Pergamon

Cement and Concrete Research 33 (2003) 55–62

CEMENT AND CONCRETE RESEARCH

The use of bulk diffusion tests to establish time-dependent concrete chloride diffusion coefficients

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Received 15 May 2001; accepted 8 July 2002

Abstract

The proper determination of chloride diffusion values, including how they change with time, is important for service life modelling. Currently, there are two major approaches for using chloride diffusion coefficients to predict the service life of structures. The average diffusion coefficient or the instantaneous diffusion coefficient can be used. Using instantaneous diffusion coefficients is a more flexible technique, but requires a more advanced evaluation of bulk diffusion test results to establish material parameters. This paper describes an analytical procedure for determining the instantaneous chloride diffusion value as a function of time for a concrete using data from bulk diffusion tests. The importance of interpreting the data correctly is illustrated with simulated bulk diffusion test data, generated using a finite-difference model for diffusion. In addition, the application of this procedure for evaluating diffusion values is illustrated with experimental data.

Keywords: Diffusion; Aging; Long-term performance; Service life modelling

1. Introduction

The durability of concrete structures exposed to chloride-containing solutions has been extensively studied. The dominant method of chloride ingress is by diffusion, and a number of different service life models have been developed to account for this [1–7]. These models require the diffusion value as an input parameter. A common method of determining diffusion coefficients is through the bulk diffusion test, where saturated samples are exposed to a chloride-containing solution for a known period of time. The chloride profiles are then established and the diffusion coefficient determined. An example of the bulk diffusion test is NT Build 443 [8]. However, concrete is not a static material—it continues to hydrate. This results in a complication in determining diffusion coefficients that is often disregarded. In this paper, the influence this continuing hydration has on evaluating diffusion coefficients is discussed and a procedure is proposed to evaluate this effect.

2. Establishing the effective age of bulk diffusion tests

In a bulk diffusion test, chloride ions are allowed to penetrate the concrete sample solely by diffusion. Diffusion of chloride ions into concrete is governed by Fick's Law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the chloride concentration, t the time, D is the diffusion coefficient and x is a positional variable. As concrete matures, additional hydration occurs which serves to reduce the diffusion coefficient. This has been modelled by [1,9]:

$$D(t) = D_{\mathrm{ref}}\left(\frac{t_{\mathrm{ref}}}{t}\right)^m \tag{2}$$

where D_{ref} is the diffusion coefficient at some time, t_{ref}, and m is a variable to describe the rate of change of the diffusion

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0008-8846/03/$ – see front matter
PII: S0008-8846(02)00925-0

coefficient. This results in an instantaneous diffusion coefficient that varies as shown in Fig. 1.

The inclusion of this changing diffusion coefficient with age is not normally considered, however, when evaluating the results of a bulk diffusion test. A constant diffusion coefficient is assumed and the following numerical solution to Eq. (1) is typically applied:

$$C(x,t) = C_0 erfc\left(\frac{x}{\sqrt{4Dt}}\right) \tag{3}$$

where C_0 is the surface chloride concentration, and the other parameters are as previously defined. The fit of Eq. (3) to the chloride profile determines a single diffusion value. This diffusion value is the average of the changing diffusion coefficient over the testing period, D_{AVG}.

The average diffusion coefficient will occur at some point during the test period. It would be useful to be able to establish at what age the instantaneous diffusion coefficient is equal to the average diffusion coefficient. To determine this age, realize that the average diffusion coefficient determined from each test /will be (Eq. (4)):

$$D_{AVG} = \frac{\int_{t_1}^{t_2} D_{ref}\left(\frac{t_{ref}}{t}\right)^m dt}{\int_{t_1}^{t_2} dt} \tag{4}$$

where t_1 and t_2 represent the age of the concrete at the start and completion of the bulk diffusion test, respectively. Now, D_{ref}, t_{ref} and m are constant for a specific concrete and thus can be taken outside the integral. This results in (Eq. (5)):

$$D_{AVG} = \frac{D_{ref} t_{ref}^m \int_{t_1}^{t_2} t^{-m} dt}{\int_{t_1}^{t_2} dt} \tag{5}$$

