Standard Sand

The standard sand used in making the mortar mixtures complied with the relevant Turkish standard. It had slightly higher water requirement for a given flow as compared with ASTM graded standard sand.

Silica Fumes

The silica fumes were obtained from the plant of Etibank Electrometallurgy Industry in Antalya. One was from the ferrosilicon furnace (SF1) and the other one was from the silicoferrochromium furnace (SF2). Their properties are shown in Table 1.

Superplasticizer

A high range water reducing admixture* complying with Type F admixture in ASTM C494 "Standard Specification for Chemical Admixtures for Concrete" was used in some of the mortar mixtures.

TESTS PERFORMED ACCORDING TO ASTM C452 METHOD

ASTM C452 standard test method determines the potential expansion of portland cement mortars exposed to sulfate. Sulfate exposure is provided by mixing the portland cement with gypsum in such proportions that final mixture has an SO_3 content of 7% by mass. The mortar mixture, proportioned as 1 part of cement plus gypsum, 2.75 parts of standard sand and 0.485 parts of water, is used to cast 25 by 25 by 285 mm prisms. After initial curing the specimens are stored in water and changes in their lengths are determined at the age of 14 days.

In the experimental program the method was applied with some modifications. In addition to the control mixture without silica fume, test mortar mixtures containing silica fume at levels corresponding to 8% and 15% of the cement mass were prepared. The quantity of gypsum was adjusted for each mix so that the SO_3 content remained constant as 1.87% of the total dry material mass as well as 7% of the cement plus gypsum.

(*) Trade name Melment L10/33

In one series of mixtures, volume of the standard sand was reduced accordingly, as silica fume partially replaced the sand. The water content of the control mixture was determined to have a flow of around 100% and was kept constant for a given set of materials. The tests were repeated using both silica fumes and different cements. The results as expansions of mortar bars at 2 weeks and 41 weeks of age are shown in Table 2a. In another group of mortar mixtures the cement was replaced with silica fume at 8% and 15% levels by mass. Again the water content was kept constant. Both silica fumes were used together with PMC2. The results as expansions of mortar bars at 2 weeks and 41 weeks of age are shown in Table 2b.

TESTS PERFORMED ACCORDING TO ASTM C1012 METHOD

ASTM C1012 standard test method covers the determination of the length change of mortar bars stored in 5% sodium sulfate solution. Mortar mixtures proportioned as 1 part of cement, 2.75 parts of sand and 0.485 parts of water, were used to cast prismatic specimens 25 by 25 by 285 mm in size and 50 mm cubic specimens. If mineral admixtures were used, the water content was adjusted to keep flow of the mortar within ±5% of that obtained with W/C of 0.485. Specimens were cured in water until the mortar cube strength reached a value of 20 MPa. At this time prismatic specimens were stored in sulfate solution for periodic length-change measurements at the ages of 1 week to 15 weeks.

In the experimental program, for a given cement and silica fume combination, one control mixture without silica fume and two test mixtures were prepared. The test mixtures contained silica fume at 8% and 15% levels of cement replacement by mass. The water content was determined to give a flow of 110±5% for the control mixture and it was kept constant for the test mixtures with the help of the superplasticizing admixture. The sulfate solutions in specimen containers were replenished at regular intervals. The results as expansions of mortar bars at the ages of 15 weeks and 41 weeks are shown in Table 3. Complete test data obtained through 65 weeks on (PMC1+SF2) is plotted in Figure 1.

OTHER TESTS PERFORMED ON MORTAR SPECIMENS STORED IN SULFATE SOLUTIONS

Effects of silica fumes on sulfate resistance of cements have been also investigated using 10% sodium sulfate and comparable magnesium sulfate solutions as the aggressive mediums. Relative deteriorations of the mortar specimens were determined by visual evaluations, and by recording the changes in the mass and compressive strength.

