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Modelling chloride diffusion in concrete Effect of fly ash and slag

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Abstract

Data from long-term field and laboratory studies of concrete exposed to chloride environments were analyzed using a chloride transport model developed at the University of Toronto. The results show that the incorporation of fly ash and slag may have little impact on transport properties determined at early ages (e.g., 28 days), but can lead to order of magnitude improvements in the long term. This means that the rate of chloride penetration during the first 6 months or so of exposure is similar for concretes with and without these materials. However, after a few years of exposure, chloride ingress slows to a much-decreased rate in fly ash and slag concretes, leading to dramatic increases in the predicted service life. Predictive models and laboratory test methods for determining chloride ingress should take account of the time-dependent nature of the transport processes in concrete, especially when supplementary cementing materials, such as fly ash or slag, are used.

Keywords: Modeling; Diffusion; Chloride; Pozzolan

The ability of concrete to resist the penetration of chloride ions is a critical parameter in determining the service life of steel-reinforced concrete structures exposed to deicing salts or marine environments. The effect of fly ash and slag on the mass transfer properties of concrete have been well documented; however, much of the available data refer to relatively short-term testing (e.g., typically 1 month to 1 year). This paper presents data from a number of long-term field and laboratory studies of chloride ingress in slag and fly ash concrete, including:

- Data for marine-exposed concrete blocks with and without fly ash and slag, between 6 months and 8 years of age,
- Diffusion testing on laboratory concretes up to 3 years old and 30-year-old field concrete, both with and without fly ash,
- Long-term field performance of a sea wall with and without fly ash exposed to sea spray for 30 years.

The data are analyzed to determine the time-dependent nature of transport properties in concrete containing fly ash and slag.

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1. Details of concretes

1.1. Folkestone blocks

Eighteen reinforced concrete blocks (1.0 × 0.5 × 0.3 m) were cast in autumn 1987 and exposed in the splash zone on the sea front at Folkestone on the southeast coast of England. Six different concrete mixes were used (three blocks from each). This paper is only concerned with three mixes: a control mix (PC only), and concretes with either 30% fly ash (P/PFA) or 70% slag (P/GBS) as partial replacement for the Portland cement. Details of the concrete mixes used are given in Table 1. The concretes were designed to provide a target 28-day, water-cured compressive strength of 40 MPa. The data shown in Table 1 indicate that the fly ash concrete significantly exceeded the design strength.

Different curing conditions were applied to each of the three blocks from the same mix. After formwork removal at 24 hours, the curing conditions were as follows:

- No further curing,
- Curing membrane applied,
- Wet sacking and plastic sheet curing applied for a further 3 days.

The blocks were then left outdoors, but protected from direct sunlight or precipitation, until placement at the marine exposure site at the age of 28 days.

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Table 1
Details of concrete mixes

	Mix proportions (kg/m^3)		
Mix designation	PC	P/PFA	P/GBS
Portland cement	288	227	110
Fly ash	—	98	—
Slag	—	—	255
Total cementitious content	288	325	365
Water	190	170	177
Water-to-cementitious materials ratio	0.66	0.54	0.48
Stone	1240	1305	1240
Sand	660	585	600
28-day strength (MPa)	39.4	49.6	37.9

Cores were taken from these blocks at various intervals, and samples were prepared for a range of tests. Complete details of this test program were presented in a series of papers by Bamforth et al. [1–4]. Chloride concentration profiles were established on 50-mm diameter cores taken from the blocks and later sliced into 10-mm-thick depth intervals for chemical analysis. Chloride contents are given in Table 2. Each result is the average of three individual results from the three different curing conditions, as the curing condition was found to have no consistent effect on the chloride ingress under these exposure conditions.

1.2. Laboratory concrete

As part of a wider program evaluating the effect of fly ash on mass transfer in concrete, diffusion coefficients are reported for three concrete mixes tested at various ages between 90 and 800 days. These mixes were all cast with water-to-cementitious materials ratio = 0.50 and contained either 0%, 25%, or 56% fly ash (meeting ASTM C 618 Class F). Samples for test were 100-mm diameter × 50-mm disks cut from cylinders that had been continuously moist cured at 23°C since demolding at 24 hours.

Chloride diffusion testing was carried out using an electrical migration test that was described in detail previously [5]. The saturated test sample is "sandwiched" between two chambers, which contain an electrolyte and a stainless steel electrode. The solutions used were 1M NaCl + 0.3M NaOH as the cathodic electrolyte and 0.3M NaOH as the anodic electrolyte. A potential difference of 12 V (corrected for polarization losses at the electrodes) was applied between the two chambers and the chloride concentration of the anodic chamber was monitored. The diffusion coefficient can be calculated from either the chloride flux at steady state or the "time of breakthrough," which is the time taken for chlorides to migrate through the sample. The latter approach was used in this study.

