Pergamon

Cement and Concrete Research 29 (1999) 1379–1386

CEMENT AND CONCRETE RESEARCH

Effects of cyclic chloride exposure on penetration of concrete cover

K. Hong, R.D. Hooton*

Department of Civil Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

Received 27 March 1998; accepted 16 March 1999

Abstract

Concretes are in a state of flux between saturated and partially saturated conditions as they undergo continuous cycles of wetting and drying. In saturated concrete, dissolved ions enter through diffusion, whereas in partially saturated concrete, ion-containing fluids are absorbed by capillary suction and concentrated by evaporation of water. The primary focus of this study was to examine the effects of cyclic wetting and drying with sodium chloride solution on chloride ingress into concrete. Chloride profiles of samples exposed to various lengths and numbers of cycles were determined for three mixtures of concrete: two containing slag and/or silica fume with a 0.4 w/cm (water to cementing materials ratio) and one with a 0.3 w/cm. It was found that longer drying times increase the rate of chloride ingress. A good relationship exists between the depth of chloride penetration and the square root of the number of cycles. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Permeability; Transport properties; Concrete

1. Introduction

Cyclic wetting and drying causes continuous moisture movement through concrete pores [1]. This cyclic action accelerates durability problems, for it subjects the concrete to the movement and accumulation of harmful materials, such as sulphates, alkalies, acids, and chlorides. Cyclic wetting and drying is a problem for reinforced concrete structures exposed to chlorides, such as:

1. marine structures, particularly in the splash and tidal zones;
2. parking garages, in areas exposed to deicer salts; and
3. highway structures, such as bridges and other elevated roadways.

Six mechanisms govern chloride ingress into concrete [2]: absorption, diffusion, chloride binding, permeation, wicking, and dispersion. For structures exposed to cyclic wetting and drying, absorption and diffusion are two of the most significant mechanisms.

Several factors can affect the extent that chlorides penetrate concrete through cyclic wetting and drying. Chloride ingress is strongly influenced by the sequence and duration of wetting and drying. Specifically, the degree of dryness and therefore the ambient drying conditions are very important. Dry or partially dry concrete when exposed to salt water imbibes the salt water by capillary suction. The concrete absorbs in the salt water until saturation, or until there is no more reservoir of salt water. Drying to a greater depth (drier concrete) allows subsequent wettings to carry the chlorides deeper into the concrete, thus speeding up the penetration of chloride ions [3]. In fact, the moisture content "has a direct influence on durability, as it governs the amount of oxygen and moisture available at the rebar, and the magnitude of the capillary suction forces, which dictates the rate of penetration of water" [4].

If the concrete remains wet, some salts may migrate inward from the concrete surface by diffusion. However, if the wetting period is short, the entry of salt water is mainly by absorption. The salts are carried into the interior of the concrete and further concentrated during the following drying cycle. Below the outer "convection zone" of the cover, the concrete remains moist and chlorides penetrate further by diffusion regardless of the external moisture conditions.

Cyclic wetting and drying can increase the rate of corrosion in reinforced concrete structures as a result of two actions. First, cyclic wetting and drying concentrates ions, such as chlorides, can increase the rate of corrosion by the evaporation of water during the drying phase. Second, once chloride thresholds have been reached at the depth of cover, drying of the concrete increases the availability of oxygen required for steel corrosion, because oxygen has a substantially lower diffusion coefficient in saturated concrete. For example, concrete structures subjected to cyclic wetting and drying of seawater are more prone to deterioration compared to concrete structures permanently submerged in seawater [5]. In this case there is an increased availability of

---

* Corresponding author. Tel.: 416-978-5912; fax: 416-978-6813 (or 7046).

E-mail address: hooton@civ.utoronto.ca (R.D. Hooton)

0008-8846/99/$ – see front matter © 1999 Elsevier Science Ltd. All rights reserved.

PII: S0008-8846(99)00073-3

Table 1
Mix properties

	0.4 w/cm, 25% slag	0.4 w/cm, 25% slag, 8% silica fume	0.3 w/cm, 25% slag, 8% silica fume
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}
Sorptivity (1-day conditioning) ($mm/min^{1/2}$)	0.0053	0.0024	0.0027
Sorptivity (3-day conditioning) ($mm/min^{1/2}$)	0.0084	0.0037	0.0024

oxygen and a higher concentration of chlorides to maintain corrosion compared to the concrete that is fully submerged.

The objective of this research project was to study the effects of cyclic wetting and drying on the rate of chloride ingress in concrete. A series of cyclic tests were performed to obtain an understanding of the physical mechanisms causing the accumulation of chlorides in the interior pores of concrete during the wetting and drying phases of the cycle. The effects of the number of cycles and the length of the drying phase on three different concretes mixtures are discussed.

