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November 1984

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THERMODYNAMICALLY COUPLED MASS TRANSPORT PROCESSES IN A SATURATED CLAY

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ABSTRACT

Gradients of temperature, pressure, and fluid composition in saturated clays give rise to coupled transport processes (thermal and chemical osmosis, thermal diffusion, ultrafiltration) in addition to the direct processes (advection and diffusion). One-dimensional transport of water and a solute in a saturated clay subjected to mild gradients of temperature and pressure was simulated numerically. When full coupling was accounted for, volume flux (specific discharge) was controlled by thermal osmosis and chemical osmosis. The two coupled fluxes were oppositely directed, producing a point of stagnation within the clay column. Solute flows were dominated by diffusion, chemical osmosis, and thermal osmosis. Chemical osmosis produced a significant flux of solute directed against the gradient of solute concentration; this effect reduced solute concentrations relative to the case without coupling. Predictions of mass transport in clays at nuclear waste repositories could be significantly in error if coupled transport processes are not accounted for.

INTRODUCTION

Saturated clays are expected to be present at nuclear waste repositories, either as components of engineered barriers or as naturally occurring fillings and linings of fractures in surrounding rocks. These materials are known to exhibit the properties of semipermeable membranes [1-7]. In the presence of gradients of temperature, pressure, and fluid composition, thermodynamically coupled transport processes - thermal osmosis, chemical osmosis, ultrafiltration, and thermal diffusion - can occur in saturated clays simultaneously with the direct transport processes - advection and mass diffusion - expressed by Darcy's law and Fick's law.

Using methods of the thermodynamics of irreversible processes, it can be shown [8] that in a semipermeable membrane supporting flow of water plus a single ideal solute the volume flux (specific discharge) is composed of three vectorially additive fluxes. These are a flux driven by the gradient of temperature (thermal osmosis), a flux driven by the gradient of pressure (advection), and a flux driven by the gradient of solute concentration (chemical osmosis). The total flux of solute is composed of six vectorially additive fluxes. Three of these are due to the flux of solute carried by the volume flux. The other three arise from the motion of the solute relative to the motion of water, and consist of additional fluxes driven by the gradient of temperature (thermal diffusion), the gradient of pressure (ultrafiltration), and the gradient of solute concentration (mass diffusion).

A previous paper [8] presented rough calculations of instantaneous fluxes of volume and solute arising from direct and coupled transport processes in near-field regions of nuclear waste repositories, and showed that fluxes due to coupled processes could be significant relative to advective and mass diffusive fluxes. The present paper extends the scope of the previous work by considering the spatial and temporal evolution of fluxes and solute concentrations arising from both coupled and direct processes.

NUMERICAL SIMULATIONS

We are currently developing a numerical simulator of coupled transport processes driven by gradients of temperature, pressure, and composition, based on methods of the thermodynamics of irreversible processes. The present version of the simulator assumes specified constant gradients of temperature and pressure, and solves the nonlinear equation of transport of a single ideal solute either with or without coupling to transport of heat and volume.

Although data relevant to thermal conductivity, permeability, and mass diffusivity of proposed engineered barrier materials are abundant in the literature, data relevant to the coupled processes are scarce. In fact, we have been unable to find a complete set of coupling coefficients for any single material. Therefore, we adopted the following strategy for the simulations reported here.

Published data, from which values of direct and coupling coefficients can be calculated, are available on chemical osmosis, advection, and mass diffusion in bentonite [9], on thermal osmosis and advection in kaolinite [10], and on thermal diffusion in alumina and pelagic clay [11]. We adopted directly the data for bentonite and assumed that a thermal diffusion coefficient characteristic of the pelagic clay would be applicable to bentonite also. We then assumed that the ratio of coefficients of thermal osmosis and advection in bentonite would be identical to the ratio of these coefficients measured in kaolinite, allowing us to estimate a coefficient for thermal osmosis in bentonite. This procedure provided a complete set of direct and coupling coefficients for a single material that, in the strict sense, should not be regarded as bentonite but rather as a hypothetical clay-like material having transport properties that are composites of the properties of bentonite, kaolinite, and a pelagic clay. Values of the coefficients used in the present simulations are listed in Table 1.

