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INFLUENCE OF Na_2SO_4 SOLUTIONS ON THE CAPILLARY ABSORPTION AND SHRINKAGE OF MORTARS MADE WITH CEMENT CONTAINING SILICA FUME

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ABSTRACT

Mortars containing cement with silica fume (sf) replacements of 0, 10, 20 and 30% were produced. Following 28 days of curing in water at 20°C ± 2°C, the mortars were kept in water, Na_2SO_4 solution of pH = 6 and in laboratory atmosphere at 20 ± 2°C and 65 ± 5% R.H. The specimens kept in water and sulfate solution were tested for absorption and unit mass, and those stored in air were tested for shrinkage. The coefficient of capillary absorption of 0% sf mortar exposed to sulfate increased up to 3.07 times that of the mortar cured in water while the value for the 30% sf mortar was 0.48; indicating a reduction when exposed to sulfate. The water absorption decreased by 12% at sf replacement of 30%. Shrinkages of the 20% and 30% sf were close to each other and were about 1.5 times that of the 0% and 10% sf, starting with the age of 7 days. © *1997 Elsevier Science Ltd*

Introduction

Silica fume (sf) is a man-made pozzolanic material of very high silica content. sf replacement of cement causes an increase in strength and durability of concrete (1,2,3,4). In many cases concrete is exposed to SO_4^{2-} ions, combined with NH_4^+, Na^+, Ca^{2+} and Mg^{2+} which significantly modify the sulphate effect. The effect of sulfate ion on the microstructure or mortar has been studied by many researchers (5,6,7,8).

The present work is an investigation of the effect of Na_2SO_4 solution on the capillary absorption and shrinkage of mortars made with cements containing silica fume.

Experimental Work

The properties of the cement and silica fume used in this work are given in Table 1. The cement (designation PC 32.5) came from Nuh Cement Industries, and the silica fume came from the Etibank Ferrochrome (Electro-Metallurgy) Works. The X-Ray diffractogram of the silica fume is given in Figure 1. It was obtained by Cu (Ni)K_α radiation and a current of (20 mA., 40 kV), at a speed of $2\theta = 1°$/minute using a Philips Diffractometer. It shows that silicafume is completely amorphous. The activity test results of the silica fume, given in Table 2, reveal its pozzolanic activity.

TABLE 1
Properties of Cement and the Silica Fume (3)

Chemical Composition by wt%	Cement	Silica fume
SiO_2	20.16	75.54
Insoluble Residue	0.40	17.46
Al_2O_3	7.00	1.00
Fe_2O_3	3.20	2.00
CaO	62.96	1.50
MgO	1.41	0.70
SO_3	2.94	0.40
Loss on Ignition	1.85	0.66
Physical Properties		
Specific Mass (Mg/m^3)	3.12	2.21
Setting time		
Initial (hr:min)	2:20	-
Final (hr:min)	3:20	-
Soundness, (mm)	3.0	-
Specific Surface (m^2/kg)	302 (Blaine)	26000 (BET)
Finess, % retained on		
90 μ	8.0	4.5
200 μ	0.6	0.3
Mechanical Properties of the Cement Age, days	Strength Flexural	(MPa) Compressive
7	5.5	32.0
28	7.3	44.6

Production of Mortars, Code Numbers, Curing, and Exposure Conditions

The silica fume (sf), was substituted by 0, 10, 20 and 30 percent by weight of the portland cement (pc). The fineness of the silica fume caused an increase in the mixing water requirement of mortars produced. A naphtalene formaldehyde sulfonate type superplasticizer (sp) was therefore added at a dosage of 2% by weight of pc + sf keeping also the (water + sp)/(pc + sf) ratio constant at (250 + 9)/(450) = 0.58.

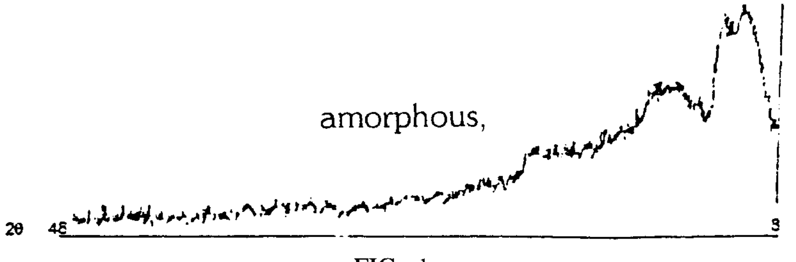

FIG. 1.
X-Diffraction of the Silica Fume (3).

