Pergamon

Cement and Concrete Research, Vol. 28, No. 10, pp. 1489–1503, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00124-0

RECURRENT STUDIES OF CHLORIDE INGRESS IN UNCRACKED MARINE CONCRETE AT VARIOUS EXPOSURE TIMES AND ELEVATIONS

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(Received March 31, 1998; in final form July 27, 1998)

ABSTRACT

Uncracked reinforced concrete slabs were field exposed mounted on a floating pontoon and partly submerged for 5 years at the Swedish west coast. The total chloride ingress was analysed at various exposure times at 3 elevations representing a submerged, a splash, and an atmospheric exposure zone. The concrete mixtures varied in w/c ratio, type of cement, and amount and type of pozzolan used in the binder. The data is unique as it represents recurrently measured total chloride penetration profiles at various exposure ages, providing a foundation for the prediction of chloride ingress in concrete in a given environment. The results after 5 years of exposure confirmed the expected inverse relationship between water-to-binder ratio and chloride ingress. The use of 5–10% silica fume in the binder had a very positive effect on reducing the chloride ingress, but little or no benefit at all was found for concrete with fly ash in the binder as compared to the use of 5% silica fume. The chloride penetration rate as expressed by a calculated effective chloride diffusivity has a tendency to decrease over time. High- performance concrete with w/c ≤ 0.4 and a minimum of 5% silica fume added as a well dispersed slurry exhibited an effective chloride diffusivity in the range of 1×10^{-13} to 5×10^{-13} m^2/s after 5 years exposure in the splash zone. *© 1998 Elsevier Science Ltd*

Introduction

Chloride-induced reinforcement corrosion is one of the most common durability problems associated with modern good quality reinforced concrete structures exposed to marine environments or to de-icing salts. The time to corrosion initiation depends on i) how fast chloride ions penetrate the concrete cover to reach the reinforcement, and ii) the critical chloride concentration needed for depassivation of the steel reinforcement.

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Chloride Penetration of Concrete

Traditionally, chloride penetration of concrete has been modeled by the use of Fick's second law of diffusion, assuming constant diffusivity and linear chloride binding (1). On the other hand, recent field studies of concrete structures have indicated that the traditional use of Fick's second law of diffusion was not applicable for long-term chloride transport into concrete (2–6). When fitting a solution to Fick's second law of diffusion to measured total chloride profiles from field exposed concrete, the calculated "effective chloride diffusivity" was found to vary with the exposure time and conditions.

More sophisticated models have been developed (7,5), still based on Fick's diffusion theories but with scientific or empirical corrections for natural phenomena that were not recognized in the traditional use of Fick's second law for prediction of chloride ingress in concrete. It was recognized that the chloride binding and the chloride penetration were affected by natural processes such as counter-diffusion of hydroxide ions, environmental load of moisture and salt, exposure temperature, surface densification, and frost action. (4–7).

Careful field exposure tests at relevant exposure conditions are most important in order to provide reference data for the development of accurate models for chloride penetration in concrete. The purpose of this study was therefore to establish reference data on chloride penetration profiles in normal and high-performance concrete exposed in a marine environment for various exposure times. The data should be useful for the calibration of existing and new models, and possibly also for the identification of any processes affecting the chloride penetration but not yet accounted for in the existing models.

The "effective chloride diffusivity" calculated from total chloride profiles fitted to a solution to Fick's second law of diffusion represents an indication of the average chloride transport rate in the concrete at the exposure time and conditions considered. Therefore, the effective chloride diffusivity has been calculated at various exposure times and conditions and compared with the effective chloride diffusivity calculated in a standard immersion test in 16% by weight NaCl solution for 35 days at room temperature (8).

The Träslövsläge Marine Field Station

The need for reliable data from field exposure tests of concrete with mixing, casting, curing, and exposure conditions as well-defined as possible, led to the establishment of a marine field station in the harbour of the village Träslövsläge on the Swedish west coast. The concrete specimens to be exposed were mounted on a floating pontoon and partly submerged in the sea. The use of a floating pontoon allowed the bottom half of each slab to be continuously submerged in sea water according to Figure 1. The floating field station was protected inside the harbour behind a breakwater, thereby minimizing wave action on the upper part of each slab. Consequently the exposure condition at the upper part of each slab was defined as "atmospheric zone" with the concrete exposed mainly to wind-borne salt, while the middle part at the water line of each slab was defined as "splash zone."

At present, 3 pontoons are carrying more than 50 different concrete qualities, with w/c ratios ranging from 0.25 to 0.75.