Table 1. Values of Transport Coefficients Used in Simulations

Process	Value of coefficient	Associated gradient	Process contributes to flux(es) of:
advection	$2.4 \times 10^{-16} \text{ m}^5/(\text{J}\cdot\text{s})$	pressure	volume, solute
mass diffusion	$6.8 \times 10^{-17} \text{ kg}^2/(\text{m}\cdot\text{J}\cdot\text{s})$	solute concentration	solute
thermal osmosis	$3.8 \times 10^{-10} \text{ m}^2/\text{s}$	temperature	volume, solute
chemical osmosis	$-0.8 \times 10^{-16} \text{ kg}\cdot\text{m}^2/(\text{J}\cdot\text{s})^*$	solute concentration	volume, solute
ultrafiltration	$-0.8 \times 10^{-16} \text{ kg}\cdot\text{m}^2/(\text{J}\cdot\text{s})^*$	pressure	solute
thermal diffusion	$8.5 \times 10^{-12} \text{ kg}/(\text{m}\cdot\text{s})$	temperature	solute

* These coefficients are equal by Onsager's reciprocal relations.

One-dimensional transport through a one-meter column of clay material was simulated. The clay was assumed to have a porosity of 0.30 and to be saturated by the fluid phase. Initial conditions were a solute concentration equal to 0.4 kg/m^3 throughout the column, a temperature gradient equal to -2°K/m , and a pressure gradient equal to -10 Pa/m . At the inner boundary the temperature was 325°K and the pressure was $1 \times 10^7 \text{ Pa}$. These conditions of temperature and pressure were maintained throughout the temporal evolution of each simulation. Although the transport coefficients are known to vary with temperature [10], their variations within the domain of these simulations were very small and could be neglected. The temperature gradient used here is based on calculations reported for a hypothetical repository in basalt [12] and the pressure gradient is equivalent to a ground-water hydraulic gradient of 10^{-3} , the order of magnitude commonly assumed in calculations of solute transport [13]. The initial solute concentration is characteristic of dissolved solids contents of basaltic ground waters [12].

Two sets of simulations were done, each with a different condition at the inner boundary ($x = 0$). In one set, a constant concentration of solute equal to 1.0 kg/m^3 was maintained at the boundary. In the other set, the total flux of solute crossing the boundary was maintained at a value equal to $2.5 \times 10^{-12} \text{ kg/m}^2\text{s}$. These values have no special significance and were chosen simply for illustrative purposes. In both sets of simulations the solute concentration at the outer boundary ($x = 1 \text{ m}$) was maintained at a constant value equal to the initial concentration, 0.4 kg/m^3 . The method of solution was to compute solute concentrations and then use these results to compute concentration gradients and the fluxes driven by them.

RESULTS OF SIMULATIONS

Figures 1-4 show results of numerical simulations of coupled and uncoupled transport processes with the constant-concentration boundary condition at 10^9 s , and Figures 5-8 show results with the constant-flux boundary condition at 10^{10} s . In the figures showing fluxes, arrows indicate the directions of the flux vectors in either the positive or negative x -direction.

Figure 1 shows solute concentration profiles with no coupling and with full coupling between transport processes. It is seen that full coupling produces significant retardation of solute migration relative to the case without coupling, and produces a very steep gradient of concentration near the inner boundary where the concentration is held at a constant value. The steep gradient is the cause of large chemical-osmotic and diffusive fluxes in this region.

Figure 2 displays fluxes of volume and solute in the case without coupling. The volume flux is constant because it is driven by a constant gradient of pressure. Near the inner boundary, solute transport by diffusion exceeds that by advection by about four orders of magnitude, a consequence of the extremely low permeability of the clay. The diffusive flux decreases monotonically with distance from the inner boundary, while the flux of solute carried by advection approaches a value that remains approximately constant to the outer boundary. These results should be compared to those in Figures 3 and 4.

