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Evidence of variable diffusivity of ions in saturated cementitious materials

Susanta Chatterji *

Carl Bernhardsvej 13B, St. 4, 1817 Frederiksberg C, Denmark

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Abstract

Evidence of variable diffusivity of ions, in both the steady and transient states, in cementitious materials are presented. In steady-state diffusion, the diffusivity of an ion, D, is related to the square root of its concentration up to at least about 0.4M, if not higher. In transient-state diffusion, the relation of D with concentration is more complicated. Some of these complicating factors have been delineated. Ion profiles in cementitious materials can be analyzed without the simplifying assumption of a single diffusivity coefficient. © 1999 Elsevier Science Ltd. All rights reserved.

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Diffusion of ions in cementitious materials plays important roles in their durability and in their use as diffusion barriers in the storage of waste radioactive materials. In these processes, diffusion takes place through a solution. It is customary to treat diffusivity of an ion as being independent of its local concentration in its solution. In a recent paper, attention was drawn to the fact that empirical analyses of reported chloride profile data in concrete samples indicate a variable diffusivity for the chloride ion [1]. Theoretical reasons for concentration-dependent diffusivity of ions were presented [2,3]. In this paper, further evidence, by way of analyses of recently reported data, of variable diffusivity of ions in cementitious materials will be presented for both steady-state and transient-state diffusion.

1. Theoretical background

Before presentation of the evidence, a short review of the theoretical background is given. Combining Nernst's conductivity equation with Kohlrausch's conductivity results, one can easily derive Eq. (1) [2,3]:

$$D_c = D_0 - k_c c^n \qquad (1)$$

where D_c and D_0 are the diffusivity at ion concentrations of c and 0, respectively (however, they include the pore characteristics of the matrix), k_c is a parameter that also includes the pore characteristics of the matrix, and n is a constant. For simple monovalent ions such as Cl^-, $n = 0.5$ is within the concentration range of up to about 0.7 M. From Kohlrausch's results, one also can predict that above about 1 M concentration, the change in diffusivity with concentration will be small. This means that if measured diffusivity at different ionic concentrations is plotted against the square root of the relevant concentrations, one first observes a linear drop and then a flattening of the curve.

There is more to diffusion of ion than its concentration dependence. It is known that halide ions have higher diffusivity in cementitious materials than alkali ions, and the diffusivity of a halide ion is higher with a divalent counter-ion, e.g., Ca^{2+}, than with a monovalent counter-ion, e.g., K^+ [4,5]. Due to the excess transport of halide ions into a cementitious material, part of $Ca(OH)_2$ dissolves, Ca^{2+} ions move with halide ions, and OH^- ions leach out to the diffusant solution [3]. This dissolution of calcium hydroxide coarsens and shortens the diffusion path and increases diffusivity of all ions. Against this background, the evidence of variable ionic diffusivity is presented.

1.1. Steady-state diffusion

Steady-state diffusion studies generally are carried out using diffusion cells, in which comparatively thin cementitious barriers are inserted between moderately concentrated and extremely dilute solutions of diffusants. During the course of investigation, the barriers become fully saturated even if they were not so at the start. Furthermore, there is no accumulation of ion within the barriers; therefore, it is not possible to determine if diffusivity changes along the length of the barriers. In these cases, the concentration difference varies over a considerable range. Eq. (1) is strictly valid

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* Tel.: 45-33-21-03-32; Fax: 45-33-21-03-32.

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over a narrow concentration range. To apply Eq. (1) to steady-state experiments, it has to be averaged over the concentration range of the experiments (L.-O. Nilsson, personal communication, 1996). For mono-monovalent diffusants, this gives Eq. (2):

$$D_M(C) = \frac{1}{C}\int_0^c D\,dc = D_0 - \frac{2}{3}k_{\hat{c}}\sqrt{C} \tag{2}$$

where $D_M(C)$ is the measured diffusivity at concentration C.

