INFLUENCE OF SILICA FUME ON CHLORIDE RESISTANCE OF CONCRETE

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ABSTRACT

A series of concrete slabs were cast with 0, 7, and 12% by mass silica fume replacement of cement at W/CM = 0.35, 0.40, and 0.45. After either moist or steam curing, a variety of chloride resistance tests were performed. These included AASHTO T259, modified T259, T277, as well as several bulk diffusion tests and sorptivity tests.

Results indicate that the use of properly dispersed silica fume results in far more dramatic reduction in chloride penetration, by all test methods, than does reduction in W/CM from 0.45 to 0.35. In general, the AASHTO T277 rapid index test provides a good indication of the reduction in chloride diffusion coefficients.

INTRODUCTION

It is well known that chloride penetration is reduced with a reduction in water-to-cementitious materials ratio (W/CM). There are numerous references [1] to the beneficial influence of supplementary cementing materials (SCM) such as silica fume. However, precast prestressed concrete producers have typically not used SCM due to a need to obtain high early strengths. The typical practice often includes steam or heat curing to further accelerate strength. In addition, recent work sponsored by PCI has suggested that the benefits from silica fume are not so great and that the use of the AASHTO T277 Rapid Chloride Permeability Test has distorted results in favor of silica fume [2,3].

The purpose of this study was to study the influence of silica fume on strength development and chloride penetration resistance of concrete using a variety of test procedures and to examine whether silica fume could reduce the need for steam curing.

EXPERIMENTAL PROCEDURE

Materials

The Portland cement (OPC) used was Lafarge's Woodstock CSA Type 10 cement (low in C_3A and alkalis, similar to ASTM Type I or II). The silica fume tested was Microsilica Slurry 970S supplied by Elkem Materials Inc. This slurry is composed of water and silica fume (each 50% by mass). The chemical admixtures used in all the mixtures were a naphthalene-sulfonate based superplasticizer (SP), a Type A ligin-based water reducer (WR), and Micro-Air air-entraining agent (AEA) from Master Builders Technologies. The coarse aggregate was 19 mm (0.75 in.) Manitoulin crushed limestone (absorption = 0.37%, specific gravity = 2.85) and the fine aggregate was Dufferin Sand from Mosport Pit (absorption = 0.86%, specific gravity = 2.68). Seven mix designs, each with a cementitious content of 375 kg/m^3 (630 pcy), were used. The W/CM ratios were 0.35, 0.40, and 0.45. The silica fume replacements of cement on a dry mass basis were 0, 7, and 12%.

Sample Preparation

Prior to mixing, the silica fume slurry was stirred thoroughly inside its pail with a small hand-held mixer to ensure uniformity. Concretes were mixed in a 140 L flat pan mixer. The AEA was added to and covered by the sand in the hopper. WR was mixed with water prior to adding to the dry ingredients in the mixer. Part of the SP was added to the mix right after the silica fume slurry in order to reduce the stiffness and enabled thorough mixing of the slurry. Three kinds of samples were cast for each mix: 350 x 250 x 75 mm (14 x 10 x 3 in.) slabs, 100 x 75 mm (4 x 3 in.) disks made from cylindrical molds, and 100 x 200 mm (4 x 8 in.) cylinders.

Curing Regimes

The steam-curing regime shown in Figure 1 was applied to four mixes. Including the preset period determined using ASTM C 403, the 18-hour cycle consisted of a rise from 23 ^oC (73 ^oF) to 70 ^oC (158 ^oF) in 2 hours, followed by about 7 hours at 70 ^oC (158 ^oF) and then cooling to 23 ^oC (73 ^oF) in 2 hours. Even though the relative humidity of the programmable environmental chamber was set at 100%, the samples were covered with moist burlap and plastic during the whole process. Table 1 summarises various curing regimes for each test conducted in this research. For most of the tests, 100 mm (4 in.) ± 3 mm (0.12 in.) concrete cores were obtained from 350 x 250 x 75 mm (14 x 10 x 3 in.) slabs to eliminate edge effects.