2. Materials and methods

Three typical mix designs for structures such as bridge decks exposed to deicing salts in the Toronto area were used that meet or exceed the requirements of CSA (Canadian Standards Association) A23.1 Exposure Class C-1 [maximum w/cm (water to cementing materials ratio) = 0.40, minimum 28-day strength = 35 MPa, air entrained]. The mix designs, plastic concrete properties, bulk diffusion coefficients, and sorptivity values are listed in Table 1. The bulk diffusion coefficients were determined from cores that had been cured for 28 days, ponded in 1.0 molar 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 used to calculate the apparent diffusion coefficient using Fick's Second Law. Sorptivity testing was performed where the samples were dried for 1 or 3 days at 23°C and approximately 50% relative humidity.

The concrete was mixed in two stages, where only one-fourth of the recommended superplasticizer dosage was added in the first stage, with the remainder added as needed

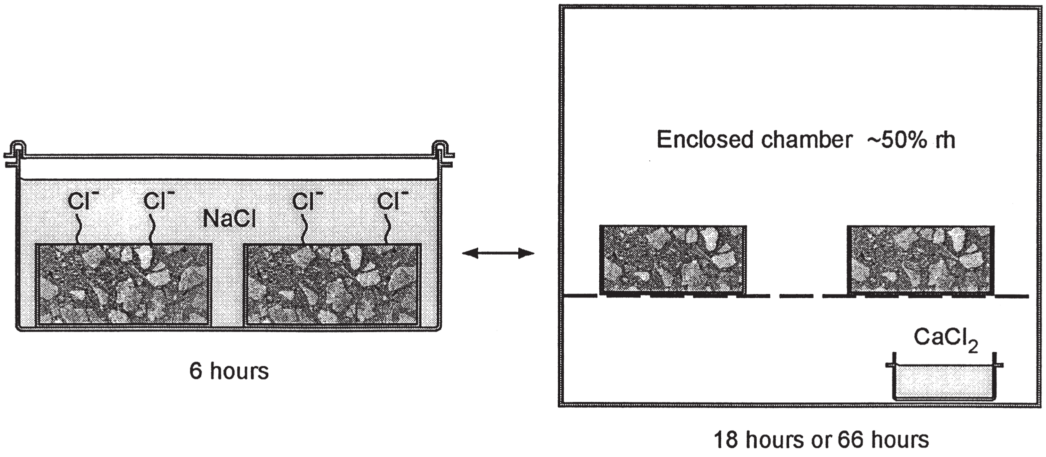

Fig. 1. Cyclic wetting and drying.

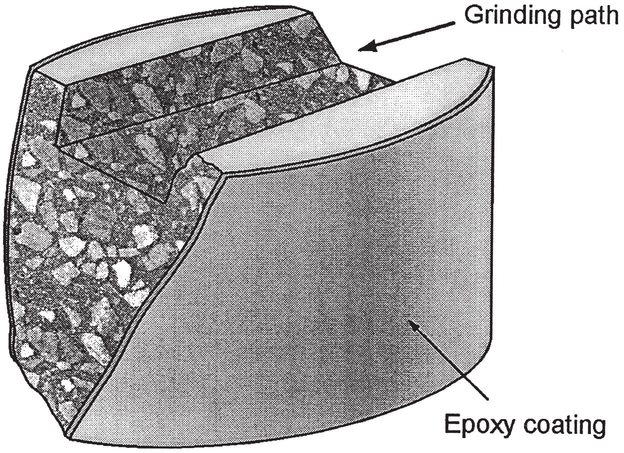

Fig. 2. Profile ground specimen.

during the second stage. All samples were cured in a saturated $Ca(OH)_2$ solution at 23°C for 28 days.

2.1. Testing program

Two wetting and drying cycle lengths were chosen. The wetting period with a 1.0 molar NaCl solution was kept constant for 6 h, but the time of drying was either 18 h (1-day series) or 66 h (3-day series). The 1-day cycle was chosen to represent a daily application of deicing salts that a reinforced concrete structure might experience during a Canadian winter. As the rate of drying is slower than the rate of wetting [4], the drying time was set at 18 h for the 1-day cycle. The 3-day cycle was chosen to test the effects of a longer drying time between salt applications. Extending the drying periods would result in deeper sorption effects since the concrete will not be fully dry after only 3 days. Six pairs of specimens were cycled in the 1-day series for 1, 4, 9, 16, 25, and 36 cycles, and five sets were cycled in the 3-day series for 1, 4, 9, 16, and 25 cycles.

To reduce the effect of wicking, specimens were sealed on all sides except for the testing surface, which also ensured unidirectional chloride penetration into the test face. Two concrete specimens of 100 ± 3 mm diameter by 50-mm depth were cored from a 350 × 250 × 75 mm slabs for each test. During the dry cycles, specimens were placed in an enclosed chamber with a relative humidity of approximately 50% at room temperature (23°C). After 18 h for the 1-day series, or 66 h for the 3-day series, specimens were then placed in a square 2.5-L plastic container filled with 1.5 L of 1.0 molar NaCl solution at 23°C and sealed for 6 h, as shown in Fig. 1. This was repeated until the prescribed number of cycles were completed.

