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Effects of fresh water exposure on chloride contaminated concrete

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Abstract

Due to its porous structure, concrete that is exposed to chlorides will eventually become contaminated through the various mechanisms of chloride ingress, such as diffusion and absorption. As the conditions of chloride exposure are continuously changing, the movement of chlorides can occur in and out of the concrete. However, these rates of chloride movement are not the same. For de-icing salt exposure, the rate with which chlorides enter concrete from salt splash is much faster than the rate the chlorides will be extracted by rainwater. It was found that continuous or cyclic exposure of chloride contaminated concrete to distilled water will decrease the chloride concentration at the surface of the concrete; however, the chloride in saturated concrete continues to diffuse inward. Essentially, once chlorides have contaminated concrete, the chlorides cannot be completely removed under normal service conditions. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the most prevalent causes of early deterioration of reinforced concrete structures is chloride-induced corrosion. Such corrosion may never be eliminated, but one way in which it can be reduced is by providing more durable concrete that limits the amount of moisture and oxygen needed to sustain corrosion, reducing the amount of chloride exposure or restricting the chloride content in materials used. In some cases, it is even possible that chlorides can be washed out of the chloride contaminated concrete, such as when directly exposed to rain.

The literature on the phenomena of chloride washout is scarce. However, in one study, the rate of chloride extraction from the surface of the concrete when exposed to fresh water was found to be much slower than the rate of chloride contamination [1]. It was also shown that once the chlorides enter concrete, very little chloride is removed by counter-diffusion. Under this process, chlorides near the surface will counter-diffuse into the chloride-free rainwater ponding on the surface and penetrating the surface pores, but some chlorides will continue to diffuse deeper into the concrete where there are lower chloride concentrations.

The washout of near surface chlorides by rainfall is typically found when structures are cored in summer. Fig. 1 shows chloride profiles for the lower inclined faces of two adjacent 9-year-old highway bridge parapet walls near Kitchener, Ontario, one of which contains 25% Class C fly ash. Both concretes, which had a w/cm = 0.41 and cementing material content of 355 kg/m^3, exhibited a 4.5-month core strength of 38 MPa.

The depth of washout or convection zone is approximately 7 mm for the Portland cement mixture and 14–15 mm for the fly ash mixture. It is also interesting to note that for the Portland cement concrete, which has a smaller convection zone, the depth of the 0.1% chloride front is 42 mm, yet only 31 mm for the fly ash concrete, due to the fly ash's lower diffusion coefficient. (Note: the background chloride levels of 510 ppm, due to locked in aggregate chlorides have been added to obtain the critical threshold.) To calculate diffusion coefficients from such field data, the depth at maximum chloride concentration can be taken as a pseudo-surface and the profile to the right can be fit using Crank's solution to Fick's Second

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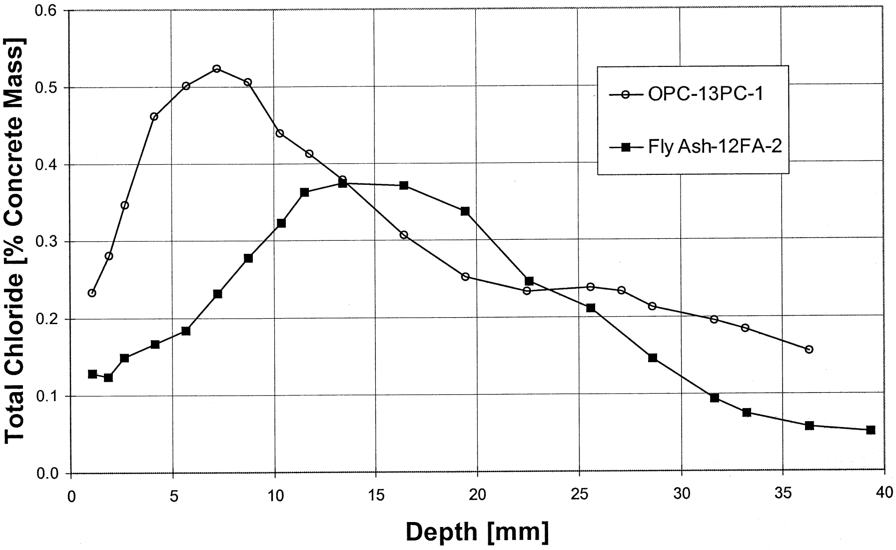


Fig. 1. Chloride profile of highway #401 at #8 barrier wall, cast June 1986, cored June 1995 (unpublished data by the second author).

