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CHLORIDE-BINDING ISOTHERMS FROM THE DIFFUSION CELL TEST

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ABSTRACT

Improved models of chloride ingress into concrete separate the effects of chloride binding and diffusion. The steady state diffusion coefficient (free from the effects of binding) is often determined in a diffusion cell experiment. This work examines a method of obtaining chloride binding data from the same experiment. This involves the measurement of the total chloride profile in the specimen under investigation, combined with an estimation of the corresponding free chloride concentration, by assuming that the concentration gradient is linear under steady state conditions. Preliminary results suggest that the chloride binding data obtained are typical of those obtained by other methods. One potential advantage of this method is that it is capable of delivering results on relatively large concrete specimens of low free water/cement ratio. However, depth-dependent variations in the properties of the test specimen should be avoided. *© 1998 Elsevier Science Ltd*

Introduction

The removal of chloride ions from the pore solution of concrete by chemical and physical reaction with the hydrated cement phases reduces the rate of all forms of chloride transport into concrete (1). This in turn will reduce the future risk of chloride-induced reinforcement corrosion. The chloride binding capacity is a non-linear function of the total chloride content and this will be reflected in the rate of chloride ingress into concrete (2,3). The binding capacity is described by a binding isotherm that may be defined as the relationship between the total, free and bound chloride contents at constant temperature.

Chloride-binding isotherms may be determined by a number of techniques, including pore solution expression under pressure (referred to as the pore press method) and equilibration with an external solution of known concentration (the equilibrium method) (4,5). All techniques have their associated difficulties. For example, the pore press method requires elaborate specimen preparation techniques on concretes and mortars of low water/cement ratio (w/c) (6), while the equilibrium method suffers from the long exposure period necessary to impose a known pore solution chloride concentration on the specimen under investigation (7,8).

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When the effects of binding and diffusion are separated in models of chloride ingress, the diffusion coefficient should be free of the effects of binding (2). It may be determined from the steady state flux of chloride ions produced by a near constant concentration gradient in a diffusion cell experiment (9). It has previously been suggested that information on the chloride-binding isotherm may also be obtained from the initial data determined in a series of such tests on specimens of differing thickness. This assumed that the binding isotherm took the form of a Freundlich or Langmuir adsorption isotherm and only the coefficients of the isotherm were derived in the reported analysis (10).

This preliminary work explores another novel approach for obtaining chloride binding data using diffusion cell experiments. This is based on the observation that a linear free chloride concentration gradient is expected in these experiments under steady state conditions (the chloride concentration at all points is stationary). Thus, in theory, the free chloride concentration as a function of specimen depth may be estimated. The corresponding total chloride profile may then be measured to give the chloride-binding isotherm.

Experimental

A preliminary investigation was undertaken using two specimens from a previous research program which had been exposed in diffusion cells for a period of 30 months (11). The 10 mm thick disc specimens were cut from the cast end of 100 mm diameter mortar cylinders with a water/cement/sand ratio of 0.45/1.0/2.5. The ordinary Portland cement had a Bogue composition of 62.3% tricalcium silicate (C_3S), 12.5% dicalcium silicate (C_2S), 7.1% tricalcium aluminate (C_3A) and 9.1% tetracalcium aluminoferrite (C_4AF), a sulphate content expressed as sulphur trioxide (SO_3) of 3%, a calcium oxide to silica ratio (CaO/SiO_2) of 3.1 and an alkali content expressed as a sodium equivalent of 0.56%. 2.4 mm sand was used. Each mortar specimen separated the two compartments of a diffusion cell. Initially, a 1 M sodium chloride (NaCl) solution was present in one compartment, with the other being chloride-free but containing 0.3 M sodium hydroxide (NaOH). The cast surface of the specimen faced the higher chloride concentration. The solutions were saturated with calcium hydroxide ($Ca(OH)_2$) to prevent it from leaching out of the specimens. Full experimental details are given elsewhere (11,12).

After removal from the cells, the specimens were frozen in liquid nitrogen and subsequently ground to produce powdered samples at 9 equal depth increments. The acid-soluble chloride content of these samples (extracted using nitric acid) and the chloride content of the storage solutions were determined by potentiometric titration against silver nitrate. The evaporable water contents of the specimens were determined by heating samples to 105°C. Independent chloride binding measurements for the purposes of comparison have previously been noted to be method dependent (8). Thus, to assess the accuracy of the above diffusion cell method, the results were compared with those obtained using a previously developed neural network model (13). This had been trained, using more than 500 sets of reported binding data extracted from 21 works, to predict the typical measured free chloride concentration as a function of 18 input variables. The average prediction error is approximately 20%.