TABLE 2
Pozzolanic properties of the Silica Fume (3)

	Quantities of the materials (g)			
According to	Silica fume	$Ca(OH)_2$	Sand	Water
TS 25 Trass standard (11)	293	150	1350	395
TS 639 Fly Ash standard (12)				
Mix No. 1*	112	450	1238	300
Mix No. 2**	111	293	1350	270
Strength of the pozzolanic activity mortars (MPa)				
Mix	Flexural	Strength	Compressive	Strength
	7-day	28-day	7-day	28-day
TS 25	1.6	-	5.8	-
TS 25 limits	≥1.0	-	≥4.0	-
TS639 Mix No. 1	4.8	7.4	24.8	46.9
Control mortar	4.5	6.1	18.3	27.2
TS639 Mix No. 2	-	6.5	-	36.1
Control mortar	-	6.1	-	27.2

*Silica fume used as replacement for sand.
**Silica fume used as replacement for cement.

The dimensions of the mortar specimens are 40 mm, 40 mm, 160 mm. The designation numbers of the specimens are given in Table 3. The mortars were kept at room temperature, in the molds for 1 day and then in water until the 28th day. Then test groups were exposed to Na_2SO_4 solution and the control groups were cured in water for 4 and 12 weeks. The sodium sulfate solution which is 0.35 M $Na_2SO_4 \cdot 10H_2O$ was kept at constant pH = 6 throughout the exposure by automatic pumping with H_2SO_4 from the acid tank, as shown in Figure 2 (3,9,10). The specimens were tested for capillary absorption, water absorption and for unit mass at the 4th and 12th weeks of curing and of exposure and the test results are given in Table 4. Other mortars were kept in the laboratory (20 ± 2°C, 65% R.H.) and specimens were tested for shrinkage. The test results are given in Table 5.

TABLE 3
Code Numbers and Compositions of the Mortars Tested (3)

Code Number	Silica Fume, wt%	Cement g	Silica Fume, g	Sand g	Water g	Superplasticizer g
S(Control)	0	450	-	1350	250	9
D1	10	405	45	1350	250	9
D2	20	360	90	1350	250	9
D3	30	315	135	1350	250	9

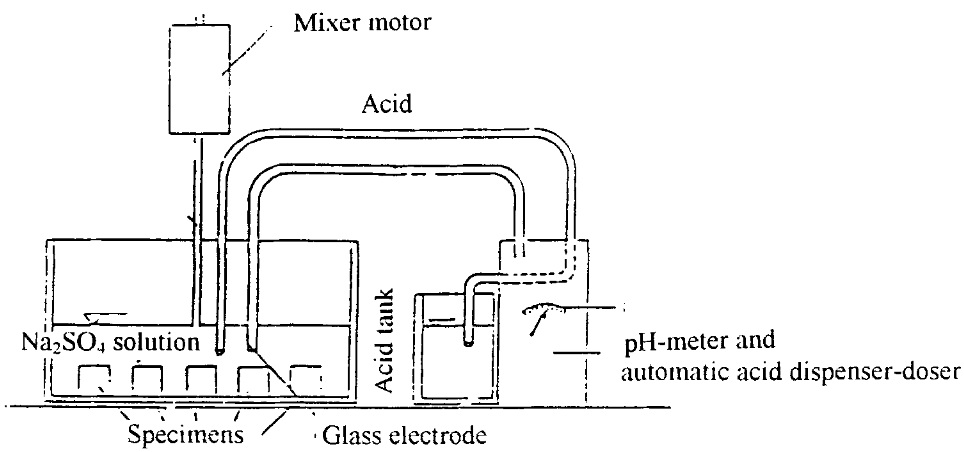

FIG. 2.
Constant pH-set-up exposure to Na_2SO_4 solution.

Evaluation and Discussion

Test results obtained on fresh and hardened mortars are evaluated below.

Properties of Fresh Mortar

The fresh unit mass flow test results can be seen in Figure 3. Samples were produced with superplasticizer.

As the silica fume content increases unit mass of mortar increases and flow decreases due to the high specific surface of the silica fume.