Solving these integrations yields an expression for the average diffusion coefficient of:

$$D_{AVG} = \begin{cases} D_{ref} t_{ref}^m \frac{t_2^{1-m} - t_1^{1-m}}{(1-m)(t_2-t_1)} & m \neq 0, 1 \\ D_{ref} t_{ref}^m \frac{\ln\left(\frac{t_2}{t_1}\right)}{t_2 - t_1} & m = 1 \end{cases} \tag{6}$$

If m is equal to 0, the diffusion value does not change with age. In this case, the diffusion coefficient at any age is equal to the average diffusion coefficient. It has been previously stated that when $m = 1$, the concrete is what is termed ‘self-blocking’, and the chloride profile remains constant [7]. This is proposed as an upper limit for the value of m. This is one of the differences between considering average diffusion coefficients and instantaneous ones. When instantaneous diffusion coefficients are used, this limit is not present. There is no reason that values of m of 1 or greater could not occur. This apparent ‘self-blocking’ effect only occurs when average diffusion coefficients are used because the equation applied (Eq. (3)) was derived for a constant diffusion coefficient. It is mathematically incorrect to then substitute a time-dependent diffusion coefficient in that solution.

Additionally, the effective age at which the average diffusion coefficient occurs, t_{eff}, can be determined using Eq. (2):

$$D_{AVG} = D_{ref}\left(\frac{t_{ref}}{t_{eff}}\right)^m \tag{7}$$

Equating Eqs. (6) and (7) and solving for t_{eff} results in:

$$t_{eff} = \begin{cases} \left[\frac{(1-m)(t_2-t_1)}{t_2^{1-m} - t_1^{1-m}}\right]^{1/m} & m \neq 0, 1 \\ \frac{t_2 - t_1}{\ln\left(\frac{t_2}{t_1}\right)} & m = 1 \end{cases} \tag{8}$$

This expression determines at what age the average diffusion coefficient will occur based upon the bulk diffusion test conditions (the age of the concrete at the beginning and end of the immersion period) and the rate of change of the diffusion coefficient with time.

3. Different approaches to service life modelling

There are two basic approaches used to evaluate the service life of a structure exposed to chloride ions. The diffusion coefficient of interest depends upon the technique that is used. The first approach to service life modelling is to use average diffusion coefficients, as typified by Weyers [5] and Maage et al. [7]. In this approach, the diffusion coefficient used at any given age is the average diffusion coefficient to that point from the beginning of exposure to chloride solution. The concentration at any given depth is then calculated from Eq. (3). In this case, the instantaneous diffusion is of no interest and the diffusion coefficients can be directly determined from bulk diffusion tests with no additional calculations. The m-coefficients can be calculated by fitting the results to Eq. (2).

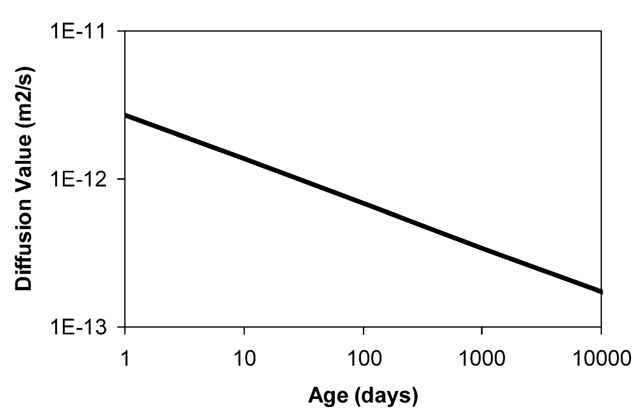

Fig. 1. Typical change in diffusion coefficient with age.

Table 1
Simulation results and fitted diffusion coefficients—various assumed times