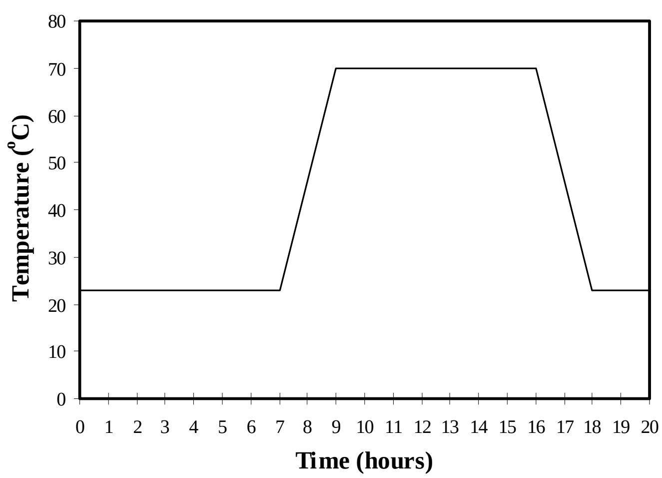


Figure 1 - 18-hour steam curing cycle

Table 1 - Summary of Curing Regimes

Test	Curing Regimes
compressive strength	ambient or steam curing for the first 24 hours + cured in lime water until test
sorptivity	ambient or steam curing for the first 24 hours + 27 days laboratory air + dry in 50 ^oC (122 ^oF) for another 7 days
RCPT (AASHTO T277)	four different curing regimes: i) 1 day moist + 27 days laboratory air ii) 18-h steam curing + 27 days laboratory air iii) 14 days moist + 14 days laboratory air iv) 28 days moist curing
bulk diffusion	ambient or steam curing for the first 24 hours + cured in lime water another 27 days
salt ponding (AASHTO T259)	ambient or steam curing for the first 24 hours + 13 days moist + 14 days laboratory air

Time of Set

The purpose of this test was to determine the optimum time for application of the steam curing cycle. The regime was applied after the initial setting of concrete (a penetration resistance of 500 psi or 3.5 MPa). The detailed procedure followed ASTM C 403.

Compressive Strength

The compressive strengths were tested at five different ages: 1, 3, 7, 28, and 56 days following ASTM C 39. For steam-cured cylinders, instead of 1-day, the 18-hour strength was determined. Two specimens were used for each test.

Surface Sorptivity

The procedure for the surface sorptivity test was based on the ASTM draft standard. Due to scheduling of the research program, cylindrical disks of 100 mm (4 in.) diameter and 75 mm (3 in.) height were cut to 50 mm (2 in.) thick on the twenty-fifth day after casting. 3 samples from each curing regime was tested. The samples were then dried in a 50 ^oC (122 ^oF) oven for 7 days. The samples were allowed to cool down to room temperature in a desiccator before testing. With the sides sealed with vinyl electrician's tape, after measuring the dry mass, the top surface was then immersed in distilled water to a depth of about 3 - 5 mm. The sample mass was repeatedly measured at times ranging from 1 to 25 minutes after wiping the surface moisture off with a damp cloth.

Rapid Chloride Permeability Test (AASHTO T277)

The same type of specimens as the surface sorptivity test was used for RCPT. The samples were epoxy-coated on the sides and vacuum-saturated before being tested with the formed face exposed to the half cell containing salt solution. The total charges at 10 minutes, 30 minutes, and 6 hours were recorded. By extrapolating the early readings to 6 hours, the heating effect in high coulomb value concrete would be minimised. This extrapolated value is considered a better estimate of concrete's chloride penetration resistance than the standard 6 hours value. It is realised that the RCPT is for the most part a measure of a concrete's resistivity, and not permeability or diffusivity directly. However, resistivity is a useful and simple index of quality.

