Microsilica and Concrete Durability

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Results from experiments to determine the effects of microsilica on concrete freeze-thaw resistance and on the permeability to chlorides and subsequent early corrosion rates of steel in the concrete are described. The results to date show that air-entrained microsilica concretes pass laboratory freeze-thaw tests and demonstrate reduced chloride permeability and corrosion rates. ASTM C 666 testing was performed on concretes with no entrained air, below-normal entrained air, and normal air-entrainment levels on numerous mix designs with and without microsilica slurry additions. In all cases, properly air entrained microsilica mixes behaved as well as or better than control mixes. When air entrainment was not added, all mixes failed. Chloride permeabilities were determined using ASSHTO 277. Results show that silica fumes significantly reduced chloride permeability. Concrete resistivity measurements were performed using the A. C. impedance method. Microsilica significantly increased concrete resistivity over that of the control concretes, indicating that macrocell corrosion should be reduced. Corrosion-rate measurements show reduced rates (essentially noncorroding) for silica-fume concretes at 0.43 and 0.5 water-cement ratios, whereas some controls have gone into corrosion. Chloride analyses are to be performed to determine whether reduced permeability, increased electrical resistivity, or a combination of the two is responsible for the better corrosion performance.

The use of silica-fume (microsilica) additions to improve the compressive strength and durability of concrete is becoming widespread. In 1985 a large-scale study on the effects of silica-fume additions on concrete properties was initiated. In this paper, the effects of water-to-cement (w/c) ratio and silica-fume content, at a constant nominal cement factor (CF) of 600 pcy, on compressive strength, freeze-thaw resistance, chloride permeability, electrical resistivity, and corrosion resistance of embedded rebar are addressed.

EXPERIMENT

Materials

A normal type I portland cement (ASTM C 150) and silica fume were used; their chemical compositions and physical properties are given in Table 1. The silica fume was added in a water slurry. The coarse aggregate consisted of an ASTM size 67 (19–4.75 mm) trap rock. The fine aggregate was a natural sand, which met the requirements of ASTM C 33.

A modified naphthalene sulfonate formaldehyde condensate high-range water reducer was used to maintain a minimum slump of 4 in. (10 cm). A Vinsol resin air-entraining agent was used.

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Concrete Design

The mix proportions and physical properties of the fresh and hardened concretes are presented in Table 2. The mix proportions are based on two overlapping factorial designs consisting of 12 different mix designs and one repetition for a total of 13 mixes. Cement factor was kept at approximately 600 pcy, and w/c ratios were 0.38, 0.43, and 0.48. Silica fume was proportioned as an additive (rather than as cement replacement) at 3.75, 7.5, and 15 percent by weight of cement. Note that sand decreased as silica fume was added to maintain yields. Minor variations in cement factor and coarse aggregate were caused by variations in air content.

The concrete mixtures were prepared at 22°C. Samples for concrete mechanical testing and rapid chloride permeability testing were cast into 4-in. × 8-in. metal cylinder molds. The cylinders were demolded at 24 hours and cured at 22°C and 100 percent relative humidity. Cylinders for rapid chloride permeability testing were removed at 28 days.

Freeze-thaw beams were cast in 4-in. × 5-in. × 16-in. steel molds. They were cured for 14 days before initiating the tests.

Resistivity samples were cast as 3-in. × 6-in. cylinders with an embedded no. 3 reinforcing bar (0.375-in. diameter) positioned 1.5 in. from the cylinder bottom and with the top 0.5 in. protected with electroplaters tape to expose 4 in. These "lollipop" samples were demolded at 24 hr and cured to 28 days as above.

Corrosion samples include the above resistivity samples plus minislabs 11 in. × 4.5 in. × 6 in. with top and bottom no. 4 reinforcing bars. The top concrete covers were 0.75, 1.38, or 2.0 in. The bottom bar was 1.0 in. from the bottom. The reinforcing bars were taped with electroplater's tape to expose 7.0 in. of bar. A 2-in.-high plastic dam with inside dimensions of 9 in. × 2.75 in. was caulked on top, and the four sides and top surface outside of the dam were coated with a concrete epoxy. Ground clamps were used to attach a 100-ohm resistor between the top and bottom bar.

Test Methods

Compressive strengths were determined in accordance with ASTM C 39. Freeze-thaw testing was in accordance with ASTM C 666, Method A. Rapid chloride permeability tests were conducted in accordance with the AASHTO T–277 test method on samples cut from 4-in. × 8-in. cylinders. Total acid soluble chloride was determined as outlined in the Florida DOT Research Report 203 PB 289620.

