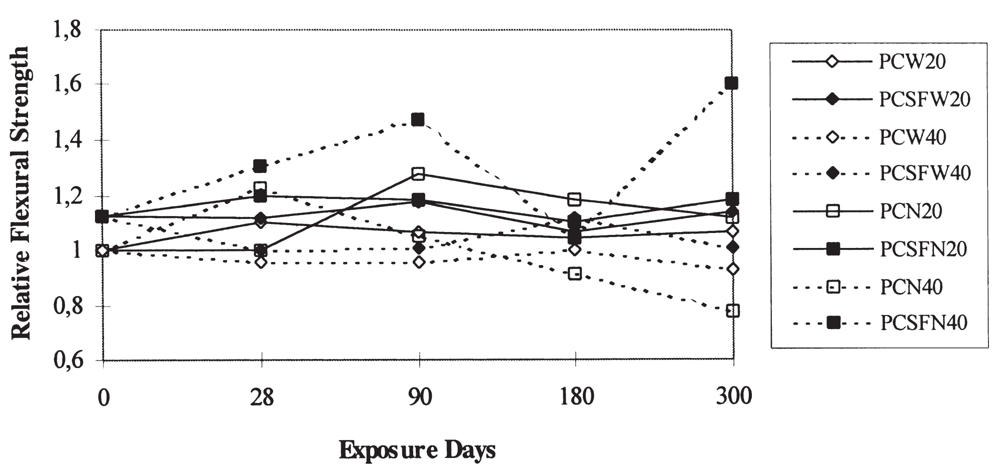

Fig. 1. Relationship between relative flexural strength and exposure days.

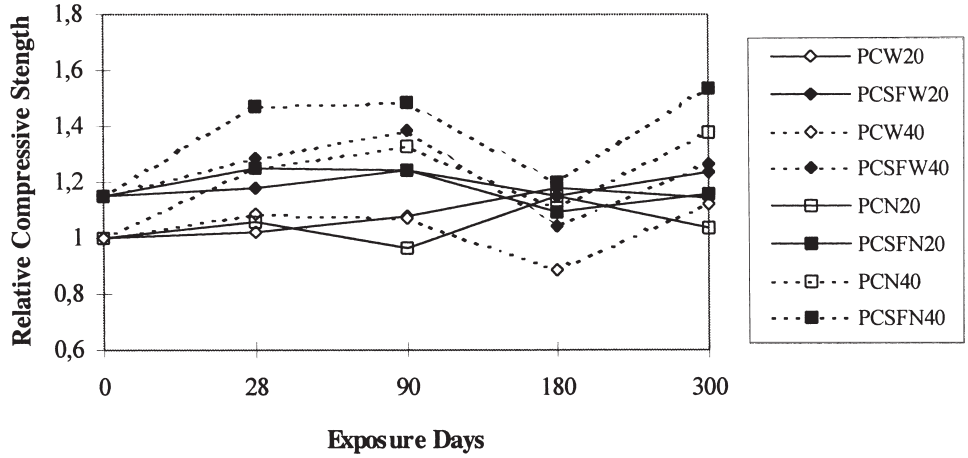

Fig. 2. Relationship between relative compressive strength and exposure days.

was insignificant except at 90 and 180 days (Fig. 2). There was significant reduction in capillarity caused by the raised temperature (Fig. 3). However, while the capillarity of PC mortars was continuously decreased in time at 20°C, it was almost constant at 40°C. Similarly, higher temperature resulted in a beneficial effect on the volumetric water absorption during the experience (Fig. 4). The beneficial effect was more significant at later days. Density was almost the same for two different curing temperatures (Fig. 5). High mass gain was observed during the first 28 days for 40°C. While the specimens at 20°C continuously gained mass up to 300 days, there were almost no changes up to 280 days and considerable decrease between 280 and 300 days at 40°C (Fig. 6).

