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Theoretical assessment of the steady state diffusion cell test

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The steady state diffusion cell test is often used to determine the chloride ion diffusion coefficient in cementitious materials. It involves the measurement of the flux of chloride ions through a specimen under near steady state conditions. It has been noted that such a test may also provide data which characterises the chloride binding capacity of the specimen. In this work a numerical model of chloride diffusion subject to the effects of chloride binding is used to assess the effect of deviations from the steady state on the data obtained from a diffusion cell test. It is noted that there will be a tendency to underestimate the diffusion coefficient, although good practice should limit this error. The predicted error in the chloride binding isotherm is smaller than that in the diffusion coefficient. Furthermore, the influence of errors in the effective porosity on model predictions is limited as the resulting effect on the values of the calculated parameters describing chloride diffusion and binding counteract each other.

1. Introduction

A major factor affecting the maintenance free service life of concrete structures is the rate of transport of aggressive species, such as chloride ions, through the concrete cover. In all practical situations diffusion contributes to the transport of these ions into concrete. It is characterised by a diffusion coefficient which may be viewed as the flux per unit of concentration gradient driving the diffusion process. A number of methods have been devised to determine diffusion coefficients. One of these, commonly applied to the determination of chloride ion diffusion coefficients, is referred to as the steady state diffusion cell test [1–3].

The diffusion cell test involves the application of a constant chloride concentration gradient across a specimen to produce steady state conditions. A typical arrangement used is given in Fig. 1 [4]. Chloride ions diffuse from an upstream reservoir of high concentration through the specimen to a downstream reservoir of low concentration (initially chloride free). The steady state flux of chloride ions (J) determined per unit area of specimen may be measured and the diffusion coefficient (D_i) may then be obtained from Fick's first law:

$$J = D_i \frac{\partial C}{\partial x} \tag{1}$$

where $\partial C/\partial x$ is the imposed concentration gradient [5]. This diffusion coefficient (D_i) has been referred to as the intrinsic diffusion coefficient [6].

The intrinsic diffusion coefficient is an average value through the full cross-section of the specimen. However diffusion only occurs in part of the porosity of the specimen [7]. The diffusion coefficient in this phase (D_p) is referred to as the pore system diffusion coefficient (also known as the pore solution diffusion coefficient in some work [6]). It is dependent on the tortuosity of the pore system but excludes all effects that result from a net uptake or release of chloride ions by the specimen. The pore system diffusion coefficient is directly related to the intrinsic diffusion coefficient by the equation:

$$D_p = \frac{D_i}{\varepsilon} \tag{2}$$

where ε is a measure of the volume fraction of the specimen accessible to the diffusing ions, hereafter referred to as the effective porosity. (This definition is deliberately vague for the reasons given below.) As ε must be less than 1, the pore system diffusion coefficient will be greater than the intrinsic diffusion coefficient [5, 6].

Another property of the concrete which affects all forms of chloride transport (including diffusion) is its ability to bind chloride ions. It has been suggested that the chloride binding relationship may be obtained on a specimen subject to a diffusion cell test [8, 9]. One method is based on the assumption that the free chloride concentration is a linear function of depth when steady state has been achieved and the properties of the specimen are independent of depth. Thus the free chloride concentration may be estimated, while the total chloride profile may be measured using standard techniques [8].

A porosity term is required to determine the quantity of bound chloride. It will be shown that, if this differs from the effective porosity used to determine the pore system diffusion coefficient (Equation 2), the chloride sink capacity of the pore volume equal to this difference must be considered when modelling chloride ingress.

An analysis of the achievement of steady state conditions in an ideal diffusion cell test has been undertaken

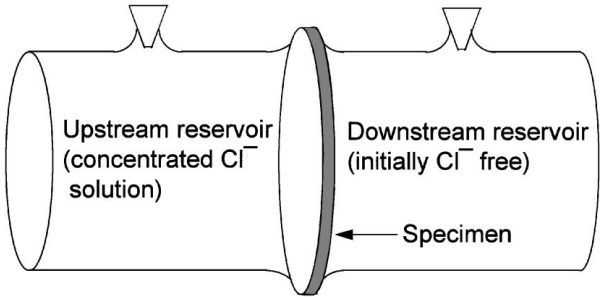

Figure 1 Typical arrangement in a diffusion cell test.

for the case where the changes in the two reservoirs of the cell (Fig. 1) are negligible [10]. However, the diffusion cell test requires a change in the downstream concentration to obtain the flux and only near steady state conditions are imposed on the specimen under investigation. This may lead to some errors which may be compounded by the effects of chloride binding.