1.3. Samples from hydraulic dams

Concrete cores (100-mm diameter) were cut from a 30-year-old hydraulic dam in Northern Ontario. The dam was constructed using a range of concrete mix designs, all of which contained 30% fly ash (ASTM Class F) except for the exposed deck (approximately 1 m thick). Test data reported here are for samples representative of two of the concretes, details of which are given in Table 3.

Samples from these cores were prepared and tested using the migration test outlined in the preceding section. The samples were approximately 35 years old at the time of test.

1.4. Sea wall

Data are also presented from a field investigation of a 30-year-old concrete sea wall in South Wales. Full details of this study were published previously [6]. The structure was built in the late 1950s at the Aberthaw Generating Station, and some of the sections were built using fly ash (25% by volume of the total cementitious content) from the nearby Portishead Generating Station. The wall is situated a few metres above the high tide level in a slightly more benign exposure condition than the Folkestone blocks. Precise details of the concrete mixes were not available, although it is

Table 2
Chloride concentration profiles for Folkestone blocks (average from three curing conditions)

		Chloride content (percent mass of concrete)					
Mix	Depth (mm)	6 months	1 year	2 years	3 years	6 years	8 years
PC	0–10	0.267	0.493	0.313	0.370	0.257	0.288
	10–20	0.140	0.193	0.273	0.273	0.237	0.264
	20–30	0.050	0.043	0.143	0.190	0.197	0.203
	30–40	0.010	0.017	0.093	0.117	0.153	0.183
	40–50	0.000	0.000	0.053	0.073	0.133	0.159
P/PFA	0–10	0.280	0.427	0.333	0.383	0.367	0.419
	10–20	0.087	0.097	0.160	0.173	0.193	0.308
	20–30	0.007	0.010	0.037	0.013	0.010	0.057
	30–40	0.000	0.023	0.010	0.010	0.010	0.012
	40–50	0.000	0.000	0.010	0.010	0.010	0.012
P/GBS	0–10	0.437	0.493	0.340	0.387	0.363	0.381
	10–20	0.173	0.140	0.173	0.153	0.227	0.216
	20–30	0.077	0.090	0.023	0.027	0.067	0.068
	30–40	0.027	0.073	0.010	0.013	0.040	0.035
	40–50	0.000	0.000	0.013	0.010	0.030	0.035

Table 3
Details of concretes from hydraulic dams

	Deck concrete	Mass exterior
Portland cement (kg/m^3)	236	147
Fly ash (kg/m^3)	—	63
Water-to cementitious materials ratio	0.57	0.59
28-day strength (MPa)	29	28

understood that the batch proportions were 1 part cement to 1.5 parts sand to 3 parts coarse aggregate (by volume), and that the water-to-cementitious materials ratio was in the range from 0.50 to 0.60 [6]. These proportions are generally consistent with the compressive strength of cores taken from the structure [6]. In addition to cores, powder samples were drilled from the seaward face of adjacent sections with and without fly ash. The powder samples were collected at 5-mm depth increments and later analyzed for chloride content by X-ray fluorescence.

2. Analysis and results

The error function solution to Fick's second law was fitted to the chloride concentration profiles from the Folkestone blocks, as given in Eq. (1):

$$C_{x,t} = C_s\left(1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right)\right) \quad (1)$$

where $C_{x,t}$ = chloride concentration at depth x and time t, C_s = chloride content at the surface, x = depth, t = time, and D_a = apparent diffusion coefficient.

Table 4
Best-fit diffusion coefficients and surface concentrations for the Folkestone blocks

		Best-fit values	
Concrete mix	Age	D_a ($\times 10^{-12}$ m^2/s)	C_s (percent concrete)
PC Control	6 months	9.5	0.35
	1 year	3.0	0.69
	2 years	7.6	0.38
	3 years	5.6	0.42
	6 years	10	0.28
	8 years	8.7	0.31
P/PFA	6 months	4.3	0.42
	1 year	2.0	0.53
	2 years	1.9	0.45
	3 years	1.1	0.54
	6 years	0.81	0.48
	8 years	0.59	0.56
P/GBS	6 months	7.5	0.58
	1 year	2.9	0.68
	2 years	1.9	0.46
	3 years	0.99	0.54
	6 years	1.0	0.46
	8 years	0.63	0.48

Values of C_s and D_a are found by iteration to produce the best fit by least squares. Results for the different profiles are given in Table 4.

The values obtained in this manner represent the average diffusivity of the concrete during the period from the start of exposure to the time of sampling and the final surface concentration at the time of sampling. This approach does not take into consideration time-dependent changes in either the diffusion coefficient or surface concentration. The data in Table 4 show that although there is no consistent change in C_s with time, the value of D_a decreases with time for the concretes containing fly ash or slag. The calculated diffusion coefficients are similar for all three concretes at early ages but are much lower in the slag and fly ash concretes at later ages. This is consistent with the chloride data, which show a similar degree of ingress between the concretes after 6 months of exposure, but considerably increased penetration into the PC control mix after 8 years.

