

Time-Dependent Diffusivities: Possible Misinterpretation due to Spatial Dependence

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Reprinted from Testing and Modelling the Chloride Ingress into Concrete. Proceedings. 2nd International RILEM Workshop. September 11-12, 2000, Paris, France, 225-233 pp, 2000.

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TIME-DEPENDENT DIFFUSIVITIES: POSSIBLE MISINTERPREATION DUE TO SPATIAL DEPENDENCE

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Abstract

To accurately predict the service life of a reinforced concrete structure exposed to chloride ions, it is necessary to estimate the temporal dependence of the diffusivity coefficient. Due to continued hydration of the cement, etc., the diffusivity of the concrete can vary considerably with time. Conventionally, a power law function is used to describe the relationship between diffusivity and time. Care must be taken in using this approach, because the fitted power law coefficient often results in diffusion coefficients which become extremely small at long times and may result in predicted service lives far larger than those actually achievable by concrete in the field. One possible reason for these "high" power law coefficients may be a misinterpretation of the field concrete cores' chloride profiles. The obtained profiles are typically fitted to a function determined by Fick's second law, where D , the determined diffusion coefficient, is assumed to be a function of time only. In fact, for most field concrete, D is spatially dependent as well, with the exposed surface of the concrete having a diffusion coefficient substantially different from that of its interior. In this paper, it will be demonstrated that when the diffusivity of the surface concrete exceeds that of the interior concrete, the conventional analysis may predict a power law type behavior for D vs. time when, in fact, none may exist.

1. Introduction

For many field concretes, one key to making an accurate prediction of the service life is having an accurate estimate (current and future) of the resistance the concrete offers to the diffusion of deleterious ions such as chlorides and sulfates [1]. In the past, a constant value for the chloride ion diffusivity, D , was often assumed and Fick's 2nd law applied for predicting the ingress of chloride ions with time, and the time needed for the

concentration at the depth of the steel reinforcement to reach the critical threshold value necessary to initiate corrosion [1]. As more data has become available from field studies, it has been recognized that D varies both spatially [2] and temporally [3,4]. While numerous authors [3-6] have quantified the "apparent" temporal variation, the spatial variation has received considerably less attention. In this paper, it will be shown that, as alluded to by Higgins [7], ignoring the spatial variation can result in significant overestimates of the reduction in D with time, which will result in equivalent overestimates in the service life of the field concrete.

2. Theory

A convenient starting point for this analysis is Fick's 2nd law for diffusion [8]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \quad (1)$$

which relates the temporal variation in concentration, C, to the local spatial variation via the diffusion coefficient, D. When D varies with time, t, usually, a power law function is used to describe this variation [3,4]:

$$D = D_i * t^{-m} \quad (2)$$

where D_i and m are the two fitting parameters used to describe the temporal variation. Mangat and Molloy [4] have derived the following solution to Fick's 2nd law when D varies with time as shown in the above equation:

$$C = C_0 * \left\{ 1 - \operatorname{erf} \left[\frac{x}{2 \sqrt{\frac{D_i t^{(1-m)}}{1-m}}} \right] \right\} = C_0 * \left\{ 1 - \operatorname{erf} \left[\frac{x}{2 \sqrt{D_A t}} \right] \right\} \quad (3)$$

with

$$D_A = \frac{D_i}{(1-m)} t^{-m} \quad (4)$$

where C_0 is the chloride ion concentration at the concrete surface, C is the concentration at depth x and time t, D_A is an apparent diffusivity, and it is assumed that the initial chloride ion concentration within the concrete is 0. The above solution is only valid for values of $0 \leq m < 1$ [9]. Values of $m > 1$ can not be used with the error function analytical solution shown above [9], as they would imply that the ingressing chloride ion front would actually recede with time instead of progressing. Despite this restriction, such values of m have been reported by several authors, including values of 1.1 to 1.3 for concretes with mineral admixtures [4] and a value of 1.2 for a concrete containing slag [5]. In the latter case, Thomas and Bamforth employed a finite difference solution to Fick's 2nd law, which makes full use of the time-dependent diffusion coefficients [5].

By this method, values of $m > 1$ can be used but result in very slow chloride ingress. Other researchers [6,9] have recognized and published these limitations on the “physically” allowable values of m when the analytical solution is employed.