Bulk Diffusion Tests

Two types of bulk diffusion tests were conducted: 90 days in 1.0 mol/L NaCl at 23 ^{o}C (73 ^{o}F) and 120 days in 5.0 mol/L NaCl at 40 ^{o}C (104 ^{o}F). Two cores of 100 mm (4 in.) diameter and 50 mm (2 in.) thickness were used for each test. The sides and bottom face were epoxy-coated and the samples were also vacuum-saturated. On the twenty-eighth day after casting, the cores were immersed in chloride solutions inside plastic containers. After the tests, the samples were profile ground and the bulk diffusion coefficients (D_B) were determined by fitting Fick's second law to the profiles.

AASHTO T259 Salt Ponding Test

Two 350 x 250 x 75 mm (14 x 10 x 3 in.) slabs from each curing regime were ponded. 25 mm (1 in.) high Styrofoam strips which acted as dams, were sealed to the edges of the top face with silicone. With all the connections properly sealed with silicone, 3% (by mass) NaCl solution was ponded on top to a depth of 20 mm (0.75 in.) on the twenty-eighth day. To minimise evaporation, the open top was then covered with Saranwrap held in place with duct tape. The slabs were ponded continuously for 90 days in a 50% relative humidity chamber. After ponding, a sample of 100 mm x 50 mm (4 in. x 2 in.) was dry cut from the center. Chloride profiling was conducted and the combined "diffusion" coefficients (D_C) were determined.

Modified Salt Ponding Tests

AASHTO T259 ponding test was modified to investigate various transport mechanisms. A 3-day ponding test was used to study initial absorption, wicking action was eliminated using a 90-day non-wicking ponding test, and the test duration was extended to one year for long-term chloride ingress. 350 x 250 x 75 mm (14 x 10 x 3 in.) slabs were used for the 1-year ponding test and 100 mm diameter (4 in.) and 75 mm (3 in.) high cores were used for the other modified tests. The sides of the cores were sealed with bithuthene adhesive sheets before air curing in order to maintain an interior moisture condition. A day before commencing the non-wicking test, specimens were epoxy-coated on the bottom face. This was to isolate the bottom face of the samples from the 50% relative humidity environment. 3% (by mass) NaCl solution was also ponded on top in these tests. By fitting Fick's second law to the profiles, sorption coefficient (S_P), non-wicking coefficient (D_W), and long-term diffusion coefficient (D_L) were calculated.
It is necessary to point out that the background chloride level (700 - 800 ppm) was subtracted from the chloride profiles before Fick's second law was fitted to it.

EXPERIMENTAL RESULTS

Plastic Properties and Compressive Strengths

The plastic properties and compressive strengths are presented in Table 2. In order to maintain similar workability, the amount of SP had to be doubled in silica fume mixes but the dosage of air-entrainer was only slightly affected. The 56-day compressive strength for the 0.35-12 concrete is not listed because, for both cylinders, the capping material failed before the cylinders. Steam curing increased the 18-hour compressive strengths but the early advantage was lost after three days. Silica fume concretes also benefited less from steam curing than the OPC ones. The use of 7% silica fume was more effective in enhancing compressive strengths than was reducing the W/CM by 0.05. A larger increase was observed between 7 and 28 days in silica fume concretes.

RCPT Results

The RCPT results shown in Table 3 are normalised to a standard diameter of 95 mm (3.75 in.) as per ASTM C 1202 and are extrapolated from the 30-minute readings by multiplying the values by 12 and the actual 6-hour readings are in brackets. The results clearly indicate that silica fume was effective in reducing the RCPT values regardless of the curing regimes applied. For each curing regime, the beneficial effect of silica fume was more profound as the W/CM ratio was increased. Moreover, silica fume enhanced chloride resistance more than reducing W/CM. This effect was confirmed by the diffusion tests shown in Table 4. The RCPT results indicate that a longer initial moist curing period was beneficial in reducing the permeability; especially for silica fume concretes. 14 days seemed to be sufficient when compared with the 28-day moist cured ones. The 18-hour steam curing cycle was found to be detrimental to OPC concretes when measured by RCPT as well as the diffusion tests. This agreed with previous research [1] ; nevertheless, for silica fume concretes, the steam-cured samples performed similar to the one-day moist cured ones.