A comprehensive chloride transport model has been developed at the University of Toronto, which takes into consideration multimechanistic transport processes (diffusion, convection, sorption, and wicking) and accounts for the temperature and time dependence of the relevant transport coefficients. The model also allows for nonlinear chloride binding and changes in the surface concentration. For analysis of the data presented here, it was assumed that the predominant transport mechanism was diffusion and that the diffusion coefficient varied with time according to Eq. (2):

$$D_t = D_{28} \cdot \left(\frac{t_{28}}{t}\right)^m \quad (2)$$

where D_t = diffusion coefficient at time t, D_{28} = diffusion coefficient at time t_{28} = 28 days, and m = constant.

The relationship is consistent with similar mathematical descriptions proposed by other investigators [7,8].

Values of D_{28} and m were selected as input variables for the model to "best fit" the experimental profiles at the six ages of sampling. The best-fit criterion used was the sum of the squares of the errors between the model prediction and the experimental data at all six ages. Surface concentrations used were the average C_s values reported in Table 4 for each concrete mix (some "outliers" were disregarded). The values of D_{28} and m that best describe the experimental data are given in Table 5. Comparisons between the predicted profiles using the model and the experimental data are shown in Figs. 1–3. There is generally a good correlation between the model predictions and the experimental data.

Table 5
Values of D_{28} and m for the Folkestone blocks

	Ordinary Portland cement	Fly ash	Slag
C_s (%)	0.35	0.50	0.50
D_{28} (m^2/s)	8×10^{-12}	6×10^{-12}	2.5×10^{-11}
m	0.1	0.7	1.2