When contrasted with the conventional solution of Fick’s 2nd law, with a time and spatially invariant D , one finds that the above solution, for $0 \leq m < 1$, is comparable, with an apparent diffusivity, D_A , as shown in Equation 4. This means that the chloride ion penetration profiles obtained after various exposure times, can be analyzed using a Fick’s 2nd law analysis, and the resulting values of D_A can then be regressed vs. t to determine D_i and m based on the equation:

$$\log(D_A) = \log\left[\frac{D_i}{(1-m)}\right] - m \log(t) \quad (5)$$

Some authors [4] using these techniques mistakenly omit the $(1-m)$ term from the regression, so that the reported values of D_i are greater than the true values, and would need to be multiplied by $(1-m)$ to obtain the true D_i values.

In addition to these commonly observed mistakes in applying a time variant D , an additional consideration is the usually ignored spatial variation in D . Higgins [7] has shown that the top 10 mm of a cast concrete has a significantly higher cement content than the “bulk” interior concrete, in agreement with the previous measurements of Crumbie et al. [10]. Due to this higher cement content and possibly inadequate curing, D for this “surface” layer could be significantly higher than for the bulk interior concrete. Regardless of the applied curing, the outer surface layer of concrete elements will be exposed to a wider extreme of both temperatures and moisture cycles than the interior sections. The depth of this spatial effect will vary with the quality of the concrete; more porous concretes will have a larger affected depth [11]. Carbonation of the outer surface will also affect the pore structure, rate of chloride penetration, and potential for chloride binding. As will be shown in the results that follow, such a spatial dependence in D could be easily misinterpreted as a diffusion coefficient that decreases with exposure time. While this paper considers only transport due to diffusion, any sorption (due to hydration of the cement [12]) of the chloride-containing exterior solution into the concrete would only further exacerbate this misinterpretation.

In his original work on developing the rapid chloride permeability test (RCPT) for concrete [13], Whiting showed that thinner samples exhibited a somewhat higher conductivity than thicker ones. Some of this effect could be due to temperature effects present in the RCPT testing protocol [13]. But, the differences could also be due to the top surface layer (5 mm to 10 mm) of the concrete having a slightly higher diffusion coefficient due to the percolation of interfacial transition zones directly in contact with the top surface, etc. Improper curing will, of course, only exacerbate this situation. While little field data exist on the variation of D with depth from the exposed concrete surface, measurements of sorptivity have indeed indicated that, depending on curing, etc., the sorption coefficients of the “outer skin” of the concrete may be up to a factor of

six greater than those of the interior concrete [11], with values of about two being typically encountered [14-16].

3. Computer Simulation Results and Discussion

Simulations were conducted using a finite difference code provided in the Computer Integrated Knowledge System (CIKS) developed by Bentz et al. and available over the Internet [17]. For these simulations, no binding was considered and the surface concentration of the chloride ions was set at 4.0 M^1 (moles/liter). The thickness of the concrete slab was set at 0.2475 m. The bulk concrete was assigned a chloride ion diffusivity of $1.0 \times 10^{-12} \text{ m}^2/\text{s}$. Conversely, the top 10 mm of the concrete was assigned a diffusivity value ten times greater, $1.0 \times 10^{-11} \text{ m}^2/\text{s}$. A factor of ten probably represents a reasonable upper bound on the ratio of surface layer D_s to bulk D_B and may thus represent a worst case scenario. To examine only the effects of this spatial dependence, both D values were considered to be invariant with time, although in practice some true reduction with time due to continued hydration, etc. would be expected. The resultant chloride profiles were computed for the following exposure times: 30 d, 90 d, 180 d, and (1, 2, 5, 10, 20, and 50) years. Figure 1 shows a selection of the resultant profiles along with the solutions based on the analytical equations developed by Carslaw and Jaeger [18] and adapted to diffusion in concrete by Andrade et al. [2]. The agreement between the finite difference solutions (solid lines in Fig. 1) and their analytical counterparts (data points in Fig. 1) is basically exact.

Next, to provide a true comparison with the practices typically employed in the field, the resultant profiles were "averaged" into 10 mm slices (the spatial resolution typically employed for powder sampling in the field). Selected averaged profiles, along with the corresponding fits based on a simple application of Fick's second law are provided in Figure 2. The fits are not exact, but are no worse than those typically found with field data [4,5]. As is typical for such an analysis, both C_0 and D were allowed to vary for each separate fitted profile. The results of fitting Fick's 2nd law to each of the simulated averaged profiles are provided in Table 1. The trend in C_0 , increasing to a maximum at intermediate exposure times and then decreasing, is consistent with the experimental results of Mangat and Molloy [4] and of Thomas and Bamforth [5].