Flexural strength of the PC-SF control mortars in water at 40°C was lower except at 180 days (Fig. 1). On the other hand, compressive strength was higher, except at 180 days. However, the difference was insignificant at 300 days (Fig. 2). Capillarity was affected beneficially at the second and third testing periods by the raised temperature and almost the same at the first and fourth periods (Fig. 3). Higher temperature resulted in lower volumetric water absorption of PC-SF mortars (Fig. 4). There was no significant effect of the raised temperature on the density (Fig. 5). Mass changes were insignificant during the test for both curing temperatures (Fig. 6).

In sodium sulfate solution, higher temperature resulted in higher flexural strength at 28 days and lower flexural strength at later days in solution at 40°C for the PC mortars. There was a significant reduction after 28 days at 40°C. Compressive strength of the PC mortars cured at 40°C was considerably higher except at 180 days. Higher temperature resulted in lower capillarity. Beneficial effect of the raised temperature was more clear at the end of 300 days. Although capillarity of the specimens at 40°C increased with time, a sharp increase in the capillarity of the specimens at 20°C after 180 days was not observed for this temperature. Volumetric water absorption for the higher temperature was higher during the first 28 days. However, raised temperature resulted in considerably lower absorption at later days. A

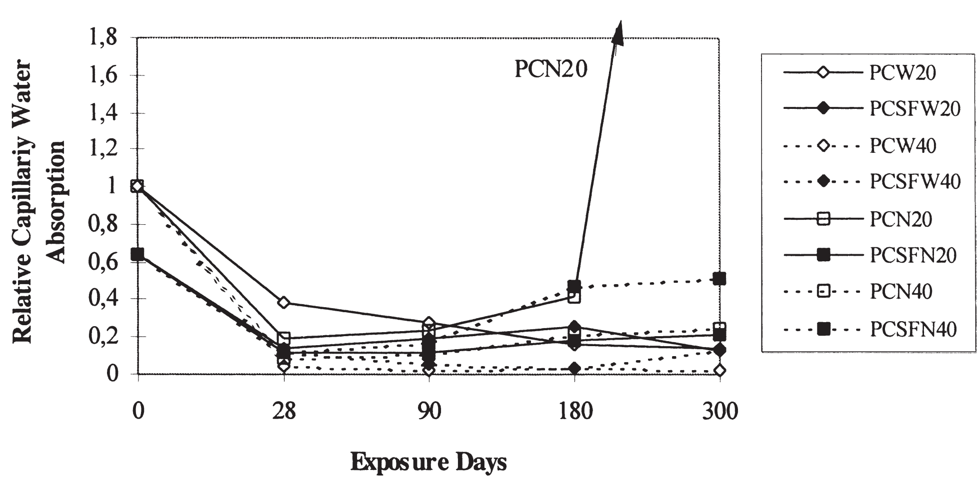

Fig. 3. Relationship between relative capillary water absorption and exposure days.

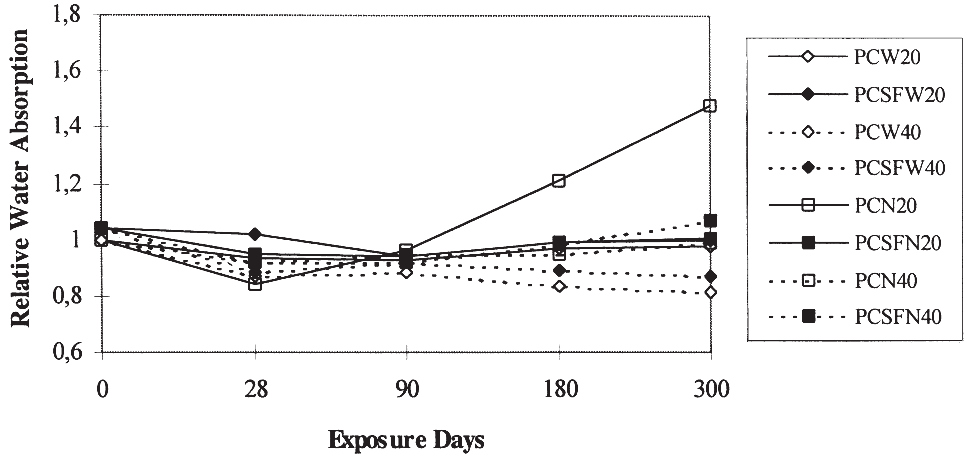

Fig. 4. Relationship between relative volumetric water absorption and exposure days.

general mass increase trend (except for some periods) was observed at 20°C (Fig. 6). Specimens showed a decrease in mass up to 70 days and thereafter continuous increase up to 300 days. This increase was higher compared to those at 20°C.