Law. Similar washout effects have been observed elsewhere [2].

This paper reports the results of distilled water exposure on the level of total chloride concentrations in previously chloride contaminated concrete. Two series of tests were performed on three different concrete mixtures. In the first series, specimens were subjected to 25 cycles of wetting and drying with 1.0 M sodium chloride solution [3], and then exposed to a various number of wetting and drying cycles with distilled water. The second series of specimens were placed in 1.0 M NaCl solution for 120 days and then exposed for various time periods in distilled water. The chloride profiles were obtained and compared to evaluate the effects of distilled water exposure on chloride contaminated concrete.

2. Materials

Three typical mix designs for structures such as bridge decks exposed to de-icing salts in the Toronto area were used. The mixtures meet or exceed the requirements of Canadian Standards Association (CSA) A23.1 Exposure Class C-1 (maximum w/cm = 0.40, minimum 28-day

Table 1
Concrete mix proportions and properties

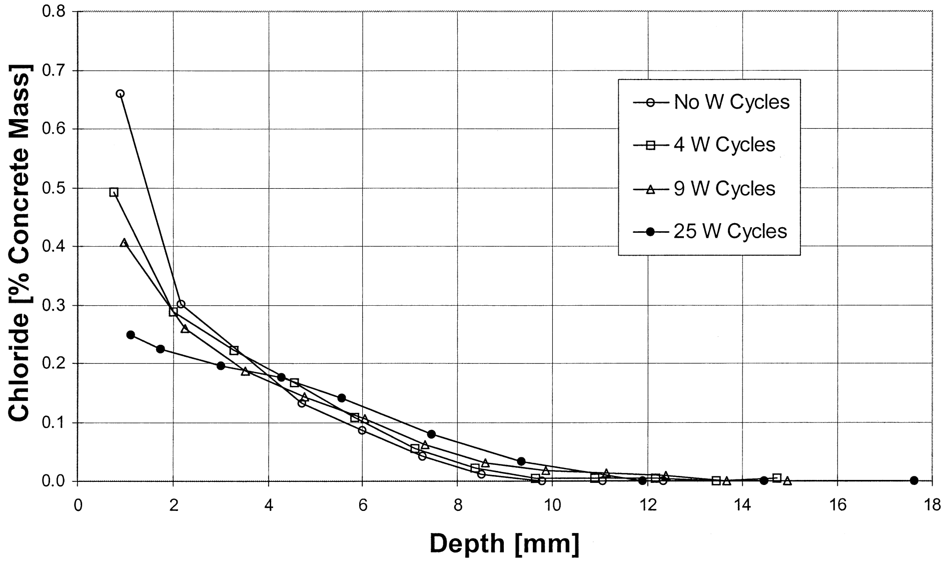
	0.4 w/cm, 25% slag	0.4 w/cm, 25% slag, 8% SF	0.3 w/cm, 25% slag, 8% SF
Portland cement (CSA Type 10 low-alkali)	285	255	308
Slag (pelletized, blaine = 400 m^2/kg)	95	95	115
Silica fume SKW becancour (undensified)	0	30	37
Coarse aggregate (10 mm crushed limestone)	1100	1100	1100
Fine aggregate (glacial sand)	654	642	600
Water	150	150	136
Water reducer (lignosulphonate based) [ml/100 kg]	325	325	325
Superplasticizer (sodium naphthalene formaldehyde condensate) [ml/100 kg]	480	640	1155
Air entrainer (pure polymeric base) [ml/100 kg]	45	40	80
Slump [mm]	150	95	135
Air content [%]	9.0	7.0	4.5
Plastic density [kg/m^3]	2274	2302	2260
7-Day compressive strength [MPa]	27.3	34.8	62.5
28-Day compressive strength [MPa]	39.6	49.2	79.0
120-Day bulk diffusion coefficient [m^2/s]	3.46×10^{-12}	1.42×10^{-12}	0.74×10^{-12}
365-Day bulk diffusion coefficient [m^2/s]	2.01×10^{-12}	0.72×10^{-12}	0.43×10^{-12}

All concrete specimens were cores of 100 ± 3 mm in diameter and 50 mm in thickness. The specimens were taken from 350×250×75 mm slabs that were cured in a saturated $Ca(OH)_2$ solution at 23°C for 27 days, after 1 day of curing under wet burlap and plastic.