Figure 3 shows the three components of the volume flux (dashed lines) and their resultant (solid line). The contribution from advection remains equal to that in the uncoupled case, but now the total volume flux is dominated by the coupled processes, thermal osmosis and chemical osmosis, which are oppositely directed. Near the inner boundary chemical osmosis, driven by the steep concentration gradient, produces a net volume flux that is negatively directed. As distance from this boundary increases, the magnitude of the chemical-osmotic flux decreases until it equals the sum of the positively directed thermal-osmotic and advective fluxes, resulting in a point of stagnation near 0.25 m . As distance increases past this point, the total volume flux, now positive, approaches the thermal-osmotic flux. The latter

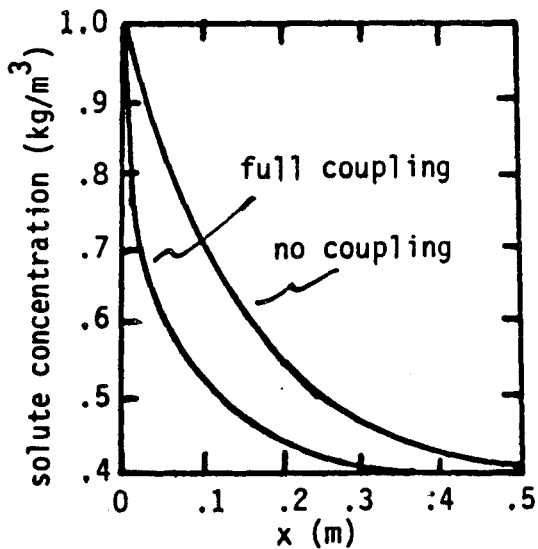


Fig. 1. Solute concentrations

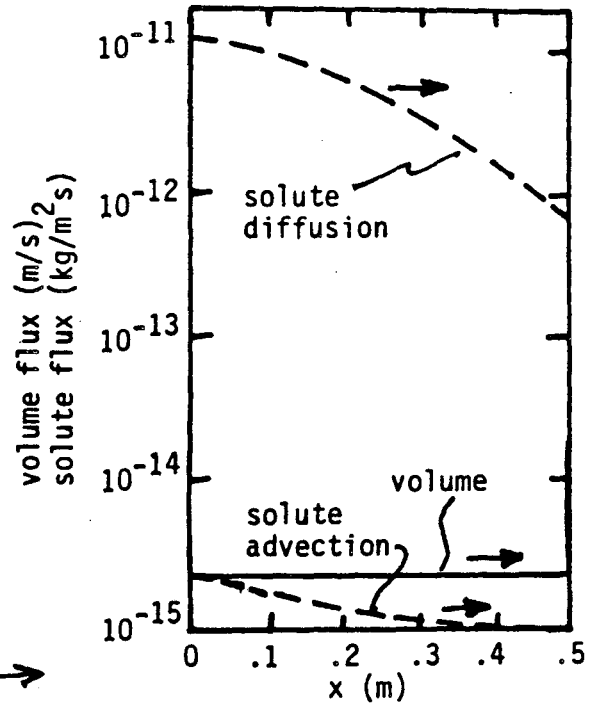


Fig. 2. Fluxes with no coupling →

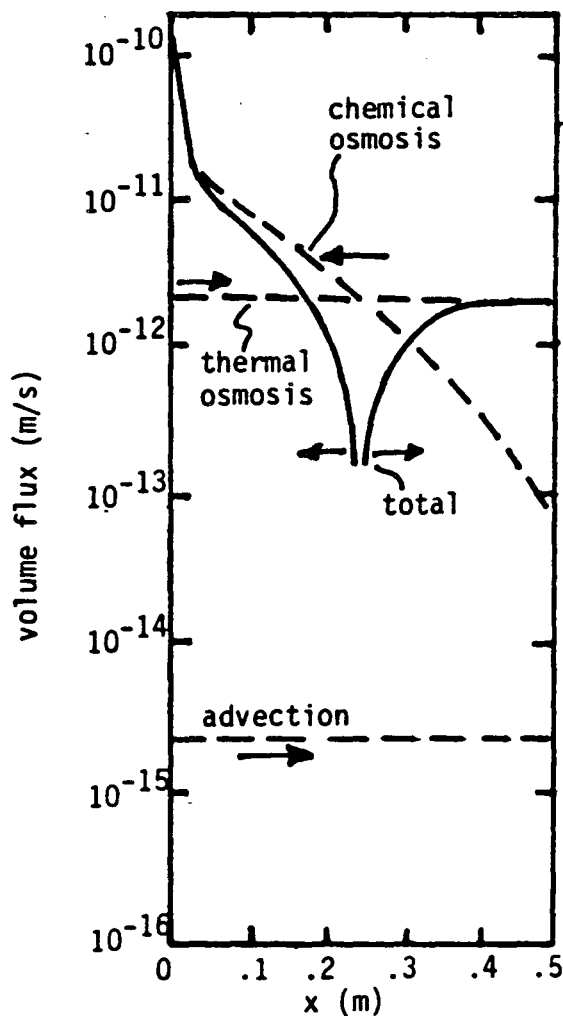


Fig. 3. Volume fluxes, full coupling

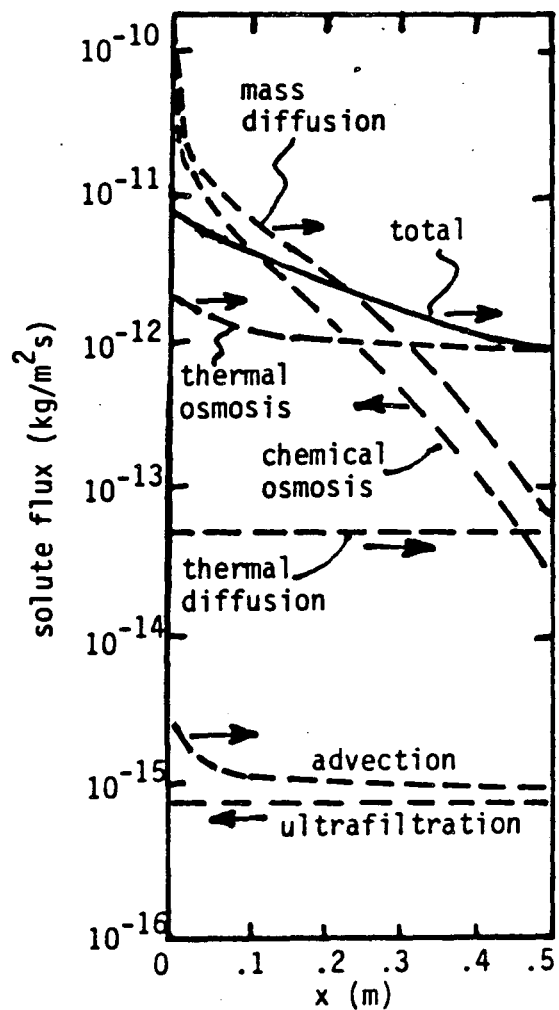


Fig. 4. Solute fluxes, full coupling

Figs. 1-4: Constant-concentration boundary condition, time = 10^9 s

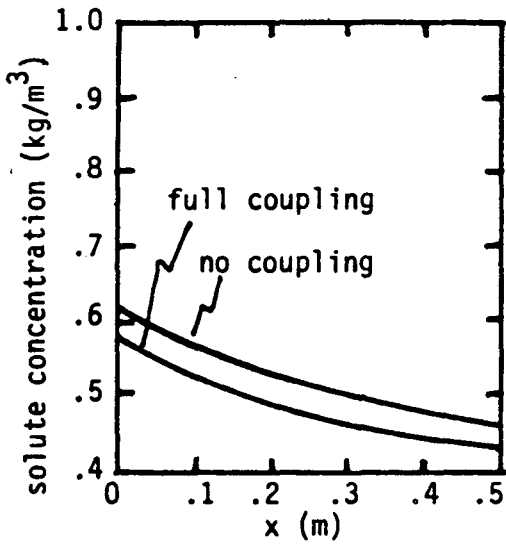


Fig. 5. Solute concentrations

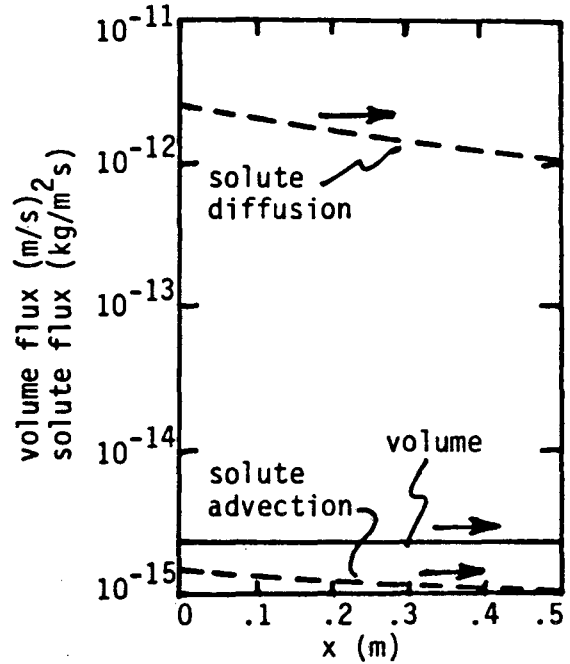