The changing trend in flexural strength of the PC-SF mortars in sodium sulfate solution was quite different from those of the PC mortars. Flexural strength at 40°C was significantly higher, except for a slight decrease at 180 days. Higher temperature also produced higher compressive strength for all the testing periods. However, the physical parameters showed a different trend. Specimens had higher capillarity at 40°C after 28 days compared to those of at 20°C. Volumetric water absorption of the mortars at 40°C was almost the same at 20°C, up to 180 days. Thereafter a slight increase was observed. Densities were almost the same for the two curing temperatures. Mass changes were not significant compared to those of PC specimens.

2.2. Magnesium sulfate solution

The results of the properties at any time (except mass changes) are related to the results of PC control mortar and shown in Figs. 7, 8, 9, 10, and 11. Mass changes are shown in Fig. 12.

Higher temperature resulted in lower flexural strength up to 300 days of sulfate exposure (Fig. 7). However, strengths were almost equal for two different temperatures at 300 days. High temperature did not have any significant effect on the compressive strength up to 180 days (Fig. 8). Thereafter, specimens in solution at 40°C had about 12% lower strength compared to those of at 20°C. Effect of high temperature on the capillarity and volumetric water absorption was similar to that on the sodium sulfate solution (Figs. 9 and 10). The beneficial effect of the raised temperature was clearer at later days of exposure. A significant density drop was observed after 90 days at 20°C (Fig. 11). There was no change in density at 40°C. An increasing trend of mass (except at some periods) was observed in sulfate solution for the two curing temperatures. However, the increase was higher at 20°C (Fig. 12).

PC-SF specimens had significantly higher flexural strength after 28 days in magnesium sulfate solution at 40°C (Fig. 7). However, there was a rapid increasing trend in

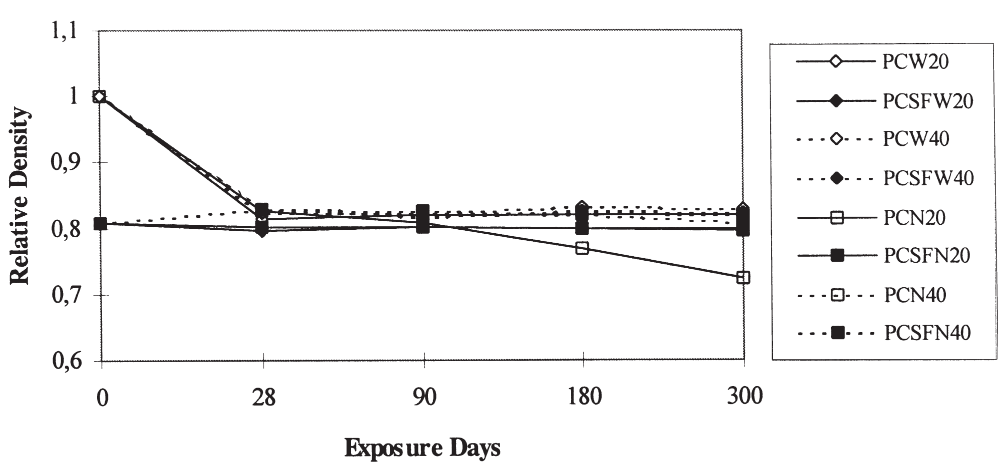

Fig. 5. Relationship between relative density and exposure days.

