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A REPLY TO A DISCUSSION BY S. CHATTERJI OF THE PAPER "A BOLTZMANN-MATANO ANALYSIS OF CHLORIDE DIFFUSION"*

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Chatterji's discussion focused on three major issues: the applicability of Fick's law for diffusion into concrete, the Boltzmann-Matano methodology, and the experimental data.

Fick's Law

Chatterji reviewed the applicability of Fick's laws for cementitious systems (1–5) and proposed that the Nernst-Planck equation was more suitable,

$$J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x} \qquad [1]$$

where, $J_j(x)$ is the flux of species j at distance x from the surface, D_j is the diffusivity, $\partial C_j(x)/\partial x$ is the concentration gradient at distance x, $\partial \phi(x)/\partial x$ is the potential gradient, F is the Faraday constant, z_j and C_j are the charge and concentration. The application of Eq.[1] to cementitious systems is complicated by a number of factors. These include the following:

- Activity coefficients are assumed to be compositionally independent which is strictly valid for ideal Raoultian or Henrian solutions. The solutions to which concrete is exposed and porewater are highly non-ideal multicomponent solutions where neither Raoult's or Henry's law holds.
- The Nernst-Einstein relationship between mobility and diffusivity implicit in Eq.[1] has not been demonstrated for multicomponent solutions like porewater.
- Eq.[1] does not incorporate non-steady state diffusion.
- The potential gradient is almost impossible to determine particularly for field exposure conditions or thick laboratory specimens.

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Therefore, Eq.[1] is not easily applied to any real concrete system without some very compromising simplifications. However, I do encourage Chatterji to develop Eq.[1] for application to real concretes.

Chatterji used a Kohlrausch equation to explain diffusivity-concentration dependence.

$$D_i = D_o - A\sqrt{C_i} \qquad [2]$$

On the basis of extremely limited experimental data, Chatterji concluded that Eq.[2] applied to cementitious systems (3, 4). In addition to the problem of chloride binding, Eq.[2] represents a limiting law which is strictly valid for dilute strongly dissociated single solute solutions. Porewater is a complex multicomponent electrolyte (6).

Boltzmann-Matano Methodology

Contrary to Chatterji's assertion, the Boltzmann-Matano methodology is not a backward fitting function. In fact, diffusivities can be determined directly from the graphical integration and differentiation of,

$$D(C_*) = \frac{1}{2t} \cdot \left(\frac{dx}{dC}\right)_{C_*} \cdot \int_0^{C_*} x \cdot dC \qquad [3]$$

For example, the value of D at $C=C_o$ is readily calculated by measuring the required area and the reciprocal of the slope. It is true, that the error in the calculated value of D(C*) is largest at the ends of the curve where C/C_o approaches one or zero, since in these regions the integral is small and dx/dc is large. To minimize the errors and to automate the procedure, the data was fitted to,

$$C = A \cdot e^{-B/x} \qquad [4]$$

where x has the units of cm. Eq.[4] is the correct equation not Chatterji's Eq.[2]. Furthermore, for the integration, the tails of the curves were truncated at $C/C_o=0.0001$. For each bath and curing condition and for each time, the experimental data was fitted to Eq.[4]. There is a unique value of B for each condition. Since B varies there is no logical contradiction with respect to the Boltzmann-Matano methodology.

Experimental Data

The reported data for exposure to Bath 2 for 12 and 18 months after 3 days hydration is correct. In general, the relationship between concentration and depth of penetration is not linear. In particular, for the 24 month data Chatterji's correlation coefficients of 0.88 and 0.94 do not indicate a linear fit.

The penetration of chloride in this experiment is a complicated process because of the composition of the salt solution. For the longer hydration times, it is true that one expects a more impermeable structure, but for the longer hydration times, there is a increase in $Ca(OH)_2$ content. The $Ca(OH)_2$ is particularly susceptible to expansive Mg^{2+} attack which allows penetration of chloride. The competing hydration and Mg^{2+} attack mechanisms are the probable source of some of the seemingly anomalous chloride penetration data.

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