Recently, Bigas et al. [6] reported results of a steady-state chloride diffusion study in cement mortar samples using NaCl solutions of 0.01709, 0.0855, 0.1709, 0.3445, and 2.89 M concentrations. Fig. 1 shows the diffusivity values plotted against the square roots of the relevant molar concentrations. Fig.1 also shows fitting of the first four diffusivity data to Eq. (2); the last one is beyond the range of Eq. (2). As expected, Fig. 1 shows an inflection in the diffusion-concentration curve above 0.4 M concentration. With the present data it is not possible to be more precise. Fig. 1 also shows that the first four measured diffusivity data could be fitted to Eq. (2) with a regression coefficient r of 0.999. The steady-state diffusivity of ions in cementitious materials is concentration dependent. Similar results were reported for the steady-state diffusion of chloride ions in clay plugs [7]. It was shown in the same study that, in contradiction to a generally held belief, chloride concentration profiles are not linear within the clay plugs [7].

1.2. Transient-state diffusion

Transient-state diffusion studies are generally carried out on long prisms. Except for one face, all other faces of the prisms are covered with a water-impermeable material. The coated prisms then are stored in diffusant solution, e.g., NaCl solution of known, rather high concentration. At the end of the experimental time, materials are sampled from different depths of the prisms and their chloride concentrations are determined. From the chloride profiles, the diffusivity of chloride ion is determined using relevant solution of Fick's second law with a further simplifying assumption of a single diffusion coefficient.

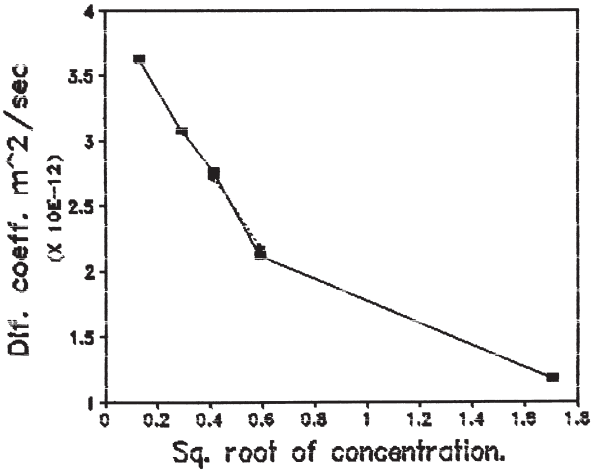

Fig. 1. Variation of diffusion coefficient with concentration.

There are some difference between steady-state and transient-state diffusion processes. In transient-state diffusion, chloride ions accumulate within the prisms. Due to their higher diffusivity, chloride ions penetrate deeper in prisms than alkali ions, i.e., the composition of the diffusing co-ion mix varies over the depth of the prisms, with the attendant variation of chloride ion diffusivity. Furthermore, in this case the dissolution of $Ca(OH)_2$ is expected to be higher near the open face than in the interior. All things taken together it is expected that concentration-dependent diffusivity will be less conspicuous.

Fick's second law of diffusion could be written as Eq. (3) without any loss of generality:

$$\frac{dC}{dt} = \frac{d}{dx}\left[D(C)\frac{dC}{dx}\right] \tag{3}$$

where D(C) is the concentration-dependent diffusivity. Recently, Nagesh and Bhattacharjee [8] reported that by applying Boltzmann's transformation, $\phi = x/\sqrt{t}$, Eq. (3) can be reduced to a ordinary differential equation, which can then be solved by finite difference technique (for further details of this technique, see Nagesh and Bhattacharjee [8]). The transformed equation becomes Eq. (4), with boundary conditions of $\phi = \infty$ and $C = C_1$, the initial free chloride concentration in the sample:

$$\frac{d}{d\phi}\left[D(C)\frac{dC}{d\phi}\right] + \left[\frac{\phi}{2}\frac{dC}{d\phi}\right] = 0. \tag{4}$$