In this work a numerical model is developed to assess the effect of small deviations from the assumed steady state condition on both the chloride binding data and diffusion coefficient data derived. The effects of varying the specimen and diffusion cell parameters on the data obtained are examined.

2. Model development

2.1. Concentration profile

The chloride concentration (C) as a function of time (t) and distance (x) under non-steady state conditions is described by Fick's second law [10]:

$$\frac{\partial C}{\partial t} = D_p \frac{\partial^2 C}{\partial x^2} \tag{3}$$

This assumes that only diffusion determines the concentration profile and there is no net uptake or release of chloride in the medium in which diffusion occurs. It may be noted that the diffusion coefficient in Equation 3 is the pore system diffusion coefficient. It may be determined from the analysis of non-steady state chloride profiles produced under conditions which may approximate one dimensional diffusion into a semi infinite medium. However such analysis is complicated by the need to subtract the effects of chloride binding which would otherwise give rise to a smaller apparent diffusion coefficient [11].

The chloride binding relationship may to a first approximation be described by a Langmuir or Freundlich adsorption isotherm [11, 12]. In this work a Langmuir adsorption isotherm given by the equation:

$$C_b = \frac{\alpha C}{1 + \beta C} \tag{4}$$

where C_b is the quantity of bound chloride and α and β are constants, is used. The time dependence of the chloride concentration (C), which is referred to as the free chloride concentration to distinguish it from bound chloride, is then given by a modified form of Equation 3 [11]:

$$\left[1 + \frac{\alpha}{w(1 + \beta C)^2}\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{5}$$

where w is a constant which converts the units of bound chloride content determined by α (typically a weight fraction of cement or moles per gram of cement) into the units of the free chloride concentration (typically moles per litre of pore solution). By setting the constant α equal to zero this reverts back to Equation 3.

Equation 5 represents an initial value problem. A solution may be obtained using finite difference methods [13]. An illustration of this method applied to diffusion in the absence of binding is described by Bard and Faulkner [14]. The boundary conditions are crucial to the solution obtained. To assess the effect of the concentration changes which occur in the two reservoirs of the diffusion cell, the boundary conditions must consider the flux of ions leaving or entering each reservoir. The time dependence of the chloride concentration in each reservoir (C_0) is given by:

$$\frac{\partial C_0}{\partial t} = J \frac{A}{\varepsilon V} \tag{6}$$

where A is the area of the specimen V is the volume of the reservoir and J is given by Equation 1.

2.2. Model validation

Inaccuracies in the model may result from both model instability and errors in the finite difference approximations to the derivatives in Equations 5 and 6. The stability of the model is determined by the relative magnitude of the distance and time increments (Δx and Δt). Instability occurs when the time increment is long compared to the distance increment and the diffusion which occurs in one time increment results in unreasonable changes in the chloride concentration in each spatial element. In the case of pure diffusion the time and distance increments are constrained by the relationship:

$$\Delta t < \frac{k}{D_p} (\Delta x)^2 \tag{7}$$

where k is a constant with a value of 0.5 [13, 14].

The accuracy of the finite difference approximations is determined by the size of the increments. A more accurate model will generally have smaller time and distance increments. These should be varied together as, while a smaller time increment combined with a relatively large distance increment will result in a very stable model, it does not significantly improve the accuracy and may require significantly more computing power.

Initially diffusion was modelled through 10 mm thick discs, 100 mm in diameter, with an intrinsic diffusion coefficient of 1×10^{-11} m^2/s, an effective porosity of 25% (by volume) and no chloride binding ($\alpha = 0$). Such

a diffusion coefficient and porosity may represent a 0.5 w/c cement paste [2, 11]. The model accuracy was assessed by comparing the effect of using distance increments of 0.1 mm and 0.01 mm. To maintain model stability corresponding time increments of 100 and 1 s, which represent 80% of the maximum value allowed by Equation 7, were used. The chloride concentration in the upstream reservoir of the diffusion cell was initially 2M. Large upstream and downstream reservoir volumes of 10 l were selected to ensure a relatively constant concentration gradient. The predicted change in chloride concentration in the downstream reservoir is given in Fig. 2. It is evident that the effect of altering the distance and time increments was negligible.