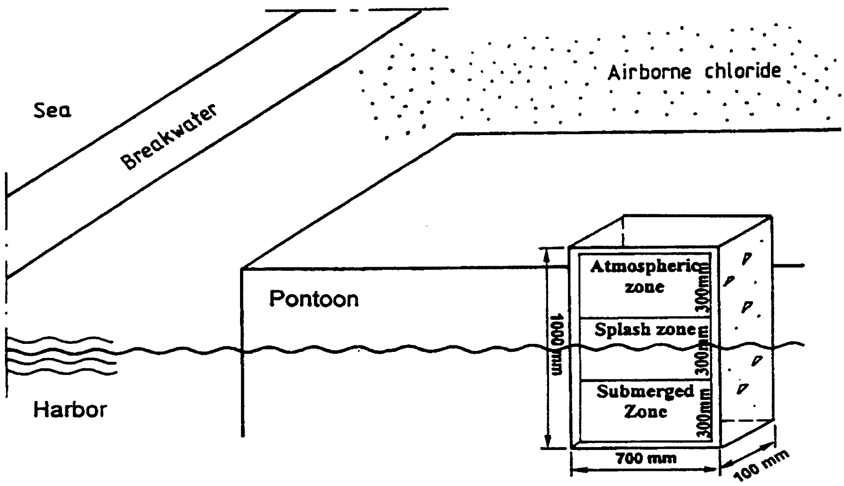


FIG. 1.
Exposure conditions at the Träslövsläge marine field station.

Experimental

Concrete Mixtures and Types of Binder

Cementing materials were used according to Table 1. Natural glacial granite aggregates were used both in the fine (0–8 mm) and the coarse (8–16 mm) aggregate fractions according to Table 2. A melamine type (formaldehyde and melamine sulfonate condensate) superplastiziser was used in the concrete mixtures with w/c ratios < 0.50 in order to achieve a slump value in the range of 10–18 cm 5 min. after mixing. A vinsol resin air entrainer was used in concrete with an air content of 3–6% according to Table 2. Thirteen different concrete qualities including 7 different binder compositions were tested, with w/c ratios between 0.25 to 0.5.

Concrete slabs, height 1000 mm, width 700 mm, thickness 100 mm, were prepared according to Tables 2 and 3, and moist cured 5 days followed by 5 days of air curing prior to marine exposure.

Analysis of Total Chloride and Binder Profiles

Total total chloride profiles were analysed after 7 or 12 months, 2 years, and 5 years exposure. Cylinders with diameter 100 mm cylinders were drilled from the concrete slabs at > 50 mm distance from the edges. The concrete cylinders were immediately sealed in airtight bags and brought to the laboratory for immediate processing and analysis.

The concrete cover was abraded from the exposed surface successively inwards in steps of 1 mm using a diamond tool according to the Nordic standard NT Build 443 (8). The pulverised samples were analysed for total chloride content according to AASHTO T 260-A,

TABLE 1
Details of cementing materials used.

Material		Sulfate resisting Portland cement (SRPC)	Ordinary Portland cement (OPC)	Silica fume (SF)	Fly ash (FA)
Fineness-% passing	45 μm	85.9	97.4	100	73
	20 μm	51.3	64.0		
	10 μm	33.1	41.7		
	5 μm	19.5	26.0		
	1 μm	3.8	5.4		
Specific surface m^2/kg	Blaine	300	360		227
	BET			23,000	625
Compressive Strength of standard 40 mm mortar cubes, MPa	1 day	10.1	18.9		
	7 days	35.6	45.2		
	28 days	56.2	55.2		
Chemical analysis %	CaO	63.8	62.5	0.4	1.87
	SiO_2	22.8	19.6	94.2*	57.0
	Al_2O_3	3.5	4.17	0.62	29.1
	Fe_2O_3	4.7	2.17	0.95	6.56
	MgO	0.80	3.45	0.65	0.79
	SO_3	1.9	3.29	0.33	0.21
	K_2O	0.55	1.29	0.5	1.76
	Na_2O	0.06	0.26	0.2	0.28
Loss of ignition		0.55	2.65	1.8	1.9
Bouge potential compounds-%	C_3S	51.5	61.4		
	C_2S	25.5	9.9		
	C_3A	1.3	7.6		
	C_4AF	14.3	6.6		

* Amorphous silica content.

by potentiometric titration using a total chloride ion selective electrode and a silver nitrate solution of 0.01 N.

After total chloride titration, 5 mL of 1:2 diluted triethanolamine was added to the sample solution, and the pH value was adjusted to pH $>$ 12 using sodium hydroxide. The calcium content was determined by potentiometric titration using a calcium ion selective electrode and a 0.1 N EDTA solution (9). Since the aggregate contained no acid soluble calcium, the binder content in each thin fraction of concrete was calculated from the measured calcium content in each fraction. The result was presented as total total chloride by weight of binder for each thin fraction.

The total total chloride profiles were analysed as described at Chalmers and Lund Institute of Technology, Sweden, AEC, Denmark, the Swedish Cement and Concrete Research Institute, and the Swedish National Testing and Research Institute (11).

Evaluation of Total Chloride Profiles

Acid-soluble total chloride profiles, expressed as % Cl by weight of binder, were evaluated by fitting the measured total chloride data to a theoretical profile calculated from a solution

TABLE 2
Details of concrete mixtures.