The finite difference form of Eq. (4) between ith and (i − 2)th data points may be written as Eq. (5):

$$\frac{1}{\Delta\phi}\left[\left\{D(C)\frac{dC}{d\phi}\right\}_i - \left\{D(C)\frac{dC}{d\phi}\right\}_{(i-2)}\right] =$$

$$\frac{1}{2}\phi_{(i-1)}(C_i - C_{(i-2)})\frac{1}{\delta\phi}. \tag{5}$$

On rearrangement one obtains Eq. (6):

$$\{D(C)\}_i = \frac{\left[\left\{D(C)\frac{dC}{d\phi}\right\}_{(i-2)} - \frac{1}{2}\phi_{(i-1)}(C_i - C_{(i-2)})\right]}{\left\{\frac{dC}{d\phi}\right\}_i}. \tag{6}$$

Thus, from a plot of ϕ vs. C, D(C) at i^{th} data point can be obtained if D(C) and $dC/d\phi$ at $(i - 2)^{th}$ data point are known. Considering the boundary condition at $\phi = \infty$, $C = C_1$, and $dC/d\phi = 0$, $D(C)_3$ may be estimated by Eq. (7)

$$\{D(C)\}_3 = \frac{\left[\frac{\phi_2}{2}(C_3 - C_1)\right]}{\left\{\frac{dC}{d\phi}\right\}_3} \qquad (7)$$

where node 1 represents the boundary $\phi = \infty$. D(C) for other data points may be obtained by repeated application of Eq. (6).

1.2.1. Analysis of a synthetic ion profile

This step was undertaken to show that the technique mentioned could also be used to analyze an ion profile with a single diffusion coefficient. A synthetic ion profile was constructed using the error function, a surface concentration of 1M, and a single diffusion coefficient of 1.17×10^{-11}. The calculated diffusion coefficients at different data points are shown in Fig. 2. Calculated point by point, D(C) values (curve 1) show fluctuation around 1.19×10^{-11} without any trend. However, a rolling average of two consecutive D(C) values (curve 2) removes most of the fluctuations and the average becomes 1.18×10^{-11}. This rolling average modification was used in subsequent analyses of ion profiles in cementitious materials.

1.2.2. Analyses of ion profiles in cement paste

Recently Sergi et al. [9] published chloride and hydroxyl ion profiles, determined on expressed pore solutions, in hardened cement paste. They analyzed their profile on the assumption of a single diffusivity constant for each ion. The original data are shown in Table 1. An examination of the table shows that there are some anomalies in the data set; the most obvious of these anomalies are underlined. In the following analyses, the profiles have been used without any correction of those anomalies. The effect of anomalies is to introduce more scatter in the calculated D(C) values than otherwise would be present.

Table 1
Hydroxyl and chloride ion profiles

Depth (cm)	C_{OH^-} (M)	C_{Cl^-} (M)
0.175	0.104	0.991
0.35	0.112	0.838
0.70	0.134	0.670
1.05	0.171	0.572
1.40	0.219	0.366
1.75	0.257	0.292
2.10	0.274	0.135
2.45	0.319	0.059
2.80	0.335	0.039
3.15	0.351	0.024
3.50	0.365	0.014
3.85	0.355	0.015
4.20	0.375	0.007
4.55	0.388	0.002
4.90	0.384	0.001

1.2.3. Chloride ion profile

Fig. 3 shows D(C) values of the point-by-point analysis (curve 1) and the rolling average (curve 2) of chloride ion concentration profile. From Fig. 3 it can be seen that both sets of D(C) values start high at the deeper end then decrease to a minima at about 0.02 m and then slowly increase toward the open face. From Fig. 3 and Table 1 it may be postulated that high D(C) values at the deeper end are due to low concentrations of chloride ion. Increase in D(C) values near the open face could not be ascribed to any decrease in chloride ion concentration; however, it may be ascribed to expected dissolution of $Ca(OH)_2$ from the paste and consequent coarsening of pores.

