

Non-Fickian ionic diffusion across high-concentration gradients

Anne E. Carey

Hydrology/Hydrogeology Program, University of Nevada, Reno

Stephen W. Wheatcraft

Department of Geological Sciences and Hydrology/Hydrogeology Program, University of Nevada, Reno

Robert J. Glass and John P. O'Rourke

Geosciences Division, Sandia National Laboratory, Albuquerque, New Mexico

Abstract. A non-Fickian physico-chemical model for electrolyte transport in high-ionic strength systems is developed and tested with laboratory experiments with copper sulfate as an example electrolyte. The new model is based on irreversible thermodynamics and uses measured mutual diffusion coefficients, varying with concentration. Compared to a traditional Fickian model, the new model predicts less diffusion and asymmetric diffusion profiles. Laboratory experiments show diffusion rates even smaller than those predicted by our non-Fickian model, suggesting that there are additional, unaccounted for processes retarding diffusion. Ionic diffusion rates may be a limiting factor in transporting salts whose effect on fluid density will in turn significantly affect the flow regime. These findings have important implications for understanding and predicting solute transport in geologic settings where dense, saline solutions occur.

Introduction

In many geologic settings, solute concentrations in fluids can be sufficiently high to affect both solution density and the thermodynamic activity of the solutes themselves. In many such geologic settings there is interest in the transport of salt from one fluid to another. Examples of these environments include playa lakes [Duffy and Al-Hassan, 1988; Macumber, 1992; R. A. Wooding et al., manuscript in preparation, 1995], midcontinent saline aquifers [McElwee, 1985; Motz, 1992], melting icebergs [Huppert and Turner, 1978], salt domes [Oldenburg and Pruess, 1995], and coastal aquifers into which seawater intrudes [Henry, 1964a, b; Voss and Souza, 1987]. Other environments where diffusion across solution boundaries is an important process include the mantle [Farber et al., 1994] and model systems like silicate melts [Liang et al., 1994]. Artificial systems where electrolyte diffusion is an important consideration for contaminant transport include repositories for radioactive [Bredhoeft and Maini, 1981; Voss and Andersson, 1993] and toxic chemical [Bradley, 1985] disposal.

Traditional [Voss and Souza, 1987] or even stochastic [Wely and Gelhar, 1992] descriptions of density-coupled fluid flow and solute transport consider the role of the solutes only in the physics of the fluids by including solution density and viscosity (as functions of solute concentration) in the local governing equations. Consideration of the chemistry of the solutes is an important part of describing the physics of density-coupled fluid flow and solute transport for ionic solutions because of the large changes in the ions' thermodynamic activities (and hence diffusivities) at high-ionic strength. Felmy and Weare's [1991] thermodynamically based diffusion model demonstrated the coupling of minor seawater ions to NaCl diffusion from a

salt dome into seawater. Those authors have been among the few to consider electrolyte thermodynamics in transport models. However, their model was not validated with experiments. Our inclusion of electrolyte physical chemistry into transport models gives rise to a new, non-Fickian transport theory for high-ionic strength solutions in groundwater. Unlike stochastic theories which have been developed to describe the greater than Fickian transport (resulting from field scale spatial variability of hydraulic conductivity) observed for ideal tracers in groundwater, this theory shows that transport rates will always be less than those predicted by a Fickian theory in a homogeneous medium.

Our model provides a theoretical basis for describing the narrow transition zone sometimes observed between salt water and fresh water in field [Lau, 1967; Voss and Souza, 1987] and laboratory studies [Wheatcraft and Peterson, 1979] of salt water intrusion. Consideration of ionic transport in such models is treated solely in a physical fashion, where the chemistry of the ions is ignored. To simulate accurately the narrow transition zone observed on Oahu, Voss and Souza [1987] developed special velocity calculations. They found that inconsistent approximation of terms involved in velocity calculations in a standard model of variable density flow led to artificially large dispersion. Voss and Souza [1987, p. 1853] commented that inconsistent approximations of the pressure and density gradients "would disperse a sharp transition zone even under hydrostatic conditions." For hydrostatic conditions, pressure is a linear function of depth only for a constant density fluid. Because the fluid velocities depend both upon the pressure and the density of the fluid, and these are usually calculated as linear functions of concentration, combining linear changes in density and pressure should result in a quadratic relationship between depth and pressure. Standard density-coupled fluid flow and solute transport models generally only calculate pressure as a linear function of depth, and this can result in velocity

Copyright 1995 by the American Geophysical Union.