Once the cycling portion of the testing was completed, the specimens were tightly wrapped four times in freezer bags, and stored in a freezer (−18°C) to prevent further chloride diffusion. At a later date these samples were profiled and analyzed for chlorides, as shown in the next section.

Bulk diffusion tests were also performed on concrete specimens that were prepared in the same manner as the specimens exposed to cycles of wetting and drying. Two specimens were placed in a square 2.5-L plastic container with 1.5 L of 1.0 molar of NaCl solution at 23°C for either 120 days or 1 year. At the completion of this test, the specimens were wrapped and stored in the freezer. These samples were later analyzed for chlorides and the chloride profiles were found.

2.2. Chloride analysis

To obtain a chloride profile, a chloride analysis is performed on a sequence of thin concrete layers. The epoxy-sealed sides of the specimen were first chipped off with a hammer and wide heavy chisel, to prevent the epoxy from contaminating the ground sample, as shown in Fig. 2. To obtain a good chloride profile, a minimum of five data points in the penetration zone and one point just beyond the penetration zone was required. An estimation of the depth of chloride penetration was made based on previously obtained profiles of similar concrete subjected to similar exposures. Generally 10 samples were taken to characterize the

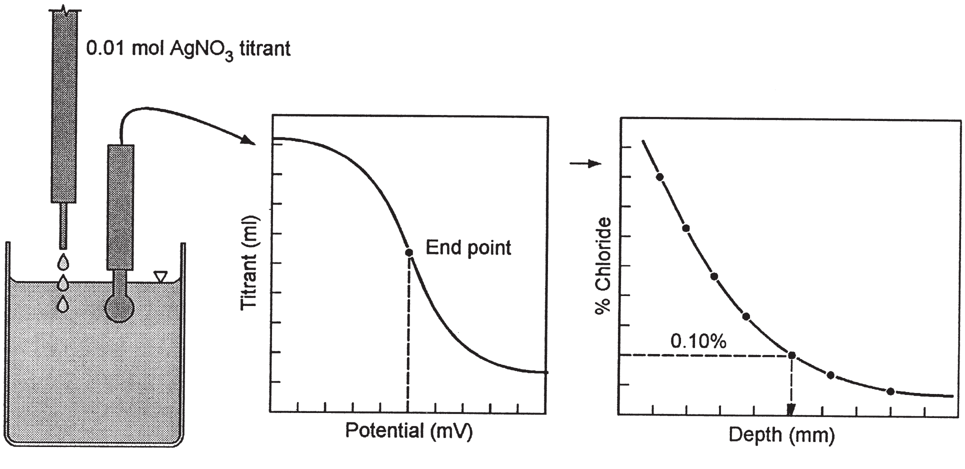

Fig. 3. Potentiometric titration.