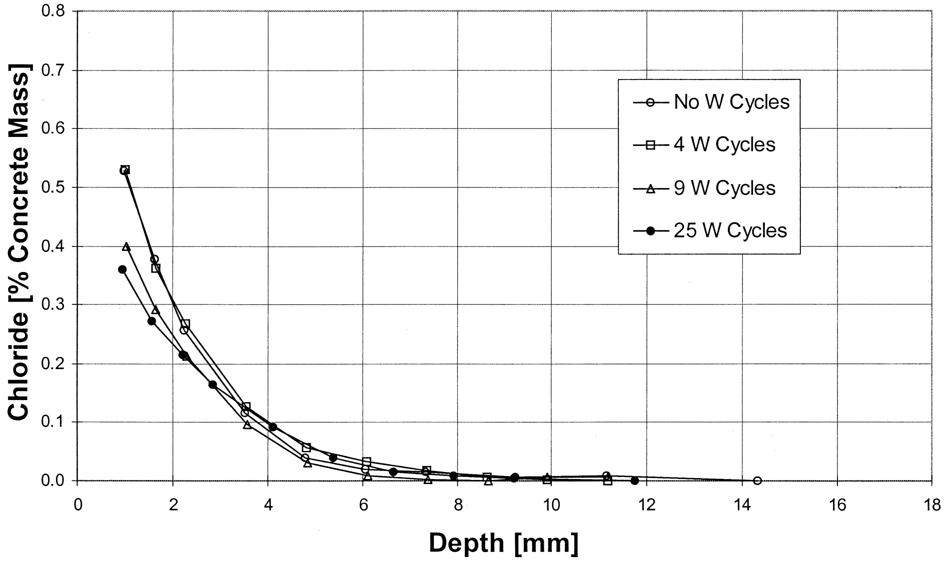
strength = 35 MPa, air entrained). The mix designs, concrete properties, and bulk diffusion coefficients are listed in Table 1. Two of the concretes contained silica fume (SF) and all mixtures incorporated 25% ground granulated blast-furnace slag as is typical in Southern Ontario. The bulk diffusion coefficients were determined from cores that had been cured for 28 days, ponded in 1.0 M NaCl solution at 23°C for 120 days or 1 year, and then analyzed for chlorides to obtain the chloride profiles. The chloride profiles were then curve-fitted to calculate the apparent diffusion coefficient using a numeric solution to Fick's Second Law.

3. Testing program

In the first series of tests, four pairs of concrete cores were exposed to 25 cycles of chloride solution. Each cycle consisted of a wetting period with a 1.0 M NaCl solution for 6 h at 23°C followed by 18 h of drying at