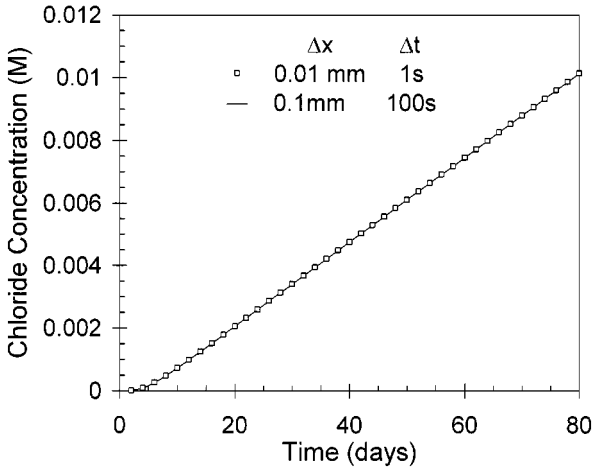

Figure 2 The predicted change in downstream concentration for two distance and time increments (model parameters: $D_i = 1 \times 10^{-11}$ m^2/s; $\varepsilon = 0.25$; $V = 10$ l; $\alpha = 0$).

TABLE I The change in the chloride content of the diffusion cell

Elapsed time (days)	$\Delta x = 0.1$ mm Amount of Cl^- (10^{-14} moles)	$\Delta x = 0.01$ mm Amount of Cl^- (10^{-14} moles)
10	−1.1	6.8
20	−5.3	11.0
30	−1.8	23.4
40	−11.0	19.2
50	−9.2	13.9
60	−11.7	17.4
70	−19.9	17.1
80	−22.4	−7.8
90	−23.1	−20.3
100	−21.7	−24.5
120	−12.5	−25.9

The model was also examined by calculating the total chloride content in the diffusion cell at various times. The deviation from the initial chloride content (20 moles) is given in Table 1. Conservation of mass requires that no change should occur. This was largely observed with only a very small discrepancy of the order of 10^{-13} moles occurring. This was marginally greater in the more refined model and may have been caused by rounding errors resulting from the numerical precision of the calculations.

The intrinsic diffusion coefficients calculated using the flux determined from various periods of predicted data together with the average concentration gradient across the specimen at the midpoint of each of these periods are given in Table II. The calculated coefficients approach the values used in the model as steady state is achieved. Such observations give some confidence in the use of the model and suggest that there is little to be gained by using distance increments below 0.1 mm.

3. Model predictions

3.1. Diffusion cell parameters

The validity of the assumption that steady state conditions have been achieved will depend on the rate of change in the chloride concentration in each reservoir of the diffusion cell. This is affected by both the diffusion cell parameters which determine the specimen area and the volume of the reservoirs, and the specimen properties which determine the chloride flux.

The influence of the specimen area and reservoir volume are related with a change occurring only when their ratio changes (cf. Equation 6). Thus an increase in the specimen area is equivalent to decreasing the reservoir volume. The predicted change in the downstream chloride concentration as a function of time when a reservoir volume of 0.5 l was used is given in Fig. 3. All other parameters were the same as those used to produce the predictions given in Fig. 2. Values of the chloride ion flux determined from various periods of data are included in Fig. 3, while the corresponding values of the calculated diffusion coefficients are given in Table II. A comparison of the data in Table II suggests that decreasing the reservoir volume from 10 l to 0.5 l, which is more typical of a diffusion cell arrangement used when testing specimens 100 mm in diameter [15], will increase the error in the diffusion coefficient determined. However the error remains relatively small (<1%).

It is also evident that, after an initial period of time, the rate of increase in the downstream concentration

TABLE II Calculated intrinsic diffusion coefficients corresponding to various periods of predicted data and maximum x-axis intercepts

Model inputs					D_i values from predicted data				
ε	D_i (m^2/s)	D_p (m^2/s)	V (l)	Chloride binding	10–20 days (m^2/s)	20–40 days (m^2/s)	40–60 days (m^2/s)	60–80 days (m^2/s)	Max. x intercept days
0.25	1×10^{-11}	4×10^{-11}	10	No	9.82×10^{-12}	9.99×10^{-12}	1.00×10^{-11}	1.00×10^{-11}	4.8
0.25	1×10^{-11}	4×10^{-11}	0.5	No	9.74×10^{-12}	9.94×10^{-12}	9.94×10^{-12}	9.94×10^{-12}	4.5
0.25	1×10^{-12}	4×10^{-12}	0.5	No	4.56×10^{-14}	3.12×10^{-13}	6.33×10^{-13}	8.11×10^{-13}	45
0.025	1×10^{-12}	4×10^{-11}	0.5	No	9.82×10^{-13}	9.99×10^{-13}	9.99×10^{-13}	9.99×10^{-13}	4.8
0.25	1×10^{-11}	4×10^{-11}	0.5	Yes	6.45×10^{-12}	9.62×10^{-12}	9.80×10^{-12}	9.82×10^{-12}	14.6

TABLE III Comparison of the calculated intrinsic diffusion coefficients after decreasing the model input parameter from 1×10^{-11} to 1×10^{-12} m^2/s