Mix no.	ID	w/c ratio*	OPC kg/m^3	SRPC kg/m^3	Silica fume† kg/m^3	Fly ash kg/m^3	fc 28d‡ MPa	Air cont. vol %
1	OPC 0.40	0.40	420	–	–	–	54	6
2	SRPC 0.50	0.50	–	370	–	–	41	6
3	SRPC 0.40	0.40	–	420	–	–	58	6
4	SRPC 0.30	0.30	–	492	–	–	96	4
5	SRPC 5%SFdry 0.50	0.50	–	351	19 dry	–	45	6
6	SRPC 5%SFdry 0.40	0.40	–	399	21 dry	–	61	6
7	SRPC 5%SF 0.40	0.40	–	399	21 slu	–	62	6
8	SRPC 5%SF 0.30	0.30	–	475	25 slu	–	112	1
9	SRPC 5%SF 0.25	0.25	–	525	26 slu	–	125	1
10	SRPC 10%SF 0.30	0.30	–	450	50 slu	–	117	1
11	SRPC 5%SF 10%FA 0.35	0.35	–	382	23 slu	45	84	6
12	SRPC 5%SF 17%FA 0.40	0.40	–	345	21 slu	75	69	6
13	SRPC 20%FA 0.30	0.30	–	493	–	123	98	3

* w/c ratio defined as w/(C + SF + 0.3FA). w = water, C = cement (SRPC = sulfate resisting portland cement, OPC = ordinary portland cement), SF = silica fume, FA = fly ash.
† Silica fume, "dry" = compacted or "slu" = as a 50% slurry. Figure denotes amount of solid.
‡ fc 28d = 28-day compressive cube strength (MPa).

TABLE 3
Concrete mixing procedure.

Step	Activity	Mixing time (min.)
1	Dry mixing of aggregates, cement, fly ash (if any), dry silica fume (if any)	1
2	Mixing with water, 50% of superplasticizer, silica fume slurry (if any), air entrainment (if any)	2
3	Mixing with remaining 50% of superplasticizer	1.5

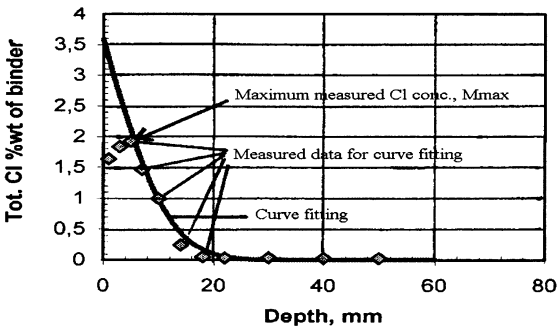


FIG. 2.
Curve fitting procedure for estimation of the "effective chloride diffusivity."

to Fick's second law of diffusion assuming a constant diffusion coefficient and linear chloride binding (10), as shown in Figure 2. The fitting procedure was started at the depth of the maximum total chloride concentration, "Cmax," which was sometimes several datapoints below the concrete surface. The theoretical total chloride profile was defined by the chloride transport coefficient, "effective chloride diffusivity," and the calculated total chloride concentration, "Ccalc," at the depth of the maximum total chloride concentration.

Results and Discussion

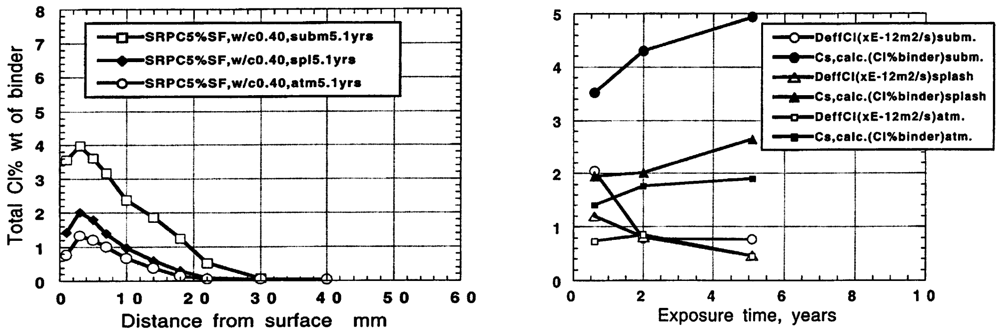
General

Due to the page limitation only selected results are presented here. A compilation of all results is available at Lund Institute of Technology, division of Building Materials (11,12).

The results presented here relate to the total chloride penetration in concrete exposed in the submerged and splash zone. The splash zone is the most critical zone in practice, but the exposure condition is better defined in the submerged zone. The chloride penetration rate may be higher in submerged concrete (Fig. 3), but the chloride threshold is also higher and it is relatively easy to prevent corrosion by the use of inexpensive protection systems (6).

Small differences in the sampling height from the water level may have large impact on the salt and moisture load, and thus on the total chloride penetration profile in the splash zone. In addition, concrete itself is an inhomogeneous material with local variations in the porosity and therefore local variations in the chloride diffusivity. As a consequence the variability in measured total chloride profiles may be relatively high, and it should be higher in the splash zone compared to the submerged zone as the exposure conditions vary less in the submerged zone.