Results

After an initial transient period, the chloride content in the low- concentration compartment of the diffusion cell increased linearly with time, indicating that steady state conditions had been reached. These data have previously been reported and used to obtain the diffusion coefficients on these specimens (12). The final hydroxyl concentration of the compartments of the diffusion cells ranged between 0.14 and 0.16 M, with the average of the four values being 0.15 M.

The total chloride profiles obtained on two mortar specimens (labeled Cell A and Cell B) are given in Table 1. The average evaporable water content was 33% by weight of cement. An unexpectedly high non-evaporable water content was determined when samples were heated to 1050°C. This may have resulted from the decomposition of some constituents in the aggregate (e.g. the conversion of calcium carbonate to calcium oxide and carbon dioxide). A relatively high value, which reflects the storage of the specimens in solution for 2.5 years, of 23% (by weight of cement) was assumed (14). These values were used in the conversion of the measured total chloride contents to values relative to the weight of cement.

The final chloride concentrations in each compartment of the diffusion cells, corresponding to a specimen depth of 0 mm (the surface in contact with the high chloride concentration) and 10 mm (the surface in contact with the low chloride concentration), are also given in Table 1. These have been used to estimate the free chloride concentration as a function of depth in the two specimens. The data are plotted in Figure 1. A small consistent difference was observed between the two sets of replicate data, and some anomalies were present in the data obtained near the cast surface.

Included in Figure 1 is the fitted Langmuir isotherm given by the equation:

$$C_t = C_b + M_{Cl}\, VC_f = \frac{\alpha C_f}{1 + \beta C_f} + M_{Cl}\, VC_f \qquad (1)$$

where C_t and C_b are the total and bound chloride contents, C_f is the free chloride concentration, M_{Cl} is the atomic mass of chlorine, and V is the pore solution volume. The best fit was achieved by adjusting the constants α and β to minimise the sum of the squared differences between the measured and fitted values. The resulting α and β values were 0.132 and 13.52, respectively.

The free chloride concentrations predicted by the neural network model (13) corresponding to both the pore press method and the equilibrium method, are also plotted in Figure 1. In addition to the total chloride content and the method, other input variables required by the neural network model described the chemical composition of the cement (C_3A, C_4AF, C_3S, SO_3, CaO/SiO_2, sodium equivalent, and absence of cement replacement materials), the mix composition (water/cement/sand ratio), and the exposure (immersed for more than 500 days, an external source of sodium chloride, and the steady state hydroxyl concentration).

Discussion

The number of previous works assessing the accuracy and reproducibility of experimental methods used to determine the free chloride content is limited. Indeed, in the only work of its kind, relatively large differences (up to 50%) were reported in the chloride binding data determined by different laboratories on specimens from the same batch using the same

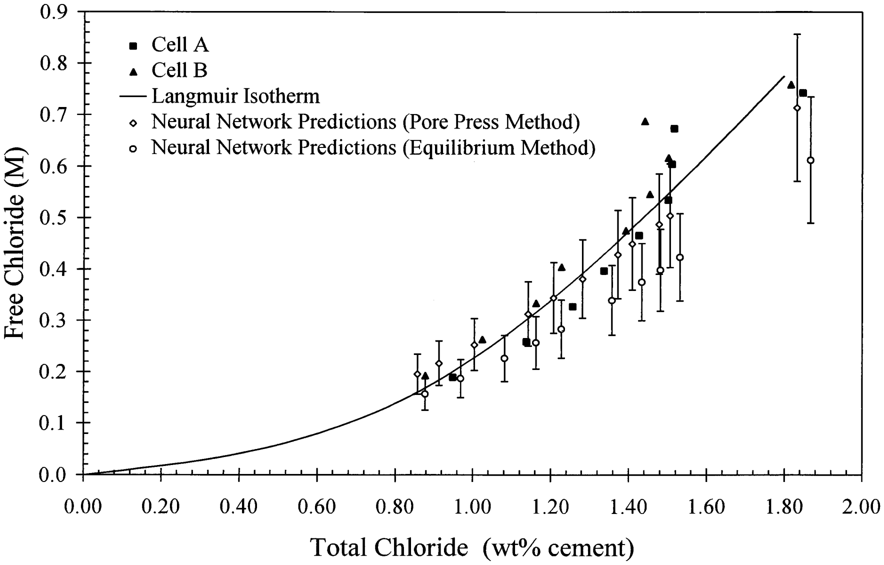

FIG. 1.

A comparison of the predicted chloride binding data corresponding to two methods (error bars represent a 20% error) with that measured using the diffusion cell method.

analysis technique (15). This presents a problem when one is attempting to assess the accuracy of a new method, which may partially be overcome by using a neural network model that has been trained on a large amount of data from a number of sources. Such a model tends to predict the effective mean values and trends present in the training data. The prediction error largely reflects the noise (unexplained variations) in the reported data (13).

