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A REPLY TO A DISCUSSION BY B. BATCHELOR OF THE PAPER "ON THE RELATIONSHIP BETWEEN THE FORMATION FACTOR AND PROPAN-2-OL DIFFUSIVITY IN MORTARS"*

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Essentially, the discussion criticized the propan-2-ol diffusivity technique. However, independent experimental evidence indicates that counter-diffusion of propan-2-ol into water-saturated cement yields diffusion coefficients similar to those for chloride diffusion. For cement pastes with w/c = 0.5, Feldman (1) reported a 4.2×10^{-12} m^{-2} s^{-1} propan-2-ol diffusivity whereas Page and co-workers (2) reported a 4.5×10^{-12} m^{-2} s^{-1} effective chloride diffusivity. Further, propan-2-ol diffusivities are in the same range as values obtained for ions such as Na^+, Cl^-, I^-, and Cs^+ diffusing through water-saturated cement paste (3). The latter diffusivities were determined with transient and steady state methods. Lastly, it is unlikely that propan-2-ol diffusivities have been compromised by convection due to the presence of cracks because cracked specimens were rejected prior to the experiment. Further, all specimens were inspected at the conclusion of the experiment. None exhibited any evidence of cracking.

Batchelor does not assess the shortcomings of the conductivity method to determine diffusivities. The basis of the conductivity technique is a simplified Nernst-Einstein equation,

$$D = M \cdot R \cdot T \tag{1}$$

where, D is the diffusivity, M is the mobility, R is the universal gas constant and T is the temperature. It is clear that diffusivities calculated with Eq.1 do not include any contributions from uncharged ion pairs. Further, for complex solutions like porewater, Eq.1 must incorporate corrections for non-ideal behavior. In this case, Eq.1 is written as,

$$D = M \cdot R \cdot T \left(1 + \frac{\partial \ln \gamma_j}{\partial X_j} \right) \tag{2}$$

where, γ_j is the activity coefficient and X_j is the concentration of the species *j*. The activity coefficients will vary with concentration and are influenced by the presence of other species. Even in dilute solutions where Henrian behavior is expected, the second effect may be

*CCR 26(9), 1301-1306 (1996).

significant. As an example, consider solutes *j*, *k*, and *l* dissolved in water. Then, the activity coefficient of *j* can be written as,

$$\ln \gamma_j = \ln \gamma_j^j + \ln \gamma_j^k + \ln \gamma_j^l \quad (3)$$

where, γ_j^j is the activity coefficient of j in the binary (j-water) solution at mole fraction Xj. γ_j^k and γ_j^l represent the effects of the solutes *k* and *l* on γ_j (which is the activity coefficient of *j* in the multicomponent solution). Another complication for the conductivity method is that the expressed pore solution does not represent the true in situ pore solution. As pressure is applied to the sample, the porewater temperature increases. Consequently, the thermodynamic state and the conductivities of the expressed pore water and the in situ pore water are not the same.

In conclusion, although both the propan-2-ol and conductivity methods have limitations, the propan-2-ol diffusion results are remarkably close to those obtained by steady state and transient techniques. To date, a similar comparison is not available for the conductivity method. Therefore, in this author's opinion, it is valid to evaluate the accuracy of the conductivity method by comparison with results from propan-2-ol diffusion.

Acknowledgment

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