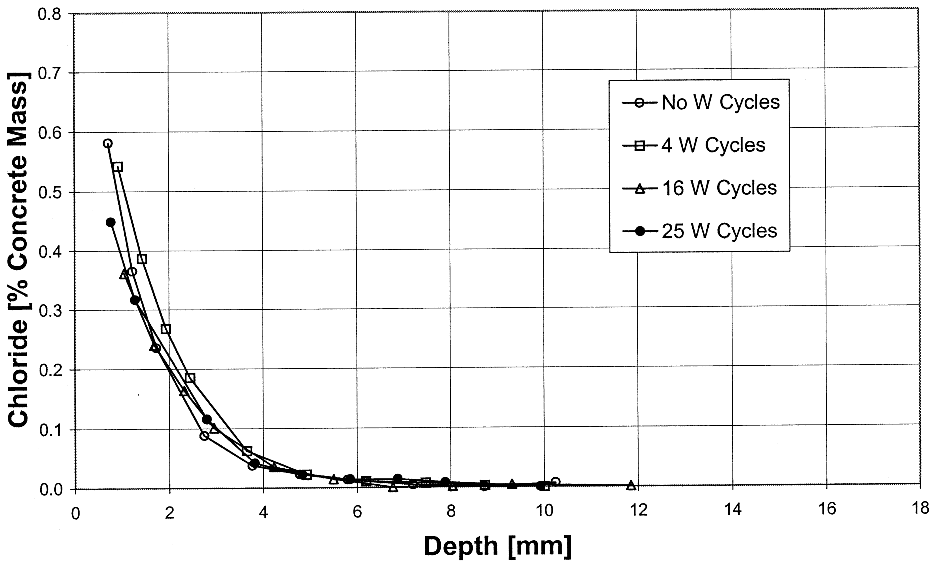


(a) Concrete with 0.4 w/cm, 25% slag



(b) Concrete with 0.4 w/cm, 25% slag, 8% silica fume

Fig. 2. Concrete exposed to 25 cycles with NaCl solution, followed by cycles (W Cycles) with distilled water (a) concrete with 0.4 w/cm, 25% slag, (b) concrete with 0.4 w/cm, 25% slag, 8% silica fume, and (c) concrete with 0.3 w/cm, 25% slag, 8% silica fume.



(c) Concrete with 0.3 w/cm, 25% slag, 8% silica fume

Fig. 2 (*continued*).

23°C and 50% relative humidity, as described in more detail in a related study [3]. All sides of each core, except for the form-faced testing surface, were sealed with epoxy to ensure unidirectional chloride penetration into the test face. After the 25 cycles with NaCl solution, the four pairs of specimens were exposed to 0, 4, 9 or 16 (where one concrete mixture was exposed to 16 cycles instead of 9), and 25 cycles with distilled water and then analyzed.

In the second series, four pairs of specimens were placed in square 2.5-l plastic containers filled with 1.0 M NaCl solution for 120 days. The specimens were then placed in similar square plastic containers filled with 1.5 l of distilled water for either 0, 30, 60, and 120 days. Small water samples (approximately 20 ml) were taken weekly to monitor the quantity of chlorides counter-diffusing into the distilled water. A total of 16 water samples were taken: the first four from the sample exposed to 30 days with distilled water, the following four from the 60-day sample and the remaining eight from the 120-day sample. This was to prevent large volumes of water being removed from any particular

Table 2
Total chlorides absorbed after wet/dry cycling with water

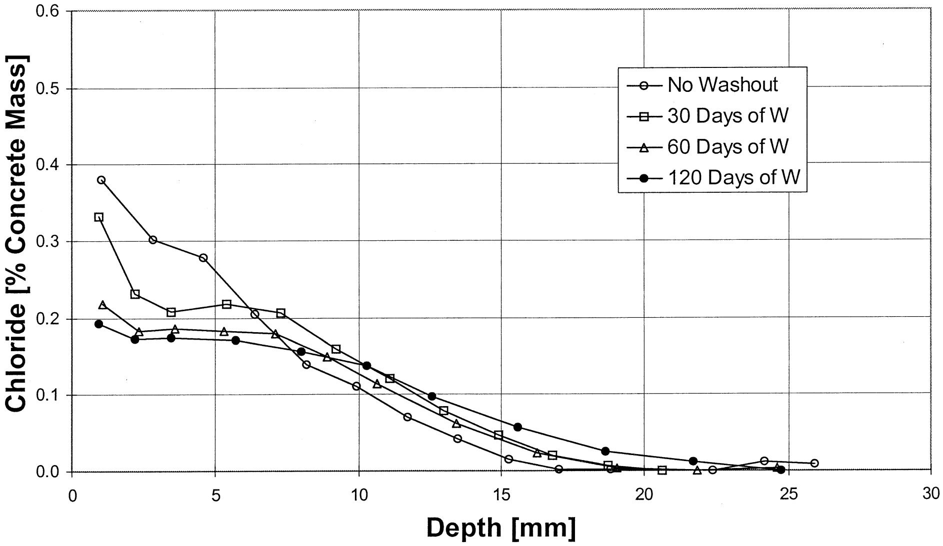
Concrete mixture	Number of W cycles	Convection depth [mm]	Near surface		Concrete at depth		Total	
			[g]	[%]	[g]	[%]	[g]	[%]
0.4 w/cm, 25% slag	0	4	0.57	100.0	0.13	100.0	0.70	100.0
	4	4	0.49	85.9	0.17	123.8	0.65	93.2
	9	4	0.43	75.4	0.19	141.3	0.62	88.1
	25	4	0.33	58.0	0.22	165.6	0.55	78.7
0.4 w/cm, 25% slag, 8% silica fume	0	3.5	0.49	100.0	0.07	100.0	0.57	100.0
	4	3.5	0.50	101.6	0.09	115.5	0.59	103.4
	9	3.5	0.39	78.3	0.04	59.1	0.43	75.8
	25	3.5	0.35	71.5	0.08	106.3	0.43	76.1
0.3 w/cm, 25% slag, 8% silica fume	0	2	0.33	100.0	0.09	100.0	0.42	100.0
	4	2	0.38	117.4	0.13	141.5	0.51	122.6
	16	2	0.26	80.8	0.10	112.0	0.36	87.5
	25	2	0.29	89.3	0.11	128.3	0.41	97.7