Table 3 - Rapid Chloride Permeability Test Results (Coulombs)

Mix	1-d moist + 27-d air	14-d moist + 14-d air	28-d moist	18-hr steam + 27-d air
0.35-0	2495 (3168)	2474 (2996)	2126 (2530)	3962 (5058)
0.35-7	637 (543)	377 (371)	293 (295)	607 (611)
0.35-12	272 (282)	230 (226)	198 (202)	--
0.40-0	2740 (3713)	2314 (3172)	2205 (3062)	--
0.40-7	567 (596)	452 (487)	432 (442)	--
0.45-0	4968 (5908)	3744 (4498)	2832 (3527)	6384 (7299)
0.45-7	1472 (1783)	665 (758)	648 (719)	1164 (1430)

Surface Sorptivity and 3-Day Salt Ponding Results

The surface sorptivities in Table 4 indicated that the values were decreased by steam curing. Besides, both W/CM and silica fume replacement affected the surface sorptivity of concretes. The sorption coefficients (Sp) calculated were found to be sensitive to W/CM and silica fume. Both tests indicated that the initial sorption was decreased by steam curing in silica fume concretes but different effects were observed in OPC samples.

Bulk Diffusion Tests

The bulk diffusion coefficients (D_B) determined from tests were also presented in Table 4. Silica fume was proved to be effective in reducing chloride diffusion similar to that indicated by the RCPT results. Steam-cured concretes were found to be less resistant to chloride diffusion than the corresponding ambient-cured ones. This was different from RCPT values where silica fume concretes were found to have higher chloride resistance after steam curing. This could be due to different curing that followed the steaming cycle. As outlined in Table 1, samples for these tests were continuously moist-cured after the steam curing cycle while those for RCPT were cured in laboratory air until coring. Silica fume replacement was more beneficial than lowering the W/CM from 0.45 to 0.35.

Table 4 - Surface Sorptivity and Various Coefficients

Mix	Sorptivity ($mm/min^{1/2}$)	S_P ($\times 10^{-12}$ m^2/s)	90-d D_B ($\times 10^{-12}$ m^2/s)	120-d D_B ($\times 10^{-12}$ m^2/s)	D_C ($\times 10^{-12}$ m^2/s)	D_W ($\times 10^{-12}$ m^2/s)	D_L ($\times 10^{-12}$ m^2/s)
0.35-0	0.116	13.0	4.7	5.9	5.3	5.8	2.8
0.35-7	0.103	3.7	1.2	1.9	1.3	1.4	0.7
0.35-12	0.112	3.2	1.0	0.9	0.7	0.7	0.3
0.40-0	0.169	26.5	5.0	9.4	7.0	6.1	3.3
0.40-7	0.109	3.9	1.2	1.8	1.3	1.7	0.7
0.45-0	0.168	24.3	7.1	10.5	8.7	7.1	3.4
0.45-7	0.180	11.9	1.6	1.9	2.3	2.2	0.8
0.35-0s	0.096	18.7	10.0	8.2	6.1	--	--
0.35-7s	0.069	3.3	1.6	3.2	1.5	--	--
0.45-0s	0.122	51.7	8.5	12.1	10.7	--	--
0.45-7s	0.094	11.5	3.9	4.5	6.3	--	--

Note: 1 $mm/min^{1/2}$ = 0.004 $in./min^{1/2}$; 1 m^2/s = 10.9 ft^2/s

AASHTO T259 Salt Ponding Test and Modified Tests

AASHTO T259 Salt Ponding Test (D_C) -- The results show that D_C was sensitive to W/CM, especially in OPC concretes. Silica fume was, again, shown to be beneficial regardless of the curing regime applied as all silica fume samples, except 0.45-7s, had a coefficient lower than that of 0.35-0. Steam curing adversely affected the chloride resistance as in previous tests. In all cases, silica fume concretes performed much better than the OPC reference concretes with a low W/CM ratio.