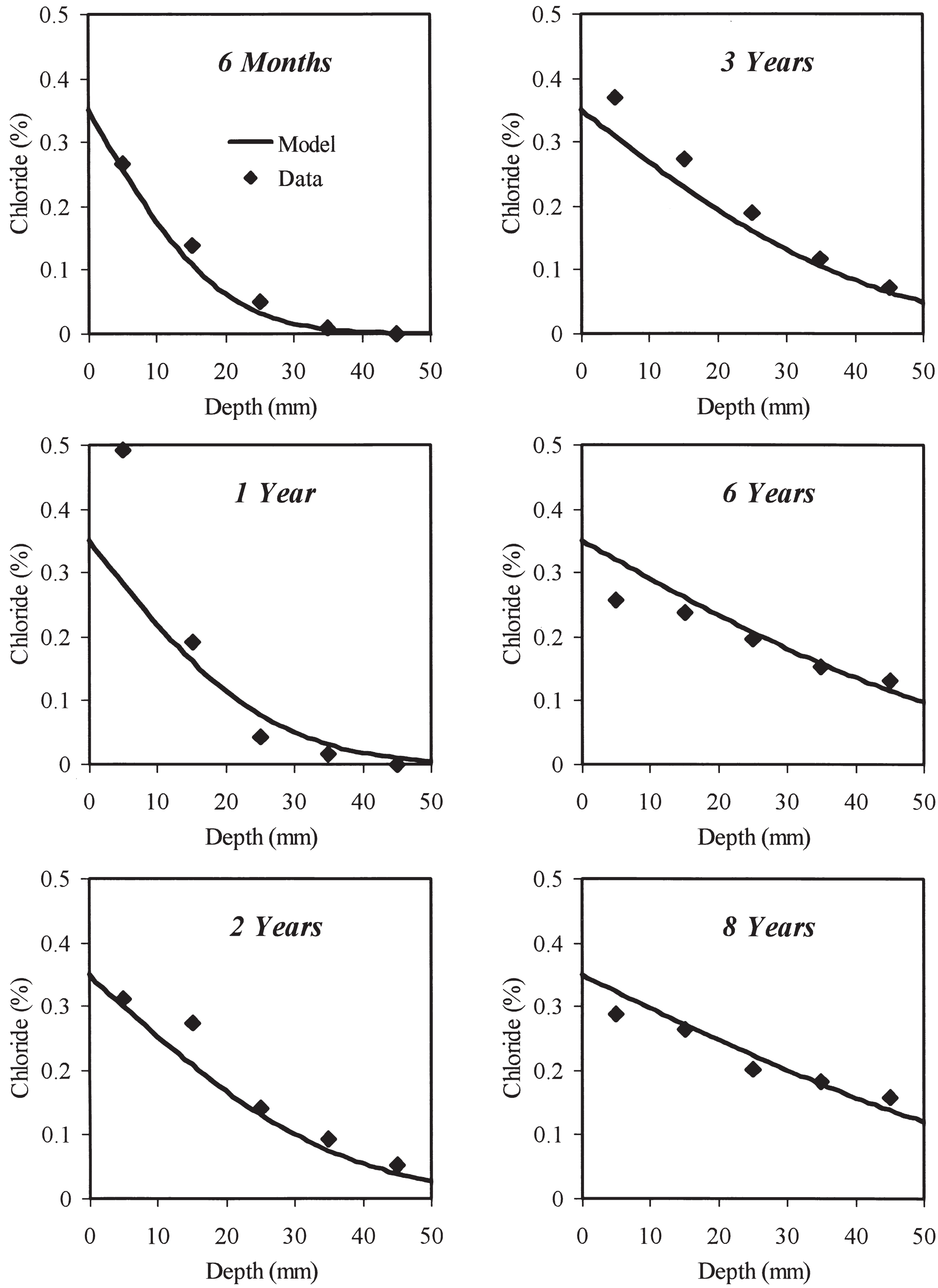

Fig. 1. Comparison between model and experimental data for PC concrete.

Fig. 4 shows the relationship between the diffusion coefficient and age as determined by the indices given in Table 5 for the three concrete mixes. Also shown in Fig. 4 is the relationship between the measured diffusion coefficient determined by the electrical migration test and the age of Portland cement and fly ash concretes produced in the laboratory and obtained from field structures. Although the laboratory and field concretes are not directly comparable, it is clear that the trend of decreasing diffusion observed in the laboratory for concrete up to 800 days old extends to much