An indication on the variability which can be expected in the submerged and splash zone is presented in Figure 4, which unexpectedly shows more chloride penetration in the splash zone for a concrete with w/c 0.30 than with w/c 0.40. One should therefore be careful not to use individual profiles for service life prediction, but rather extract information from trends observed from several profiles. The reason for the unexpectedly high chloride penetration in

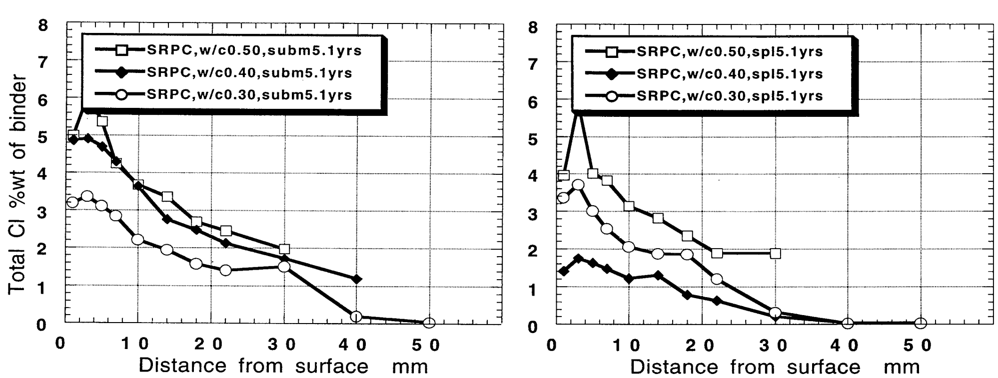


A B

FIG. 3.

Total chloride profiles (*A*) and corresponding calculated curve fitting results (*B*) for SRPC concrete with 5% silica fume in the binder, w/c 0.40, exposed for 5 years in the submerged, splash, and atmospheric zone.

the concrete with w/c 0.30 is not clear, as no examination of the micro structure was carried out. It is possible, however, that the existence of cracks has accelerated the chloride penetration in the concrete with w/c 0.30. High-performance concrete, w/c $\leq$ 0.40, is considered as being more sensitive to the formation of cracks as compared to normal concrete (13). A similar unexpectedly high chloride penetration was found for concrete with w/c 0.25 exposed in the splash zone (Fig. 5). It was found in (4) that cracks $>$ 0.1 mm wide and open to the surface may have a strong influence on the measured profile of total chloride.



A B

FIG. 4.

Total chloride profiles in SRPC concrete exposed in the submerged zone (*A*) and in the splash zone (*B*) for 5 years.

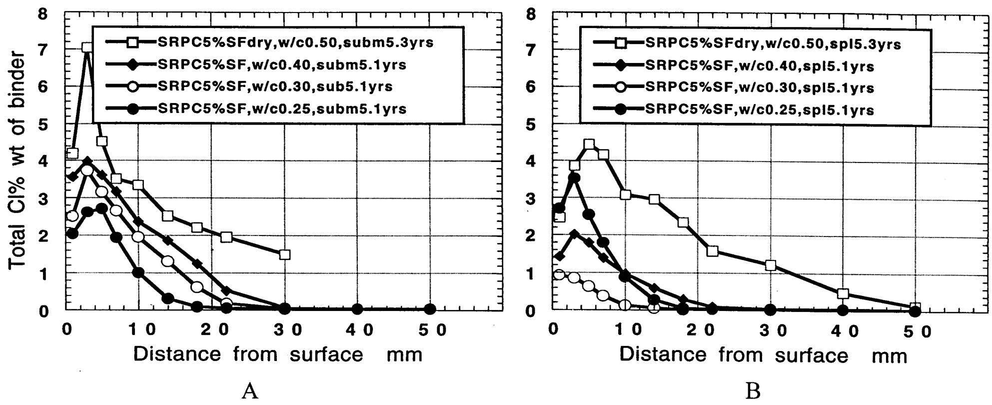


FIG. 5.
Total chloride profiles in SRPC concrete with 5% silica fume in the binder fraction, exposed in the submerged zone (*A*) and in the splash zone (*B*) for 5 years.

Presentation of Results

The chloride profiles expressed as total Cl by weight of binder as a function of the distance from the exposed concrete surface were measured after 3 or 4 different exposure times and presented as shown in Figure 3. Each total chloride profile was labelled according to the ID label in Table 2, with the addition of the exposure condition, "atm" (atmosphere) "spl" (splash zone) or "subm" (submerged), as indicated in Figure 1, and the exposure time. The corresponding calculated chloride transport coefficient, DeCl ($\times 10^{-12}$ m^2/s), and the calculated total chloride concentration, Ccalc., at the depth of the maximum measured total chloride concentration (Cl % by weight of binder), are presented in Tables 4 and 5.

The Effect of Exposure Elevation

The effect of exposure elevation on the total chloride penetration profile is shown in Figure 3 for a typical modern Swedish bridge concrete with w/c 0.40 and 5% silica fume in the binder, exposed for 5 years in the submerged, splash, and atmospheric zone.