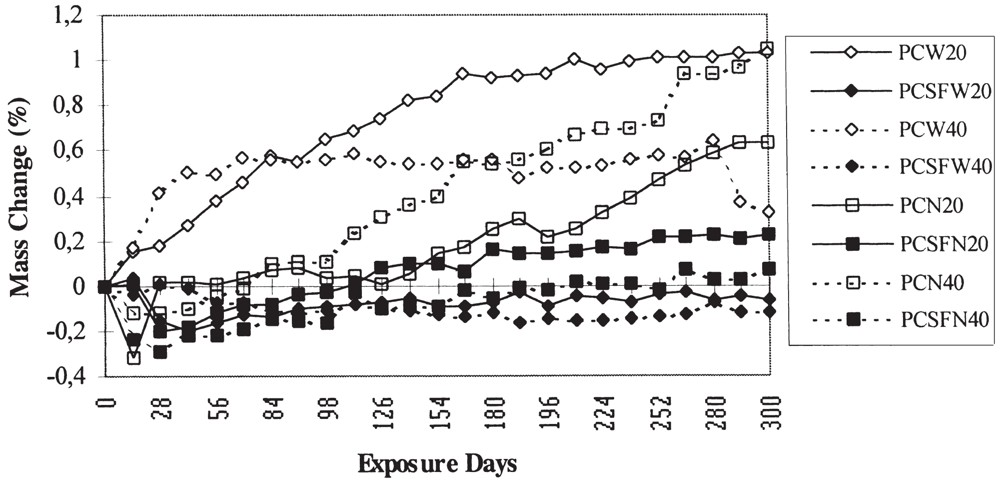

Fig. 6. Relationship between mass change and exposure days.

time. While the compressive strength at 40°C was higher up to 90 days, thereafter it was lower compared to those of at 20°C (Fig. 8). A rapid decreasing trend could be observed at 40°C, a reversal of the case of sodium sulfate solution. Capillarity of the specimens was lower up to 180 days at 40°C but higher at 300 days (Fig. 9). Higher temperature resulted in slightly higher volumetric water absorption during all the test (Fig. 10). Specimens had equal density for the two curing temperatures and there was no change in time (Fig. 11). Mass of the specimens cured at 20°C showed increasing and decreasing cycles during the test. Specimens showed a general increase in mass (except some periods) up to 300 days at 40°C (Fig. 12).

3. Discussion

Although flexural strength was continuously lower for the specimens cured in sodium sulfate solution at 40°C, physical properties and compressive strength did not indicate any negative effect of high solution temperature. Gypsum and ettringite are the main products produced by the cement hydration products and sulfate solution [7,8]. Gypsum forms mainly near the material surface and ettringite in the interior part by the sodium sulfate attack. Torii and Kawamura [9] said that these products lead to expansion of plain mortar and formation of microcracks. At higher temperature the hydration reaction will be accelerated. Thus, more $Ca(OH)_2$ will be produced. It could be expected that more gypsum and ettringite would be formed at high temperature. On the other hand, higher temperature leads to more adsorption of the SO_4^{2-} ions on the surface of C-S-H [10]. This is a reversible phenomenon and SO_4^{2-} ions can be released later to form ettringite crystals. These are the phenomena that reduce the performance of the material. On the other hand, higher temperature reduced capillary and volumetric water adsorption as can be seen from the results obtained from the specimens cured in water at 40°C. So, the diffusion rate of sulfate ions will be reduced. Experimental

