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Influence of Silica Fume Replacement of Cement on Physical Properties and Resistance to Sulfate Attack, Freezing and Thawing, and Alkali-Silica Reactivity



by R. D. Hooton

Between 1983 and 1990, a series of test programs was conducted into the physical properties and durability of pastes, mortars, and concretes made with silica fume replacements for part of the portland cement. From these test programs, it was found that silica fume: 1) reduced the permeability of both cement pastes and concretes; 2) reduced the size of pores and total porosities of both cement pastes and concretes; 3) reduced the leachable calcium hydroxide contents of cement pastes (in some cases to zero); 4) reduced the level of alkalis leached from pastes (this has implications for reduced alkali-aggregate reactivity); 5) improved the resistance of ASTM C 441 Pyrex mortar bars to deleterious expansion (10 percent replacement was adequate to meet limits); 6) provided resistance superior to that of a sulfate-resistant portland cement in ASTM C 1012 tests for sulfate resistance (10 percent replacement was adequate to meet limits); and 7) provided resistance to freezing and thawing to a series of high-strength, non-air-entrained concretes. (Indirect evidence suggested that ultra-low permeabilities and unreacted silica fume caused self-dessication resulting in noncritical saturation levels).

Keywords: alkali-aggregate reactions; durability; freeze-thaw durability; permeability; silica fume; sulfate attack.

For provision of durable concrete to most aggressive environments, the most important property is permeability. Most deleterious reactions, such as sulfate attack, alkali-aggregate reactions, corrosion of reinforcement, and freezing and thawing, initially involve the ingress or movement of water or aggressive solutions.

Designing concrete for low permeability results in restricted access of water or solutions from external sources and can also impair the internal movement of pore solutions to reaction sites. While permeability of good quality concretes can be difficult to measure,^{1,2} the study of porosity and the size distribution of pores can provide some qualitative insight into permeability.

The results of several laboratory studies on the use of silica fume as a cement replacement, especially with respect to its effects on permeability, pore structure, and durability to specific aggressive environments, are described. While much of this work was directed toward developing durable concrete

materials for engineered barriers for radioactive waste management,^{1,3,4} it is for the most part relevant to other end uses requiring durable concrete.

RESEARCH SIGNIFICANCE

The use of silica fume in concrete has become widespread in North America in the areas of both high-strength concrete and where durability is of prime concern, especially in parking structures. In spite of its increasing use, little data has been published with respect to the effects of silica fume on permeability, as well as resistance to sulfate attack and alkali-aggregate reactivity. Data is presented on these topics for silica fume replacements of 5 to 20 percent by mass of the cement. In addition, data is provided on the controversial topic of resistance to freezing and thawing of nonair-entrained concretes. The good resistance observed in this study is explained by several pieces of evidence which indicate that the concretes had self-desiccated and were therefore not critically saturated.

MATERIALS

Compositions of normal (CSA Type 10; ASTM Type I) portland cement (NPC), sulfate-resisting (CSA Type 50; ASTM Type V) portland cement (SRPC), and silica fume (SF) used in the various studies are given in Table 1. The silica fume powder was undensified and was obtained from a plant in Quebec. The superplasticizer was a melamine formaldehyde condensate with 20 percent solids content and a relative density of 1.105.

For comparison, a commercially available, preslurried, silica fume product containing a superplasticizer was used in the concrete program. This product contained 45 percent silica

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fume, 51 percent water, and 4 percent other solids (the solids fraction of the admixtures) by mass with a relative density of 1.345.

Aggregates for the mortar programs were either standard Ottawa quartz sand, as outlined in ASTM C 1012, or graded and washed Pyrex, as outlined in ASTM C 441.

The concrete sand was an Ontario Hydro Laboratory standard Paris sand with a fineness modulus of 2.75, bulk density of 2680 kg/m³ (167.2 lb/ft³), and an absorption of 1.50 percent. The 20-mm maximum-size coarse aggregate was laboratory standard Dundas crushed limestone having a bulk density of 2730 kg/m³ (170.4 lb/ft³) and an absorption of 1.00 percent.

SPECIMEN PREPARATION

Pastes

Pastes were mixed under vacuum in a high-speed, stainless steel, 3.8-l (1-gal)-capacity blender. The cubes cast for compressive strength determinations were 50 mm (2 in.).

Specimens for permeability and pore size determinations were obtained from paste cast into a 100 x 200-mm (4 x 8-in.) metal cylinder mold, sealed with a rubber membrane, then rotated about its axis for 18 to 21 hr to avoid bleeding and segregation. All molds were stripped at 24 hr and specimens were moist-cured subsequently. Each cylinder was later sliced into three 40-mm (1.5-in.) discs and one 25-mm (1.0-in.) disc, three for permeability measurements and the thinner one for pore size determinations and x-ray diffraction (XRD).

Mortars

For sulfate resistance, 25 x 25 x 125-mm (1 x 1 x 5-in.) gage-length mortar bars were cast to measure length change and 50-mm cubes for compressive strength.

For alkali-aggregate reactivity tests, 25 x 25 x 250-mm (1 x 1 x 10-in.) gage-length mortar bars were cast to measure length change.

