

**Reply to the discussion by S. Chatterji of the paper "Effects of  
speciation on the apparent diffusion coefficient in nonreactive  
porous systems"**

by

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## Discussion

Reply to the discussion by S. Chatterji of the paper “Effects of speciation on the apparent diffusion coefficient in nonreactive porous systems”<sup>☆</sup>

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We received two copies of the discussion: one from the journal and a corrected version directly from Dr. Chatterji. Based on the differences between the two versions, we realized that our choice of wording in the paper could be improved upon. While we were careful in the paper to distinguish between a field and a gradient in a field, the reader may have been confused by our use of the word “potential” for both the field quantity and the voltage one would measure across the system. The first has both spatial and temporal dependence, the latter only temporal dependence. This distinction was also obfuscated by our omission of explicit dependence on the equations in an effort to achieve visual clarity.

The electrostatic potential  $\psi$  that arises in diffusive systems is a conservative (scalar) field [1] that varies with both position  $\mathbf{x}$  and time  $t$ :  $\psi(\mathbf{x}, t)$ . (Here, as in the paper, bold typeface is used to denote vector quantities.) The associated electrical (vector) field  $\mathbf{E}$  is the negative gradient [2] of the field:

$$\mathbf{E}(\mathbf{x}, t) = -\nabla\psi(\mathbf{x}, t) \quad (1)$$

Although the scalar potential field  $\psi$  is a macroscopic quantity, it is not measured directly in the laboratory. Rather, one measures differences in the scalar field. The macroscopic change in potential  $\Psi$  (volts in SI, statvolts in cgs, etc.) measured across a specimen of length  $L$  is the integral over the gradient of the scalar field:

$$\Psi = \int_0^L \nabla\psi dx \quad (2)$$

The notation used in the discussion suggests that the reader has inferred that the gradient  $\nabla\psi$  is the voltage drop across

the system and is a single value used in the transport equation. In our effort to achieve brevity, it may not have been clear to the reader that both  $c(\mathbf{x}, t)$  and  $\psi(\mathbf{x}, t)$  are field variables that are solved throughout the entire system.

The question of whether the systems are additive can be answered by studying the source of the scalar field  $\psi$ . Although the paper uses the zero total current condition to determine the (gradient of the) scalar field  $\psi(\mathbf{x}, t)$ , one could alternatively solve for  $\psi$  using Poisson’s equation ( $c$  is charge density,  $F$  is Faraday’s constant and  $z_i$  is the valence of the  $i$ -th species) [1]:

$$\nabla \cdot \mathbf{E} = \frac{4\pi}{F} \sum_i z_i c_i \quad (3)$$

Since the field  $\psi$  is conservative, electrical fields are additive with respect to each ionic species  $i$ :

$$\sum_i \left( \nabla \cdot \mathbf{E}_i = \frac{4\pi}{F} z_i c_i \right) \quad (4)$$

From this, it might be tempting to infer that the KI/NaCl system can be decomposed into separate experiments with the same initial conditions, as Dr. Chatterji has conjectured. One might then assert that, because the fields are additive, the divergences should also be additive:

$$\sum_{i=\text{Na}^+, \text{Cl}^-, \text{K}^+, \text{I}^-} \nabla \cdot \mathbf{E}_i = \sum_{i=\text{Na}^+, \text{Cl}^-} \nabla \cdot \mathbf{E}_i + \sum_{i=\text{K}^+, \text{I}^-} \nabla \cdot \mathbf{E}_i \quad (5)$$

While this equation is still correct, the systems are separable only if each term on the right hand side does not depend upon information about species in the other summation.

To determine whether the terms in Eq. (5) are separable, return to the approach used in the paper for determining the electrical field. Consider the following abbreviated transport equation for the total ionic species flux  $\mathbf{j}_i$ :

$$\mathbf{j}_i = -D_i \nabla c_i - z_i u_i \nabla \psi \quad (6)$$

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The total charge flux (with no external electrical field) must be zero:

$$\sum_i z_i j_i = 0 \quad (7)$$

Substituting Eq. (6) into Eq. (7) and using Eq. (1) solve for the electrical field:

$$\mathbf{E}(\mathbf{x}, t) = \frac{\sum_i z_i D_i \nabla c_i}{\sum_j z_j^2 u_j} \quad (8)$$

From this, one could partially separate the electric fields:

$$\mathbf{E}_i = \frac{z_i D_i \nabla c_i}{\sum_j z_j^2 u_j} \quad (9)$$

Hence, the systems are not completely separable via Eq. (5) because each summation requires information about other species in the denominator. Therefore, the response of the NaCl/KI composite is not the sum of the NaCl and KI systems.

As a concrete demonstration, the systems can be simulated and the equilibrium diffusion potential  $\Psi$  calculated. Using the (1.0 mol/l) NaCl/KI system mentioned in the discussion as an example, the predicted voltage drop  $\Psi$  across the three possible systems are the following:

System	$\Psi$ (mV)

As expected, the NaCl/KI system is not the sum of the other two systems.

By contrast, if the experiment is a migration test and the applied external electrical field  $\mathbf{E}_{\text{ext}}$  is sufficiently strong so that electrical migration overwhelms diffusion, the species flux  $j_i$  is approximately proportional to the external field:

$$\approx z_i u_i \mathbf{E}_{\text{ext}} \quad (10)$$

For a sufficiently large electrical field  $\mathbf{E}_{\text{ext}}$ , the flux of each species is a constant throughout the system. Based on this equation, one might then assert that the systems are additive. This approach assumes that the mobility  $u_i$  is independent of the solution ionic strength. Recent research, however, suggests that the mobility of an ion is measurably dependent on the quantity and type of species present [3] so that systems containing strong electrolytes, which concrete pore solution would qualify as, would no longer be additive. The consequence being that estimations of sample diffusivity based on migration tests must be able to distinguish between

material and chemical influences on the migration of the target ionic species.

Note also that above equations apply, regardless of the volumes on either side of the specimen. Therefore, contrary to the assertion made in Dr. Chatterji's discussion, these effects apply to either finite volume or "natural" systems. Here, a clarification is required. In the discussion, the negative apparent diffusion coefficient is described as "long time" behavior. As explained in the paper, this effect only occurs at intermediate times. At long times, the ion species arrange themselves in such a way as to drive the macroscopic voltage  $\Psi$  to zero. Interestingly, in a "natural" system, as ions attempt to arrange themselves to drive  $\Psi$  to zero, they will be swept away at the boundary. The effect is that the transport of ions across the interface may not occur as one would expect and the system remains eternally coupled. For example, consider a 0.5 mol/l NaCl solution separated from a 0.35 mol/l KOH+0.15 mol/l NaOH solution by a 10-mm thick porous material with formation factor 10 and porosity 0.10. The concentration of the solutions at each boundary is held constant. At intermediate times, the apparent sodium diffusion coefficient becomes less than zero. At long times, the ion concentrations within the interface eventually arrange themselves so that the apparent diffusion coefficient becomes positive. Even at equilibrium, the apparent diffusion coefficient of sodium is almost one half the value expected from Fick's law. This is due to coupling among the various species present.

It was not, nor is not, our intention to suggest that one will see negative apparent diffusion coefficients (of significance) in cementitious systems under field conditions. Rather, our assertion was that the effect of speciation can still be quite significant—more significant, in fact, than concentration. Because the number of species in a cementitious system can be numerous, and since the solution to the complete transport equation can only be solved numerically, one should investigate possible effects before ignoring them.

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