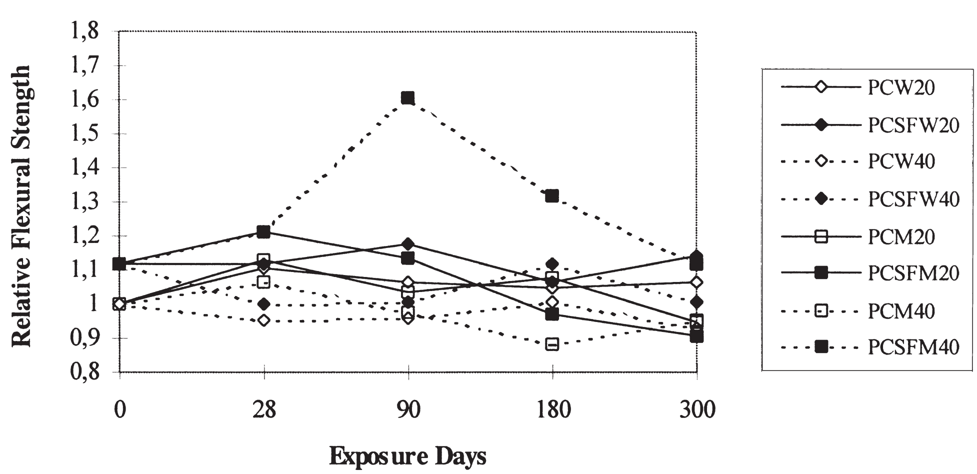

Fig. 7. Relationship between relative flexural strength and exposure days.

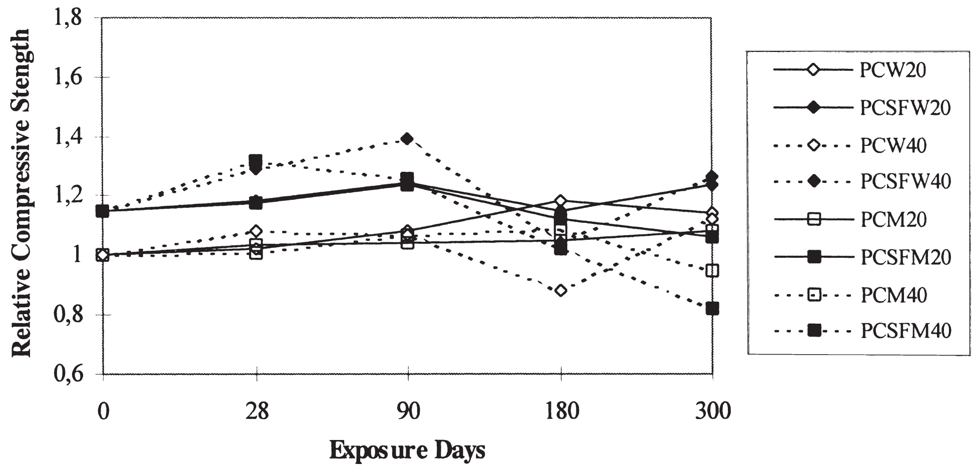

Fig. 8. Relationship between relative compressive strength and exposure days.

results showed that all the properties of mortars except flexural strength were generally better in sodium sulfate solution at 40°C than those of at 20°C. Due to our experimental results, it cannot be said that the sodium sulfate solution at 40°C produced a reduction in the performance of PC mortars.

Physical changes in the PC specimens in magnesium sulfate solution at 40°C were similar to the changes in sodium sulfate solution. Raised temperature had beneficial effect on water absorption properties of the specimens. There was no significant effect of raised temperature on the mechanical strengths. It is not possible to say that raised solution temperature resulted in lower performance of PC mortars in magnesium sulfate solution, as in the case of sodium sulfate solution.

Results showed that mechanical strengths of the PC-SF mortars were generally affected beneficially by the raised temperature in sodium sulfate solution. On the other hand, a similar trend could not be observed for the water absorption properties. Although there were some slight decreases at 40°C up to 180 days compared to the lower curing temperature condition, a negative effect of the raised temperature, especially for the capillarity, could be observed at later periods. This is a different development for PC-SF mortars compared to that of PC mortars and it is difficult to explain the reason for this result. The presence of silica fume results in a decreased $Ca(OH)_2$ content, decreased permeability [9,11] and more C-S-H gel of different composition [12]. Higher temperature accelerates hydration reactions of cement, pozzolanic reactions, and the formation of more C-S-H gel. Reduced permeability and the $Ca(OH)_2$ content beneficially affect the performance of mortars in sulfate solution. Increased amount of C-S-H gel may negatively affect the performance of mortars in sulfate solution by increasing the sites for adsorption of sulfate ions. It is not possible to determine the dominant factor affecting performance of the material in the sodium sulfate solution at 40°C. Although increasing in the absorption properties at later periods, it cannot be said that this temperature resulted in a lesser performance of the PC-SF mortars in sodium sulfate solution at 40°C compared to those of at 20°C.