Table 1 — Composition of cementing materials

	Normal portland cement (NPC)	Sulfate-resisting portland cement (SRPC)	Silica fume (SF)
CaO, percent	62.2	62.82	0.30
SiO ₂	20.7	22.46	93.89
Al ₂ O ₃	5.8	2.79	0.19
Fe ₂ O ₃	2.64	3.92	0.32
MgO	2.97	3.27	0.71
SO ₃	3.11	2.03	0.28
Na ₂ O	0.39	0.45	0.13
K ₂ O	1.18	0.41	0.93
Na ₂ O equivalent	1.17	0.72	0.74
LOI	1.72	0.91	2.72
Bogue C ₃ A	10.9	1.4	—
Relative density	3.12	3.13	2.32
Blaine, m ² /kg	359	406	4870*

*Nitrogen BET surface area = 23,000 m²/kg.

Concretes

Concretes were mixed in a 0.04-m³ (1.5-ft³) flat pan mixer. Both coarse and fine aggregates were presoaked in water for 24 hr prior to mixing. Specimens for compressive strength, split tensile strength, and elastic moduli tests were 150 x 300-mm (6 x 12-in.) cylinders. Drying shrinkage and freezing and thawing tests were performed on 75 x 100 x 350-mm (3 x 4 x 16-in.) gage-length prisms.

TEST PROCEDURES

Cumulative pore size distributions were obtained by mercury intrusion using an automatic scanning porosimeter with intrusion pressures up to 414 MPa (60,000 psi), and assuming a contact angle of 140 deg. Specimens were dried for 16 to 20 hr at 110°C, crushed to pass a 4.7-mm (# 4) sieve and be retained on a 2.4-mm (# 8) sieve, then dried again at 110°C prior to testing. For concretes, only the mortar fractions were crushed for testing.

X-ray diffraction traces were made using a diffractometer with Copper k α radiation at a scan rate of 1 deg/2θ/min from 6 to 70 deg/2θ.

Water permeabilities of pastes were measured using specimens and test cells adapted from those described by MacInnis and Nathawad.⁵ For each composition, sand-filled epoxy rings were cast around the roughened perimeters of the paste or concrete discs. Each cell consisted of two stainless steel end plates fitted with O-rings to bear against the epoxy ring. The bottom faces of the specimens were exposed to deaired, deionized water that was pressurized with a piston driven by nitrogen gas. The top faces of the specimens were saturated and the flows of permeating water were measured in calibrated 10-ml glass tubes attached to the top plates of the cells (readings were taken to the nearest 0.01 ml). For the pastes, constant pressures of 172 kPa (25 psi) were applied for 7-day-old specimens, and 690 kPa (100 psi) for later ages for periods of up to 96 hr.

For the concrete permeabilities, 100 by approximately 200-mm cores were placed in a high-pressure triaxial permeability cell. Deaired, deionized water was used with the pressure system described for the paste specimens. Confining pressures were 17.2 MPa (2500 psi), while pressure differentials across the cores ranged up to 12.5 MPa (1800 psi) for periods of up to 2 months.

For both paste and concrete permeability tests, specimens were saturated in water under vacuum for at least 24 hr prior to each test. Flow volume-time curves were plotted, and after initial, nonlinear portions were deleted, permeability constants were calculated using Darcy's equation. Where no flow was observed, the permeability was estimated assuming a flow of less than 0.01 ml of water over the period of test. Such results are denoted by "less than" symbols.

Rapid chloride permeabilities were measured according to AASHTO T 277 (ASTM C1202) on 50 x 100-mm (2 x 4-in.) discs cut from cylinders.

CEMENT PASTE TEST PROGRAM AND RESULTS

Cement pastes consisting of SRPC, partially replaced with 0, 10, and 20 percent by volume SF, were mixed at a water-to-cementing materials ratio (W/CM) of 0.25 and were moist-

cured at 23 C. Measurements of compressive strength, permeability, pore size distribution, and calcium hydroxide content were made after 7, 28, 91, and 182 days. More details are given elsewhere.¹

Strength development

Values for compressive strength development are given in Table 2(a). At all ages, the paste containing 20 percent silica fume exhibited higher strengths than the one containing 10 percent. The lower strengths relative to the SRPC paste may be due to microcracking caused by higher plastic shrinkage, or self-desiccation due to the low permeabilities.

Permeability

The permeability coefficients calculated for the pastes are given in Table 2(b). In some cases, no flows could be determined, as indicated by the "less than" symbol. The paste containing 20 percent SF replacement was more effective in minimizing permeability at 28, 91, and 182 days.

Chemical effects on permeated water

Water samples were taken from the cavity in the top plate of each permeability cell after 24 hr of exposure and analyzed for sodium, potassium, and calcium concentrations, as well as pH. The average results for both 28- and 182-day curing are given in Table 3. Calcium hydroxide (CH) contents of the pastes obtained by XRD are also shown. At 28 days, variations in permeability (also shown as k) may have influenced results, but at 182 days all permeabilities were low. Therefore, at the later age, the deionized water was likely altered only by contact with the top surface of the paste disc—similar to a static leach test. It can be seen that SF generally reduced the ion concentrations in the water, with the 20 percent replacement being the most effective. The results give a crude indication that a condensed silica fume mix would be more leach-resistant, and also that the alkali available for potential alkali-aggregate reactions would be reduced greatly.

Pore structure

The total mercury-intruded porosities for the various pastes and moist-curing periods are shown in Table 2(c). The 20 percent SF paste exhibited the lowest porosities at all ages. However, total porosity is not a good indicator of quality (i.e., permeability), since very small-size gel pores would not contribute to increased permeability. While a unique relationship between permeability and pore size distribution has not been found, in general, a smaller volume of coarse pores (greater than approximately 0.025 to 0.05 μm radius^{6,7}) results in a lower permeability. The volumes of pores larger than 0.025 μm radius are given in Table 2(d). The volume of these large-size pores is generally reduced with increasing SF content.