Electrochemical tests were used to determine concrete resistivity and corrosion rates as a function of time. Concrete resistivities were determined by measuring the A. C. impedance of steel rebars in the 3-in. × 6-in. cylinders at 20 KHz.

TABLE 1 CHEMICAL COMPOSITION OF PORTLAND CEMENT AND CONDENSED SILICA FUME

Chemical Analysis	Portland Cement 170 (ASTM Type I)	Microsilica
Silicon Dioxide (SiO_2)	20.78	95.75
Aluminum Oxide (Al_2O_3)	4.44	0.35
Ferric Oxide ($Fe_2)_3$)	2.88	0.21
Calcium Oxide (CaO)	64.20	0.17
Magnesium Oxide (MgO)	3.66	0.09
Sulfur Trioxide (SO_3)	2.75	0.42
Alkali as Na_2O	0.46	0.51
Loss on Ignition	0.61	1.44

Each cylinder was submerged in a 3-percent NaCl solution to within 1 in. of the top surface to provide a high conductivity environment and to minimize resistance drops outside of the concrete.

The A. C. impedance measurements involved the use of a potentiostat to provide the current necessary to sinusoidally vary the potential between a calomel reference electrode and the steel rebar. The current was provided through graphite auxiliary electrodes in the NaCl solution. At high frequencies, any capacitive effects were eliminated as the impedance of a capacitor is inversely proportional to the frequency, and thus quite low relative to the resistance. This is a fast (less than 5 min) nondestructive test. A detailed explanation of the technique can be found in Dawson et al. (*1*), and a description of the PAR Model 368 Corrosion System used to make the measurements is in Scali et al. (*2*).

Corrosion-rate measurements consisted of polarization resistance and macrocell corrosion techniques. Both methods have been successfully used to measure corrosion rates of steel in concrete (*1*, *3–10*).

The polarization resistance method is a nondestructive means of determining the corrosion rate, and thus one can monitor the corrosion rate as a function of time on the same specimen. The technique uses a potentiostat to supply the current necessary to vary the potential between a reference electrode and the specimen away from the corrosion potential (typically ±20 MV). The voltage versus current curve is plotted on a linear scale.

The polarization measurements were performed using a PAR Model 351 system with current interrupt circuitry (eliminates concrete resistivity errors) as described in Berke (*3*). Specimens tested included the 3-in. × 6-in. cylinders with embedded rebars. These samples are continuously ponded in 3 in. of 3 percent NaCl to stimulate wicking action. Measurements were also performed on the minislabs.

Macrocell corrosion measurements are performed by measuring the voltage drop across the 100-ohm resistor connecting the top and bottom bars of the minibeams. The specimens are ponded with 3 percent NaCl for 2 weeks, vacuumed, allowed to room-dry for 2 weeks, and then reponded. Macrocell currents are measured at the beginning of the second week of ponding. The method is very simple and determines the galvanic corrosion susceptibility of a top salt-rich rebar mat coupled to a salt-free bottom mat with good access to oxygen.

RESULTS AND DISCUSSION

Compressive Strength

As can be seen in Table 2 and Figure 1, compressive strength increases substantially when silica fume is added to concrete. Lowering the w/c ratio also increases strength. However, at any given w/c ratio silica-fume additions increase strengths.

Freeze-Thaw Resistance

The freeze-thaw data summarized in Table 2 show that all properly air-entrained concretes with or without silica fume offer good resistance to freeze thaw. This finding is in good agreement with others who have properly air-entrained concretes with silica fume (*11*, *12*).

Chloride Permeability

The FHWA rapid chloride permeability test is a qualitative test for estimating the chloride ion permeability of concrete. The test method assumes that the total electrical charge (coulombs), which passes through the concrete, is directly related to chloride ion permeability.

Figure 2 graphically depicts the rapid chloride data in Table 2 as a function of w/c and silica-fume content. Clearly, silica-fume additions are more influential than is lowering the w/c ratio.

At this time, chloride data are available on six of the mixes (Table 2). On a gross scale, the rapid chloride test values agree with the chloride contents, e.g., mix 13 (75 coulombs/0.53 pcy chloride) vs. mix 1 (3,663 coulombs/4.9 pcy chloride) and mix 10 (3,485 coulombs/1.63 pcy chloride), even though the latter two rapid chloride values are similar. Nevertheless, both of these high-coulomb-value mixes have higher chloride concentrations then mix 13 (75 coulombs/0.53 pcy chloride).