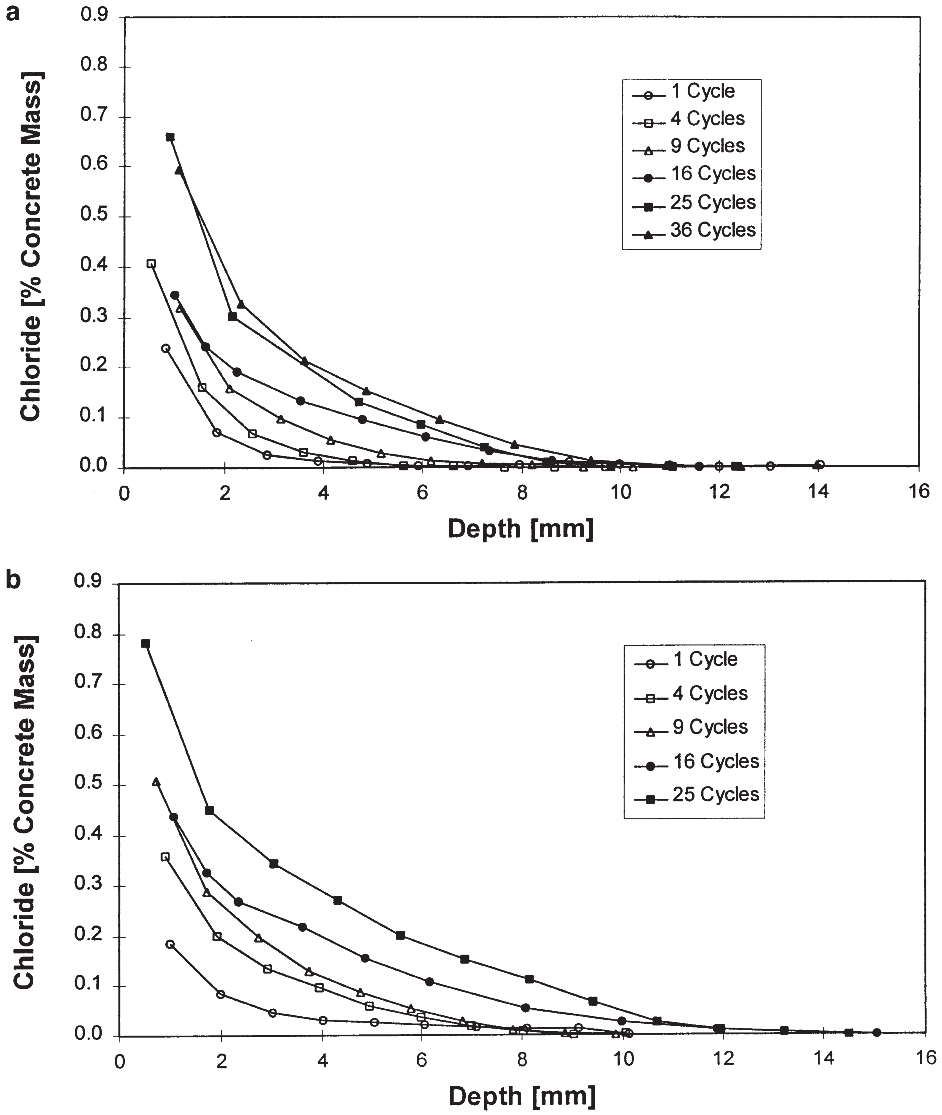

Fig. 4. Chloride profiles for concrete with 0.4 w/cm, 25% slag. (a) One day cycle; (b) three day cycle.

chloride profile, with more points taken at the surface of the specimen.

The core was then mounted on the bed of a Van Norman milling machine (Van Norman, Springfield, MA, USA), and ground with a 50-mm diamond-tipped core barrel [6]. Layers of 0.6 ± 0.1 mm thickness were sequentially ground, but not every layer was kept. The first layer was discarded, as surface imperfections tend to cause accumulation of the chloride solution, resulting in higher values of chloride concentrations in this layer.

These layers were then decomposed with nitric acid brought to a boil and digested to release the chlorides into solution [6]. The concentration of the chlorides at the given depth was determined through potentiometric titration with a 0.01 molar silver nitrate ($AgNO_3$) solution, using a Metrohm DMS 716 (DMS 716 Titrino, Herisaw, Switzerland) automatic titrator as shown in Fig. 3. The chloride concentrations were computed from the inflection point of a potential vs. titrant volume plot. The chloride value obtained from the analysis was the acid soluble chloride content.

The lowest concentration value obtained was taken to be the background chloride content of the concrete. These values were then reduced by the background chloride level to obtain the chloride gradient, and with this information, a chloride profile was made for each sample in terms of chloride content by percent of concrete mass.

3. Results

Chloride profiles for the three concrete mixtures (Figs. 4, 5, and 6) were first analyzed visually. This first step was to note the overall shape of the profiles and to obtain some evidence regarding the type of processes that had occurred. Several replicate specimens were also analyzed and it was found that for a chloride front with a chloride concentration of 0.1% by mass of concrete, the spread of results was ±0.3 mm. As expected, these figures clearly demonstrate that