Calcium hydroxide

The pastes were examined by x-ray diffraction after 7, 28, 91, and 182 days of curing. Amorphous calcium silicate hydrates (by a diffuse halo between 28 and 35 $\text{deg}/2\theta$), unreacted SRPC (by alite peaks), and calcium hydroxide were observed. From a calibration curve, the quantities of CH were determined from the averaged intensities of the 4.90, 2.68, and 1.80 \AA diffraction peaks. From Table 2(e), it can be observed

Table 2 — Properties of cement pastes at W/CM = 0.25¹

Paste	(a) Compressive strength, MPa			
	7 days	28 days	91 days	182 days
100 percent SRPC	82.0	99.7	109.0	112.8
10 percent SF	71.9	75.8	86.6	88.7
20 percent SF	76.3	89.8	97.9	107.2
(b) Coefficients of permeability, 10^{-13} m/s				
100 percent SRPC	6.3	3.8	1.3	0.3
10 percent SF	10.0	0.9	0.6	0.4
20 percent SF	6.3	<0.1	0.3	<0.1
(c) Total intruded porosity, percent				
100 percent SRPC	14.4	14.9	11.1	11.5
10 percent SF	15.4	12.6	11.7	10.7
20 percent SF	11.7	9.8	8.1	7.6
(d) Volume of pores larger than 0.025 μm radius, percent				
100 percent SRPC	7.5	3.6	2.2	1.3
10 percent SF	4.5	2.1	1.4	1.4
20 percent SF	0.9	0.9	1.1	1.1
(e) Calcium hydroxide contents, percent				
100 percent SRPC	16	18	17	19
10 percent SF	7	7	8	8
20 percent SF	4	2	0	0

Table 3 — Chemical effects on deionized water from permeability tests, contact time = 23 \pm 2 hr

W/CM = 0.25	SRPC	10 percent SF	20 percent SF
28 days: Na ⁺	26.7	6.5	2.9
K ⁺	35.7	5.9	4.5
Ca ²⁺	33.0	19.0	19.3
pH	11.4	11.0	10.6
k, 10^{-13} m/sec	100	7	<1
CH, percent	18	7	2
182 days: Na ⁺	5.6	2.4	1.8
K ⁺	7.7	2.7	2.4
Ca ²⁺	17.2	8.5	7.1
pH	10.7	10.8	10.4
k, 10^{-13} m/sec	2	3	<1
CH, percent	19	8	0

that silica fume replacement results in substantial reductions in CH levels, well beyond those expected by dilution effects.

MORTAR TEST PROGRAM AND RESULTS

Alkali-aggregate reactivity

Four ASTM C 441 Pyrex mortar bars were cast with a high-alkali cement (Table 1, Na₂O equivalent = 1.17 percent) partially replaced by volume with 0, 5, 10, 15, and 20 percent SF. The mortar mixes were made to a constant flow of 110 \pm 5 using a constant 30 ml/kg dose of superplasticizer and increasing W/CM (0.429, 0.430, 0.450, 0.460, and 0.464, respectively, corrected for liquids in the superplasticizer). The expansion results for up to 1 year are shown in Fig. 1.

It can be observed that expansions were reduced with increasing replacements by SF, and a 10 percent by volume SF replacement almost meets the ASTM C 618 expansion limit (for fly ash) of 0.020 percent at 14 days. However, using the CSA CAN-A23.5-M86 requirements for silica fume of 80 percent reduction in expansion at 14 days, a 5 percent SF re-

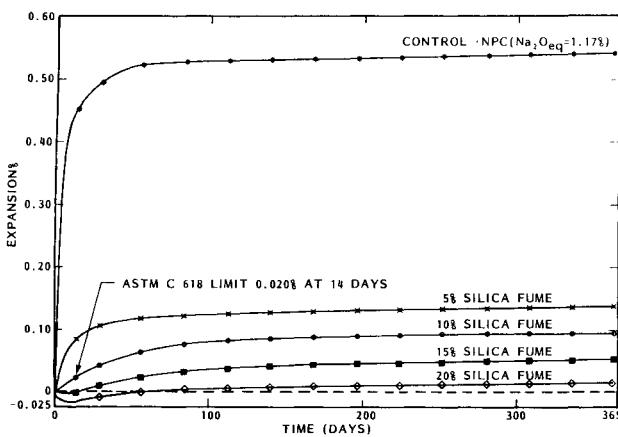


Fig. 1—Expansion of ASTM C 441 Pyrex mortar bars with various silica fume contents

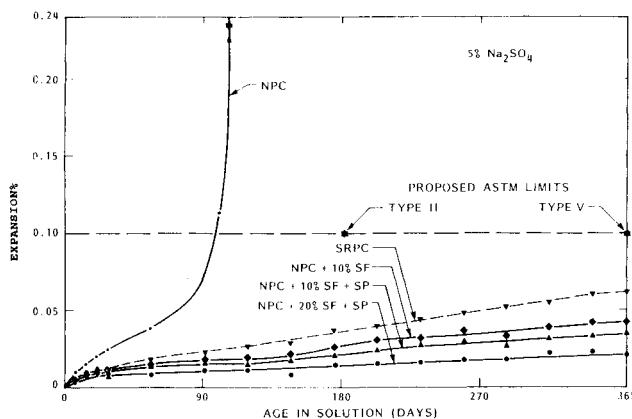


Fig. 2—ASTM C 1012 mortar bar expansions in sulfate solutions

placement was sufficient. By the ASTM C 33 and ASTM C 227 maximum mortar bar expansion limit of 0.10 percent, 10 percent SF should be adequate.