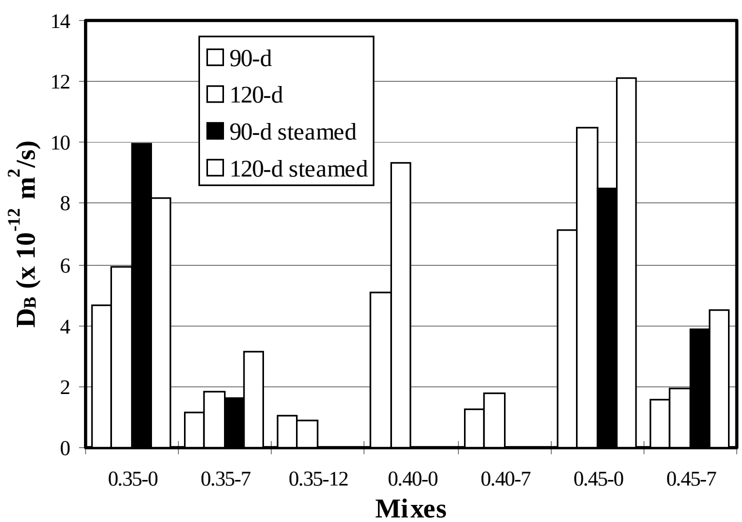
Non-wicking Salt Ponding Test (D_W) -- Unlike AASHTO T259, D_W of OPC and silica fume concretes were equally sensitive to the W/CM. The chloride resistance was increased by the addition of silica fume and the decrease in diffusion coefficients were comparable to those indicated by AASHTO T259.

1-year Salt Ponding Test (D_L) -- The influence of W/CM was less obvious in the 1-year data, especially in silica fume concretes. The increase in chloride resistance by silica fume was consistent with AASHTO T259 results. Silica fume was also more effective than W/CM in resisting chloride ingress in the long term.

DISCUSSION OF RESULTS

Bulk Diffusion Tests

The results from these tests are presented graphically in Figure 2. Both tests were able to demonstrate the influences of W/CM and silica fume on chloride resistance of concrete. Silica fume was shown to be more effective in enhancing the durability. Steam curing consistently decreased the resistance. Except for the steam-cured 0.35-0, the 120-day bulk diffusion coefficients calculated were higher than the 90-day ones. Chloride ingress was promoted by the higher solution temperature and salt concentration. Both tests were highly reproducible and generated a clear indication of the concrete quality.