TABLE 2 CONCRETE PROPERTIES

		Mix Proportions (pcy)				Properties of Fresh Concrete				Properties of Hardened Concrete					
Mix ID	% Silica Fume by Mass of Cement	Portland Cement	MS	Fine Agg.	Coarse Agg.	w/c	Slump (in)	% Air	Unit Weight (pcf)	28-Day Comp. Strength (psi)	28-Day Chloride Perm. (coulombs)	28-Day Resistivity (kohm-cm)	300 Cycles Freeze Thaw (RDME)	Scale Factor	10 Month Total Chloride 0.5-1.0 inch (pcy)
1	0	587	0	1194	1819	0.48	6.0	7.0	144	5160	3663	7.7	105	1	4.90*
2	3.75	588	22.0	1197	1822	0.48	5.4	7.0	144	5417	3175	16.3	—	—	ND
3	7.5	585	44.6	1268	1813	0.48	6.75	9.0	147	6346	348	45.4	100	0	ND
4	15.0	591	89.0	1204	1834	0.48	5.75	7.0	145	7357	198	94.7	102	1	0.43
5	0	556	0	1205	1723	0.43	9.75	10.5	138	5264	2585	9.3	—	—	ND
6	3.75	593	22.2	1261	1838	0.43	4.0	7.4	147	6547	2210	22.1	—	—	ND
7	7.5	573	43.0	1167	1779	0.43	8.25	8.0	140	7214	213	67.7	100	0	0.54
8	7.5	575	43.1	1246	1782	0.43	9.1	10.0	143	6751	—	67.0	—	—	ND
9	15.0	598	91.2	1295	1853	0.43	7.0	6.0	149	8582	98	118.0	—	—	ND
10	0	571	0	1312	1770	0.38	8.75	8.0	144	5782	3485	10.8	104	1	1.63*
11	3.75	585	21.9	1344	1814	0.38	3.5	8.0	147	9312	736	24.3	—	—	ND
12	7.5	591	44.3	1358	1832	0.38	8.25	7.0	149	9288	132	73.9	104	1	0.41
13	15.0	599	90.0	1377	1858	0.38	6.0	6.0	151	12119	75	161.0	102	1	0.53*
Mean Values		584	39.3	1264	1811	0.43	6.8	7.8	145	7318	1410	55.0	102	1	ND

Notes: RDME is the relative dynamic modulus of elasticity. Scale Factor ratings: 1 = Very slight scaling (no coarse aggregate visible); 2 = slight to moderate scaling; 3 = moderate scaling (some coarse aggregate visible).

* These chloride values are at 18 months.

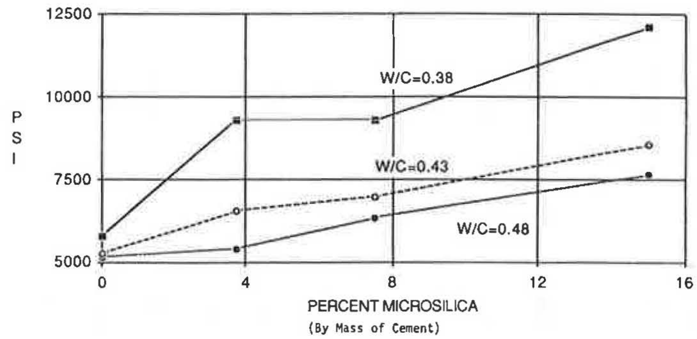

FIGURE 1 Compressive strength vs. microsilica and w/c.

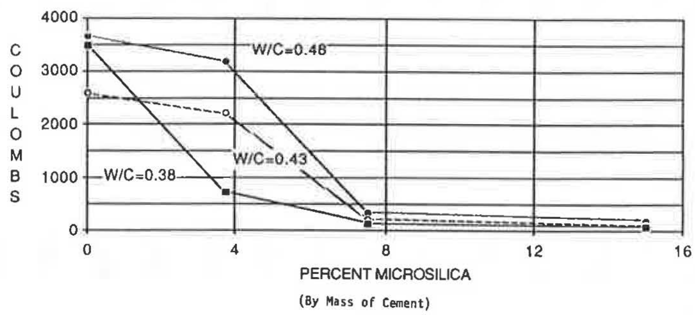

FIGURE 2 Rapid chloride permeability vs. microsilica and w/c.

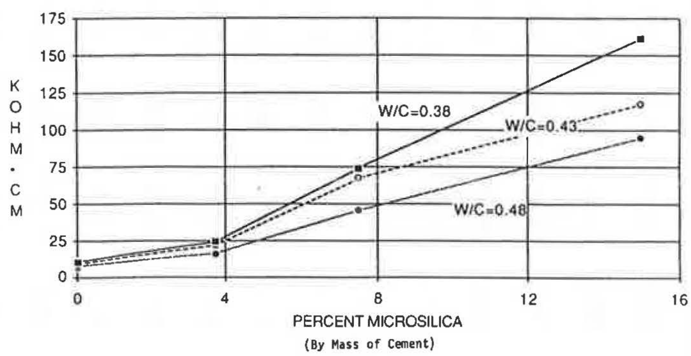

FIGURE 3 Resistivity vs. microsilica and w/c.