Therefore, it appears that silica fume may be effective in reducing deleterious alkali-silica expansions, but job-specific combinations of cement, SF, and aggregate should be evaluated before SF is recommended for use.

Sulfate resistance

Mortar bars were cast according to ASTM C 1012 for a high C₃A (10.7 percent, Table 1). NPC partially replaced 0, 10, and 20 percent by mass with SF to a constant flow of 110 ± 5. For the NPC and one of the 10 percent SF mixes, the W/C_M was 0.485 and 0.535, respectively. A superplasticizer (SP) was used for mixes with 10 and 20 percent SF, and a W/C_M of 0.485 was maintained. For comparison, an SRPC mix was cast at W/C_M = 0.465. In accordance with ASTM C 1012, all bars were immersed in 5 percent Na₂SO₄ solution at 21 ± 1 MPa (3000 ± 100 psi) strength. Expansions of the bars in this strong sulfate solution are shown for up to 1 year in Fig. 2.

It can be seen that, while the NPC bars failed quickly, all of the SF mortar bars expanded less than the SRPC. The SRPC and all the SF mixes easily passed the proposed ASTM criteria of 0.10 percent expansion at 1 year. After 1.7 years

in the solution, the SRPC failed the 0.10 percent criteria (above 0.10 percent, cracking and visual deterioration are noticed), but the SF mixes continue to perform satisfactorily after 5 years.

It appears that a high C₃A cement can be made to be more sulfate-resistant than an SRPC when 10 percent SF replacement is used. However, it is stressed that each source of SF and portland cement should be evaluated, and that good concrete practice must be followed to obtain sulfate-resistant concrete.

CONCRETE TEST PROGRAM AND RESULTS

Mix design

Normal density concretes were designed with total cementitious materials contents (cement plus SF) of 400 kg/m³ (674 lb/yd³), at approximately W/C_M = 0.35, and slumps of 40 to 90 mm (1.5 to 3.5 in.). The mixes were also nonair-entrained. Details of each of the five mixes are given in Table 4.

Mix 1 is a control mix using SRPC as the sole cementing material (see Table 1). Mixes 2, 3, and 4 have 10, 15, and 20 percent by mass replacement with SF.

Mix 5 contains 10 percent by mass replacement with SF incorporated in the proprietary preslurried admixture. Since the desired quantity of SF was 40 kg/m³ and the admixture contained 45 percent silica fume, the product dose rate was 88.9 kg/m³ (150 lb/yd³).

The 51 percent water content of the proprietary product was included in the mix water. A trial mix had been made at W/C_M = 0.37, yielding a slump greater than 250 mm (10 in.). This mix was discarded and, for Mix 5, the W/C_M was reduced to 0.32 to attain an acceptable 70-mm slump. Unlike Mix 5, in Mixes 1 through 4, the water component of the superplasticizer was not included in the mix water. Therefore, the actual W/C_M ratio was slightly greater than 0.35 (ranging from 0.360 to 0.369).

The SF powder was preslurried with 35 percent of the total mixing water and up to 30 percent of the total superplasticizer dose using a drill mixer. The slurry and the remainder of the mixing water were added to the cement, and presoaked aggregates were added during the first minute of mixing in a flat-pan mixer. Later in the mixing cycle, the remainder of the superplasticizer was added until the required slump was achieved.

Note from Table 4 that increased dose rates of superplasticizer were required as SF contents increased. This is due to the high surface area of the SF.

Fresh concrete properties

Slump, air content, and density tests were performed on the fresh concrete, as shown in Table 4. Air contents of Mixes 1 through 5 ranged between 1.0 and 1.5 percent, while slumps were maintained between 60 and 75 mm (2.5 to 3.0 in.).

Mechanical properties

Compressive strength tests were performed at 1, 7, 28, 56, 91, 182, and 365 days, and 2, 3, and 5 years, as shown in Table 5, on two moist-cured 150 x 300-mm (6 x 12-in.) cylinders (except that only one cylinder was tested at 1 day and three were tested at 28 days). In addition, long-term com-

Table 4 — Concrete mix proportions

Mix no.	Mix proportions, kg/m ³					Superplasticizer, ml/kg CM	Design,* W/CM	Initial properties		
	Cement	Silica fume	Fine aggregate	Coarse aggregate	Water			Slump, mm	Air, percent	Fresh density, kg/m ³
1	401	0	729	1211	141*	11.1	0.35*	75	1.2	2483
2	361	40	725	1205	141*	18.2	0.35*	75	1.0	2472
3	341	60	719	1196	140*	21.4	0.35*	60	1.2	2455
4	320	80	716	1191	139*	26.2	0.35*	60	1.1	2446
5	363	41†	728	1211	131	‡	0.32	70	1.5	2477

*Water in superplasticizer not included in mix water (NET W/C = 0.360 - 0.369).

†Silica fume content of proprietary preslurried admixture.

‡Superplasticizer content of proprietary product is unknown.

Table 5 — Moist-cured concrete compressive strength development, MPa

Concrete mix no.	Number* tested	1	2	3	4	5
		Control	10 percent SF	15 percent SF	20 percent SF	10 percent SF in slurred product
1 day	1	25.6	25.2	28.0	27.2	33.2
7 days	2	44.6	59.8	63.2	64.5	69.9
28 days	3	55.6	70.7	75.2	74.2	85.0
56 days	2	63.5	74.0	76.4	72.9	82.6
91 days	2	63.4	77.6	72.9	74.0	83.7
182 days	2	72.5	73.2	71.4	77.7	82.7
365 days (1 year)	2	79.0	76.7	70.0	80.3	80.2
2 years	2	86.1	81.5 (1)	71.4	82.0	—
3 years	2	88.2	89.7	85.1	88.3	—
5 years	2	86.0	79.6 (1)	68.6	70.3	—

*Except as noted in parentheses.