PC-SF mortars showed different response to magnesium sulfate attack at 40°C curing condition. All the physical and

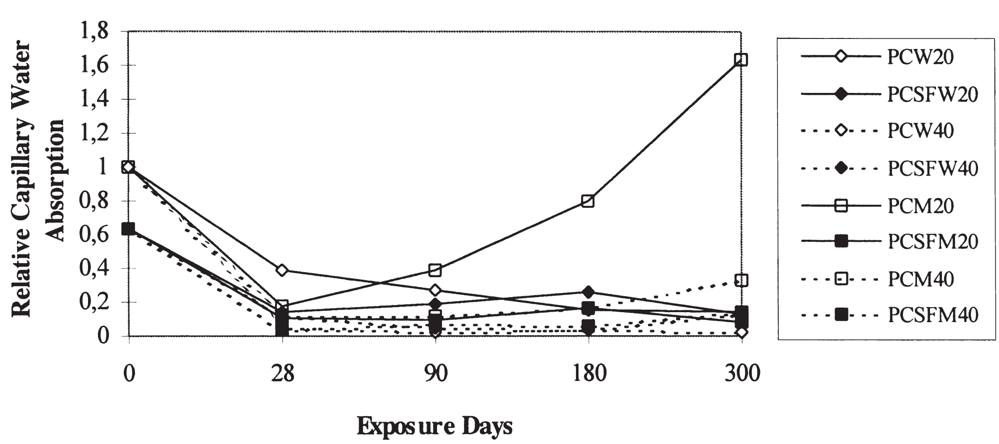

Fig. 9. Relationship between relative capillary water absorption and exposure days.

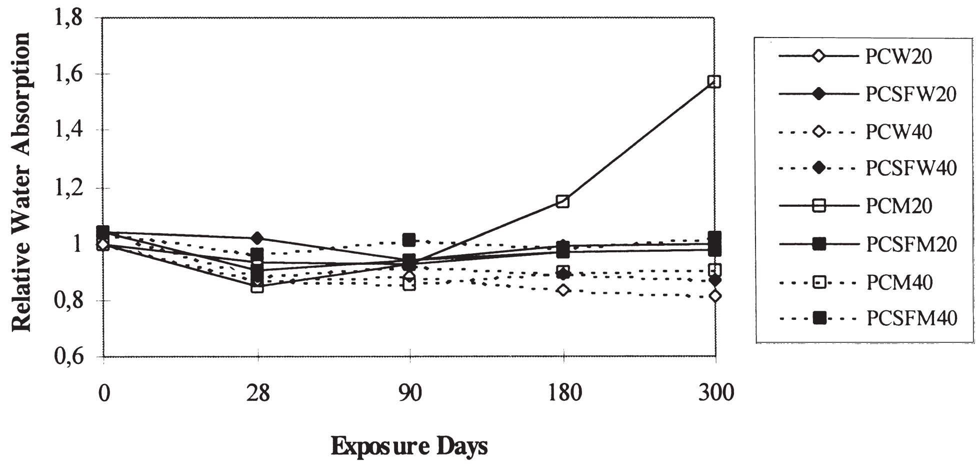

Fig. 10. Relationship between relative volumetric water absorption and exposure days.