Figure 3 shows a log-log plot of D_A vs. time for the values provided in Table 1. As can be seen in the figure, a linear fit to the log-transformed data (as shown in Equation 5) seems quite reasonable. Even though D has no temporal dependence in this simulation, our analysis (based on fitting only the first ten years of simulation data) indicates that one could easily characterize D by $D_i = (3.85 \times 10^{-10}) \cdot t^{-0.3095} \text{ m}^2/\text{s}$, where t is in units of seconds. Thus, because the surface layer (with a higher D) is sampled earlier in time

¹ The accepted SI unit of concentration, mol/L, has been represented by the symbol M [small capital M] in order to conform to the conventions of this proceedings.

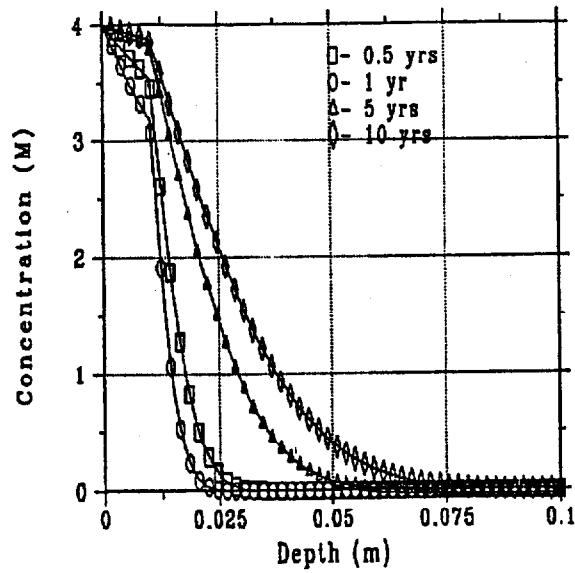


Figure 1: Concentration profiles vs. time from finite difference simulation (data points) and analytical solution (solid lines).

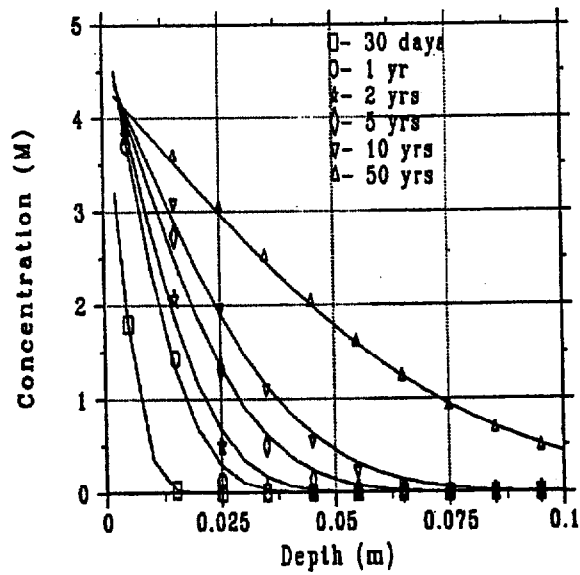


Figure 2: "Averaged" concentration profiles vs. time, along with the fits obtained by fitting a Fick's 2nd law error function solution.

Table 1. Fitted parameters (Fick's 2nd law) vs. exposure time

Exposure time	C_0 (M)	D_A^* (10^{-12}) m ² /s
30 days	4.9154±0.0002 [^]	5.8889±0.0003
90 days	5.703±0.007	3.91±0.01
180 days	5.631±0.033	3.23±0.05
1 year	5.327±0.081	2.68±0.10
2 years	5.087±0.101	2.16±0.11
5 years	4.839±0.087	1.67±0.08
10 years	4.677±0.067	1.44±0.05
20 years	4.535±0.048	1.28±0.03
50 years	4.379±0.029	1.16±0.02

[^] indicates standard deviation in parameter estimate.

than the lower D interior, a simple two-layer spatially dependent D can be easily misinterpreted as a temporal dependence. This simple example clearly illustrates the need to characterize both the spatial and temporal dependence of D for a field concrete in order to perform an accurate analysis. From a practical standpoint, analyzing the spatial variation in cement content as a function of distance from the cast concrete surface, and increasing the spatial resolution of the powder analysis technique (from 10 mm to 2 mm for example) would both be beneficial in separating spatial from temporal effects. The method of inverse cores [19] also allows a more direct evaluation of the current D value of the interior concrete.