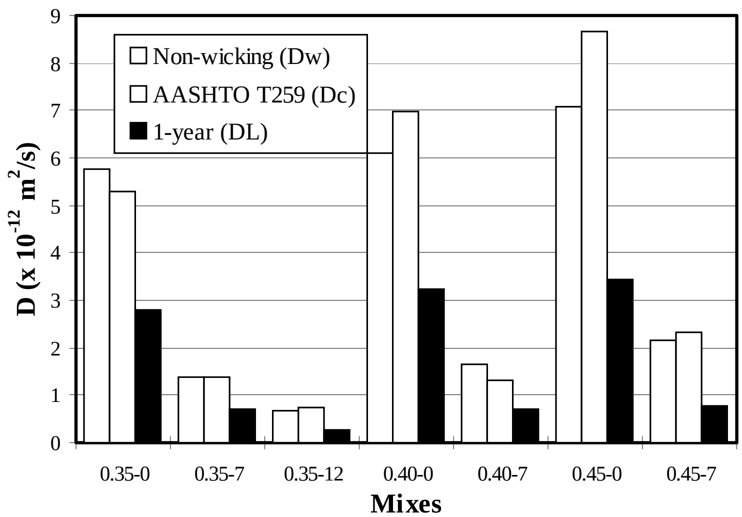


Note: 1 m^2/s = 10.9 ft^2/s

Figure 2 - Bulk diffusion coefficients (D_B) of all the mixes

AASHTO T259 and Modified Salt Ponding Tests

Figure 3 is a plot of the different coefficients calculated for each mix. Similarly, the chloride resistance was influenced more by silica fume than by W/CM. The diffusion coefficients of silica fume concretes were comparable regardless of the W/CM. For most cases, chloride ingress was increased by the wicking action, particularly in OPC concretes. In comparing D_C with D_L, the chloride diffusion coefficient of concrete decreased by 50% between 90 days to 1 year. This percentage increased with the W/CM.

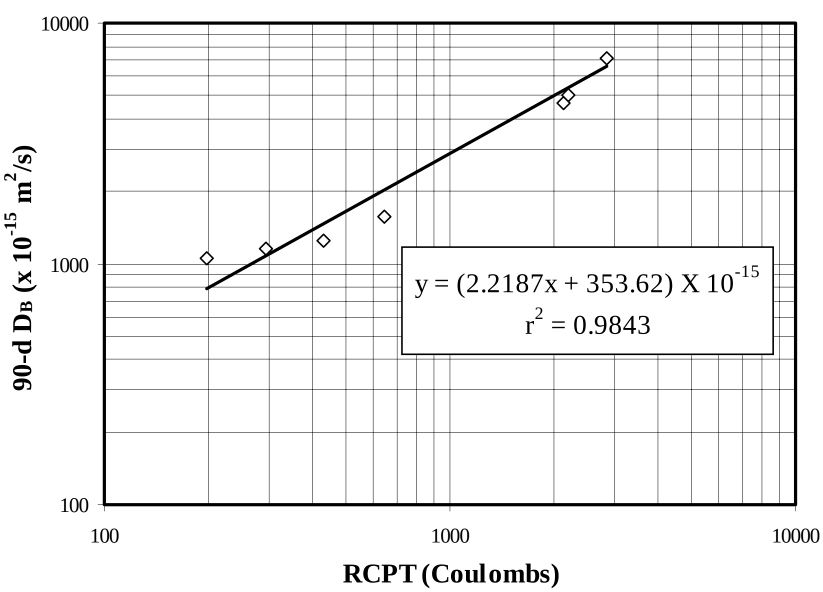


Note: 1 m^2/s = 10.9 ft^2/s

Figure 3 - Comparison of diffusion coefficients from salt ponding tests

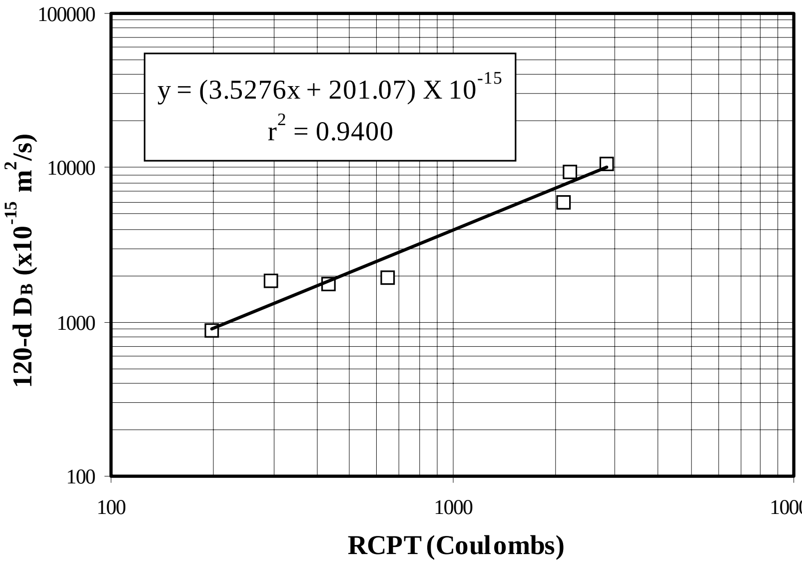
Bulk Diffusion Tests and RCPT

In Figure 4 and Figure 5 the 90-day and 120-day bulk diffusion coefficients (D_B) are plotted against the RCPT values, respectively. All the samples were moist cured for 28