Fig. 6. Fluxes with no coupling

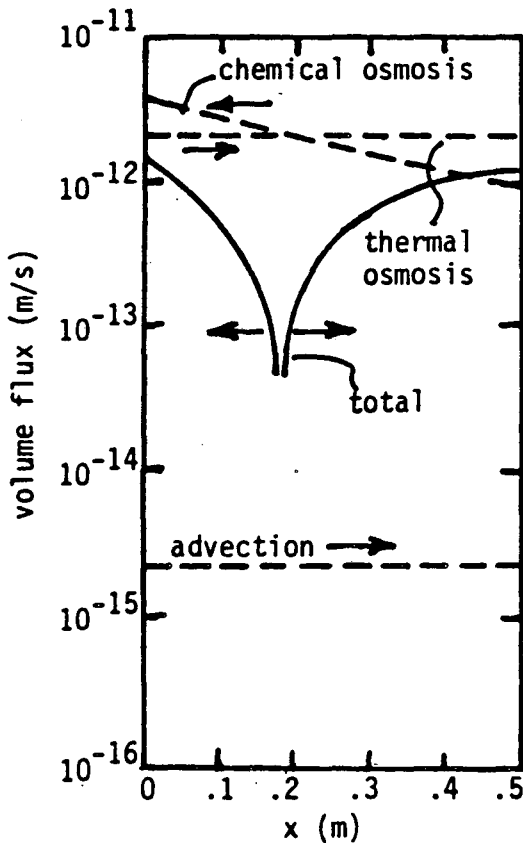


Fig. 7. Volume fluxes, full coupling

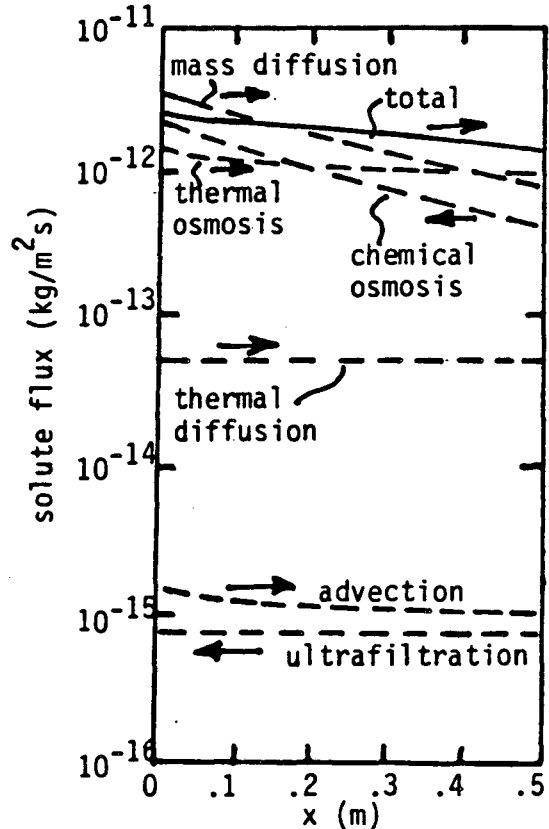


Fig. 8. Solute fluxes, full coupling

Figs. 5-8: Constant-flux boundary condition, time = 10^{10} s

remains constant at a value approximately three orders of magnitude larger than the advective flux. In these simulations the contribution to the volume flux from thermal osmosis is constant because the gradient of temperature is constant. It is important to note that the point of stagnation is neither a source nor a sink of matter, but is simply a point of zero total flux. As noted below, it is mobile and transient.

Figure 4 displays the six components of the solute flux (dashed lines) and their resultant (solid line). In this case, the total flux of solute is dominated by diffusion and two coupled processes, chemical osmosis and thermal osmosis. Near the inner boundary, the diffusive and chemical-osmotic fluxes are each about one order of magnitude larger than the diffusive flux in the uncoupled case because of the larger concentration gradient here. However, the diffusive flux is largely cancelled by the negatively directed chemical-osmotic flux, and the resultant of these two fluxes plus the positively directed thermal-osmotic flux is slightly smaller in