The Effect of w/c Ratio

The effect of w/c ratio on the total chloride penetration profiles in concrete exposed submerged and in the splash zone for 5 years is shown for plain SRPC concrete in Figure 4 and for SRPC concrete with 5% silica fume in the binder in Figure 5. As expected, the effect of w/c ratio is significant for chloride penetration in concrete.

The Effect of Pozzolan in the Binder

The effect of silica fume and/or fly ash in the binder on the chloride penetration in concrete exposed in the submerged and splash zone for 5 years is shown for w/c 0.40 in Figure 6 and

TABLE 4
Curve fitting results at various exposure times for concrete exposed submerged.

Concrete exposed in the submerged zone			DeCl × 10^{-12} m^2/s Ccalc. Cl % by weight of binder							
Mix no.	Exposure time		0.6–0.8 years		1.0–1.3 years		2.0–2.3 years		5.1–5.4 years	
	ID	w/c	DeCl	Ccalc	DeCl	Ccalc	DeCl	Ccalc	DeCl	Ccalc
1	OPC 0.40	0.40	–	–	2.1	2.7	2.4	3.2	1.9	4.2
2	SRPC 0.50	0.50	4.7	2.5	–	–	5.1	2.9	2.3	4.5
3	SRPC 0.40	0.40	4.5	2.5	3.6	3.1	2.8	3.1	1.4	4.3
4	SRPC 0.30	0.30	–	–	1.8	2.7	2.4	2.4	1.5	3.6
5	SRPC 5%SF dry 0.50	0.50	4.8	2.2	–	–	2.6	3.6	1.2	4.1
6	SRPC 5%SF dry 0.40	0.40	3.4	3.1	–	–	1.4	3.0	1.3	4.2
7	SRPC 5%SF 0.40	0.40	2.0	2.6	–	–	0.8	3.2	0.8	4.1
8	SRPC 5%SF 0.30	0.30	–	–	0.9	2.7	0.7	3.9	0.5	3.7
9	SRPC 5%SF 0.25	0.25	–	–	0.4	1.0	0.5	2.9	0.2	2.4
10	SRPC 10%SF 0.30	0.30	–	–	0.6	1.6	0.5	1.9	0.2	2.8
11	SRPC 5%SF 10%FA 0.35	0.35	1.0	1.3	–	–	0.9	2.9	0.8	4.2
12	SRPC 5%SF 17%FA 0.40	0.40	1.6	2.3	–	–	0.8	2.4	0.8	5.1
13	SRPC 20%FA 0.30	0.30	–	–	1.4	2.3	1.1	2.3	0.5	4.1

for w/c 0.30 in Figure 7. The relative efficiency of silica fume seems far higher than that of fly ash under these test conditions.

The Effect of the Type of Silica Fume in the Binder

The effect the type of silica fume in the binder on the total chloride penetration profiles in concrete exposed in the submerged and in the splash zone for 5 years is shown for w/c 0.40 in Figure 8. The anticipated higher efficiency of silica fume when added as a well dispersed slurry was confirmed in submerged concrete, but not for concrete exposed in the splash zone.

The Combined Effect of w/c Ratio and of Pozzolan in the Binder

The combined effect of w/c ratio and silica fume in the binder on the calculated effective chloride diffusivity is shown in Figure 9, for concrete exposed in the splash zone and for the same concrete when tested in a standard laboratory immersion test according to NT Build 443

TABLE 5
Curve fitting results at various exposure times for concrete exposed in the splash zone.

Concrete exposed in the splash zone			DeCl × 10^{-12} m^2/s Ccalc. Cl % by weight of binder							
Mix	Exposure time		0.6–0.8 years		1.0–1.3 years		2.0–2.3 years		5.1–5.4 years	
No.	ID	w/c	DeCl	Ccalc	DeCl	Ccalc	DeCl	Ccalc	DeCl	Ccalc
1	OPC 0.40	0.40	–	–	0.6	1.3	1.6	2.4	0.9	2.2
2	SRPC 0.50	0.50	4.8	3.2	–	–	2.6	3.8	1.9	4.8
3	SRPC 0.40	0.40	2.3	1.1	–	–	2.6	1.8	1.4	1.9
4	SRPC 0.30	0.30	–	–	0.5	1.2	1.4	2.1	1.2	3.6
5	SRPC 5%SFdry 0.50	0.50	2.0	1.2	–	–	2.3	3.0	1.5	4.4
6	SRPC 5%SFdry 0.40	0.40	1.4	1.2	–	–	0.7	2.2	0.4	1.5
7	SRPC 5%SF 0.40	0.40	1.2	1.3	–	–	0.8	1.5	0.5	2.2
8	SRPC 5%SF 0.30	0.30	–	–	0.4	1.6	0.2	1.6	0.2	1.3
9	SRPC 5%SF 0.25	0.25	–	–	0.3	1.3	0.2	2.0	0.2	4.3
10	SRPC 10%SF 0.30	0.30	–	–	0.4	1.2	0.4	3.3	0.2	1.6
11	SRPC 5%SF 10%FA 0.35	0.35	0.9	0.9	–	–	0.8	2.5	0.3	1.5
12	SRPC 5%SF 17%FA 0.40	0.40	0.5	1.1	–	–	0.4	1.7	0.3	2.1
13	SRPC 20%FA 0.30	0.30	–	–	0.7	1.8	0.5	2.3	0.4	2.5