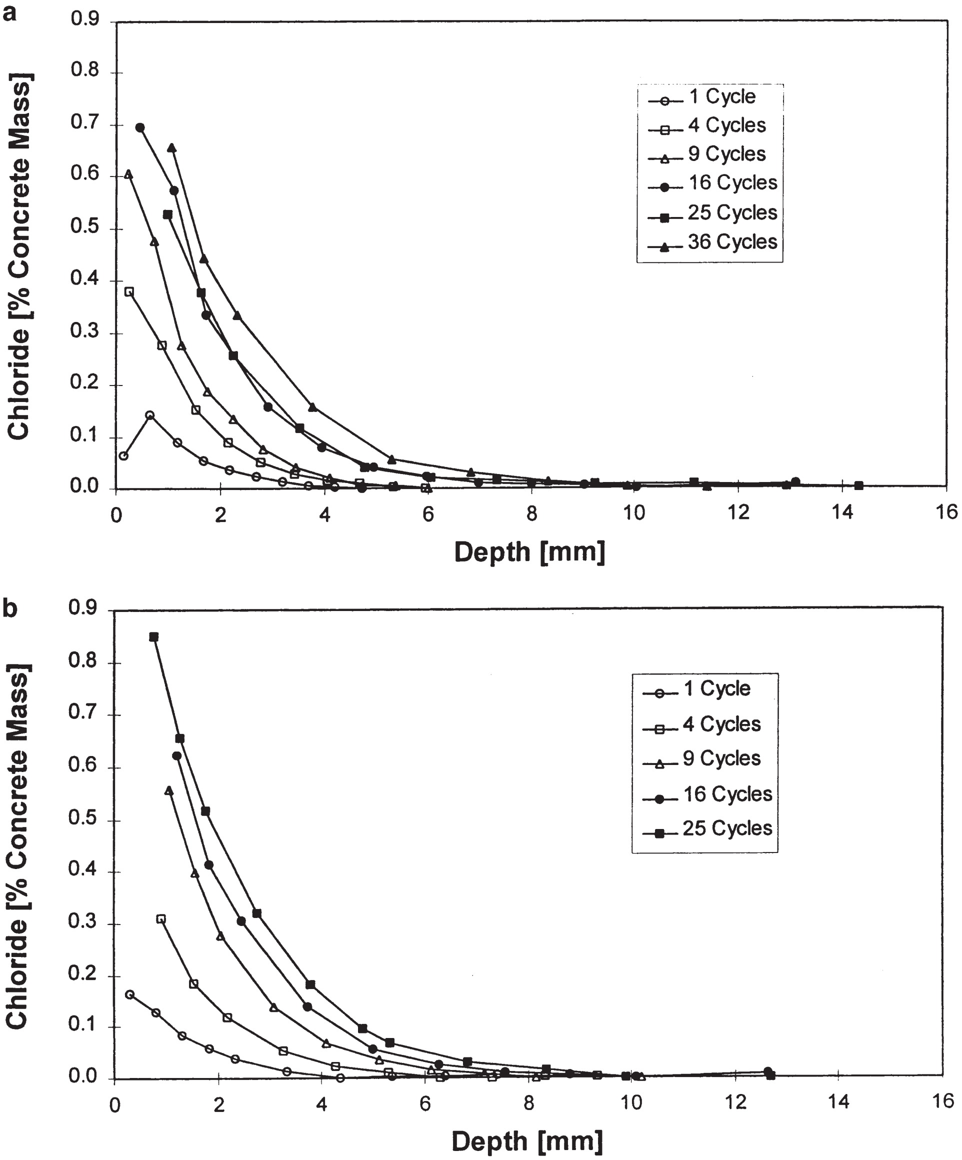

Fig. 5. Chloride profiles for concrete with 0.4 w/cm, 25% slag, 8% silica fume. (a) One day cycle; (b) three day cycle.

chloride ingress increased as the number of cycles of salt-water exposure increased.

The results for the bulk diffusion tests were also analyzed to obtain the best fit for the diffusion coefficients using Crank's solution to Fick's second law. Each diffusion curve was characterized by its equivalent diffusion coefficient and the surface concentration. The results are show in Table 1. It was found that the diffusion values reduced with the addition of silica fume, as replacement materials result in a reduction in pore size [7] and reduced w/cm. As well, the bulk diffusion values decrease with exposure period from 120 days to 365 days due to increased maturity and binding effects [8]. Intuitively a lower diffusion value will increase service life but no modeling has been done here to quantify this effect.

Sorptivity results can be found in Table 1. The results are in agreement with previous studies that show the rate of absorption is a function of the square root of time [9–11]. However, these mild drying conditions were not sufficient to obtain results with a sufficient r^2 from the linear regression.

4. Discussion

In general the results show that for the three concretes, 3-day cycles resulted in a greater chloride ingress compared with the corresponding number of 1-day cycles, in terms of concentration and depth. The degree of increased chloride ingress due to a longer drying time was not the same for the three concretes. This is most evident in the 0.4 w/cm with slag mixture. The 0.4 w/cm with slag and silica fume mixture yielded a milder increase, while the 0.3 w/cm with slag and silica fume mixture showed only a slight increase, as a result of the longer drying period.

The results show that with higher quality concrete, longer drying times have a reduced effect. This illustrates that concretes of higher quality, which have a finer pore