Note: Cylinders also cast for 10-, 15-, 25-, 50-, and 100-year tests.

pressive strength tests will be performed after 10, 15, 25, 50, and 100 years on cylinders buried below the frost line at Ontario Hydro's outdoor exposure site in Toronto. This type of long-term testing has been done previously and will help provide assurance as to the long-term retention of physical properties of silica fume concretes.

Observe that the SF is so reactive that 1-day strengths were not reduced and were actually increased in most cases over that of the SRPC control mix. After 7 days of moist-curing, the compressive strengths of all of the SF mixes were 34 to 57 percent higher than the control, with higher increases as SF contents were increased. Mix 5, containing the proprietary preslurried silica fume, developed higher early strengths than Mixes 2 through 4. The same trend held for 28-day compressive strengths, except that 15 percent SF appears to be the optimum replacement level. The control mix (Mix 1) continued to gain strength, and after 182 days, it caught up to the SF mixes. At ages greater than 56 days, the SF concretes practically stopped developing strength, likely due to self-dessication effects.⁸ The results between 56 days and 5 years show more scatter, including some reduced strength values. On first inspection, the observed strength losses between 3 and 5 years appear significant. However, on closer inspection, the 3-year results for Mixes 2, 3, and 4 appear abnormally high (by 6 to 13 MPa), showing an anomalously large strength gain between 2 and 3 years. If the 3-year results are ignored, the losses of Mixes 2 and 3 are within normal scatter.

Note that this type of wide scatter is typical in long-term strength tests when there is little or no continued strength increase.⁹ Even portland cement concretes have shown apparent losses in strength of up to 10 MPa between 3 and 5 years, but they recover at later age tests. This may be due to random

Table 6 — Tensile strengths, moduli, and densities of concretes

Concrete mix no.	1	2	3	4	5
	Control	10 percent SF	15 percent SF	20 percent SF	10 percent SF in slurred product
Splitting tensile strength, MPa					
28 days	5.2	6.3	6.2	4.6	6.2
91 days	6.8	6.7	6.2	5.6	6.6
182 days	7.1	6.2	6.5	5.6	7.1
Elastic modulus, GPa					
28 days	43.2	43.7	42.8	43.4	43.4
91 days	48.0	46.2	45.0	45.7	46.0
182 days	49.2	46.7	45.5	46.1	48.6
365 days	51.8	48.4	45.9	48.1	56.6
Density of hardened concrete, kg/m ³	2499	2489	2475	2466	2515

chance when selecting only two cylinders from a large group at any given test age.

Tensile splitting strengths were made from two cylinders at each of 28, 91, and 182 days, as shown in Table 6. Except at 28 days, the splitting tensile strength was not improved for the SF mixes.

Elastic moduli were measured at 28, 91, 182, and 365 days using three surface-mounted 100-mm (8-in.) gage-length, polyester embedded strain gages at 120-deg separation on a cylinder. In Table 6, the elastic modulus of the portland cement concrete was approximately equal to the silica fume concretes at 28 days but continued to rise at later ages, reaching 51.8 GPa (7.5×10^6 psi) after 1 year. With the ex-

Table 7 — Average length change of ASTM C 157 shrinkage prisms, percent

	1	2	3	4	5
Mix no.	Control	10 percent SF	15 percent SF	20 percent SF	10 percent SF in proprietary product
28 days in lime water	+0.0051	+0.0033	+0.0044	+0.0075	+0.0056
Time at 50 percent RH, weeks					
0.5±	+0.0007* (3 day)	+0.0012* (3 day)	-0.0002* (4 day)	+0.0026* (4 day)	+0.0021* (2 day)
1	-0.0028	-0.0012	-0.0037	+0.0019	0.0000
2	-0.0054	-0.0012	-0.0063	-0.0035	-0.0044
4	-0.0117	-0.0105	-0.0110	-0.0096	-0.0119
8	-0.0182	-0.0173	-0.0209	-0.0170	-0.0175
16	-0.0229	-0.0231	-0.0241	-0.0237	-0.0236
32	-0.0276	-0.0296	-0.0322	-0.0320	-0.0304
64	-0.0325	-0.0358	-0.0386	-0.0370	-0.0398
64, referenced to 28-day length	-0.0376	-0.0391	-0.0430	-0.0445	-0.0454

*Referenced to length as stripped at 1 day.

Table 8 — Air-void parameters by ASTM C 457 modified point count method

Mix	1	2	3	4	5
Silica fume, percent	0	10	15	20	10 in proprietary product
Air content, percent					
a) Fresh concrete	1.2	0.9	1.1	1.0	1.5
b) Hardened concrete	0.9	1.4	0.8	0.9	1.9
Specific surface, α , mm^{-1} *	13	7.8	18	13	17
Spacing factor, L , mm^*	0.69	0.96	0.50	0.70	0.23

*For freeze/thaw-resistant concrete: α min = 24 min^{-1} , L max = 0.20 mm; and for 19-mm aggregate, air content = 5 → 8 percent.

ception of the preslurried silica fume product, the moduli of the silica fume concretes did not rise after 91 days, consistent with their compressive strengths.