	Model inputs		D_i values from predicted data					
ε	D_i (m^2/s)	D_p (m^2/s)	Period days	D_i (m^2/s)	Period days	D_i (m^2/s)	Period days	D_i (m^2/s)
0.25	1×10^{-12}	4×10^{-12}	100–200	9.74×10^{-13}	200–400	9.94×10^{-13}	400–600	9.94×10^{-13}
0.25	1×10^{-11}	4×10^{-11}	10–20	9.74×10^{-12}	20–40	9.94×10^{-12}	40–60	9.94×10^{-12}

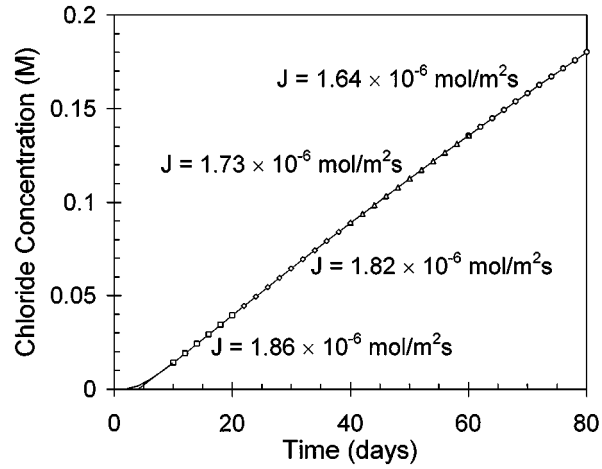

Figure 3 The predicted change in downstream concentration on decreasing the reservoir volume to 0.5 l, together with calculated values of the flux (model parameters: $D_i = 1 \times 10^{-11}$ m^2/s; $\varepsilon = 0.25$; $V = 0.5$ l; $\alpha = 0$).

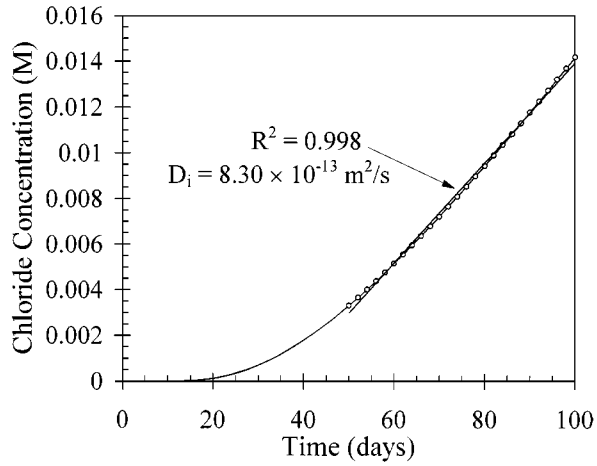

Figure 4 The effect of decreasing the intrinsic diffusion coefficient to 1×10^{-12} m^2/s (cf. Fig. 3), together with the correlation coefficient of a line fitted to the 50 to 100 day data and its corresponding calculated intrinsic diffusion coefficient.

begins to decrease (cf. the values of flux given in Fig. 3). This results from the decrease in the concentration difference between the two reservoirs. However such deviations from a linear rate of change in low concentration reservoir are easily masked by random errors in measured chloride concentrations.

Included in Table II is the maximum x-axis intercept extrapolated from a near linear portion of the relationship in Fig. 3. This gives a measure of the time required for detectable quantities of chloride to pass through the specimen. It also represents the lower bound of the time required to achieve near steady state conditions. A small decrease in this intercept (from 4.8 to 4.5 days) occurred on decreasing the reservoir volume. This would have resulted from the more rapid decrease in concentration gradient between the two diffusion cell reservoirs.

3.2. Specimen properties

The specimen properties which determine the chloride flux are the diffusion coefficient, the effective porosity and chloride binding.

The change in downstream chloride concentration after decreasing the intrinsic diffusion coefficient from 1×10^{-11} m^2/s to 1×10^{-12} m^2/s is given in Fig. 4. All other parameters were the same as those used to produce the predictions given in Fig. 3. This indicates that, if the period of time over which the data is collected is not increased, the measured chloride concentrations will be relatively low. However the high correlation coefficient of the line fitted to the data between 50 and 100 days (included in Fig. 4) suggests that detecting non-linearity in the trend will be difficult.

The calculated intrinsic diffusion coefficients from this data are given in Tables II and III. Significant errors resulted from the use of the first 80 days of data due to the absence of steady state conditions (Table II). However when the downstream concentration was allowed to increase to the same level as that resulting from the use of an intrinsic diffusion coefficient of 1×10^{-11} m^2/s, the errors were again small (data compared in Table III). The only difference between these two cases is the order of magnitude change in the time required to obtain such data.