Assumed coefficients		Simulated bulk diffusion tests				Calculated coefficients from bulk diffusion data					
		Test A		Test B		Iterative approach		Assuming endpoint of each test		Assuming midpoint of each test	
D_{28} (m^2/s)	m	Test duration (days)	D_{AVG} (Eq. (3)) (m^2/s)	Test duration (days)	D_{AVG} (Eq. (3)) (m^2/s)	D_{28} (m^2/s)	m	D_{28} (m^2/s)	m	D_{28} (m^2/s)	m
1×10^{-12}	0.30	28–68	8.61×10^{-13}	28–393	5.87×10^{-13}	1.00×10^{-12}	0.300	1.05×10^{-12}	0.218	9.90×10^{-13}	0.259
1×10^{-12}	0.70	28–68	7.12×10^{-13}	28–393	3.09×10^{-13}	1.00×10^{-12}	0.701	1.09×10^{-12}	0.476	9.65×10^{-13}	0.565
1×10^{-12}	0.30	28–68	8.61×10^{-13}	28–3678	3.22×10^{-13}	1.00×10^{-12}	0.300	1.07×10^{-12}	0.247	9.95×10^{-13}	0.269
1×10^{-12}	0.30	28–68	8.61×10^{-13}	3650–3678	2.32×10^{-13}	1.00×10^{-12}	0.300	1.15×10^{-12}	0.328	1.01×10^{-12}	0.302
1×10^{-12}	0.30	28–68	8.61×10^{-13}	365–405	4.56×10^{-13}	1.00×10^{-12}	0.300	1.18×10^{-12}	0.356	1.01×10^{-12}	0.305
7×10^{-12}	0.30	28–68	6.03×10^{-13}	28–393	4.11×10^{-12}	7.00×10^{-12}	0.300	7.32×10^{-12}	0.219	6.93×10^{-12}	0.259

Table 2
Effect of different parameters on time to corrosion

Example	Time to corrosion based on D_{28} and m using		
	Fitted ages (years)	End of test (years)	Midpoint of test (years)
1	51.6	28.3	39.4
2	>10,000	227.7	1003.0
3	51.8	32.8	41.9
4	51.5	52.2	51.9
5	51.5	62.4	53.0
6	3.5	2.5	3.1

The other method is to use the instantaneous diffusion coefficients, and to apply a finite difference approach using Eq. (1). An example of a model using that approach is the one developed by the University of Toronto [2]. In this case, the diffusion coefficients and m-values need to be determined for the instantaneous diffusion values and not the average diffusion values determined by bulk diffusion techniques. This is more difficult mathematically to determine but is a more powerful approach. When the average diffusion coefficient is used to estimate the service life, inherent in that assumption is that the conditions in service are identical to the conditions during testing. For example, the age at which the concrete is first exposed to chloride ions is identical, the surface concentration is constant throughout the life of the structure and the surface concentration is identical in both cases. If this is not the case, then the average diffusion coefficients projected from the test results are invalid. The average diffusion coefficients are a function of both the material properties of the concrete and the test conditions. However, if the instantaneous diffusion coefficient is used, this is not the case. The instantaneous diffusion coefficient is a property of only the materials. The use of instantaneous diffusion coefficients and a finite difference approach allows the inclusion of varying environmental parameters in a straightforward manner. It is a more powerful approach. The procedure to use bulk diffusion tests to determine the

Table 3
Diffusion test data

	56% Fly ash	25% Fly ash	Control mix
Test 1	90–180 days 1.53×10^{-12} m^2/s	90–180 days 1.56×10^{-12} m^2/s	90–180 days 5.53×10^{-12} m^2/s
Test 2	90–270 days 1.40×10^{-12} m^2/s	90–270 days 1.23×10^{-12} m^2/s	90–270 days 5.03×10^{-12} m^2/s
Test 3	90–455 days 7.59×10^{-13} m^2/s	90–455 days 9.62×10^{-13} m^2/s	90–455 days 5.98×10^{-12} m^2/s
Test 4	90–1550 days 5.13×10^{-13} m^2/s	90–1550 days 5.77×10^{-13} m^2/s	90–1550 days 3.32×10^{-12} m^2/s

Table 4
Fitted coefficients

	Fitted parameters	
	m	D_{28} (m^2/s)
Control	0.32	9.72×10^{-12}
25% Fly ash	0.66	4.07×10^{-12}
56% Fly ash	0.79	5.01×10^{-12}

required instantaneous diffusion coefficients and *m*-values is outlined.

4. Using bulk diffusion data to determine diffusion vs. age parameters

The equation establishing the effective age of the average diffusion coefficient during a bulk diffusion test can now be used to determine the parameters required to describe concrete diffusion coefficients according to Eq. (2). In Eq. (2), there are two independent unknowns, *m* and the reference diffusion coefficient. The reference age can be selected as any age. In this work, a reference age of 28 days will be used. Since there are two unknowns, at least two test results are required using two different testing periods. While two tests are the minimum required, additional tests can be included to account for any uncertainty in the test results. These tests can either start at the same age and have different exposure times, or start at different ages with possibly the same exposure duration. The information thus available for each of the bulk diffusion tests is the age at which the concrete was first exposed to chlorides (t_1), the age at which the test was ended (t_2) and the average diffusion coefficient between these two ages (D_{AVG}). This average diffusion coefficient is the result of fitting the chloride profile to Eq. (3).