Paper number 95WR01679.
0043-1397/95/95WR-01679\$05.00

discontinuities when the fluid density changes from element to element.

One method to avoid these inconsistent velocities, developed by *Frind* [1982], assigns only one velocity to each element of a finite element mesh, at the centroid of the element, based on the average density of the fluid in the element. This method requires rather fine mesh discretization. *Voss and Souza's* [1987] consistent approximation of the velocities was achieved by allowing both the density of the fluid and the local gravity vector to vary over each finite element. Their method removed some artificial numerical dispersion from their simulations, while our physico-chemically based model provides a theoretical basis for further improvements beyond those made by *Voss and Souza*.

In this paper we present results of our model predictions for ionic diffusion in one-dimensional, high-ionic strength aqueous systems using published mutual diffusion coefficients which vary with concentration. We have also performed one-dimensional diffusion experiments for the purpose of verifying our theoretical model. Our model predicts that the physico-chemical effects on diffusion in high-ionic strength solutions serve to reduce diffusion from that predicted using Fick's Law with the infinite dilution diffusion coefficient. These initial one-dimensional results have relevant applications to multidimensional models for density-coupled fluid flow and solute transport problems.

Theoretical Model

The general governing equation for solute flux in a multi-component, ionic system can be developed by relating the flux of each ion to the gradients of all the thermodynamic forces in the system. The resultant governing equation is

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left[\sum_{i=1}^N D_{ij}^v(c) \frac{\partial c_j}{\partial x} \right] \quad (1)$$

where

- c_i concentration of species i mol/L;
- x spatial coordinate cm;
- $D_{ij}^v(c)$ volume-fixed mutual diffusion coefficient as a function of concentration of i and j cm²/s;
- c_j concentration of ion j mol/L;
- N number of ions.

Using the electroneutrality condition, the general equation for multicomponent diffusion reduces to

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D^v(c) \frac{\partial c}{\partial x} \right] \quad (2)$$

in a binary system.

We use this equation to predict CuSO₄ diffusion, using published [*Miller et al.*, 1980], volume-fixed, mutual diffusion coefficients (Figure 1). For our numerical simulations of this one-dimensional problem, we used a Crank-Nicolson approximation [*Crank*, 1975], time step length of 100 s and spatial discretization of 0.001–0.01 cm. Initial conditions were that for

$$\begin{aligned} 0.0 < x/L \leq 0.5 & \quad C = C_0 \\ 0.5 < x/L \leq 1.0 & \quad C = 0.0. \end{aligned}$$

Initial estimates for new CuSO₄ concentrations were that they were equal to the old concentrations. We calculated diffusion

Copper Sulfate Diffusion Coefficients

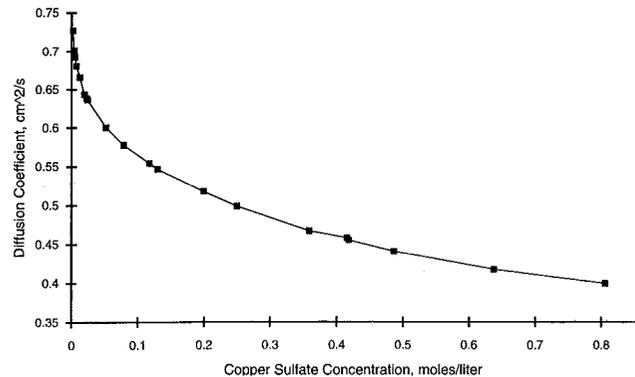


Figure 1. Copper sulfate diffusion coefficients, measured by *Miller et al.* [1980], used to simulate CuSO₄ diffusion.

coefficients by averaging the estimates for the new concentrations between adjacent nodes and then calculated the volume-fixed diffusion coefficient for each averaged concentration using the equations of *Miller et al.* [1980]. Boundary conditions fulfilled the semi-infinite column assumptions [*Li and Gregory*, 1974] and were fixed at each time step to C_0 or to 0.0, as appropriate. The solution matrix was tridiagonal and solved with the Thomas algorithm using a subroutine from *Press et al.* [1992]. Then volume-fixed diffusion coefficients were recalculated for the new concentrations, and the new coefficients were compared to the old coefficients. The error tolerance between the old and the new volume-fixed diffusion coefficients was set to 0.5%. If the maximum difference between old and new coefficients exceeded the error tolerance, the coefficients were calculated again and another iteration was performed before calculating the flux of water to replace the electrolyte which had diffused. Then the electrolyte concentrations were updated. Iteration occurred only during the first time step, when there was a large difference in concentration between the water and the CuSO₄ solution. Coefficients changed little between subsequent time steps due to the small spatial and temporal discretization scheme.