Coefficient of Capillary Absorption and Water Absorption of the Mortars

The variation of coefficients of capillary absorption with the duration of exposure given in Table 4 is illustrated in Figure 4. Figure 4 shows that the capillary absorption of control

TABLE 4
The Coefficients of Capillary Absorption, Unit Mass and Water Absorption of Control and Test Specimens Exposed to Na_2SO_4 Solution

	Coefficient of capillary absorption, $K*10^9$ m^2/s				Unit mass, Mg/m^3				Water absorption, wt%			
Duration of exposure												
Weeks	4	12	4	12	4	12	4	12	4	12	4	12
Code No												
S	0.94	0.52	0.68	1.59	2.04	2.02	1.97	1.96	6.9	7.6	8.2	8.3
D1	0.44	0.30	0.53	0.24	2.03	2.01	2.00	2.02	5.6	6.7	6.1	6.6
D2	0.49	0.37	0.55	0.22	2.02	2.04	2.06	2.05	6.5	5.8	5.2	6.0
D3	0.63	0.83	0.71	0.40	2.04	2.07	2.07	2.07	7.0	5.8	5.5	5.6

TABLE 5
Shrinkage of Mortars ($\times 10^{-6}$ mm/mm)

Age Days/Mortar Code	7	14	21	28	56	70	84	112
S	11.1	13.9	13.9	13.9	16.2	16.9	17.1	17.6
D1	7.7	15.9	17.9	17.9	20.9	14.4	21.7	18.8
D2	18.4	23.6	26.3	25.6	29.5	26.6	28.8	27.2
D3	20.8	22.9	25.0	25.5	26.6	26.3	27.6	26.6

specimens cured in water, except the specimen with 30% silica fume decreased between the 4th and the 12th weeks as the silica fume content increased. As for the capillary absorption of the test mortars exposed to sulfate solution a decrease is observed in the 10% and 20% silica fume mortars while a very significant increase was taking place in the capillary absorption of the control specimens. The variation in the capillary absorption of the mortars at 4-week and 12-week exposure are given in Figure 4.

The relative changes in the variation of capillary absorption with respect to the 4-week control mortar specimens and K12 sulfate/K12 water are given in Table 6.

The capillary absorption of control specimens cured in water decreased with time and with increasing silica fume content, except that of the 30% silica fume mortar which increased by 31%, from 4th to 12th week.

As for the specimens exposed to sulfate solution, the capillary absorption of the 0% silica fume control mortar increased by 169% within the same period, whereas reductions of 25 to 42% were observed in the mortars containing silica fume. In a previous research it was also observed that exposure to Na_2SO_4 solution caused no reduction in the strengths of mortars containing varying amounts of silica fume while it caused a reduction in the strengths of mortars containing silica fume (3). In other words, the Na_2SO_4 solution kept at constant pH by sulfuric acid dosing causes a reduction in the mechanical strength and durability of

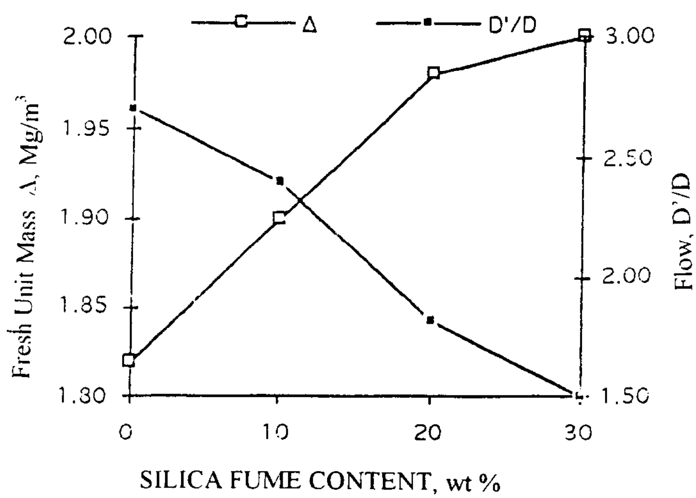

FIG. 3.
Effect of Silica Fume on Fresh Unit Mass and Flow.