Drying shrinkage

Drying shrinkage tests were performed in accordance with ASTM C 157. Three concrete prisms from each mixture were stored initially in limewater at 23°C for 28 days and then dried at 23°C and 50 percent relative humidity for 64 weeks. The results are given in Table 7 for length changes referenced to the original length after the molds were stripped at 1 day. While differences in shrinkage are minor up to 16 weeks of drying, at 32 and 64 weeks all of the silica fume concretes exhibited 10 to 22 percent higher shrinkages than the control concrete. The concrete with 10 percent SF did not shrink as much (10 percent more than the control) as the ones with the higher replacements and the proprietary preslurried admixture.

If the total shrinkage is referenced to the length after 28 days of moist-curing, then it can be calculated that at 64 weeks, shrinkage increased from 4.0 to 18.4 percent with increasing replacements of silica fume from 10 to 20 percent.

Freezing and thawing resistance

Standard freezing and thawing tests were performed on Mixes 1 through 4 using ASTM C 666 Procedure A. This was done because it had been suggested that silica fume may provide resistance to freezing and thawing without air entrainment.^{10,11} In addition, 300 x 300 x 450-mm (12 x 12 x 18-in.) blocks were cast for outdoor exposure testing. These blocks are stored outdoors in Toronto semi-immersed in water and annually measured for changes in length, mass, and ultrasonic pulse velocity. Further description of outdoor exposure testing is given elsewhere,^{12,13} but the concretes at this location undergo between 45 and 72 freezing and thawing cycles annually. The blocks were placed outdoors in 1986 and are in good condition after six winters.

Air-void parameters of the hardened concretes were determined by modified point count according to ASTM C 457. It can be seen that none of Mixes 1 through 4, as shown in Table 8, had higher than 1.4 percent total air content, and all spacing factors were far from acceptable. It is interesting to note that Mix 5, containing the preslurried proprietary silica fume product, had an almost acceptable spacing factor in spite of a low air content. This is likely due to interactions of some of the proprietary admixtures. In addition, during the air-void analyses, a number of discrete microcracks were noticed in all the concretes, and the quantity appeared to increase with higher silica fume replacements. Therefore, a linear traverse was performed at 70 X magnification to count the total number of cracks intersected on 8 lines of 150 mm (6 in.) each. The cracks, which were less than 0.01 mm (0.0004 in.) wide and 2 to 3 mm (0.08 to 0.12 in.) long, numbered 13, 12, 20, and 44 for the 0, 5, 10, and 20 percent silica fume concretes, respectively. A typical crack is shown in Fig. 3. The increased number of cracks, which were distributed uniformly over the polished sections, were taken as evidence of self-desiccation, as will be discussed later.

The six freezing and thawing prisms for each mix were cured for 14 days in lime water prior to placement in the freezing and thawing cabinets for freezing and thawing in

water (Procedure A). With these cabinets, between 6 and 7 freezing and thawing cycles were achieved in a 24-hr period, with a thermocouple embedded in the center of one prism in each cabinet to insure proper cycle control.

The results are given in Tables 9 and 10. The control mix failed the usual 60 percent of original dynamic modulus criteria after 58 cycles (typical, normal strength, nonair-entrained prisms usually fail in 25 to 35 cycles in this apparatus).

However, as shown in Table 9, after the standard 300 cycles of freezing and thawing, all of the SF concretes exhibited durability factors in excess of 90 percent. Therefore, it was decided to extend the testing to 600 cycles, but even then, durability factors remained excellent. Because it was thought that the prisms must not be critically saturated, half of the prisms were continued to 900 cycles, while the rest were first vacuum-saturated and left immersed in water for 40 days. These prisms were then exposed to another 300 cycles. The vacuum-saturation and immersion had little adverse effect, since durability factors remained high for all of the SF concretes, as shown in Table 9.

In Table 10, the length and mass changes are given as well for 900 cycles, but no problem is indicated for any of the SF concretes.

DISCUSSION OF FREEZING AND THAWING RESULTS

Two possible explanations are offered for the unexpected excellent performance of these nonair-entrained concretes. Feldman¹¹ postulated that SF may create its own micro-air-void network around fine aggregate particles. Normally, the calcium hydroxide liberated by the hydration of portland cement preferentially deposits in the transition zone around aggregates. The SF would use up the CH in secondary hydration, leaving voids. If the fine aggregate content is high enough, these created voids might be close enough together to provide freezing and thawing protection.

The other explanation, and the one favored by the author, is that the concrete is not saturated critically. In spite of pre-soaking the aggregates and continuous storage in water, the SF concretes could have become internally self-desiccated due to a combination of very low permeabilities (not allowing ingress of water) and an abundance of very reactive but as yet unreacted material. Any water that did penetrate would be consumed immediately in hydration and make the concrete even less permeable. There are a number of indirect pieces of evidence for this explanation:

1. The pore size distributions of all the SF concretes are much finer (i.e., fewer coarse pores) than the control mix, even after 7 days, as shown in Table 11 and Fig. 4. This trend continues at later ages, as shown in Table 11 and Fig. 5 and 6. The pore size distributions also become slightly finer with increasing SF contents.