Thus, the rapid chloride method appears to give a qualitative indication of chloride permeability, but should not be used as a quantitative test. Note that chloride ponding is still in progress, and long-term results will be reported when available.

Resistivity

Resistivity data at 28 days is plotted in Figure 3 as a function of w/c ratio and silica-fume content. Silica fume plays the predominant role in increasing resistivity as was the case for the rapid permeability test. At any given silica-fume content, resistivity increased as w/c decreased. Note that in several cases, resistivity is substantially above 30 kohm-cm.

Corrosion processes, which are electrochemical in nature, can be affected by concrete resistivity. In general, concretes having resistivities greater than 30 kohm-cm do not exhibit evidence of corrosion (*13*). As will be shown below, this finding appears to hold for the concretes in this study.

Corrosion Studies

Corrosion data to date are summarized in Table 3. The lollipop data were determined by use of the polarization resistance method. Previous experiments in our laboratory indicate that severe corrosion is occurring at 1/Rp (Rp = polarization resistance) values above 20 umho/cm^2 (*3–5*). Note that 1 umho/cm^2 is approximately 0.01 mpy (*3*). Thus, only the control

TABLE 3 CORROSION-RATE DATA FOR LOLLIPOPS AND MINIBEAMS

					Lollipop Data 18 Months			Minibeam Data			
Mix ID	% Silica Fume by Mass of Cement	CF (pcy)	Silica Fume (pcy)	w/c	Ecorr (mV vs SCE)	1/Rp (umho/cm^2)	Cover (in)	Ecorr (mV)	12 Months Macrocell Current (uA)	Ecorr (mV)	21 Months Macrocell Current (uA)
1	0	587	0	0.48	-456	22	1 3/8	-79	0.1	-287	10.3
							3/4	-50	0		
2	3.75	588	22.0	0.48	-71	7	1 3/8	-47	0	—	—
3	7.5	585	44.6	0.48	-40	3	1 3/8	-32	0.2	—	—
4	15.0	591	89.0	0.48	-26	4	1 3/8	-35	0.1	-45	0.2
5	0	556	0	0.43	-55	5	1 3/8	-71	0.05	—	—
6	3.75	593	22.2	0.43	-83	5	1 3/8	-9	0.1	—	—
7	7.5	573	43.0	0.43	+7	4	3/4	-36	0.1	—	—
8	7.5	575	43.1	0.43	-13	4	2.0	-23	0.2	—	—
9	15.0	598	91.2	0.43	-53	3	1 3/8	-30	.1	—	—
10	0	571	0	0.38	-286	7	1 3/8	-63	0	-69	0.1
							3/4	-10	0.1		
11	3.75	585	21.9	0.38	-58	3	1 3/8	-13	0.1	—	—
12	7.5	591	44.3	0.38	-38	1	1 3/8	-32	0.1	—	—
13	15.0	599	90.0	0.38	53	4	1 3/8	-32	0.1	-46	0.1

Note that 1/Rp is proportional to the corrosion rate. Values above 20 umho/cm^2 are indicative of the onset of severe corrosion.

lollipops at 0.48 w/c are into corrosion at 18 mo of accelerated testing.

The minibeam macrocell current data indicate that, once again, only the control samples at 0.48 w/c are corroding. Note that these beams started to corrode at 17 mo.

Polarization resistance and macrocell current measurements show that the steel reinforcement in the highest w/c ratio mix without silica fume is corroding, whereas additions of silica fume have delayed the onset of corrosion. Based on previous experiments, we expect the controls at lower w/c ratios to begin to show corrosion activity at 2–2.5 yr of testing (*3*). Nevertheless, at this point, we clearly see that silica fume has prevented the onset of corrosion at 0.48 w/c.

The improved corrosion resistance with silica fume is probably due to the noted reductions in chloride permeability and to the increase in concrete resistivity. A prior study of microstructure by our laboratory (*2*) showed that silica fume significantly reduced the porosity of concrete, especially at the paste-aggregate interface. We believe that this reduced porosity is responsible for the reduced chloride permeability and increased resistivity.

CONCLUSIONS

- The addition of silica fume to concrete improves the compressive strength and resistivity while reducing chloride permeability.
- Silica fume improves the resistance to the onset of chloride-induced corrosion of steel in concrete.
- Lowering the w/c ratio of concrete improves the performance gain of adding silica fume.
- Properly air-entrained concretes with silica fume have excellent resistance to freeze-thaw damage as measured by ASTM C 666.

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