magnitude than the diffusive flux in the uncoupled case. As distance from the inner boundary increases, the total solute flux does not decrease monotonically (as in the uncoupled case), but approaches the magnitude of the thermal-osmotic flux and thenceforth remains approximately constant at a value about three orders of magnitude larger than the flux of solute carried by advection.

Simulations with the constant-flux condition at the inner boundary produced results, shown in Figures 5-8, that are similar to the results obtained with the constant-concentration boundary condition. The principal differences between the two sets of simulations result from the smaller gradients of solute concentration near the inner boundary in the constant-flux case, and from the larger elapsed time of these simulations. This is evident from the profiles of solute concentrations shown in Figure 5, which indicate slight retardation of solute migration when full coupling is considered, relative to the case without coupling.

In Figure 6, without coupling, the solute flux is due largely to diffusion and again decreases monotonically, but at a lower rate with distance than in the case of the constant-concentration boundary condition.

Figure 7 shows the contributions to the volume flux with full coupling, and their resultant. Although the chemical-osmotic flux is not as prominent near the inner boundary as in Figure 3, it exceeds the thermal-osmotic flux in magnitude and a point of stagnation is reached near 0.18 m. At greater distances the total volume flux approaches the constant thermal-osmotic flux.

Figure 8 shows that the contribution to solute flux from chemical osmosis opposes a diffusive flux that is larger than the diffusive flux without coupling. However, the resultant solute flux, including a significant contribution from thermal osmosis, is almost identical to the solute flux without coupling for several tenths of a meter from the inner boundary, and thereafter approaches the thermal-osmotic flux.

Results of the simulations at other elapsed times, not shown here, show that the point of stagnation in the volume flux with full coupling moves away from the inner boundary as elapsed time increases and as the system approaches a steady state. The rate of movement is larger in the case of the constant-concentration boundary condition. At the largest simulated elapsed time, 10^{12} s, the point of stagnation has vanished in both cases, and the total volume flux is negative throughout the spatial domain included in the simulations.

DISCUSSION

Several generalizations can be drawn from the results of the simulations reported here.