Note: 1 m^2/s = 10.9 ft^2/s

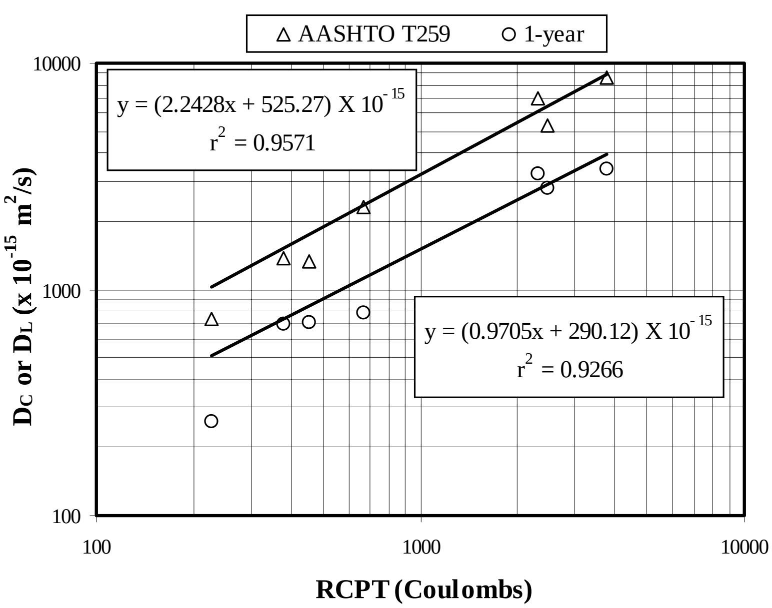
Figure 4 - 90-day bulk diffusion coefficients vs. RCPT values



Note: 1 m^2/s = 10.9 ft^2/s

Figure 5 - 120-day bulk diffusion coefficients vs. RCPT values

days. A linear regression was applied to both graphs. High coefficients of correlation were found from the plots; therefore, a linear function existed between the tests.



Note: 1 m^2/s = 10.9 ft^2/s

Figure 6 - Salt ponding diffusion coefficients vs. RCPT values

Salt Ponding Tests and RCPT

Both D_C and D_L are plotted against the RCPT results in Figure 6. The same curing regime was used for all the tests: 14-day moist curing then 14-day air curing. Through regression analysis, a linear relationship was found between the ponding tests and RCPT.

Effects of Silica Fume on Diffusion Coefficients

Various diffusion coefficients were normalised and the relative reduction of these coefficients is shown in Figure 7. It is clearly indicated that silica fume could enhance concrete durability by lowering the diffusion coefficients. The rate of decrease was reduced as the silica fume replacement level was beyond 7%. The diffusion coefficients were consistently lowered by 75% at this replacement level. A further 10% reduction was resulted when the silica fume replacement level was increased to 12%.