Preparing the Specimens and the Sulfate solutions

The mortar mixtures used in this phase of the experimental program were identical with those produced for ASTM C1012 tests. From each mixture twelve 50 mm cubic specimens were cast following the ASTM C109 standard procedure. After an initial curing period of 28 days in lime-saturated water, nine of the specimens were removed from the water. Of these, three were tested to determine the compressive strength of the mixture, three were immersed inside a 10% sodium sulfate solution and the remaining three were immersed in 8.4% magnesium sulfate solution. Both solutions had the same SO_4 ion concentration of 67.6 g/l. The solutions were replenished at 8 week intervals and the liquid level over the top surface of the specimens were kept constant.

Visual Durability Index Values

Mortar specimens stored in sulfate solutions undergo progressive deterioration accompanied by typical cracking and erosion patterns over their surfaces.Based on previous experiences with such patterns, a numbering system was developed to identify specimens at various stages of deterioration. A visual durability index (VDI) of 10 was assigned to a perfect specimen and zero was assigned to a completely destroyed specimen. During their storage in sulfate solutions cubic mortar specimens were periodically examined and rated for visual durability index values. Figure 2 shows the appearance of the specimens from the same mortar mixture group after 60 weeks in sulfate solution together with their VDI ratings. The variations in index value of the specimens from another group of mixtures through the test period are plotted in Figure 3. The values are the averages of the observations on three specimens belonging to the same mixture.

Mass Change in Specimens

The mass change of the specimens stored in sulfate solutions were determined periodically. The specimens were brought to a surface dry condition before weighing over a balance with 0.1 g sensitivity.Average values obtained from three specimens were recorded for each mixture. These values were used to plot diagrams such as the ones shown in Figure 4.

Change in Compressive Strengths of the Specimens

The effect of sulfate exposure on the strength development of mortars with and without silica fume could be studied by testing the specimens stored in the sulfate solutions and in the lime saturated water at the end of the experimental program and comparing the results with each other and with the 28-day strength of the mixture. During the laboratory studies, this phase of the test program was planned to terminate for each mixture when the specimens reached an age of 60 weeks in sulfate solution. The results available at this time are presented in Table 4.

DISCUSSION

Results of the ASTM C452 Tests

All cements used in the experiments seemed to have good sulfate resistance as determined by the ASTM C452 method. As shown in Table 2, the 14-day expansion of the control mixtures were similar to each other and remained below the 0.04% limit. However, according to the results at 41 weeks PMC2 and SRC were performing better at later ages. At constant water content, partial replacement of sand with silica fume decreased the W/(C+SF) while partial replacement of cement with silica fume increased the W/C. In both cases flow values were decreased and the effect of silica fume addition on mortar bar expansions were similar. At 14 days the effect was not significant, silica fume even causing some increase in the expansion of mortars made with PMC2 and mortars with 15% cement replacement. On the other hand, silica fume addition caused a sharp decrease in all 41-week expansions. Silica fume additions at 15% level were more effective. Of the two silica fumes SF2 caused smaller decreases in flow and seemed to perform slightly better.

Although ASTM C452 method is recommended only for portland cements it seems that it may be a useful supplementary method to evaluate the effect of the silica fumes on long-term sulfate resistance of cements.

Results of the ASTM C1012 Tests

According to the results of the ASTM C1012 test at 15 and 41 weeks the cements used in the test again showed similar sulfate resistance. One exception was PMC1 whose control mixture exceeded 0.1% expansion at the age of 41 weeks in the sulfate solutions as shown in Figure 1 and Table 2. Addition of silica fume was beneficial in reducing the expansions both at 15 and 41 weeks of age. In general 15% addition was more effective although mixtures with 8% addition could also perform well occasionally during the test period. Again SF2 seemed to be slightly more effective than SF1 in reducing the expansions at these observation periods.

Findings mentioned above are in agreement with the results of the previous work where the expansion of the portland cement mortars in 5% sodium sulfate solution and in ASTM C1012 test could be effectively controlled by the addition of silica fume (4,5).