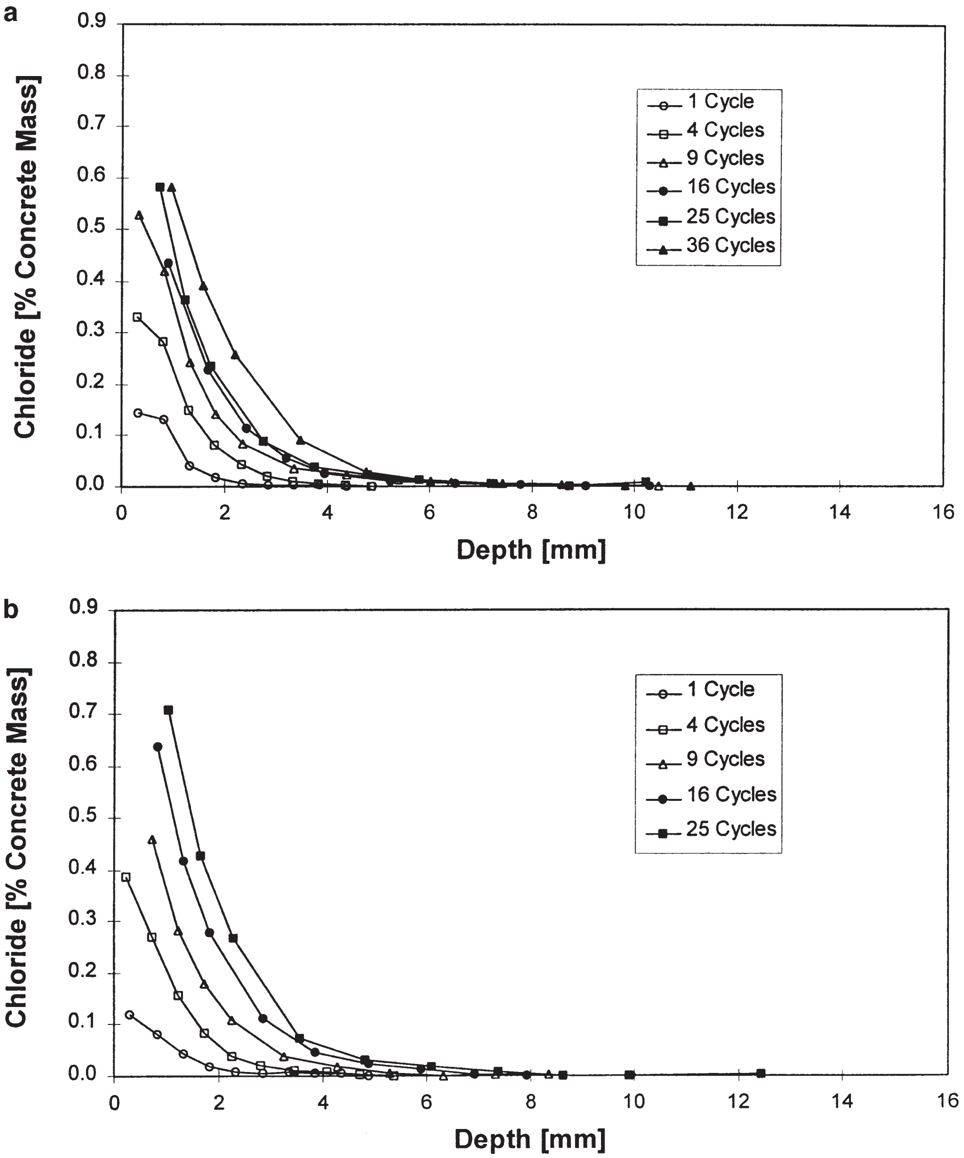

Fig. 6. Chloride profiles for concrete with 0.3 w/cm, 25% slag, 8% silica fume. (a) One day cycle; (b) three day cycle.

structure, require longer drying times to obtain a particular moisture content. Since the drying times were the same for the three concrete mixtures, the results indicate that concretes with respectively lower moisture content will result in an increase rate of chloride ingress, when experiencing cyclic chloride exposure. As the moisture content of the concrete decreased, the amount of capillary sorption should increase, likely causing the chlorides to be pulled further into the concrete.

To compare the two cycling regimes at similar total test times, the 25 1-day cycles (25 days) were compared with the nine 3-day cycles (27 days). It was found that in general, the nine 3-day cycles resulted in slightly lower chloride concentrations. This may be attributed to the longer total NaCl exposure time in the 25 cycles.

To obtain a better understanding of the mechanisms controlling this increase in chloride ingress due to longer drying periods, a more thorough analysis was needed. In both series the concretes were exposed to salt solution for 6 hours. The chlorides that have entered the concrete during the wetting phase will likely continue inward, due to diffusion during the drying phase. Diffusion will stop when saturation is no longer maintained at a given depth; however, it is difficult to know when this will occur. To determine whether diffusion was occurring during the drying phase and to what extent, the 120-day bulk diffusion curve was used to predict the amount of diffusion that could be expected for a given time without wetting and drying.