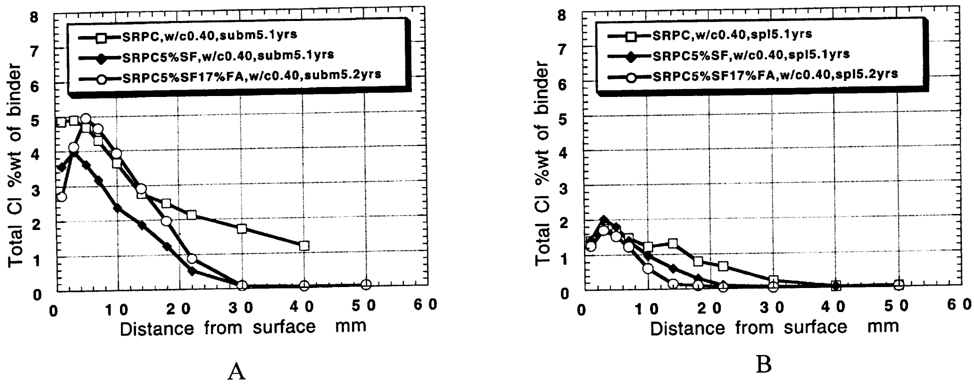


FIG. 6.
Total chloride profiles in plain concrete and in concrete with silica fume and/or fly ash in the binder fraction, w/c ratio 0.40, exposed in the submerged zone (*A*) and in the splash zone (*B*) for 5 years.

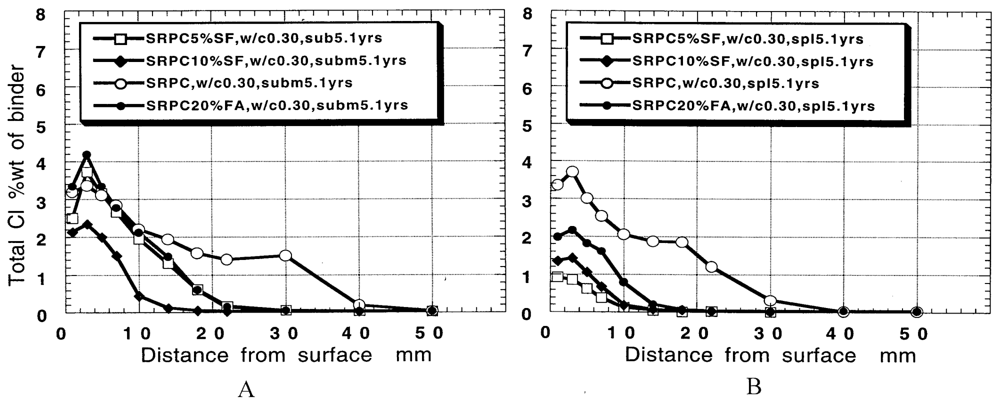


FIG. 7.
Total chloride profiles in plain concrete and in concrete with silica fume and/or fly ash in the binder fraction, w/c ratio 0.30, exposed in the submerged zone (*A*) and in the splash zone (*B*) for 5 years.

(6,8). The results in Figure 9 indicate that for a w/c ratio of 0.40, which is the maximum w/c ratio recommended for marine concrete in several codes of practice (5), the effective chloride diffusivity can be reduced by a factor of 3–5 by using 5% silica fume in the form of a well dispersed slurry in the binder fraction of the concrete. If on the other hand the w/c ratio is reduced from 0.40 to 0.30 in addition to the use of 5% silica fume in the binder, it appears that the effective chloride diffusivity can be reduced by a factor of 8–10.