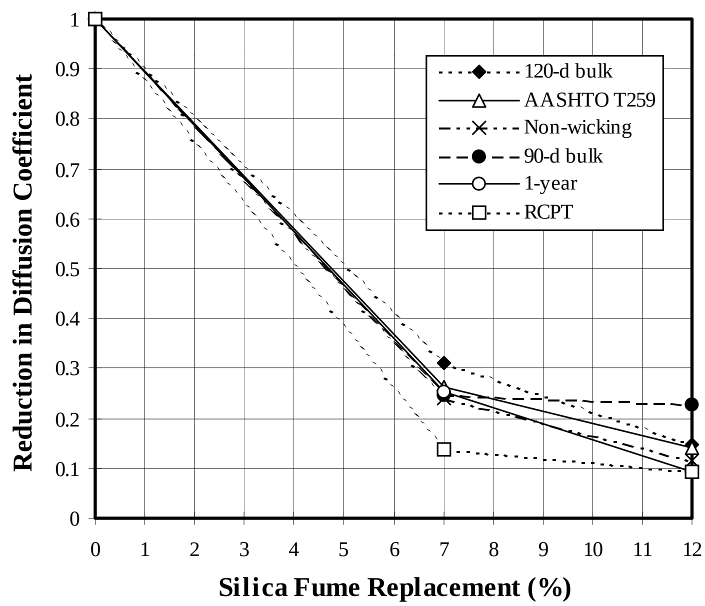


Figure 7 - Relative reduction in diffusion coefficients with silica fume (W/CM = 0.35)

CONCLUSIONS

The study has confirmed the beneficial effect of silica fume on chloride penetration resistance of concrete.

1. 7% silica fume provides a dramatic improvement in chloride penetration resistance regardless of the test procedure used.
2. The reductions exhibited by silica fume concretes in Rapid Chloride Permeability Test (AASHTO T277) are indicative of the reductions shown by both bulk diffusion tests and the AASHTO T259 90-day ponding test.
3. The AASHTO T259 test and the bulk diffusion tests indicate that steam curing is having an adverse effect on chloride penetration but the steam-cured silica fume concretes have greater resistance to chloride penetration compared to the Portland cement controls.

4. One day, ambient-cured strengths were not as high as the same mixture when steam cured. However, the 12% silica fume strength was similar to the 18-hour strength of the 0.35 W/CM Portland cement concrete. From 3 to 56 days, at the same W/CM, 7% silica fume concretes had higher strengths than the steam-cured Portland cement concretes.

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Table 2 - Plastic Properties and Compressive Strengths Results

Material (kg/m^3)	**0.35-0**	**0.35-7**	**0.35-12**	**0.40-0**	**0.40-7**	**0.45-0**	**0.45-7**	**0.35-0s**	**0.35-7s**	**0.45-0s**	**0.45-7s**
Portland Cement (Type 10)	380	356	334	374	353	369	350	370	357	369	347
Silica Fume	0	27	46	0	27	0	26	0	27	0	26
Coarse Aggregate	1193	1194	1174	1141	1150	1098	1108	1162	1197	1098	1101
Fine Aggregate	731	732	719	699	705	672	679	708	733	672	674
Water	133	133	132	149	152	165	169	151	131	165	167
Water Reducer (mL/100 kg)	325	325	325	325	325	325	325	325	325	325	325
Superplasticizer (mL/100 kg)	1232	1194	1555	436	1255	154	550	482	952	154	611
Air Entrainer (mL/100 kg)	74	49.9	52	45	62.8	52.1	54	52.1	52	52.1	54.2
Air (%)	5.0	4.4	5.4	6.8	5.2	8.0	6.3	5.7	4.5	8.0	7.0
Slump (mm)	100	100	180	110	165	190	125	110	80	190	80
Fresh Density (kg/m^3)	2443	2449	2414	2368	2394	2307	2336	2395	2452	2307	2320
Compressive. Strength (MPa)											
1-day/18-h	11.4	24.8	26.0	10.7	23.4	12.1	10.7	28.8	41.4	19.8	37.8
3-day	39.0	47.8	44.6	31.3	42.6	22.2	24.9	29.7	50.2	20.2	40.0
7-day	50.3	55.6	64.0	38.9	54.8	24.8	37.2	32.1	57.9	21.4	42.1
28-day	58.8	82.2	76.1	46.1	62.9	31.8	51.6	37.4	58.4	29.3	46.3
56-day	69.0	85.6	--	49.6	69.6	35.7	59.1	45.9	61.0	31.1	47.1

Note: 1 kg/m^3 = 1.7 pcy; 1 mm = 0.004 in.; 1 MPa = 143 psi, 1 mL/100 kg = 0.015 fl. oz./100 lb