The 36-cycle curve from the 1-day series was compared with a predicted curve for 36 days of diffusion, shown in Fig. 7(a). The 25-cycle curve for the 3-day series was also compared with a predicted curve for 75 days of diffusion, shown in Figure 7(b). It was found that for both cases the wet/dry-cycled chloride concentrations were higher near the

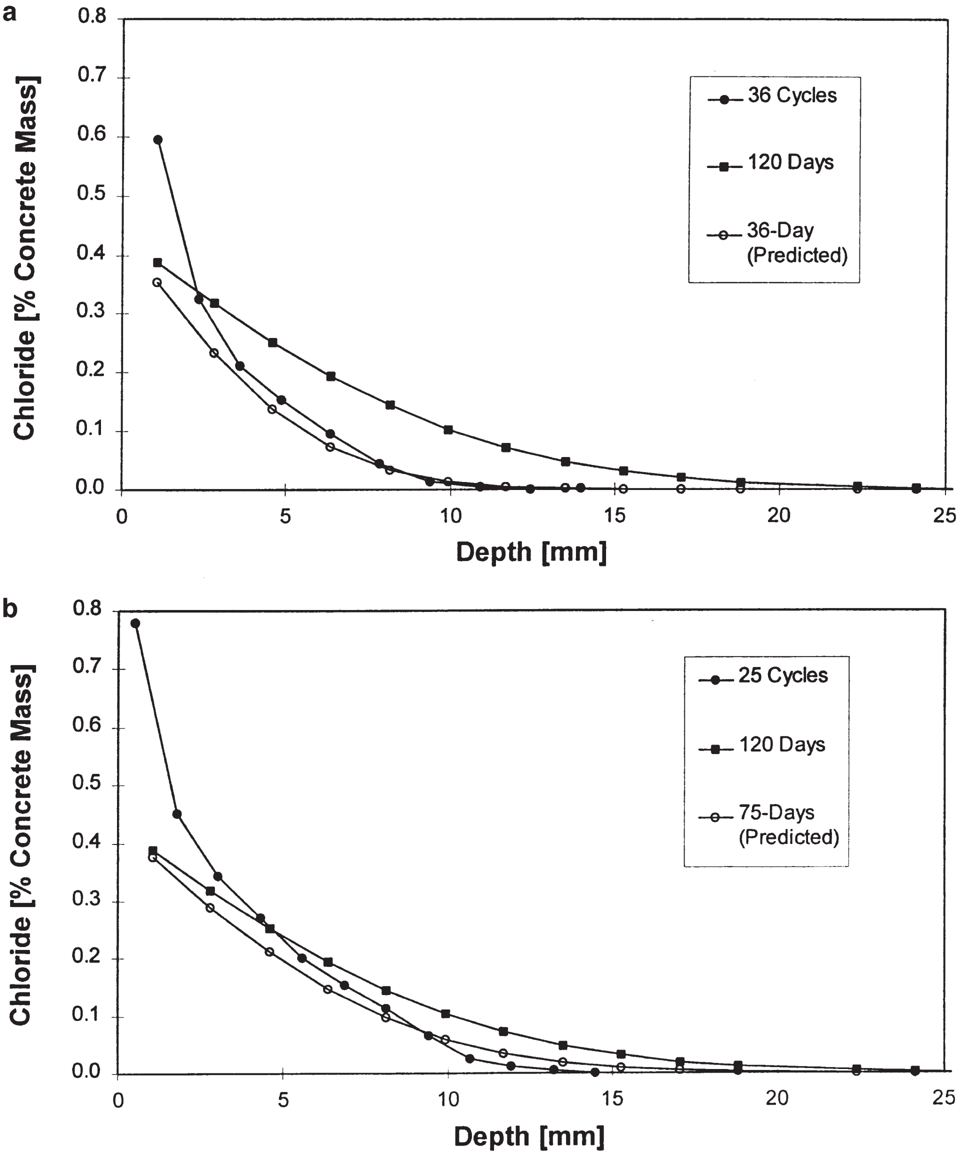

Fig. 7. Diffusion for concrete with 0.4 w/cm, 25% slag. (a) One day cycle; (b) three day cycle.

surface, but lower deeper into the concrete, and this effect was greater for the 3-day series. The near surface zone, or the cover, is the part of the concrete most effected by cyclic wetting and drying. It would appear that the high chloride concentration levels near the surface can be attributed to cyclic wetting and drying [12]. Since the predicted diffusion curves are based on the surface concentrations for a 120 days, the near surface portion of the curve is likely to be overestimated. This overestimation on the predicted curve would actually magnify the difference between the actual and predicted chloride concentrations at the surface.

However, at deeper levels where concretes tend to remain saturated, diffusion is the dominant mechanism. The lower chloride levels would imply that diffusion is not occurring for the full 18 h of the 1-day series, and certainly not for the 66 h of the 3-day series. As this effect was more prominent in the 3-day series, it is likely that a similar amount of diffusion is occurring in the drying phase of both series. This also confirms that the increase in chloride ingress is likely due to the dryer moisture conditions, rather than diffusion during a longer drying period.

5. Model

The results confirm, as anticipated from the onset of the testing program, that an increase in the number of cycles will increase the depth of chloride penetration. A good correlation was found between the depth of chloride ingress and the square root of the number of cycles, at least for the outer 10 mm of cover where sorption is the dominant mechanism. Fig. 8 shows this model for the 0.4 w/cm, 25% slag concrete mixture.