Percentage values are relative to the original value before fresh water exposure. Near surface is the depth between the surface and convection depth. Concrete at depth is the region beyond the convection depth.

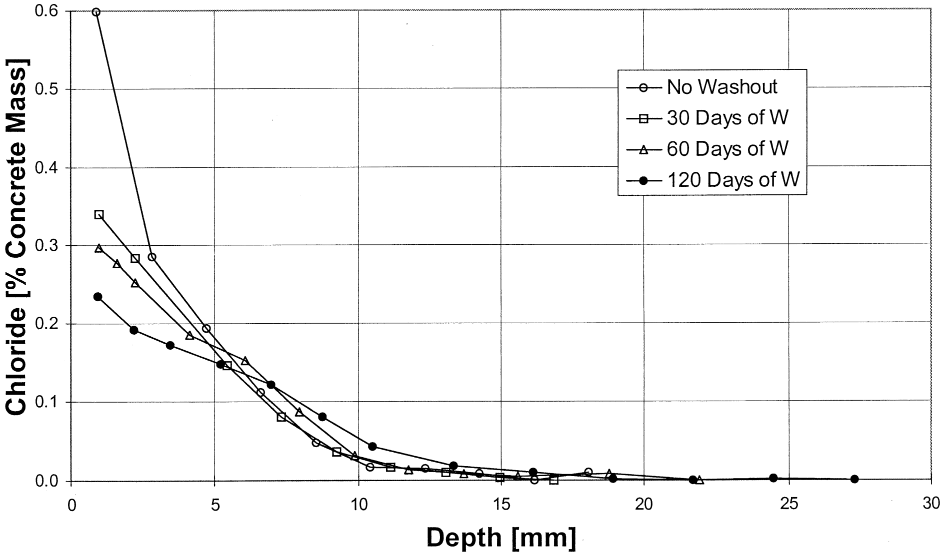
container, as the change in volume was not accounted for in the chloride analysis. These specimens were wrapped and frozen, for later chloride analysis.

4. Analysis

Once the cyclic portion of the testing was completed, the specimens were tightly wrapped in freezer bags and stored in a freezer (−18°C) to prevent further chloride diffusion prior to analysis. Later, thin layers of concrete were obtained at various depths into the specimen, and these samples were analyzed for total chloride content. These layers were first decomposed with nitric acid, and then using a Metrohm DMS 716 automatic titrator, the chloride concentrations were found. Only external chlorides that were introduced into the concrete during the test were considered by subtracting the background chlorides. The details of the chloride analysis are given elsewhere [3].