In the systems simulated in this work, full coupling of processes affecting mass transport leads to retardation of solute movement and significant enhancement of volume fluxes in comparison to results predicted without coupling. Retardation of solute movement is larger in the case of a con-

stant-concentration condition at the inner boundary where gradients of solute concentration can be very large, producing correspondingly large negative contributions to solute fluxes due to chemical osmosis. Thermal osmosis alone can, in the presence of a rather mild gradient of temperature, produce a volume flux several orders of magnitude larger than the advective flux. The addition of chemical osmosis can produce a large negative contribution to the volume flux, resulting in a point of stagnation which migrates away from the inner boundary with increasing time. These effects would not be predicted by application of Fick's law and Darcy's law without inclusion of coupling.

Chemical osmosis is a large contributor to fluxes of both volume and solute in the systems studied here, and the nature of these contributions deserves detailed examination.

In the most commonly used development, the thermodynamics of irreversible processes provides two kinds of phenomenological equations relating matter fluxes to the forces driving them. In the present case these forces are gradients of temperature, pressure, and solute concentration. One equation expresses the fact that the volume flux (defined to be the sum of volume fluxes of solvent and solutes) consists of contributions from thermal osmosis, advection (Darcy's law) and chemical osmosis. This equation is used directly in our calculations of volume flux. The other equations pertain to the fluxes of solutes in a reference frame moving with the mean motion of the solvent, and state that each such "diffusive" flux is the sum of contributions from thermal diffusion, ultrafiltration, and mass diffusion (Fick's law). (Here we ignore contributions from coupled mass diffusion in multi-component systems.) To calculate the total flux of any solute in the reference frame used for the volume flux (the "laboratory" frame) it is necessary to combine the contribution from the volume flux with the diffusive flux of that solute. Thus, thermal osmosis, advection, and chemical osmosis contribute to both the volume flux and the total flux of a solute. In a semipermeable membrane, a quantity called the "reflection coefficient" is used as a measure of the membrane's ability to block passage of a solute when acted upon by gradients of pressure and composition; the reflection coefficient ranges in value from zero for a nonselective membrane such as a porous glass frit to unity for an ideal membrane in which the net flux of solute is zero in the absence of thermal gradients [14]. The data reported [9] for bentonite and used in this work indicate a value of the reflection coefficient equal to about 0.88. This extent of "leakiness" allows chemical osmosis to be a major contributor to the total flux of solute. If the reflection coefficient were unity in the present system, the solute flux due to mass diffusion would exactly cancel that due to chemical osmosis, that due to advection would exactly cancel that due to ultrafiltration, and only thermal osmosis and thermal diffusion could contribute to migration of solute. Volume fluxes would be relatively unaffected. However, it is noted that thermal osmosis is a major contributor to solute fluxes in the present system.

CONCLUSIONS

The results of numerical simulations presented here have indicated the possible significance of thermodynamically coupled transport processes in saturated clay materials and the magnitudes of errors that could result by omission of coupled processes from transport calculations in such materials. However, application of these methods to predictive analyses of the performance of clay-containing engineered barriers at nuclear waste repositories will require further development along the following lines.

The simulator used in this work assumed gradients of temperature and pressure that remained constant over times of 10^9 - 10^{10} s. These assumptions may be untenable in a repository environment, and reality dictates a need to consider heat transport and to account for the equation of state of a multi-component fluid phase. Addition of a heat transport equation will require

consideration of two more coupled effects, thermal filtration and the diffusion thermo-effect. However, if the phenomenological coefficients for the coupled processes considered in the present work were determined experimentally, no new coefficients for the additional coupled processes would be required. This is because the Onsager reciprocal relations provide equality between the coefficients associated with thermal osmosis and thermal filtration, and between those associated with thermal diffusion and the diffusion thermo-effect.

Further development also should include imposition of a condition of zero volume flow at the inner boundary, addition of an outer layer of material of dissimilar properties, and extension to a higher number of spatial dimensions.

Finally, there is a need for experimental measurements of coupled transport processes in candidate materials for engineered barriers to provide both input data for, and verification of, predictive numerical simulations. Highest priority should be given to determination of direct and coupled transport coefficients and their variations with ambient conditions and substrate compositions. Experimental methods for such measurements are well established (e.g., [9]-[11] and references therein).

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