One effect which will decrease the intrinsic diffusion coefficient is a decrease in the effective porosity (cf. Equation 2). The effect of an order of magnitude decrease in the intrinsic diffusion coefficient which is entirely due to an order of magnitude decrease in the effective porosity is given in Table II. In this case the pore system diffusion coefficient remains at 4×10^{-11} m^2/s. It is evident that despite the low chloride concentrations, no increase in time is required to obtain such data. Indeed the accuracy of the calculated intrinsic diffusion coefficients has improved while the maximum x-axis intercept is again less than 5 days.

This suggests that it is the pore system diffusion coefficient which determines the rate at which steady state is achieved (cf. Equation 5). It may however be noted that, in practice, a reduction in effective porosity would also produce a reduction in the pore system diffusion coefficient due to factors which include an increase in pore wall interactions.

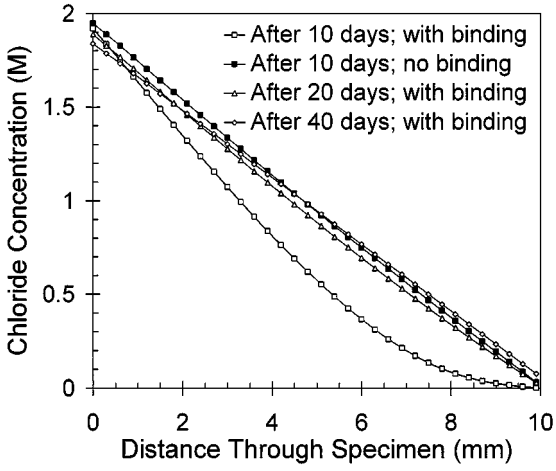

Figure 5 The predicted free chloride profile through specimens in the presence and absence of binding (cf. Fig. 3 and Table II).

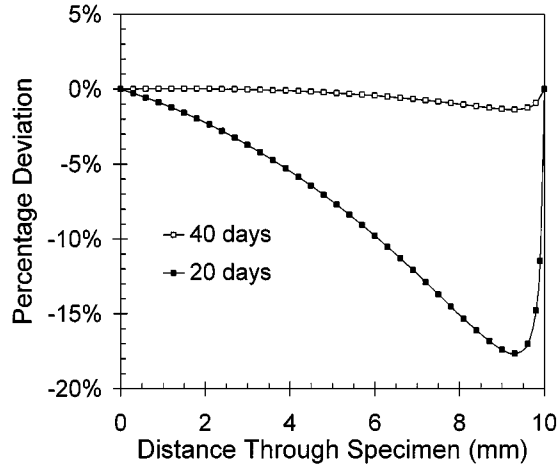

Figure 6 The percentage deviation from an ideal linear free chloride profile in a specimen which binds chloride.

The effect of binding was determined using a previously reported Langmuir binding isotherm for an ordinary Portland cement specimen with the values of the constants α and β in Equation 4 being 6.46%/M and 3.79%/M respectively (the units of bound and free chloride were percentage by weight of cement and Molar respectively) [16]. The constant w in Equation 5, which converts the units of bound chloride to moles per litre of pore solution, was obtained using a cement content of 1200 kg/m^3 (typical of a cement paste) and a water filled porosity of 25% [17].

The calculated intrinsic diffusion coefficients in the presence of chloride binding are included in Table II. They suggest that chloride binding will increase the error in the diffusion coefficient determined although this remains relatively small after a sufficient period of time has elapsed (<2% after 80 days). Furthermore such a typical chloride binding capacity will increase the maximum x-axis intercept (also given in Table II) by a factor of more than 3.

The predicted free chloride profiles after 10, 20 and 40 days in specimens which bind chloride are given in Fig. 5. Also included is the profile after 10 days in a specimen which does not bind chloride but is otherwise the same (cf. model parameters in Table II). It is evident that chloride binding increases the time required to achieve a near linear profile (cf. the predicted profiles after 10 days). This might be expected in view of the increase in the maximum x-axis intercept. However, the predicted profiles rapidly adopt a linear nature as time increases.

The percentage deviation from an ideal linear profile determined using the chloride concentration in the two reservoirs after 20 and 40 days in specimens which bind chloride is given in Fig. 6. The largest deviation occurs near the downstream reservoir of the diffusion cell.