Changes in Visual Durability Index of Specimens

The visual durability index concept was developed and successfully applied in a previous research program (6). In the current study it was again useful as an additional method to assess the gradual deterioration of the specimens by quantifying the subjective observations. The six specimens shown in Figure 2 clearly illustrate the different corrosion patterns of mortar specimens in different sulfate solutions, the effects of silica fume addition and the VDI rating system.

The deterioration of the cubic mortar specimens in concentrated sodium sulfate solutions progressed with the formation and growth of circumferential cracks along the edges of the faces. In such solutions the gypsum and ettringite formations can be considered as corrosive mechanisms. The expansive nature of gypsum formation is questioned (1). The results of this study indicated the occurence of expansions in the specimens which could be effectively controlled by the addition of silica fume.

The behaviour of the mortar specimens in concentrated nagnesium sulfate solutions was completely different. The deterioration progressed by softening and uniform erosion of the specimen surfaces. The corrosive mechanism is the magnesium attack, which decomposes the cementitious calcium silicate hydrate gel (CSH) into noncementitious magnesium silicate hydrate (1,2). Addition of silica fume to the mortar was detrimental as seen from Figure 2. This could be explained by the pozzolanic action of the silica fume resulting in the elimination of protective magnesium hydroxide layer and by the formation of a lower quality CSH gel (2).

The relative deterioration of the mortar specimens belonging to the same mixture group could be studied by plotting the VDI values as shown in Figure 3.

Results of the Mass Change Measurements on Specimens

Mass change of the mortar specimens stored in sodium and magnesium sulfate solutions followed different patterns, in line with the possible corrosive mechanisms mentioned above. As seen from Figure 4, the mass of the specimens stored in sodium sulfate solution initially showed an increase before beginning to decrease . Specimens containing silica fume had smaller mass change. In specimens stored in magnesium sulfate solution mass loss occured almost from the beginning. Addition of silica fume increased the magnitude of the mass losses. The findings were consistent with the results of a previous work performed on paste specimens in sulfate solutions of similar concentrations (2).

Results of the Compressive Strength Tests

The test data presented in Table 4 on compressive strength of the mixtures made with NPC1 supported the results of the VDI and mass change studies. According to the 60-week strength values of the specimens stored in water and in sulfate solutions, silica fume again had beneficial effect in sodium sulfate and detrimental effect in magnesium sulfate solutions. SF1 seemed to be more effective than SF2. Contribution of silica fumes to strength development seemed to diminish at the later ages.

CONCLUSIONS

- Blending with silica fume improved the sulfate resistance of cements as determined by ASTM C1012 and ASTM C452 methods.
- ASTM C452 method could be useful in studying the effect of silica fume on sulfate resistance of cements and mortars at later ages.
- Addition of silica fume improved the durability of mortars in concentrated sodium sulfate solution. However it had a detrimental effect on mortars stored in magnesium sulfate solution of similar concentration.
- In general, addition of silica fume to replace 15% of the cement by mass proved to be more effective than the 8% level.
- Of the two silica fumes, the one from SiFeCr furnaces had lower water demand and SiO_2 content. Most of the time it performed better in controlling mortar expansions.
- Cements used in the study so far had comparable sulfate resistance and the test results did not seem to be significantly affected by the type of cement.

- Visual durability index concept and measurement of mass changes were very useful in studying the deterioration of mortar specimens in sulfate solutions.

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TABLE 1 — CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF CEMENTS AND SILICA FUME