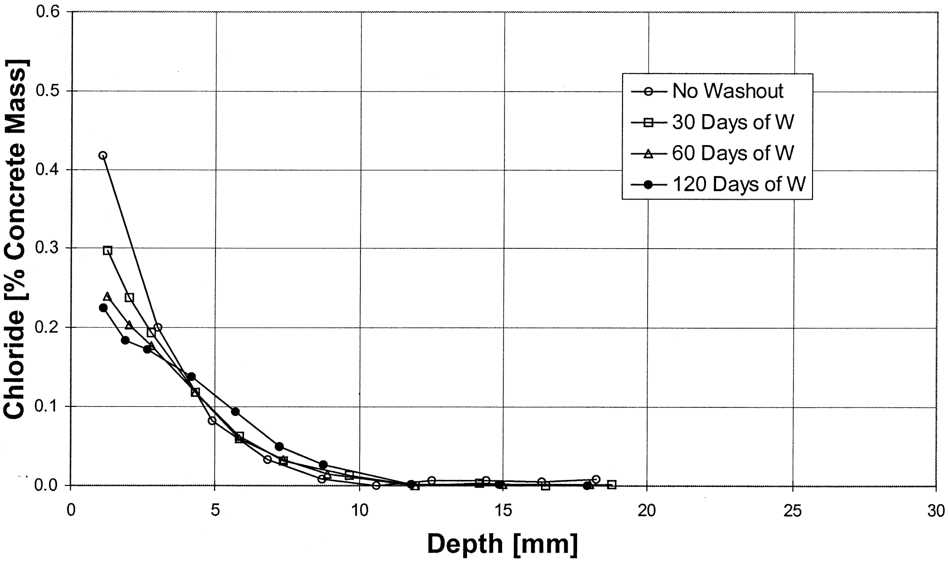


(a) Concrete with 0.4 w/cm, 25% slag



(b) Concrete with 0.4 w/cm, 25% slag, 8% silica fume

Fig. 3. Concrete exposed to 120 days of NaCl solution, followed by exposure to distilled water (a) concrete with 0.4 w/cm, 25% slag, (b) concrete with 0.4 w/cm, 25% slag, 8% silica fume, (c) concrete with 0.3 w/cm, 25% slag, 8% silica fume.



(c) Concrete with 0.3 w/cm, 25% slag, 8% silica fume

Fig. 3 (*continued*).

The mass of chlorides penetrated into the concrete were determined by integrating the area under the profile curve. The mass of chlorides absorbed was found using the following formula:

$$\text{Mass of Chlorides Absorbed [g]} = \frac{\text{Integrated Area} \times \text{Concrete Density} \times \text{Area of Specimen}}{100}$$

where Integrated Area = area under the chloride profile curve [100% mm], Concrete Density = density of the concrete, taken to be 2300 [kg/m^3]; and Area of Specimen = surface area exposed to test [m^2].

5. Results

The chloride profiles from the first series of tests for the three concrete mixtures are shown in Fig. 2 (W Cycles are the washout cycles with distilled water). It can be seen that in each case, with an increasing number of distilled water cycles, the concentration of chlorides near the surface decreased with respect to the control specimen.

It was noted that the chloride concentrations near the surface decreased quickly, while deeper in the concrete, the concentrations generally increased. To separate these two areas, an approximate depth was chosen for each

Table 3
Total chlorides absorbed after continuous water immersion

Concrete mixture	Days in water	Convection depth [mm]	Near surface		Concrete at depth		Total	
			[g]	[%]	[g]	[%]	[g]	[%]
0.4 w/cm, 25% slag	0	7	0.75	100.0	0.28	100.0	1.03	100.0
	30	7	0.63	83.8	0.39	139.3	1.02	99.1
	60	7	0.49	66.1	0.35	122.7	0.84	81.6
	120	7	0.45	60.5	0.44	155.3	0.89	86.6
0.4 w/cm, 25% slag, 8% silica fume	0	6	0.63	100.0	0.13	100.0	0.76	100.0
	30	6	0.55	86.9	0.13	96.9	0.67	88.6
	60	6	0.50	79.7	0.15	118.7	0.66	86.3
	120	6	0.41	64.9	0.21	158.9	0.62	80.8
0.3 w/cm, 25% slag, 8% silica fume	0	4	0.44	100.0	0.09	100.0	0.54	100.0
	30	4	0.36	81.8	0.12	124.7	0.48	89.4
	60	4	0.31	69.7	0.12	122.0	0.42	78.9
	120	4	0.28	63.3	0.15	162.3	0.43	80.8

Note: Percentage values are relative to the original value before fresh water exposure. Near surface is the depth between the surface and convection depth. Concrete at depth is the region beyond the convection depth.