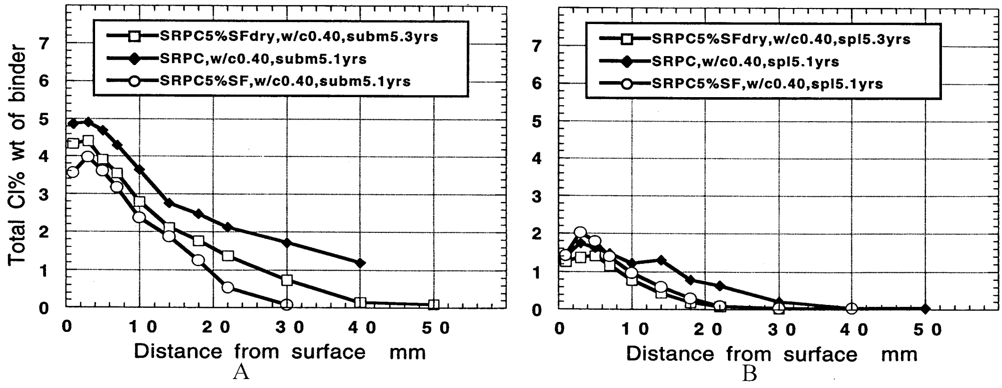
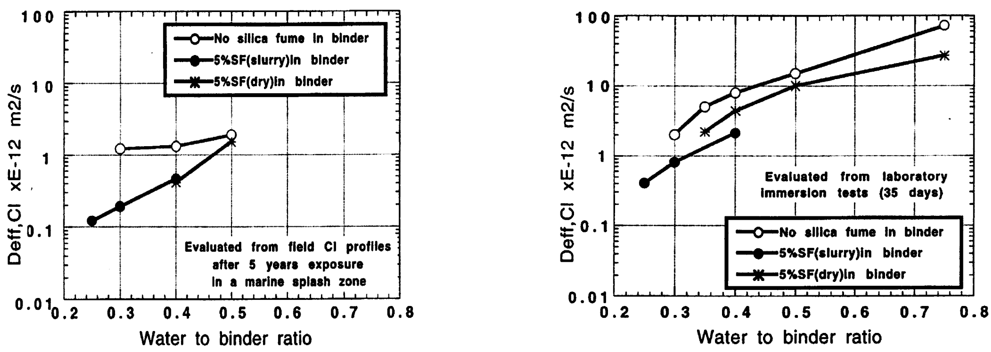


FIG. 8.
Total chloride profiles in concrete with 0–5% silica fume added as 50% slurry or as compacted powder, w/c ratio 0.40, exposed 5 years in the submerged zone (*A*) and in the splash zone (*B*).

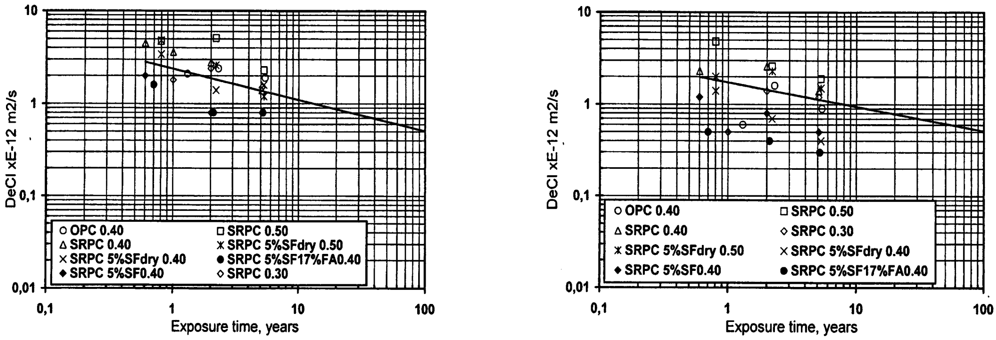


A B

FIG. 9.
Calculated effective chloride diffusivity in plain SRPC concrete and in concrete with silica fume and/or fly ash in the binder, exposed in the splash zone for 5 years (*A*) and exposed in a standard laboratory immersion test for 35 days in 16% NaCl (*B*).

Evaluation of Data Trends for Service Life Prediction

An attempt to evaluate the trends in calculated chloride penetration parameters with respect to the effective chloride diffusivity and the calculated/apparent surface concentration, as presented in Tables 4–5, was carried out as shown in Figures 10-13. The data were plotted versus the exposure time and linear or logarithmic trend lines were calculated as indicated. Figure 10 shows the calculated effective chloride diffusivity for concrete mixtures with w/c ≥ 0.40 and for plain SRPC concrete with w/c 0.30, exposed submerged and in the splash zone. Figure 11 shows the calculated effective chloride diffusivity for concrete mixtures with



A B

FIG. 10.
Calculated effective chloride diffusivity for concrete mixtures with w/c ≥ 0.40, and for plain SRPC concrete with w/c 0.30, exposed in the submerged zone (*A*) and in the splash zone (*B*).

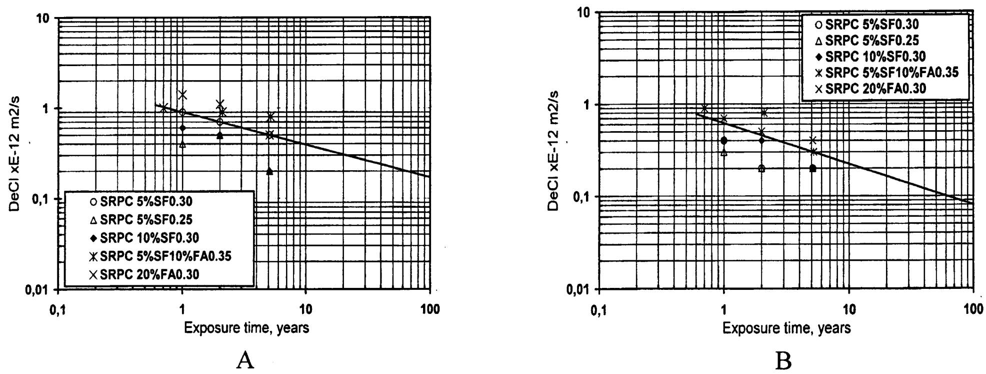


FIG. 11.
Calculated effective chloride diffusivity for concrete mixtures with pozzolan in the binder and w/c ≤ 0.40, exposed in the submerged zone (*A*) and in the splash zone (*B*).

pozzolan in the binder and w/c ≤ 0.40, exposed submerged and in the splash zone. Note the difference in the scaling of the y-axis. Figures 12–13 show the corresponding maximum measured total chloride concentrations.