	Cements					Silica Fumes	
	NPC1	NPC2	PMC1	PMC2	SRC	SF1	SF2
Chemical Composition (%)							
SiO_2	20.84	19.93	22.33	26.36	20.74	90.00	77.82
Al_2O_3	4.57	5.60	5.38	6.35	4.74	0.40	1.62
Fe_2O_3	3.96	3.60	3.98	3.28	4.92	0.36	2.54
CaO	63.75	63.20	60.06	54.84	63.77	1.63	2.09
MgO	2.38	2.66	3.09	1.70	1.29	1.02	1.10
Na_2O	0.21	-	0.23	0.43	0.16	0.50	0.91
K_2O	0.80	0.91	0.80	0.68	0.63	2.28	1.50
SO_3	2.69	2.39	2.67	2.78	2.15	0.44	1.08
Cr_2O_3	-	-	-	-	-	-	3.83
L.O.I.	0.77	0.76	1.11	2.61	1.44	3.03	5.64
Insoluble	0.98	0.50	2.29	9.03	0.80	-	-
Physical Properties							
Specific Gravity	3.15	3.16	3.08	2.96	3.15	2.50	2.37
Specific Surface (m^2/kg)	294	310	334	348	271	-	-
Bogue Composiotion (%)							
C_3S	57.10	56.23	-	-	56.85	-	-
C_2S	16.76	14.80	-	-	16.66	-	-
C_3A	5.42	8.76	-	-	4.25	-	-
C_4AF	12.04	10.94	-	-	14.96	-	-

Note: NPC1, NPC2 - Normal portland cements; PMC1, PMC2 - Pozzolan modified portland cements
SRC - Sulfate resisting portland cement; SF1 - FeSi silica fume; SF2 - SiFeCr silica fume

TABLE 2 — RESULTS OF ASTM C452 TESTS

a) Silica Fume Partially Replacing Sand

Type of Cement + Silica Fume* in Mortar Mixture	W/C	W/(C+SF)	Flow (%)	Expansion (%)		Expansion as % of Control Mix	
				2 weeks	41 weeks	2 weeks	41 weeks
NPC1 (Control)	0.67	0.67	96	0.029	0.198	100	100
NPC1+ 8% SF1	0.67	0.60	85	0.026	0.095	90	48
NPC1+15% SF1	0.67	0.55	80	0.028	0.061	97	31
PMC1 (Control)	0.71	0.71	110	0.028	0.200	100	100
PMC1+ 8% SF1	0.71	0.65	81	0.027	0.105	96	53
PMC1+15% SF1	0.71	0.59	53	0.025	0.064	89	32
PMC1+ 8% SF2	0.71	0.65	100	-	0.095	-	48
PMC1+15% SF2	0.71	0.59	73	-	0.095	-	28
PMC2 (Control)	0.65	0.65	115	0.029	0.168	100	100
PMC2+ 8% SF1	0.65	0.58	76	0.030	0.068	103	40
PMC2+15% SF1	0.65	0.53	55	0.035	0.053	121	32
PMC2+ 8% SF2	0.65	0.59	104	0.030	0.064	103	38
PMC2+15% SF2	0.65	0.54	85	0.033	0.047	114	28
SRC (Control)	0.63	0.63	110	0.028	0.174	100	100
SRC+ 8% SF1	0.63	0.57	80	0.028	0.065	100	37
SRC+15% SF1	0.63	0.52	52	0.029	0.048	104	28
SRC+ 8% SF2	0.63	0.57	100	0.028	0.065	100	37
SRC+15% SF2	0.63	0.52	80	0.028	0.048	100	28

(*) Silica fume replacing sand expressed as % of cement

TABLE 2 — RESULTS OF ASTM C452 TESTS (CONT'D.)

b) Silica Fume Partially Replacing Cement

Type of Cement+Silica Fume**	W/C	W/(C+SF)	Flow (%)	Expansion (%)		Expansion as % of Control Mix	
				2 Weeks	41 Weeks	2 Weeks	41 Weeks
NPC2 (Control)	0.67	0.67	111	0.029	0.197	100	100
NPC2+ 8% SF1	0.76	0.67	79	0.028	0.074	97	38
NPC2+15% SF1	0.87	0.68	52	0.032	0.054	110	27
NPC2+ 8% SF2	0.76	0.67	100	0.029	0.062	100	32
NPC2+15% SF2	0.87	0.68	86	0.033	0.045	114	23

(**) Silica fume replacing % of cement by mass