A comparison of the neural network predictions with the values measured using the diffusion cell method shows that, in most cases, the differences fall within the average

TABLE 1

Total and free chloride contents as a function of specimen depth

	Cell A		Cell B	
Specimen depth mm	Total Cl wt.% cement	Free Cl M	Total Cl wt.% cement	Free Cl M
0 (NaCl Solution)		0.7766		0.7936
0 to 1.1	1.8477	0.7420	1.8160	0.7582
1.1 to 2.2	1.5172	0.6729	1.4417	0.6875
2.2 to 3.3	1.5111	0.6038	1.5018	0.6168
3.3 to 4.4	1.5018	0.5347	1.4543	0.5461
4.4 to 5.6	1.4275	0.4656	1.3926	0.4754
6.7 to 7.8	1.2570	0.3274	1.1620	0.3340
7.8 to 8.9	1.1380	0.2583	1.0247	0.2633
8.9 to 10	0.9496	0.1892	0.8770	0.1927
10 (NaOH Solution)		0.1546		0.1573

prediction error (Fig. 1). Indeed, the differences between the measured and predicted values tend to be less than the differences observed between the two most generally acceptable methods of obtaining chloride binding data, namely the pore press and the equilibrium methods (8,13). This suggests that chloride-binding isotherms may be obtained from the diffusion cell experiments used to determine steady state diffusion coefficients.

A major assumption made in the derivation of chloride-binding isotherms using the above analysis is the linearity of the free chloride concentration across the specimen. This will be the case if steady state conditions have been achieved (the change in chloride concentration gradient with time is negligible) and the diffusion coefficient across the specimen is constant. Furthermore, to prevent anomalies in the determination of the total chloride content, a depth-independent binding capacity and pore solution volume are required.

The achievement of near steady state conditions is widely assumed in the determination of diffusion coefficients by this method (9). However, the specimens used in this preliminary work had a cast surface. This may have a chloride diffusion coefficient which differs from the bulk of the material. A higher surface-zone diffusion coefficient would be expected if the only difference with the bulk of the specimen was a decrease in the aggregate content (16). However, such a local variation would cause minimal distortion in the free chloride profile if the diffusion process remains under the control of the bulk of the specimen.

A more likely explanation for the anomalies in the data observed near the cast surface (Fig. 1) is based on the expected variation in cement content at this location. A high surface cement content and its accompanying depletion in adjacent segments will affect the local level of bound chloride. This in turn affects the measured total chloride content.

Another factor which may affect the results is the prolonged exposure to a chloride-containing solution. However, the full depth of the specimen was contaminated with chloride, and therefore depth-dependent variations in the pore structure induced by a reaction between chloride ions and constituents of the hydrated cement paste would be limited. It may also be noted that in practice concrete is exposed for even longer periods to a chloride-containing environment.

The total error in the results may well be determined by other less controllable sources. For example, the consistent difference between the two replicate sets of data (Fig. 1) could not result from the non-linearity in the free chloride profile, as the error in estimating the free chloride concentration would be smaller near the surfaces of the specimen. This reflects the presence of a systematic error, the reasons for which are less clear.

One of the advantages of the diffusion cell method is that the binding isotherm may be determined on a single relatively large specimen under conditions close to those often encountered in practice. The determination of binding isotherms using the pore press and equilibrium methods requires a number of small samples, which in some cases may be crushed. Such sample preparation may increase the risk of carbonation, change the reactive surface area, and expose unhydrated cement grains to moisture. The diffusion cell method will also deliver results on concretes of low free water/cement ratio. However, a long measurement duration may be required.

The experimental method may be improved by using specimens with cut as opposed to cast surfaces to minimise any depth dependence in the specimen properties. Further developments could include applying a higher initial concentration gradient across the specimen and limiting the exposure time of the specimens in the diffusion cell after steady state conditions are established. This would increase the spread of values obtained. However, the absence of these developments did not prevent the acquisition of some promising results in this preliminary work.

Conclusions

Chloride-binding isotherms for use in modeling chloride ingress into concrete may be obtained from the diffusion cell experiments used to determine steady state diffusion coefficients. This involves the determination of the total chloride profile in the specimens under investigation, combined with the estimation of the free chloride concentration, by assuming that the concentration gradient is linear under steady state conditions.

The chloride binding data obtained using the diffusion cell method are typical of those obtained by other methods. Indeed, the predictions of a previously developed neural network model suggest that it generally produces values which fall within the prediction error levels which largely result from unexplained differences in reported data. Depth-dependent properties in the specimen used should be avoided, as these may cause some distortion in the trends observed.

The method is capable of delivering results on relatively large concrete specimens of low free water/cement ratio. Potential problems, such as carbonation, associated with the use of the small samples required by other methods, are absent. Furthermore, a complete binding isotherm may be obtained on a single specimen. However, the method may be time consuming.

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