4. Discussion

4.1. Diffusion coefficients

The above analysis would suggest that deviations from the steady state in the diffusion cell test result in an underestimation of the intrinsic diffusion coefficients determined. These errors were small for most cases examined if a sufficient period of time was allowed to achieve near steady state conditions. However chloride binding affects chloride transport and amplifies the errors resulting from small deviations from steady state conditions (Table II). Increasing the ratio of the diffusion cell reservoir volume to the specimen area will improve the accuracy of the steady state conditions achieved, but will also decrease the downstream chloride concentration which may increase the measurement error.

A larger error may arise from the difficulty in detecting near steady state conditions from the rate of change in concentration of the downstream reservoir. Measurement error may easily mask any non linearity in the rate of concentration change. This gives rise to the risk of determining diffusion coefficients using data obtained under non-steady state conditions. This risk may well depend on the time required to achieve steady state.

The achievement of steady state conditions is determined by the intrinsic diffusion coefficient, effective porosity and chloride binding capacity with the influence of the intrinsic diffusion coefficient and effective porosity being related through the pore system diffusion coefficient (Equation 2). Indeed it is this parameter that gives a measure of the velocity of the ions transported by diffusion in the specimen and therefore the penetration rate of chloride ions.

One approach to minimise the risk of using too short a duration of diffusion cell test data is to ensure that a given quantity of chloride passes through the specimen when a typical concentration gradient is applied. In the present work the errors were always relatively small by the time 5% of the chloride present in the cell had entered the downstream reservoir. However, in some cases, this may give rise to unnecessarily long and impractical test durations.

Near steady state conditions will be achieved after much smaller quantities of chloride have passed through the specimen when a low intrinsic diffusion coefficient is produced by a low effective porosity (Table II). Indeed it would not have been possible to accurately determine some very low reported values

of the intrinsic diffusion coefficient in a reasonable time period if these did not result from a low effective porosity (cf. data in references [2] and [4]). The smaller change in chloride concentration of the diffusion cell reservoirs, and therefore the smaller deviation from steady state, improves the accuracy of the diffusion coefficients determined in this case.

An alternative method of determining whether steady state conditions have been achieved is to ensure that the period over which the rate of change downstream concentration appears to be linear constitutes a significant proportion of the duration of the test. Thus the time axis intercept of the linear portion of the downstream concentration versus time graph must be small compared to the total measurement period. An examination of Figs. 3 and 4 suggests that this should be less than 20% of the test duration.

It may be noted that neither the x-axis intercept nor the intrinsic diffusion coefficient should increase if successive periods of the linear portion of the graph are used. However it is possible for these parameters to decrease. Reasons for this include further hydration of the specimen and changes in the pore structure due to reaction with chloride ions. This may require further measures to ensure the achievement of steady state.

Underestimation of the intrinsic diffusion coefficient would also occur if the concentration gradient initially imposed, as opposed to that existing at the time when the flux was determined, was used in the calculation. In the typical cell geometry used in this work, changes in upstream and downstream concentrations could relatively easily result in a 10% reduction in the concentration gradient driving diffusion.

The greatest predicted change in concentration in the diffusion cell occurred in the upstream reservoir (Fig. 5). However as steady state conditions are approached, the rate of concentration change in each reservoir tends to the same value. Thus, in terms of the accuracy of the steady state conditions achieved, there is no advantage to be gained by increasing the volume of one reservoir at the expense of the other reservoir in the diffusion cell.

4.2. Binding isotherms

It was noted in the introduction that information on the chloride binding capacity of the specimen in a diffusion cell test may be obtained by measuring the total chloride profile and estimating the free chloride profile based on the assumption that it is a linear function of depth. The small deviation from linearity of the free chloride profile suggests that the resulting error may be relatively small (Fig. 6). The percentage error is smaller in that half of the specimen closer to the high concentration reservoir, it having been exposed to chloride for a longer period of time.

The maximum predicted error in the free chloride profile obtained by linear extrapolation is significantly smaller than the error in the diffusion coefficient obtained using a corresponding period of data (18% maximum as opposed to 36% after 20 days and 1.4% maximum as opposed to 3.8% after 40 days). One reason for this is that the free chloride concentration is determined at the end of the test while the flux used to determine the diffusion coefficient is derived from data obtained over an extended period running up to the end of the test. Furthermore it is the concentration gradient at the interface of the specimen with the downstream reservoir that determines the flux into the downstream reservoir and deviations from a linear concentration gradient are greatest at this interface (Fig. 6).