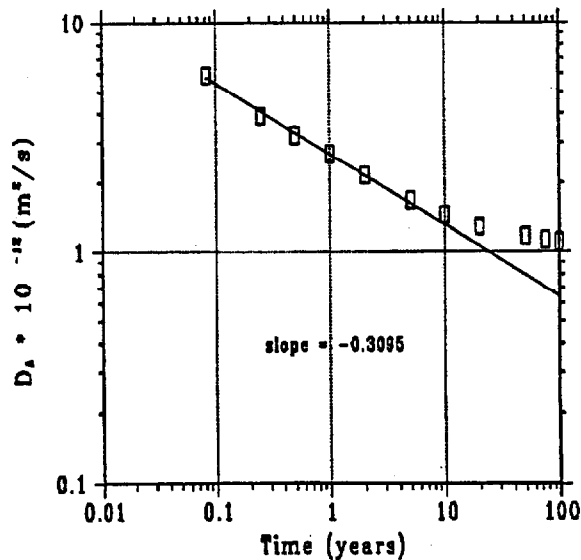


Figure 3: Apparent diffusivity vs. time, along with the fitted power law relationship.

To further extend this example, one can calculate a projected service life under two circumstances: the “true” service life with a spatially dependent D value, and the service life computed using the incorrect assumption that D is only temporally dependent. For this calculation, it is assumed that the steel reinforcement is at a depth of 50 mm in the concrete. Furthermore, for the case of a temporally dependent D , values of both 5.17 M (the average of the values in Table 1 for times less than or equal to ten years) and 4.0 M (the true value) were used for C_0 . Figure 4 shows the predicted concentrations at the depth of the reinforcement as a function of exposure time. Here, the curves are fairly similar for lower concentrations, with the time-dependent analysis with $C_0=5.17$ M slightly underestimating the “true” service life. The higher concentrations predicted by the time-dependent D analysis are consistent with the fits of Fick’s 2nd law slightly overestimating the profile data shown in Figure 2, at a depth of 0.05 m. However, for higher “threshold” concentrations (e.g., > 0.5 M), the service lives predicted using both time-dependent D analyses are significantly greater than the actual service life based on the true spatial dependence. For example, for a true service life of 50 years, the time-dependent D analyses would result in predicted values of about 65 years ($C_0=5.17$ M) and over 100 years ($C_0=4.0$ M), both significant overestimates. This reinforces the need to consider both spatial and temporal dependence when trying to execute a detailed service life prediction, especially when the analysis is being used to try to justify service lives of 50 years or more.

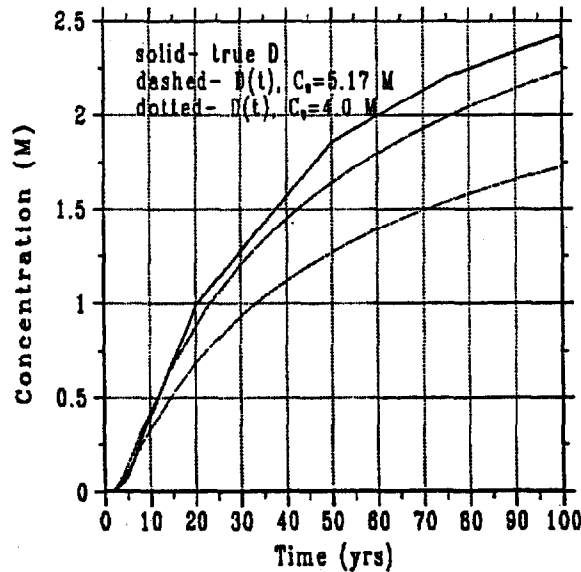


Figure 4: Concentration at rebar depth (50 mm) vs. time for the three cases examined in this study. Line types from top to bottom are solid, dashed, and dotted.

4. Conclusions

It has been shown that when applying a conventional time-dependent D analysis to chloride ion profiles, relevant values of the power law exponent, m, are limited to the range [0,1] when the analytical solutions are to be used. A simple two-layer spatially dependent D can be easily misinterpreted as a temporal dependence due to the fact that the usually higher D surface layer is "sampled" earlier in time than the lower D interior. Ignoring this spatial dependence could lead to severe overestimates in the predicted service lives for reinforced concrete structures.

5. Acknowledgments

Partial funding for this research was provided by the NIST Partnership for High Performance Concrete Technology program.

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