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Discussion

A discussion of the paper "Effect of speciation on the apparent diffusion coefficient in nonreactive porous systems" by K.A. Synder and J. Marchand☆

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It is a very interesting and informative paper. Even with my limited knowledge of ionic diffusion, I think I can follow most of the theoretical side. However, it may be useful to examine the situation from a slightly different point of view to see how much I have understood.

Best way I can start is to take the concrete situation of KI ‖ NaCl system. Fig. 1 depicts the experimental setup used by the authors. The setup is a small-volume closed system. The system is closed in the sense that the total masses of individual ions remained essentially constant throughout the diffusion experimental in spite of their diffusion, in general, from the high to low concentration side. As a thought experiment, the KI ‖ NaCl system may be divided into two subsystems. In one subsystem, KI solution is separated from NaCl solution by a semipermeable barrier. The barrier only allows K^+ and I^- ions to diffuse to NaCl solution. Due to diffusion, two diffusion potentials, $\nabla\psi_{DK}$ and $\nabla\psi_{DI}$, develop across the barrier. In the other subsystem, NaCl solution is similarly separated from KI solution by a semipermeable barrier. In this case also, two diffusion potentials, $\nabla\psi_{DNa}$ and $\nabla\psi_{DCl}$, develop. As the concentrations of all these ions are changing with time in both compartments, all these four potentials are also changing with time. The original KI ‖ NaCl system may be looked up on as two subsystems joined in opposition. The macroscopic diffusion potential across the barrier, at any time, is given by $\sum(\nabla\psi_{Di})_T$ where the subscript T stands for instantaneous time. In this summation, signs of the individual terms have to be taken into account. Only four terms are involved so their combinations could be worked out easily. The net instantaneous macroscopic diffusion potential can be negative, zero or positive or may even be oscillating for any particular ion. This net instantaneous diffusion potential determines the direction of diffusion of that particular ion at the relevant time. If I have understood the authors correctly, this is how they have explained the apparent negative diffusion coefficient of I^- in the system KI ‖ $CaCl_2$ at long time. In that case, one can expect various diffusion effects—both time dependent and time invariant. These are what the authors have got.

However, these effects and calculated counterdiffusion coefficients are relevant only to small-volume, closed and coupled systems. Natural systems are generally large and often open or nearly so, for example, the movement of nutrients from soil to plants. Another example would be the exchange of Cl^- and OH^- ions between seawater and concrete. In this case, both Cl^- and OH^- ion concentrations in seawater remain constant throughout the process. Most of the natural systems are not even coupled. Obviously, these effects and counterdiffusion coefficients are not relevant to most of the natural systems.

If I have misunderstood the authors, then I hope the authors will correct me.

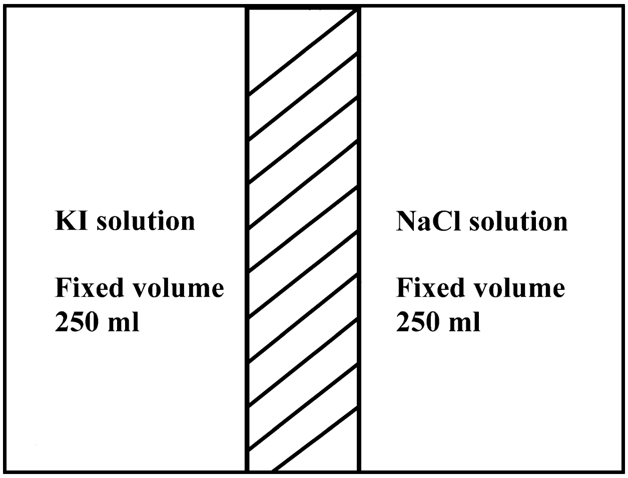

Fig. 1. Diffusion setup used by the authors.

☆ Cem Concr Res 31(2001)1837–1845.

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