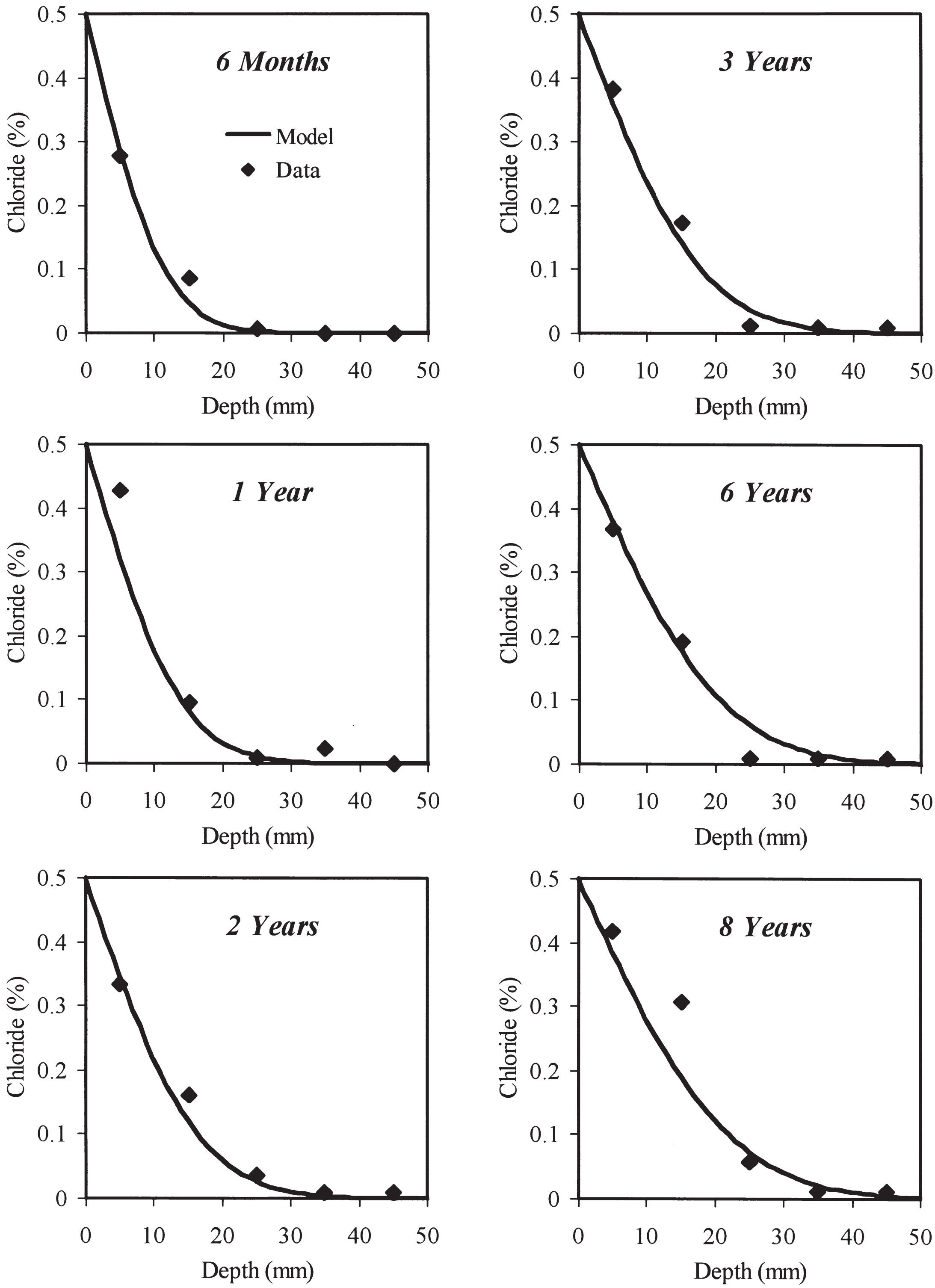

Fig. 2. Comparison between model and experimental data for fly ash concrete.

greater ages. Assuming a single relationship for the laboratory and field concretes yields values of $m = 0.14$ and 0.60 for the Portland cement and fly ash concrete, respectively. These values are in close agreement to those derived from fitting the model to the data from the Folkestone blocks.

Fig. 5 shows the predicted chloride concentration profiles for the Folkestone blocks at 30 years using the model with the input data given in Table 5. The differences between the Portland cement concrete and the concretes containing either fly ash or slag are substantial. Such differ-

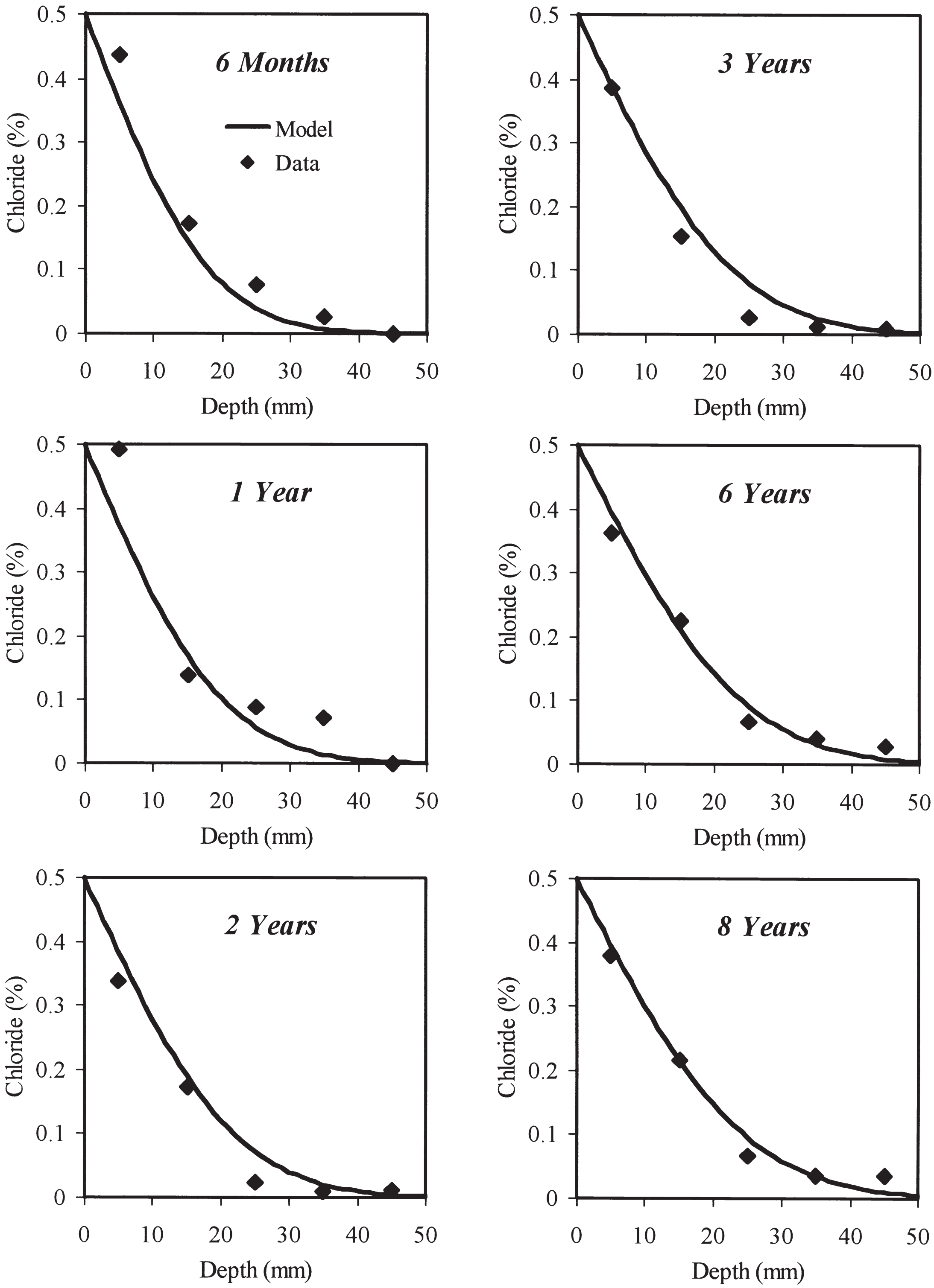

Fig. 3. Comparison between model and experimental date for slag concrete.