To establish the diffusion parameters (*m* and D_{ref}), this iterative procedure can be followed:

1. Assume a value of *m*.
2. For each bulk diffusion test, calculate the effective age from Eq. (8) using the assumed value of *m* and the test parameters.
3. Determine the logarithms of the average diffusion coefficients (D_{AVG}) and the effective ages from Step 2 for each test.
4. Determine the value of m from the negative slope of the line of best fit using the logs of the average diffusion coefficients as the *y*-values and the logs of the effective ages as the *x*-values.
5. Repeat Steps 2 through 4 with the new value of *m*. When the *m*-value determined from Step 4 is equal to the *m*-

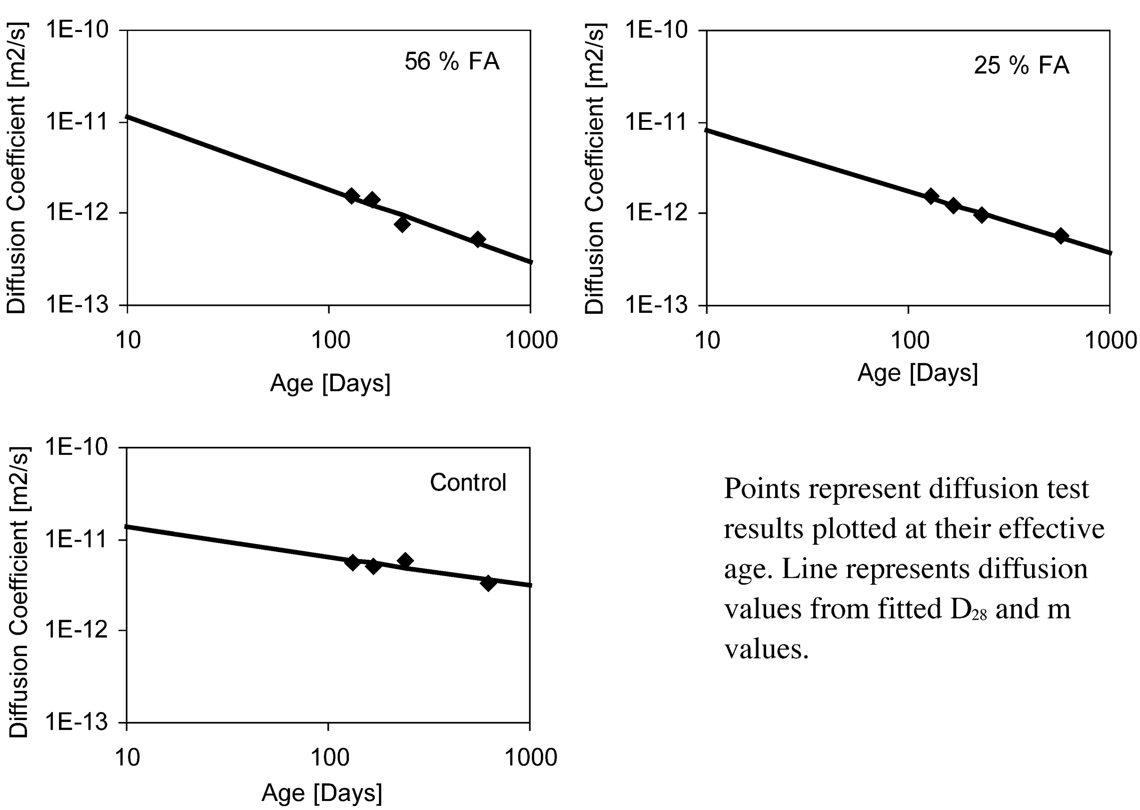

Fig. 2. Comparison between fitted and experimental diffusion coefficients.

value used in Step 2, the value of m is established for the concrete.