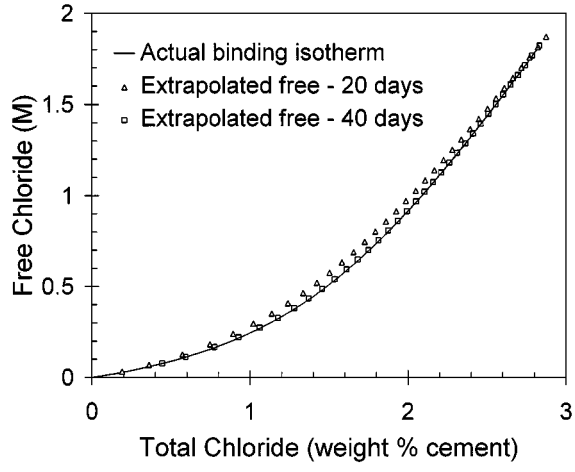

Figure 7 The actual and estimated relationship between free and total chloride.

The total chloride content may be obtained as a function of depth following a diffusion cell experiment. The total-free relationship determined using a linear free chloride profile and the predicted total chloride profile after 20 and 40 days is given in Fig. 7. It may be noted that the estimated binding isotherms converge relatively rapidly on the actual values. Indeed the errors resulting from the assumption of a linear free chloride profile appear to be small in comparison to the errors in other methods of binding isotherm determination (typically 20%) [16].

The accuracy of this diffusion cell method of binding isotherm determination will be limited by the accuracy with which the total chloride profile may be measured as well as by the time and depth dependent properties of the specimen. Depth dependent properties such as a variation in the cement content and therefore the binding capacity at a cast surface should be avoided [8]. Time dependent properties could include pore structure refinement resulting from continued hydration, as well as the slow release of bound chloride. This latter effect may hinder the maintenance of equilibrium in the specimen adjacent to the upstream reservoir as its chloride concentration falls [18]. The influence of these time dependent effects is more difficult to minimise.

The determination of binding data by this method at low chloride contents may be limited by the relatively large quantity of chloride that may pass through the specimen prior to the detection of near steady state conditions. This may necessitate an increase in the volume of the downstream reservoir to keep its concentration low. Another problem arises from the porosity term required to calculate the quantity of bound chloride. This term is poorly defined. However this is true for most methods of bound chloride determination.

4.3. Effective porosity

As noted above, the effective porosity determines the relationship between the intrinsic and pore system diffusion coefficients. It might be considered to be the volume fraction of capillary pores in the sample which contribute to the net transport of chloride through the specimen under steady state conditions [7]. However all pores which are accessible to chloride ions may affect chloride transport under non-steady state conditions. While blocked pores that are connected to the pore system at only one point do not contribute to the net throughput of chloride, they will act as a chloride sink which will slow the achievement of steady state in a similar manner to chloride binding.

To directly address the effect of the chloride sink capacity of blocked pores presents problems associated with obtaining values for some of the parameters that describe it. However, to a first approximation, it may be addressed by using a larger effective porosity and a correspondingly smaller pore system diffusion coefficient. This assumes that this chloride sink effect acts in a linear manner. Indeed it can be shown that, when the average concentration in the blocked pores at a given depth is the same as that in the pores through which transport is occurring, the influence of the chloride sink capacity of blocked pores on chloride transport is to increase the effective porosity by the volume fraction of the blocked pores and decrease pore system diffusion coefficient by the same factor.

If there is no depth dependence of the geometry (volume, length and direction) of blocked pores in the specimen and the concentration in these pores is equal to that at their point of connection with the rest of the pore system, the average concentration in the blocked pores will be the same as that in the pores through which transport is occurring at a given depth. However the finite time required for chloride to diffuse into blocked pores will result in a below average chloride concentration in the blocked pores. In this case a lower effective porosity that does not include the entire volume of the blocked pores could be used. It may be noted that defining the effective porosity in these terms results in it being equivalent to that required to calculate the quantity of bound chloride from the free chloride concentration and total chloride content.

Attempts may be made to estimate the value of the effective porosity from a comparison of the intrinsic diffusion coefficient and the time required to achieve steady state after subtracting the effects of chloride binding (cf. the influence of the effective porosity on the maximum x-axis intercept in Table II when the intrinsic diffusion coefficient remains unchanged). However, while a lower pore system diffusion coefficient calculated using a higher effective porosity would be expected to increase the predicted time to steady state, a higher porosity would also decrease the calculated chloride binding capacity which in turn would decrease the time to steady state.

The effect of using calculated binding isotherms and diffusion coefficients corresponding to different porosities on subsequent predictions made using these calculated model inputs is illustrated in Figs. 8 and 9. The parameters used to generate the simulated actual data for this comparison are the same as those given in Table II for the case where chloride binding occurred. The diffusion coefficients were calculated using the data which extended up to 80 days while the binding isotherm was obtained by fitting a Langmuir isotherm (Equation 4) to the actual total versus extrapolated free chloride relationship at 80 days.