ences are consistent with data obtained for the concrete sea wall, which are shown in Fig. 5. The chloride contents reported for the sea wall have been corrected by subtracting the "background" chloride content of 0.15% from all of the data points. This background level was determined on a sample of the fly ash concrete at a depth of 300 mm. The high background level is believed to be the result of using sea-dredged sand for construction.

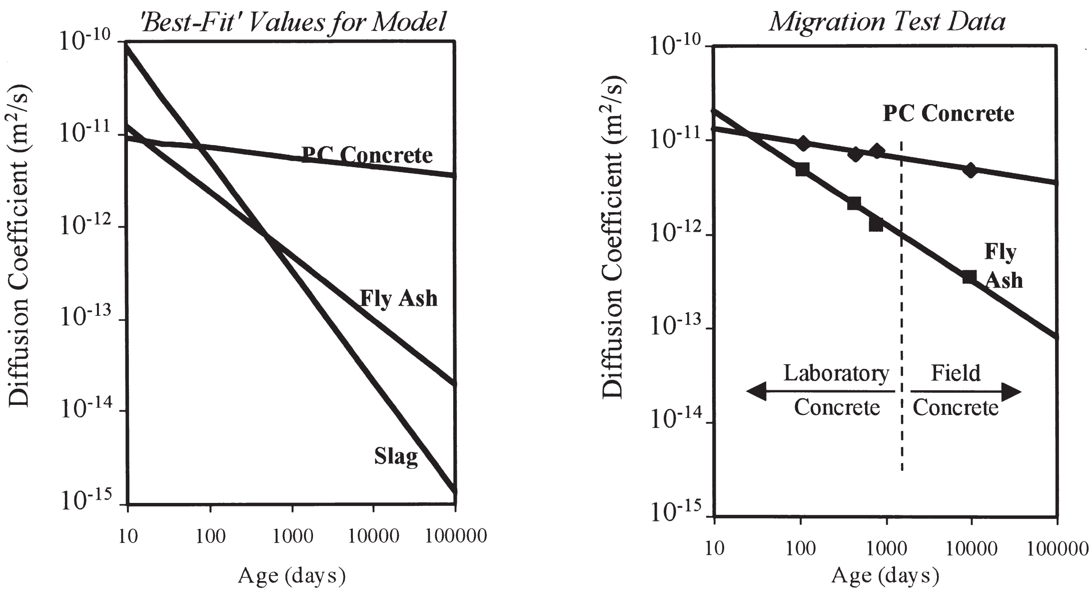

Fig. 4. Change in diffusion coefficient with time.

3. Discussion

It is evident that the diffusivity of concrete containing either fly ash or slag is considerably more sensitive to aging than that of plain Portland cement concrete. The data presented here show that at early ages (e.g., 1 month), the diffusivity of concrete containing 25% to 30% fly ash may be expected to have a similar chloride ion diffusivity as an equivalent grade Portland cement concrete. However, after approximately 2 years the diffusivity of the fly ash concrete may be one order of magnitude lower than the Portland cement and decrease to two orders of magnitude lower after 100 years. This has a significant impact on the long-term performance of concrete in chloride environments and on the interpretation of data from short-term (or accelerated) tests.

The results from the slag concrete indicated a much higher diffusion coefficient at very early ages (e.g., $\leqslant$ 28 days) compared with the other two concretes, but the diffusivity decreased very rapidly with time. This dramatic behaviour is attributed to the high slag content (70%) of the concrete, and it is expected that concrete with more moderate levels of slag (e.g., 50%) would behave in a similar fashion to the fly ash concrete.