2. While the permeability to water of Mix 1 at 6 months was 1.8×10^{-14} m/sec, the permeability of Mix 2 was so low that it could not be measured ($< 1 \times 10^{-17}$ m/s), even under a differential pressure of 12.5 MPa and after 2 months in testing. The permeabilities of the other SF concretes could not be measured either. In fact, in some cases at the low-pressure end, water started flowing back into the specimens. AASHTO

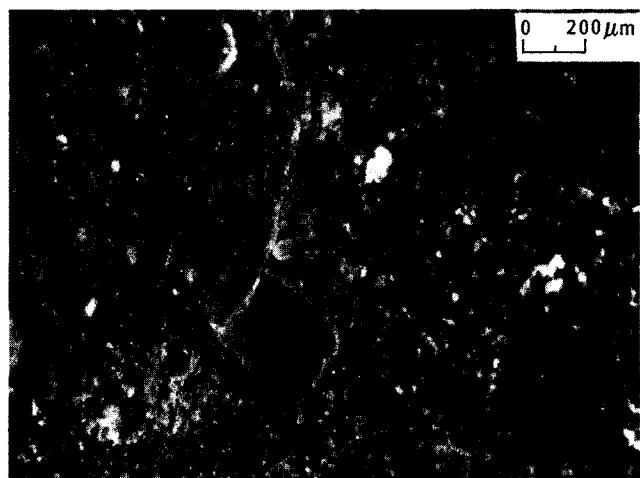


Fig. 3—Photo of microcrack through paste and fine aggregates in 20 percent silica fume concrete

Table 9 — Freezing and thawing resistance (ASTM C 666 Procedure A — Relative durability factor, percent, from dynamic moduli)

Mix no.	1	2	3	4
Number of cycles	Control	10 percent SF	15 percent SF	20 percent SF
300, standard	11.5*	94.2	94.4	90.2
400	—	95.4	93.7	91.0
500	—	95.6	92.8	91.8
600	—	96.2	91.5	92.1
700	—	96.1	94.1	92.5
800	—	97.9	95.2	92.1
900	—	97.5	93.4	92.8
After vacuum-saturation at 600 cycles followed by water immersion for 40 days				
0	—	105.8	104.0	98.3
100	—	99.7	96.9	92.8
200	—	96.5	93.7	89.5
300	—	95.7	93.0	89.8

*Failed the 60 percent limit after 58 cycles.

Table 10 — Silica fume (SF) concretes — Freezing and thawing resistance at 900 cycles

Mix no.	Description	Weight change, percent	Length change, percent	Relative durability factor, percent
1	Control	+0.30*	+0.142*	60.0*
2	10 percent SF	-0.10	+0.031	97.5
3	15 percent SF	-0.25	+0.045	93.4
4	20 percent SF	0.00	+0.022	92.8

* After 58 cycles.

T 277 rapid chloride permeability testing indicated that all silica fume mixes had much lower change passed than the control mix, as shown in Fig. 7. Permeability values decreased slightly with increasing silica fume replacements.

3. Moist-cured, split-tensile cylinders were observed to have almost no evaporable water except for the outer few millimeters.

4. As described earlier, on the polished, air-void specimens, with the exception of the 10 percent SF mix, the occurrence of internal microcracking was found to increase with increasing SF contents. These discrete microcracks were less than 0.01 mm wide and 2 to 3 mm long, and uniformly distributed over the cross section.

Table 11 — Mercury intrusion porosity of concretes, on mortar fraction only

Mix no.	1	2	3	4	5
Moist-curing period, days	Control	10 percent SF	15 percent SF	20 percent SF	10 percent SF in proprietary product
(a) Total intruded porosity, percent					
7	16.0	14.3	13.7	13.0	11.7
28	14.7	13.4	12.9	11.7	11.6
91	14.3	13.3	11.7	10.6	10.5
182	10.8	10.8	9.6	8.6	9.6
365	10.7	9.5	10.5	9.1	10.2
After 900 cycles F/T*	12.6	11.6	11.5	11.4	—
(b) Volume of pores > 0.025 μm radius, percent					
7	8.5	3.0	2.7	2.0	3.2
28	6.3	2.8	2.2	2.3	3.1
91	7.5	2.8	1.8	1.7	2.4
182	5.3	3.2	2.4	2.3	2.9
365	5.1	2.1	2.5	2.0	2.8
After 900 cycles F/T*	4.9	2.4	2.8	2.5	—

F/T = freezing and thawing.