6. The intercept of the line of best fit will be the log of the 1-day diffusion coefficient (if age is given in days). Correct to the reference age using Eq. (2) and the value of m just determined.

In this manner, the parameters required to completely describe the change in diffusion coefficient with age according to Eq. (2) can be determined. This procedure is relatively simple to incorporate into a commercial spreadsheet package and typically converges to the m-value in four or five iterations.

5. Validation of the technique—theoretical data

To explore the effect of using this technique for determining the m-coefficient, six theoretical examples were analyzed. For each example, a 28-day reference value and an m value were assumed and then a finite difference program developed at the University of Toronto [1] was used to simulate chloride profiles for two bulk diffusion tests. The resulting chloride profiles were then fit to Eq. (3) and the average diffusion coefficients were determined. The average diffusion coefficients and the test start and stop ages were then used to calculate the m-values and the reference diffusion coefficients using the iterative procedure described above. The results of this process are shown in Table 1. Also in Table 1 are the m-values that would be determined if the endpoint of the exposure time was assumed as the effective age and the m-value that would be determined if the midpoint of the exposure period $[1/2(t_1 + t_2)]$ was assumed as the effective age.

An examination of Table 1 reveals the importance of properly evaluating the effective age of the calculated diffusion coefficients in order to adequately establish the age reduction factor, m. There is an insignificant difference between the assumed parameters used to model the tests and parameters determined when the iterative procedure described herein is used, and any difference is attributable to round-off error in determining the average diffusion coefficient of the simulated bulk diffusion tests. If either the endpoint or the midpoint of the chloride exposure period is assumed as the effective age, however, a significant error is introduced. The magnitude of the error is greater when the m-coefficient is higher or the tests are of different durations and occur when the concrete is at a young age. Unfortu-