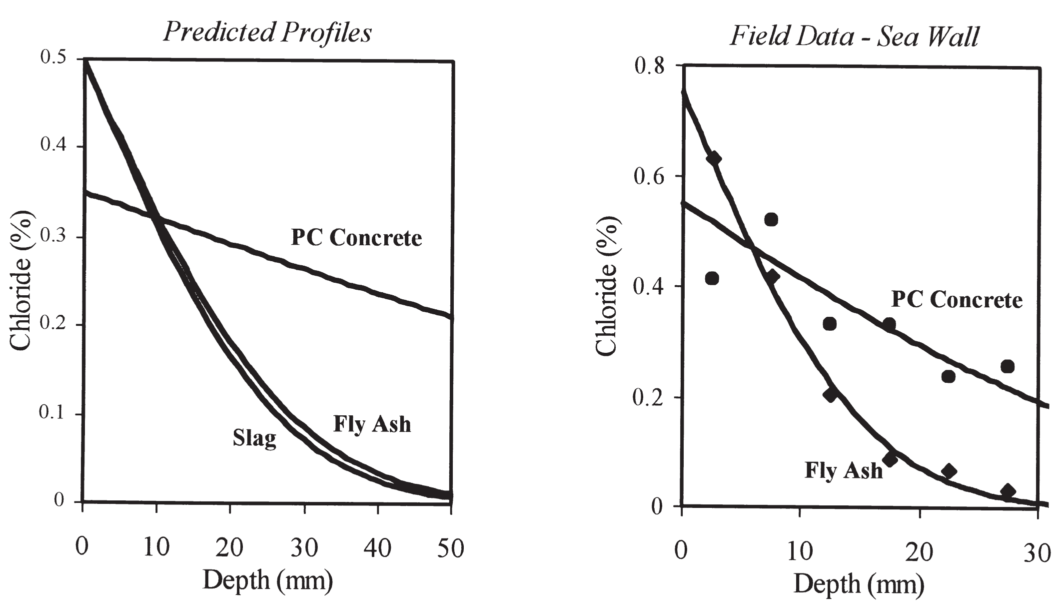

Fig. 5. Predicted and measured chloride profiles at 30 years.

The beneficial effect of fly ash and slag on the service life of reinforced concrete structures is adequately demonstrated by the predicted and measured profiles in Fig. 5. The level of chloride at the 50-mm depth is negligible in the fly ash and slag concrete after 30 years of marine exposure. However, at the same depth in the Portland cement concrete the level of chloride is substantially in excess of that required to initiate corrosion. Another approach to examining influences on service life is to determine the rate of penetration of the "critical chloride threshold" into the concrete. For this analysis a chloride content of 0.05% (by mass of concrete) has been assumed as the threshold quantity required to initiate corrosion. Fig. 6 shows the rate of penetration of this threshold value into the Folkestone blocks (fly ash and Portland cement concrete shown). The data shown compare predictions from the model with interpolated values from the actual measured profiles. Also shown in Fig. 6 are data from the Building Research Establishment for concrete specimens exposed on a marine exposure site on the Thames Estuary in England; details of this study were presented previously [9]. The chloride data for these specimens were expressed as a mass percentage of the cementitious material, and the threshold used is 0.40% Cl by mass of cement (which is comparable to 0.05% Cl by mass of concrete). The data show a broad agreement between the two separate studies.

Fig. 6 indicates that the critical threshold concentration rapidly penetrates the Portland cement concrete and reaches 50 mm after only 3 years. For concrete with 30% fly ash, the initial penetration is also rapid, but the rate diminishes sharply with time. It is estimated that approximately 10 years would be required for the threshold value to compromise the outer 30 mm of cover of the fly ash concrete, but at this time the rate of penetration has decreased to an extremely slow value. Indeed, the model estimates that it would take almost 200 years in this environment for the threshold content to reach steel at a depth of 50 mm. This analysis emphasizes the importance of achieving proper cover to the steel reinforcement.

The analysis presented here shows the importance of using time-dependent transport coefficients in modelling chloride ingress in concrete, especially when either fly ash or slag is present. The weakness of using a constant diffusion coefficient can be demonstrated by attempting to make predictions using Eq. (1). Curve fitting Eq. (1) to the 8-year data for the fly ash block at Folkestone yields the values for D_a and C_s given in Table 4. The value $D_a = 5.9 \times 10^{-13}$ m²/s is really an average diffusivity for the period from 28 days to 8 years. If it assumed that this value is actually constant throughout exposure and the value is then used in predicting the time for the threshold concentration to reach the steel, the analysis will result in significant error. For example, if the