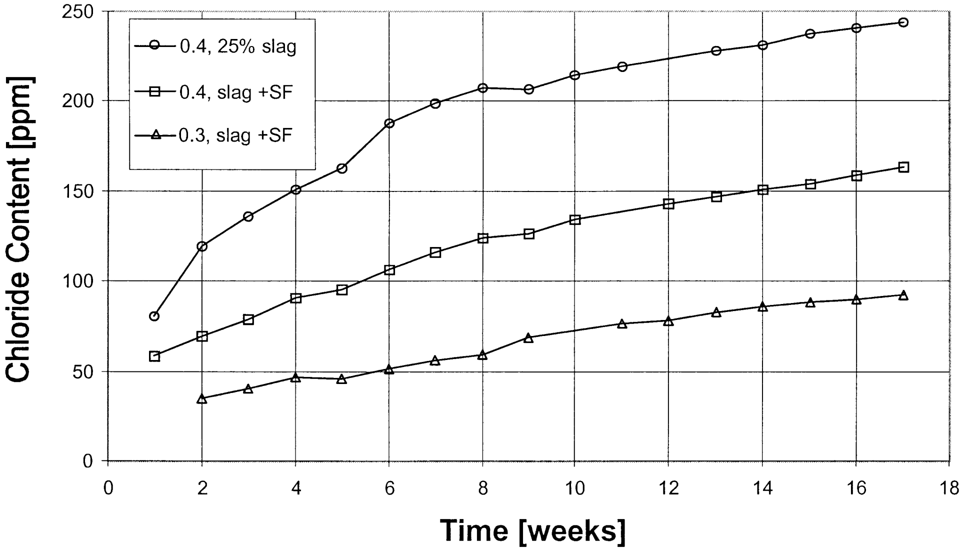


Fig. 4. Chloride concentration of water samples.

concrete, where the chloride profile of the specimen treated with distilled water crossed the original chloride profile. The depth defining the outer zone is referred to as the convection depth. The mass of chlorides absorbed in each of the two zones was determined and compared with the control specimen. These results can be found in Table 2.

The results from the second series are shown in Fig. 3. The mass of chlorides absorbed by the concrete was also found by integrating the area under the chloride profile, and can be found in Table 3. Fig. 4 shows the chloride concentrations found from in the weekly water samples.

6. Discussion

Fig. 2 shows that with each higher quality concrete, the effect of cyclic exposure with distilled water has a reduced ability to wash out the chlorides. For higher quality concretes, chlorides enter more slowly into the concrete, and they also exit more slowly. In general, with the decrease in

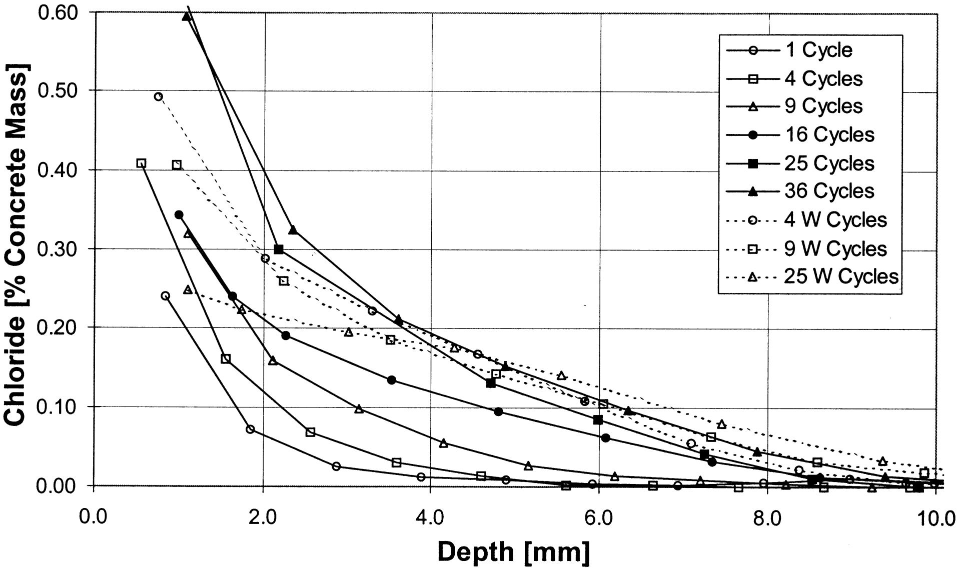


Fig. 5. Chloride profiles for concrete with 0.4 w/cm, 25% slag, with various number of (chloride and fresh water) cycles.