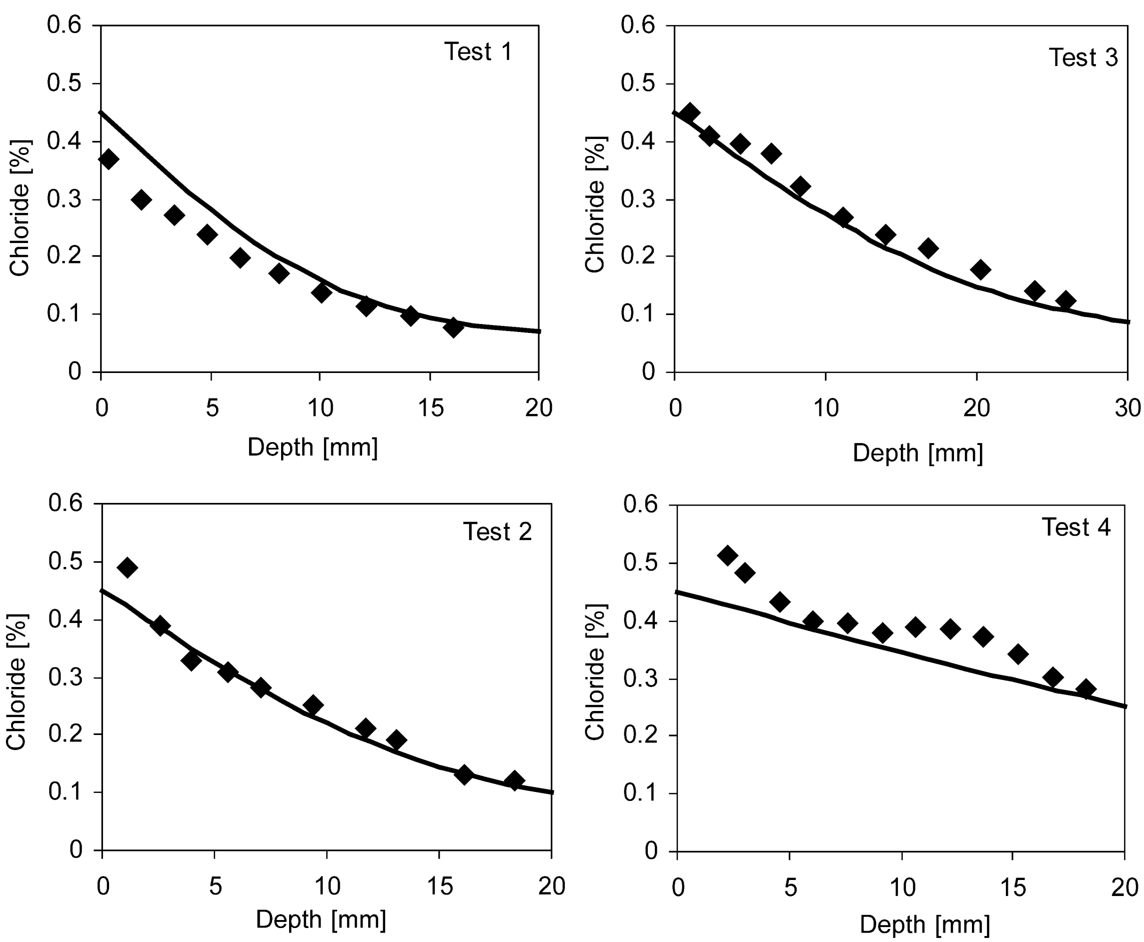

Fig. 3. 0% Fly ash bulk diffusion results—simulated and experimental. Test numbers refer to Table 3.

nately, practical considerations require the use of tests that are completed as early as possible. The determination of m using a standard point in the exposure time is improved if tests are of relatively short durations starting at different ages. Using an improper evaluation procedure did not change the reference value of the diffusion coefficient as much as its influence on m.

To illustrate the influence that the improper evaluation of test data will have on service life prediction, the time to corrosion initiation using the coefficients in Table 1 was calculated assuming a cover thickness of 50 mm, a constant surface chloride concentration of 1% by concrete mass and an onset of corrosion at a chloride concentration of 0.05% by concrete mass. These predictions were performed using a finite difference program developed at the University of Toronto [1] based upon Eq. (1) and instantaneous diffusion coefficients. The results are shown in Table 2. It should be pointed out that the predictions are based solely upon diffusive transport through undamaged concrete, and thus are likely not achievable in practice.

It can be seen that utilizing the correct evaluation procedure for determining the diffusion coefficients results in significantly different predicted times to corrosion. In general, using different procedures results in an earlier predicted corrosion time, though this is not always the case.

6. Application of procedure to experimental data

To demonstrate the applicability of this technique to laboratory data, three different sets of concretes were examined. The concretes had a water-to-cement ratio of 0.50 and a cementitous material factor of 300 kg/m^3. One set contained 56% Class C fly ash, one contained 25% Class C fly ash and one contained no fly ash. The 28-day strengths were 25, 36 and 42 MPa, respectively. Each concrete had average diffusion coefficients reported from four different tests, all tests started at 90 days of concrete age and continued for various durations (90, 180, 365 and 1460 days). A summary of the test information and the test results including the diffusion coefficient, D_{AVG}, calculated for the chloride profiles is presented in Table 3. These data were then used to calculate the m-value and the diffusion coefficient at 28 days, following the iterative procedure previously outlined. These values are reported in Table 4. A comparison of the experimental diffusion coefficients (plot-