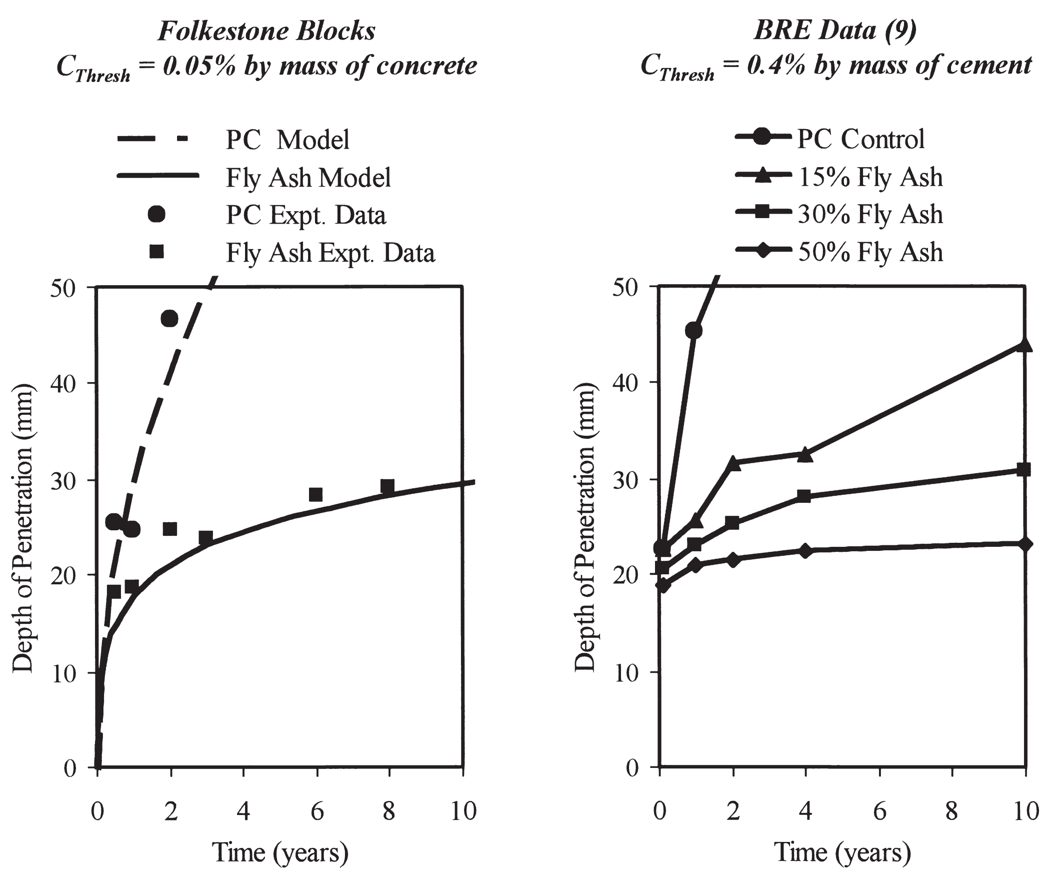

Fig. 6. Depth of penetration of critical chloride threshold.

threshold is assumed to be 0.05% and the depth of cover is 50 mm, the predicted "age at corrosion" will be just over 23 years (or 15 years after the profile was established). Using the time-dependent model, the actual "instantaneous" diffusivity at the time of establishing the 8-year profile was $D_a = 2.3 \times 10^{-13}$ m^2/s. Using the model for predictive purposes yields an "age at corrosion" of 197 years!

Based on the results presented in this paper, the usefulness of using simple numerical solutions to Fickean Law [e.g., Eq. (1)] to predict the residual service life of existing structures or for the purposes of designing and specifying new structures is questioned. Also, the considerable reductions in diffusivity with time observed for concrete containing fly ash or slag raises concerns regarding the use of short-term tests for characterizing or comparing concrete mixtures. Consideration must be given to the ability of the cementitious system to refine its pore structure as it matures, thereby decreasing transport rates. Coefficients that account for the decay in transport rate [i.e., the index m in Eq. (2)] must be included for reliable predictions to be made. Such coefficients may be determined empirically using published literature (where available) or it may be possible to account for maturity effects by using elevated temperature curing in laboratory determinations of transport properties. This last item is currently under investigation at the University of Toronto.

There is a need for more field exposure and long-term laboratory studies to calibrate both mathematical models for predicting and test methods for measuring chloride ingress in concrete. Furthermore, existing studies such as those presented here need continued monitoring to assist in the development of long-term performance databases.

4. Conclusions

1. Experimental chloride profiles from concrete blocks exposed to sea spray for up to 8 years were fitted to a chloride transport model using time-dependent diffusion. The rate of reduction of diffusivity is far greater for concrete containing fly ash or slag than for plain Portland cement concrete.
2. The rates of diffusion reduction observed for the marine-exposed blocks are similar to values obtained by comparing experimentally determined diffusion coefficients for laboratory and field concretes ranging in age from 90 days to 30 years.
3. Differences in chloride penetration rates between plain Portland cement concrete and concrete containing either fly ash or slag become much more marked with the duration of exposure. Diffusion coefficients for fly ash or slag concretes are likely to decrease to one or two orders of magnitude less than similar grade Portland cement concrete during a 100-year service life.
4. The use of fly ash or slag will considerably increase the service life of structures exposed to chloride environments. The increase may actually be greater than an order of magnitude provided sufficient cover is provided to the steel.

Acknowledgments

The computer model used in this analysis was developed by Evan Bentz and Michael Thomas of the University of Toronto.

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