Results of a linear regression for all the points show $r^2 >$ 0.95 for both the 1- and 3-day series. Consequently, there is

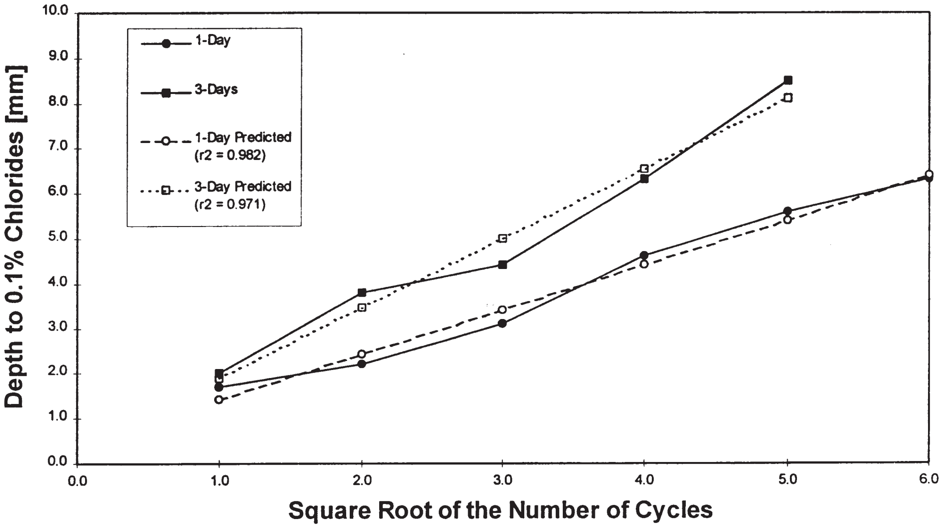

Fig. 8. 0.4 w/cm, 25% slag depth vs. square root of the number of cycles.

potential for estimating the effects of cyclic wetting and drying using this model.

A good relationship between the depth of penetration and the square root of the number of cycles is expected as cyclic wetting and drying is governed by sorptivity and diffusion, both of which are functions of the square root of time. However, further study is needed to extend this model to predict chloride penetration at greater depths. Tests performed on ordinary portland cement concrete of similar w/cm would likely show deeper chloride penetrations due to a coarser pore structure.

6. Conclusions

1. Wetting and drying cycles with 3-day drying periods accelerate chloride penetration more than 1-day drying cycles due to the increased drying resulting in deeper sorption.
2. Diffusion of chlorides in saturated pores at greater depths continues to occur during the drying phase.
3. Extending the drying period appears to increase the chloride ingress by capillary sorption in subsequent wetting cycles, rather than by continued diffusion during the drying phase.
4. The rate of drying is dependent on the pore structure of the concrete and as a result higher quality concretes dry at a slower rate.
5. As sorptivity and diffusion are related to the square root of time and these two mechanisms govern the effects of cyclic wetting and drying, it is reasonable that chloride penetration due to cyclic wetting and drying would also be related to the square root of time, as was shown in the results.
6. The rate of penetration of the chloride front was found to be linearly related to the square root of the number of cycles of wetting and drying at least in the outer 10 mm of cover where sorption dominates.

References

[1] C.F. Crumpton, B.J. Smith, G.P. Jayaprakash, Transportation Research Record 1250 (1989) 8.
[2] R.D. Hooton, P.F. McGrath, Proceedings of RILEM Workshop on Chloride Penetration into Concrete, L.O. Nilsson, J.P. Ollivier (Eds.), 1997, p. 388.
[3] A.M. Neville, Properties of Concrete, 4th Ed., Longman, New York, 1996.
[4] W.J. McCarter, D. Watson, Proceedings of the Institute of Civil Engineers—Structures and Buildings, 22 (2), 1997, p. 227.
[5] Abdul-Hamid, J. Al-Tayyib, M.M. Al-Zahrani, ACI Materials 87 (4) (1990) 363.
[6] P.F. McGrath, R.D. Hooton, ACI SP-170 1 (1997) 331.
[7] W.J. McCarter, Cement, Concrete, and Aggregates, 18 (1) (1996) 55.
[8] M. Maage, S. Helland, J.E.C. Carlsen, Proceedings of RILEM Workshop on Chloride Penetration into Concrete, L.O. Nilsson, J.P. Ollivier (Eds.), 1997, p. 398.
[9] S.J. DeSouza, Test methods for the evaluation of the durability of covercrete, MASc Thesis, University of Toronto, Ontario, 1996.
[10] C. Hall, M.H.R. Yau, Building and Environment 22 (1) (1987) 77.
[11] C. Hall, Magazine of Concrete Research, 41 (147) (1989) 51.
[12] W.J. McCarter, H. Exirim, Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, 1992, p. 39.