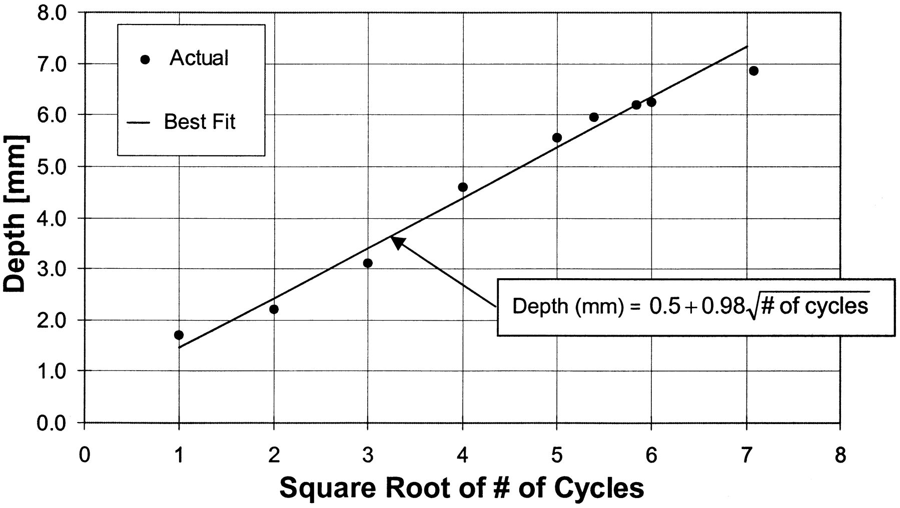


Fig. 6. Depth of a chloride concentration of 0.1% vs. the square root of number of cycles (chloride and fresh water) for concrete with 0.4 w/cm, 25% slag.

w/cm, and the use of silica fume, a finer and more discontinuous pore structure is produced, which could be the reason for the slower transport properties.

It was also found that the rate of chloride intake was much faster than the rate of chloride removal. For all three concrete mixtures, there was a slight decrease in surface concentration and total mass of absorbed chlorides after 25 cycles with distilled water. In particular, for the 0.3 w/cm, with 25% slag and 8% silica fume concrete, shown in Fig. 2(c), the amount of chlorides removed is almost negligible compared to the amount absorbed during the 25 cycles with NaCl solution. This slower chloride removal rate was also found in a study done by Tritthart [1].

From the second series of tests, where the overall exposure time to salt solutions and distilled water was longer, the results show a notable difference in chloride concentrations and mass of chlorides absorbed between the control specimen and the specimens exposed to distilled water. In Fig. 3, concrete mixtures showed a definite decrease in chloride concentration near the surface, and an increase in chloride concentration deeper in the concrete, at least after 120 days of washout. This could be attributed to continuing diffusion in deeper pores, which remain saturated. The substitution of distilled water for the chloride solution at the surface of the concrete reverses the chloride concentration gradient in the convection zone, causing some chlorides to counter-diffuse. Given a constant concentration gradient, diffusion is governed by time. The gradual increase in chloride concentration in the distilled water (Fig. 4) is indicative of diffusion being the primary mechanism causing the outward movement of chlorides.

The overall conclusion from these results is that once the chlorides enter the concrete, they will not be easily removed except near the surface, without an active form of removal such as electrochemical methods. As long as the pores are saturated, inward chloride diffusion will continue to act, drawing more chlorides toward regions of lower chloride concentration unless they become bound.

It was interesting to notice from the chloride profiles in Fig. 5, that with an increase in the number of cycles, whether with NaCl solution or distilled water, the chloride concentration continued to increase at depth where the concrete is most likely saturated. The data in Fig. 5 show the results of tests performed in a previous study [3] in combination with the chloride profiles of the specimens exposed to 25 cycles of chloride solution and cycles with fresh water.

Because of the continued inward chloride diffusion at greater depths during washout cycles, it was possible to plot the relationship between the depth of an arbitrarily chosen 0.1% chloride concentration front by mass of concrete and the square root of the number of cycles regardless of the cycle being due to chloride solution or fresh water exposure. This is shown for one concrete mixture (0.4 w/cm with 25% slag) in Fig. 6, derived from the data shown in Fig. 5. The best-fit line is based on a linear regression of the data from the 1, 4, 9, 16, 25, and 36 cycles with NaCl solution. Fig. 6 also includes the additional 25 cycles of washout (total = 50).

7. Conclusions

(1) Higher-quality concretes slow down the rate of chloride entry, as well as the rate of chloride removal.

(2) For a given concrete, the rate of chloride removal is much slower than the rate of chloride ingress.

(3) When chloride contaminated concrete is exposed to distilled water, chloride concentrations will decrease at the surface, but increase at depths below the convection zone. In saturated pores, free chloride ions continue to diffuse to regions of lower chloride concentrations, both outside the concrete surface, and deeper into the concrete.

(4) Once chlorides have entered into concrete, they will never be completely removed by freshwater exposure.

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