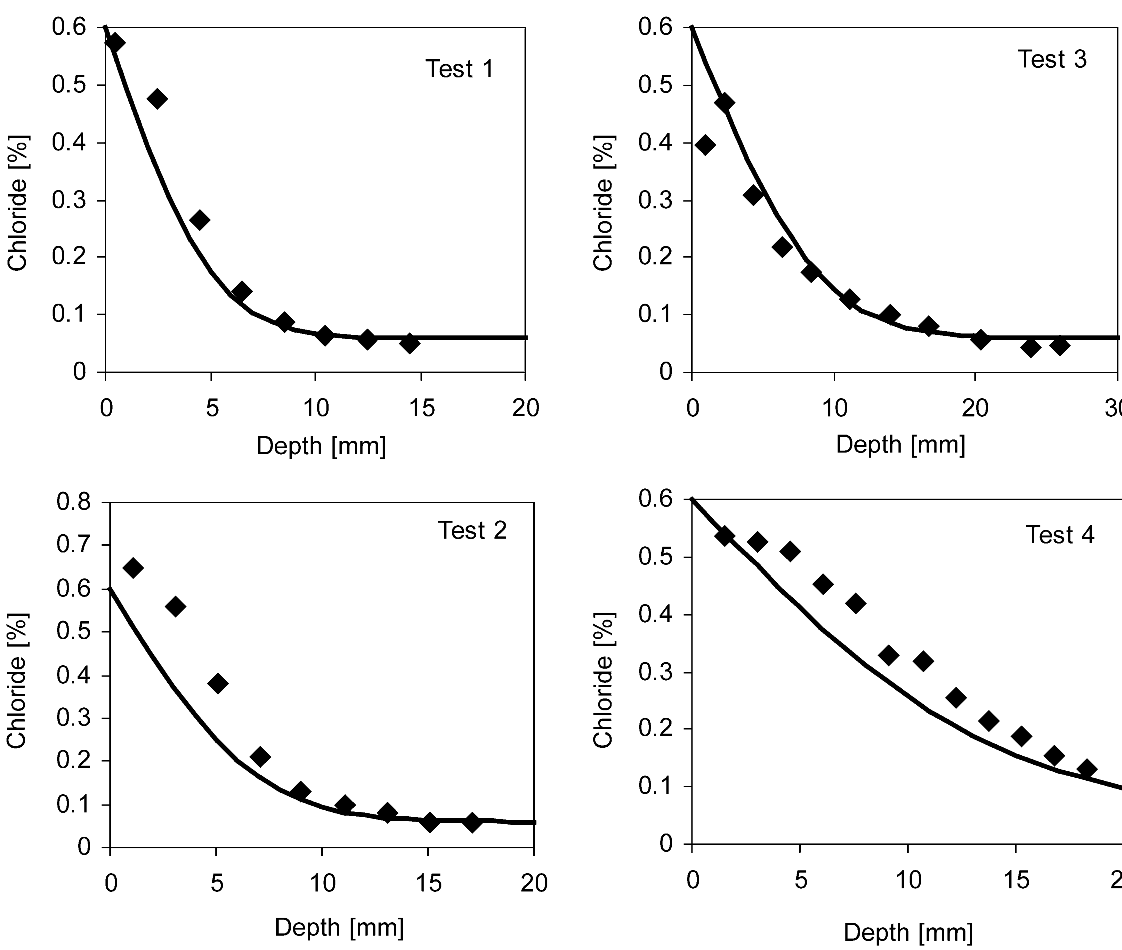

Fig. 4. 25% Fly ash bulk diffusion results—simulated and experimental. Test numbers refer to Table 3.