1.2.4. Hydroxyl ion profile

Fig. 4 shows both point-by-point (curve 1) and rolling average (curve 2) D(C) values. In this case, the direction of diffusion is opposite to that of chloride ion. The diffusivity of hydroxyl ion increase from low values at the deeper end to higher values toward the open face, i.e., they increase with decreasing concentration of hydroxyl ion in the paste. However, dissolution of $Ca(OH)_2$ and coarsening of pores also play their parts.

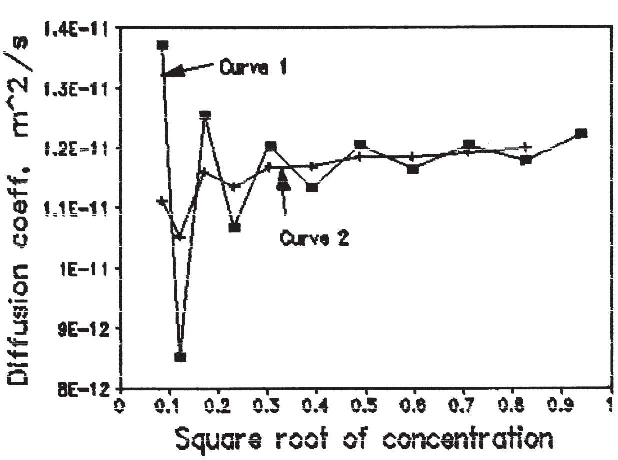

Fig. 2. Analysis of a synthetic ion profile.

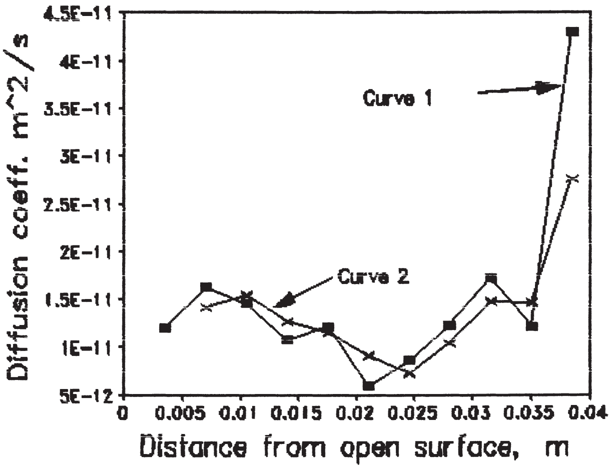

Fig. 3. Analysis of a chloride ion profile.

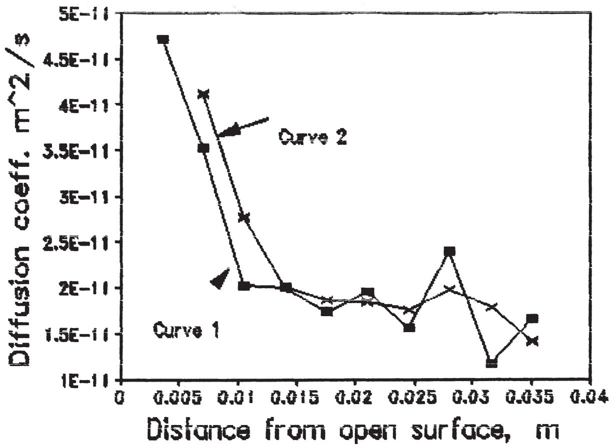

Fig. 4. Analysis of an hydroxyl ion profile.

2. Conclusions

It could be said that analyses of published ion profiles strongly indicate a variable diffusivity of both chloride and hydroxyl ions in cementitious materials. In the case of transient-state diffusion, a dissolution of $Ca(OH)_2$ from the paste and consequent coarsening of pores also are indicated. It has been shown that ion profiles can be analyzed without the simplifying assumption of a single diffusivity constant. The result of the analysis itself indicates if a single or variable diffusivity constant was operative in the diffusion.

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