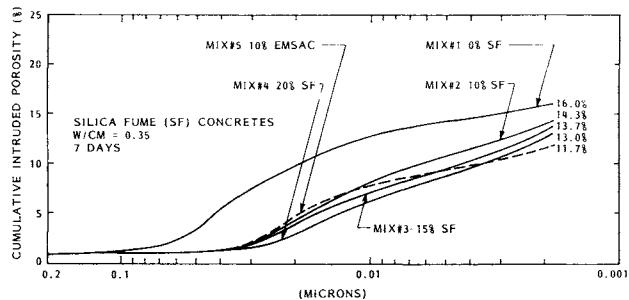


Fig. 4—Cumulative pore size distributions of concretes after 7 days of curing

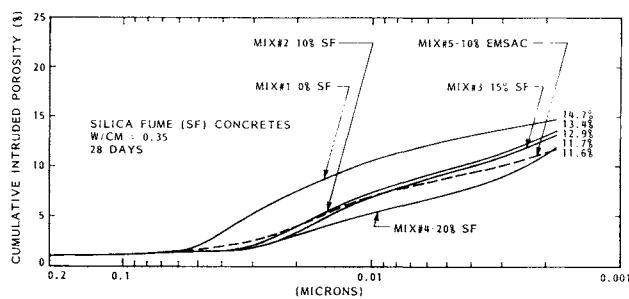


Fig. 5—Cumulative pore size distributions of concretes after 28 days of curing

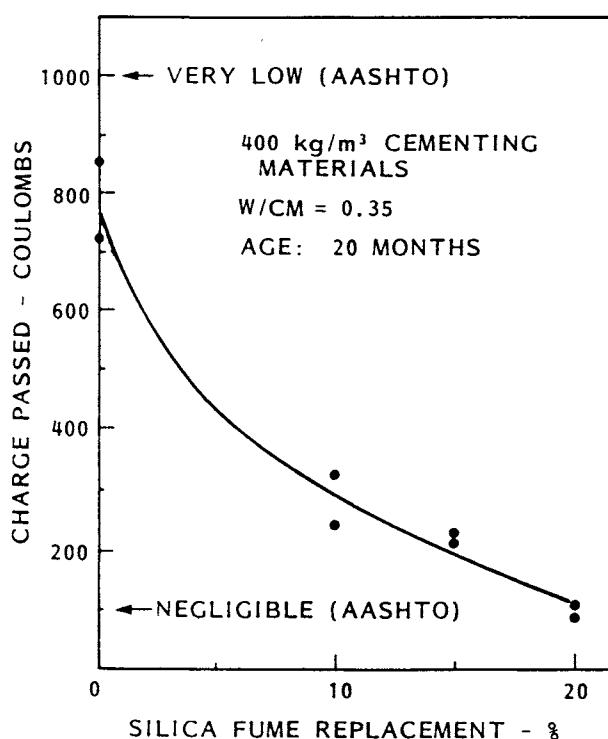


Fig. 7—AASHTO T 277 Rapid Chloride Permeability Test results

As direct evidence of self-desiccation, a recent study of silica fume concretes has shown that if the W/CM is low enough and sufficient silica fume is used, then self-desiccation can be observed, as evidenced by reduced internal relative humidities.⁸ When relative humidities of less than 90 percent were obtained, this was an indication of good performance in ASTM C 666.

Because all others have not found good resistance to freezing and thawing of nonair-entrained SF concretes,¹⁴ it appears that there are limits to this good performance. If any

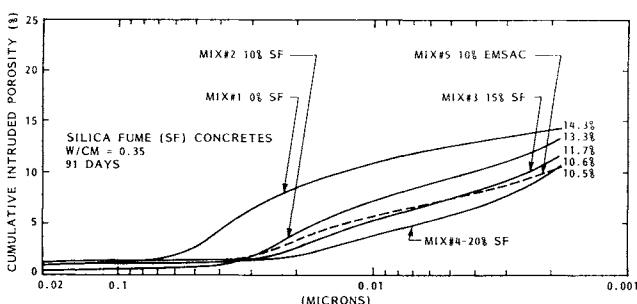


Fig. 6—Cumulative pore size distributions of concretes after 91 days of curing

advantage is to be made of nonair-entrained silica fume concretes, there is a need to identify those limits (e.g., quality of cementing materials and aggregates, mix proportions, degree of saturation, and freezing rates).

Because of this, it is not recommended that the requirements for air entrainment in CSA CAN A23.1-M90 or ACI 318-89 be ignored when producing high-strength SF concretes. While not studied here, air-entrained silica fume concretes have been shown to be resistant.¹⁴

CONCLUSIONS

Several independent studies on the use of silica fume as a cement replacement have been shown to impart higher resistance to sulfate attack, alkali-reactive aggregates, and freezing and thawing.

1. Cement pastes with low water-to-cementing materials ratios (*W/CM*) exhibited reduced porosity, lower permeability, and a complete utilization of the easily leachable calcium hydroxide component (provided that 20 percent condensed silica fume was used).

2. ASTM C 441 Pyrex mortar bar tests showed 10 percent condensed silica fume to be effective in reducing deleterious alkali-silica expansions. ASTM C 1012 mortar bars exposed to 5 percent Na₂SO₄ were found to be more resistant than sulfate-resistant portland cement at the 10 percent replacement level, even when combined with a 12 percent C₃A cement. Higher replacement levels or combinations with a lower C₃A cement improved performance even further.

3. A series of nonair-entrained concretes having 400 kg/m³ cementitious content and *W/CM* = 0.35 were made with 0, 10, 15, and 20 percent silica fume replacement. Permeabilities of the silica fume concretes were unmeasurable (less than 10⁻¹⁷ m/sec) and rapid chloride permeabilities decreased with increasing silica fume replacements.

4. While strengths of the concretes containing silica fume were higher at ages between 7 and 91 days, the portland cement concrete continued to gain strength at later ages, with a 55 percent increase between 28 days and 5 years. In contrast, the long-term strengths gain of silica fume concretes were very low, and 5-year strengths were \pm 12 percent of the 28-day strengths. While some reductions in strengths were noted, these are thought to be within the normal variation of strengths observed in other long-term strength studies with portland cement concretes.

5. While the control portland cement concrete rapidly failed in freezing and thawing (ASTM C 666 Procedure A), all of the silica fume concretes easily survived 900 cycles (three times the normal duration) even after vacuum-saturation. Indirect evidence indicates that the excellent performance was due to self-desiccation obtained from a refined pore structure, combined with low permeability and an abundance of unreacted cementitious material, resulting in less-than-critical saturation levels. This mechanism has been confirmed by measurement of reductions in internal relative humidities in another study.⁸

From all of the results described in this paper, it appears that a 10 percent by mass replacement of portland cement by silica fume is adequate with respect to resistance to freezing and thawing, sulfate attack, or alkali-silica reactivity, and does not result in a large increase in drying shrinkage. The early

age strengths with 10 percent SF are not as high as with 15 or 20 percent SF, but 10 percent SF did not result in any increase in microcracking in the hardened concrete.

Because of the potential variability of all concrete materials, it is suggested that each job-specific combination of materials be evaluated prior to using silica fume concretes for particular environmental exposures.

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