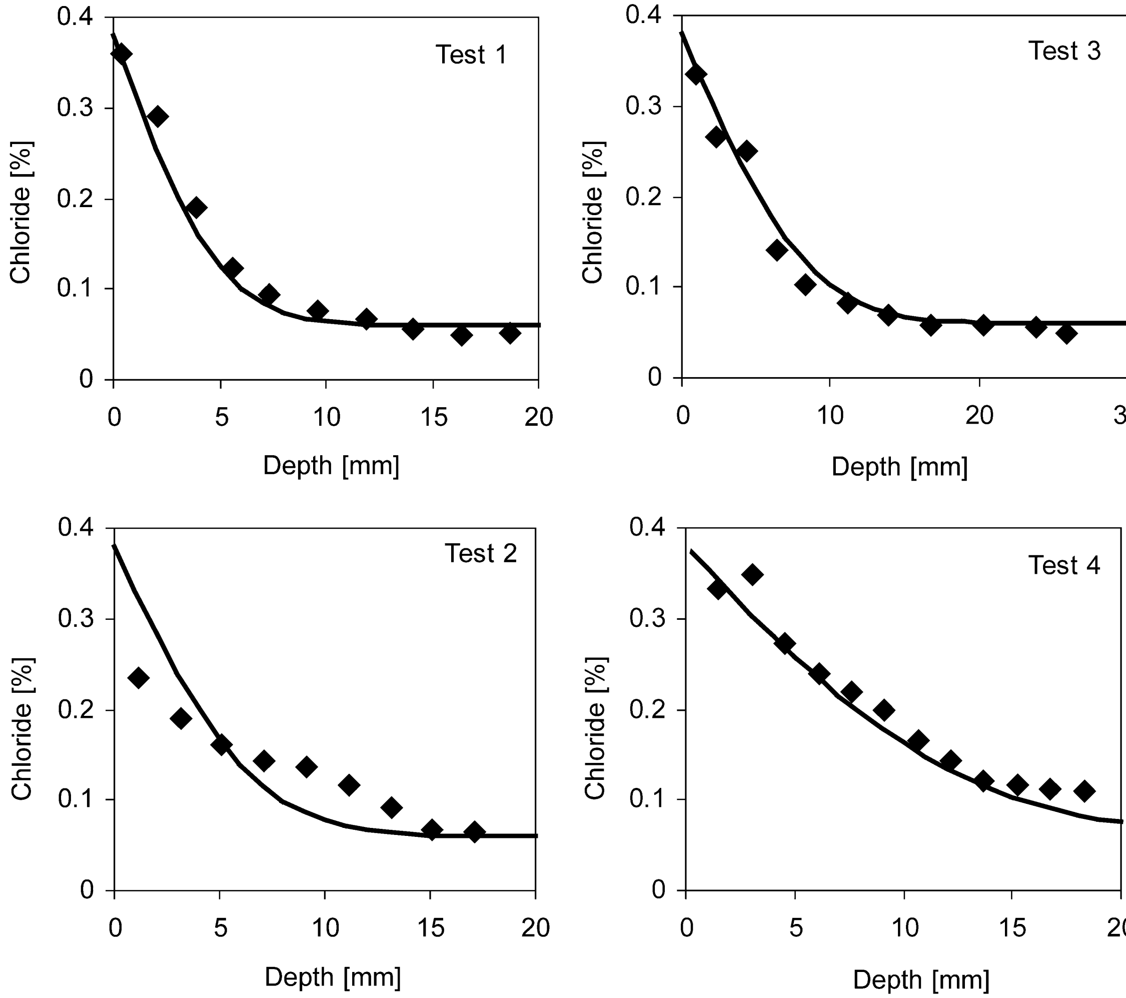

Fig. 5. 56% Fly ash bulk diffusion results—simulated and experimental. Test numbers refer to Table 3.

ted at their effective age according to Eq. (8)) and the diffusion coefficient as a function of age according to Eq. (2) is shown in Fig. 2 for the three concretes.

In addition, the predicted diffusion parameters (D_{28} and m) were used to simulate the diffusion tests conducted and a comparison of the experimental profiles and the predicted profiles is shown in Fig. 3 for the control concrete, in Fig. 4 for the 25% fly ash concrete and in Fig. 5 for the 56% fly ash concrete. For the control concrete, a surface concentration of 0.45% was assumed; for the 25% fly ash concrete, a surface concentration of 0.60% was assumed; and for the 56% fly ash concrete, a surface concentration of 0.38% was assumed. These values were selected based upon the surface concentrations of all four profiles for each concrete. While there are some data in the literature to indicate that the surface chloride concentration will increase with time [7,10], there were insufficient data available to establish the time dependence of the surface concentration for these concrete mixtures and exposure conditions. A constant surface concentration was thus assumed. In all cases, a background chloride concentration of 0.06% was assumed. There is a generally good agreement between the model predictions using the determined parameters and the experimental data, with much of the discrepancy likely attributable to differences between the assumed surface chloride concentration and the actual surface concentration.

7. Conclusions

A technique for evaluating diffusion tests for establishing m-values and reference diffusion values is reported. This technique is simple enough that it can be done quickly using any commercial spreadsheet package. While it is iterative, it normally closes in four or five iterations. It is shown that the use of a fixed point in the bulk diffusion test as the assigned age (e.g. end or middle of exposure period) can introduce significant errors in establishing these reference values. While the magnitude and the direction of these values depend upon the exact parameters of the tests used to establish the values, for the type of tests that are often used there is a tendency to underestimate the m-values. This can lead to a significant underestimation of the service life of structures. This effect is heightened for concrete types that change more rapidly with time. The use of this procedure to evaluate the characteristics of four laboratory concretes produced diffusion coefficients (D_{28} and m) which were able to predict the profiles of the bulk diffusion tests.

Nomenclature

C chloride concentration
C_0 chloride surface concentration
D diffusion coefficient
D_{AVG} average diffusion coefficient over test period
D_{ref} diffusion coefficient at reference age
m coefficient controlling rate of change of diffusion coefficient
t time or age
t_1 age at start of test
t_2 age at end of test
t_{eff} effective age of average diffusion coefficient from test
t_{ref} reference age
x depth

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