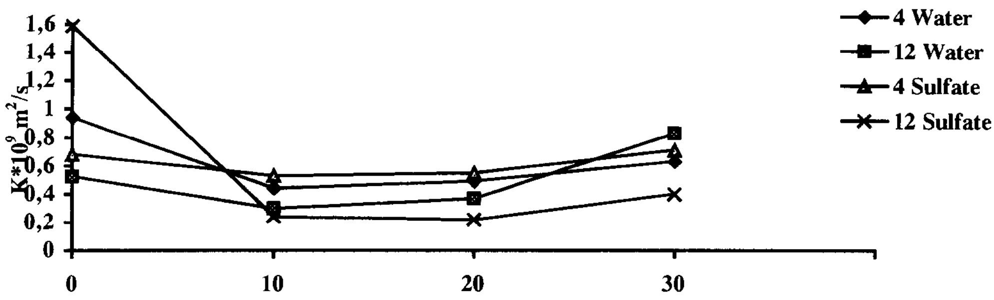

FIG. 4.
Capillary absorption of mortars.

mortars containing no silica fume at the end of an exposure applied from 4th week to 12th week reckoned from the day of production. Figure 4 illustrates the variation of the coefficient of capillary absorption as a function of silica fume content for the mortars exposed to sulfate solution and water at the 4th and 12th weeks of age.

The variation of water absorption of mortars cured in water and exposed to sulfate solution as functions of time and silica fume content of the binder are illustrated in Figure 5. Figure 5 shows that, in general, the absorptions of both control and exposure specimens decrease with increasing silica fume content on the 4th and 12th weeks, respectively. There is no significant difference between the 12th-week absorptions of control and exposure specimens.

Conclusions

Based on the evaluation and discussions given above, it can be concluded that:

1. The coefficients of capillary absorption decreased by 48% for silica fume replacement of 30%, whereas it had increased up to 3.07 times that of the control at 0% replacement at the end of sodium sulfate solution exposure period of 8 weeks. Starting at the age of four weeks and continuing up to the twelfth week, silica fume replacement resulted in a

TABLE 6
Variations of Capillary Relative to Control Specimens

Duration of exposure	Relative K Values Exposure Conditions: Water 4	Water 12	Sulfate solution 4	Sulfate solution 12	Relative Effect at 12 week $K_{sulfate}/K_{water}$: Capillary Absorption	Water Absorption
Code No						
S	100	55	72	169	3.07	1.09
D1	47	32	56	25	0.78	1.01
D2	52	39	58	23	0.59	1.03
D3	67	88	75	42	0.48	0.96

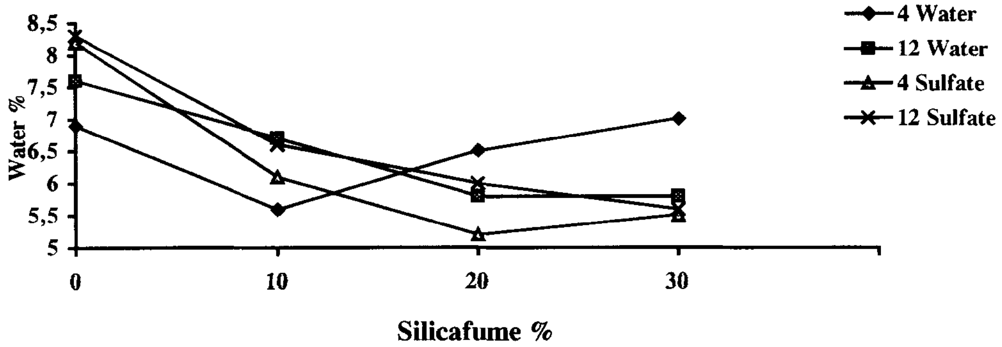

FIG. 5.
Water absorption of the mortars.

significant decrease in capillary absorption and total absorption, the decrease in total absorption being less significant.

2. Silica fume replacement of 30% resulted in an increase of about 10% in the fresh unit mass. This is in compliance with the 12% reduction in water absorption or apparent porosity of the hardened mortar. The reduction in water absorption with increasing silica fume replacement is probably partly due to the lower air content and partly due to the lower permeability of the binder paste.

   The increase in fresh unit mass despite the reduced workability as measured by flow table test can be explained by the increased cohesion due to the silica fume replacement.

3. The shrinkages of 20% and 30% silica fume replacement mortars are significantly higher than those of the control and 10% silica fume mortars starting at the age of 7 days. The shrinkage beyond the age of 28 days is insignificant.

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