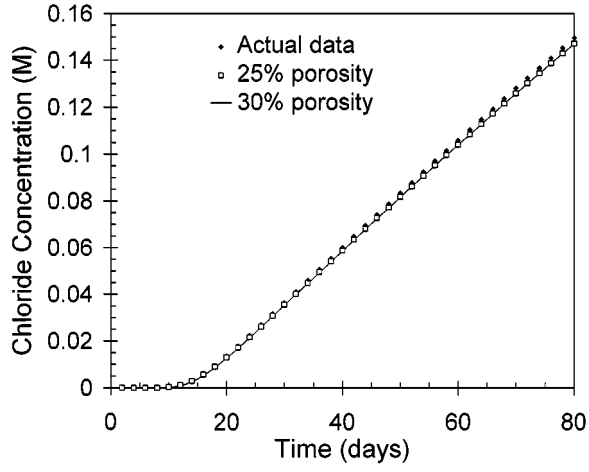

Figure 8 The predicted change in downstream concentration using a binding isotherm and diffusion coefficient calculated from diffusion cell test data at two porosity values.

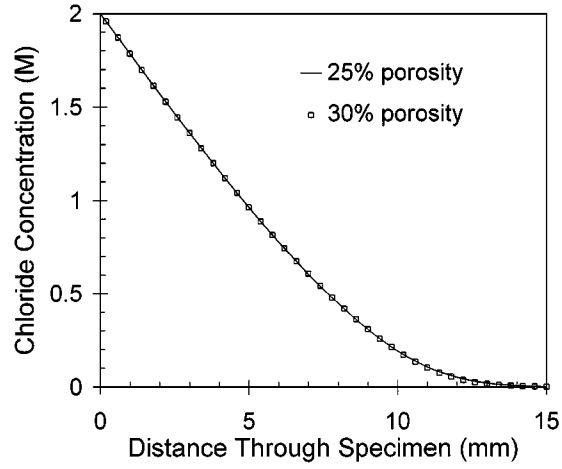

Figure 9 The predicted chloride profiles after 20 days in a 25 mm thick specimen using the parameters calculated from simulated diffusion cell test data at two porosity values.

Fig. 8 gives the predicted change in concentration in the downstream reservoir of the diffusion cell, while Fig. 9 gives the free chloride profiles after 20 days in a 25 mm thick specimen of the same material exposed to a chloride source with a constant concentration on one face and sealed on the opposite face. It is evident that no difference in the predictions occurred when the value of the effective porosity used was increased from its actual value of 25% to a value of 30%. The small difference which occurred between the actual data and the data predicted using the calculated parameters in Fig. 8 was most likely to have resulted from the small error in the calculated intrinsic diffusion coefficient.

It should be noted that the calculation of the binding isotherm is constrained by the condition that a given

total chloride content corresponds to a given free chloride concentration irrespective of the value of porosity used to determined the bound chloride content. Thus the similarities between the free chloride concentration profiles in Fig. 9 will also exist between the corresponding total chloride content profiles.

The above observation suggests that the effect of errors in the value of the porosity used to calculate the binding isotherm is cancelled by their effect on the calculated pore system diffusion coefficient. Thus the sensitivity of the model predictions to such errors is limited when the same effective porosity is used to determine both the binding isotherm and the pore system diffusion coefficient from the data produced by a diffusion cell test.

5. Conclusions

1. In theory the steady state diffusion cell test provides a relatively accurate method of determining the intrinsic diffusion coefficient. However deviations from steady state conditions will result in some tendency to underestimate its value. Important factors affecting the accuracy are the chloride binding capacity of the specimen and the geometry of the diffusion cell. Furthermore, near steady state conditions are difficult to detect from changes in chloride concentration and the period over which near linear behaviour is observed should constitute a significant proportion (say 80%) of the total duration of the test.

2. In addition to the determination of the diffusion coefficient, the diffusion cell test also offers a method for determining the chloride binding isotherm on relatively large specimens through which diffusion is occurring. The free chloride concentration in the specimen may be estimated by assuming that it is a linear function of depth when near steady state conditions have been achieved. The errors resulting from this assumption are less than the errors in the diffusion coefficient calculated using data determined over a similar period of time. The bound-free relationship may then be obtained at the end of the test by measuring the total chloride profile.

3. The effective porosity is required to calculate both the pore system diffusion coefficient and the bound chloride content from the data generated in a steady state diffusion cell test. However, the sensitivity of model predictions to errors in the value used is limited as the effect of the resulting error in the pore system diffusion coefficient tends to be cancelled by the resulting error in the chloride binding isotherm.

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