Conclusions

1. The use of 5–10% silica fume in the binder has a very positive effect on reducing the chloride ingress in concrete. Little or no benefit at all was found for concrete with fly ash in the binder as compared to the use of 5% silica fume, under these test conditions of 5 days moist curing followed by 5 days of air curing prior to exposure.

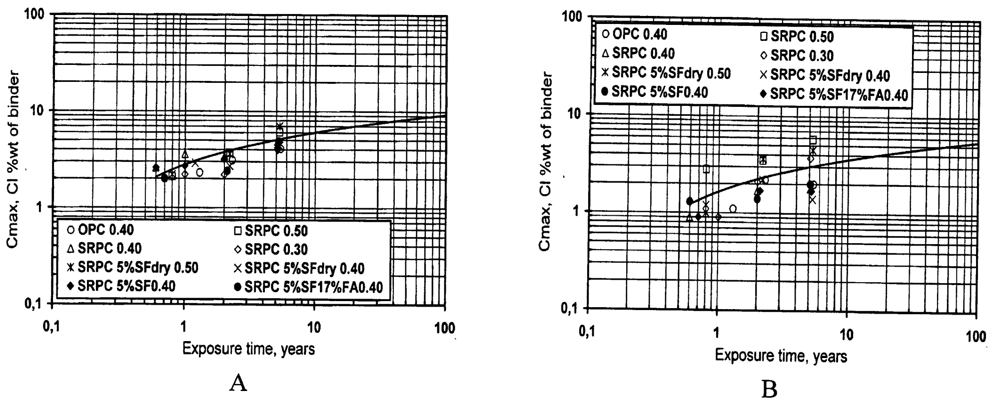


FIG. 12.
Measured maximum total chloride concentrations for concrete mixtures with w/c ≥ 0.40, and for plain SRPC concrete with w/c 0.30, exposed submerged (*A*) and in the splash zone (*B*).

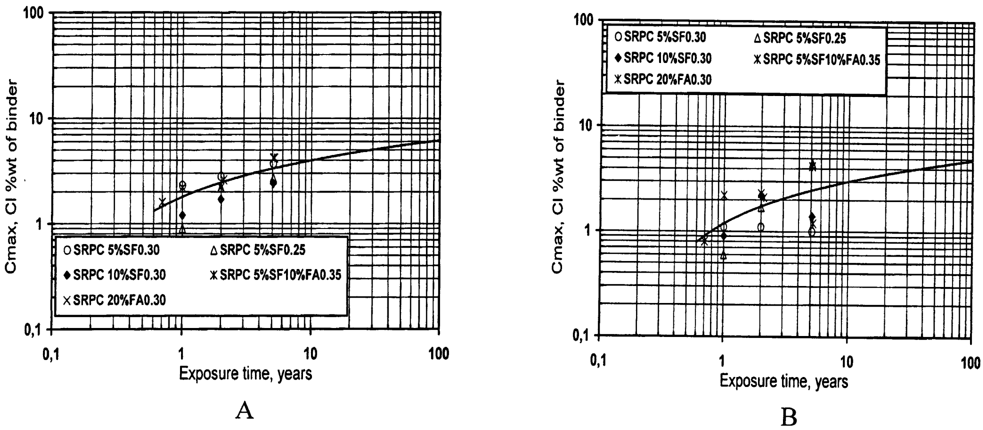


FIG. 13.

Measured maximum total chloride concentrations for concrete mixtures with pozzolan in the binder and w/c $\leq$ 0.40, exposed in the submerged zone (*A*) and in the splash zone (*B*).

2. High-performance concrete with w/c 0.25–0.3 and 5–10% silica fume exhibited an effective chloride diffusivity in the range 2×10^{-13} to 4×10^{-13} m^2/s after 5 years exposure in the splash zone. The corresponding range of values found for a typical Swedish bridge concrete with w/c 0.4 and no pozzolan in the binder was 9×10^{-13} to 14×10^{-13} m^2/s.
3. The chloride penetration rate as expressed by a calculated effective chloride diffusivity, assuming linear chloride binding and constant diffusivity, has a tendency to decrease in a linear fashion over time.
4. The maximum measured total chloride concentration has a tendency to increase in a non-linear fashion over time.
5. The presented results are based on recurrent studies of total chloride ingress in well-defined concrete mixtures at various exposure ages. The data can be very useful for the prediction of chloride ingress in marine concrete structures exposed in a similar environment.

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