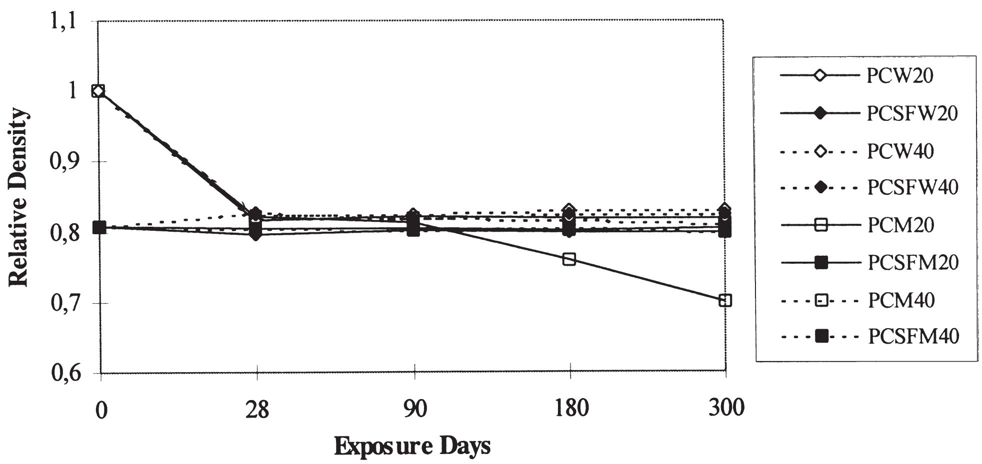

Fig. 11. Relationship between relative density and exposure days.

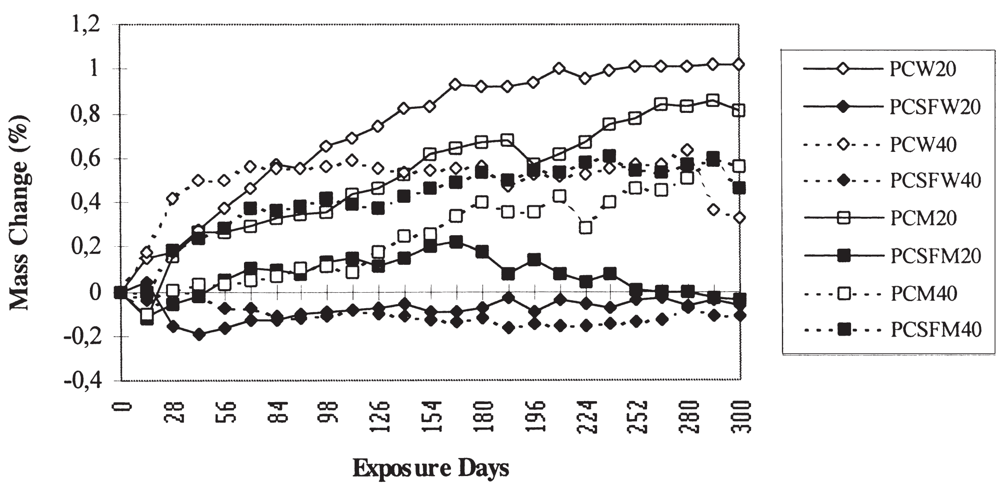

Fig. 12. Relationship between mass change and exposure days.

mechanical properties indicate a reduction in the performance of mortars cured at 40°C at later days. The main deteriorating process is decalcification of C-S-H gel to M-S-H gel in magnesium sulfate solution [12,13]. Torii and Kawamura [9] stated that this transformation leads to a porous and noncementitious structure. On the other hand, C-S-H formed by the pozzolanic reaction may be more susceptible to the magnesium sulfate attack [14]. Since more C-S-H gel would be produced by the accelerated pozzolanic reactions at the condition of high temperature, a larger part of the structure will be decomposed by the magnesium sulfate attack. Probably this change is the main cause of the performance drop of PC-SF mortars in magnesium sulfate solution at 40°C.

4. Conclusions

Results of this research showed that raising temperature of sodium sulfate solution to 40°C led to some changes in the PC and PC-SF mortar properties. These changes were generally beneficial, especially at early days of sulfate attack. It is not possible to reach a conclusion about the performance of the material in sodium sulfate solution at later days by using the results of early days. Hence, raised temperature of solution cannot be used as a rapid test method. However, it should be noted that this conclusion is limited for the solution at 40°C.

The above mentioned conclusion is valid for the PC mortars in the case of magnesium sulfate solution. For the mortars containing silica fume, there was a significant performance drop after 180 days.

Although negative effects of the raised temperature on the mortar properties in magnesium sulfate solution were observed, further research is needed to reach a satisfactory conclusion on the usability of raised temperature of sulfate solutions as an accelerated test.

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