Predictions for the Fickian model were made with the error function solution to the diffusion equation

$$C = \frac{1}{2} \operatorname{erfc} \left[\frac{x}{2\sqrt{Dt}} \right] \quad (3)$$

where D for CuSO₄ = 8.58×10^{-6} cm²/s (the infinite dilution diffusion coefficient [*Miller et al.*, 1980]).

Methods

One-dimensional copper sulfate diffusion experiments were conducted in rectangular cross-section glass tubing (1 cm by 2 cm) oriented with an optical path length of 1 cm. The column was filled with deionized water which was pumped into the column from the bottom, using a peristaltic pump (Cole-Parmer). Then the CuSO₄ solution (concentration, $C_0 = 0.4$ mol/L; density, $\rho = 1.063$ g/cm³) was pumped into the column from the bottom, at a slow rate (volumetric flow rate of ~ 0.5 mL/min or a linear velocity of ~ 0.2 cm/min), displacing the water. When the interface between the solutions was at the desired location (which usually took about 15 min), the pump was turned off, the tubing clamped, and the doors of the en-

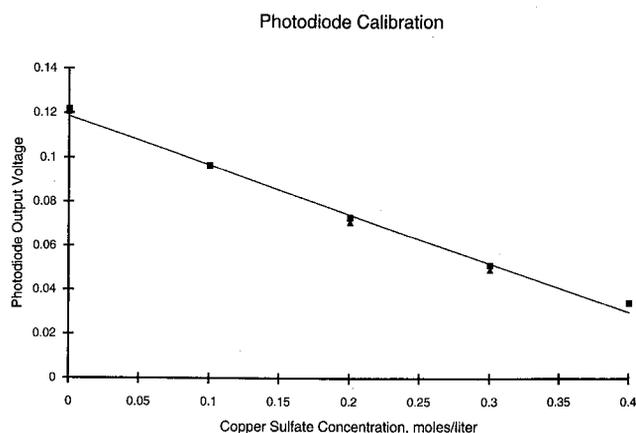


Figure 2. Calibration curve for photodiode output voltage as a function of CuSO_4 concentration. The best fit line to the data (from linear regression) was voltage = $-0.2202(\text{CuSO}_4 \text{ concentration}) + 0.1186$, with $r^2 = 0.991$.

vironmental chamber closed. Data collection began immediately. All experiments were conducted in the dark in a temperature-controlled chamber maintained at $25^\circ \pm 0.5^\circ\text{C}$. Monochromatic light at the absorbance maximum of CuSO_4 (660 nm) was provided using the diffraction grating of a modular spectrophotometer (Sargent Welch ChemAnal) and transmitted to the column with fiber optic cable. Light transmittance through the column was measured with a planar-diffused silicon photodiode (United Detector Technologies model PIN-2DI). Light transmittance through the column was measured at spatial intervals of 1 mm. The output voltage from the photodiode was amplified on a multiplexer board which served as the input board to a PC-based data acquisition system (Lab Tech Notebook). For each measurement made for a diffusion front

profile, the light source and sensor were moved along the column by a microprocessor-controlled linear positioning system (Daedal). After the linear positioning system placed the sensor and light source at the first location for a measurement, there was a wait of 2 min (which allowed sufficient time for the photodiode output voltage to stabilize), then the data acquisition system collected 50 measurements of light transmittance at a data collection rate of 2.5 Hz. The sensor was then moved 1 mm to the next position, paused 2 min and measurements collected. Each scan of the column was over a total distance of 4 cm. The times in the legend are times at which the measurements at the midpoint of each curve were taken. Photodiode output voltages were converted to CuSO_4 concentrations with a calibration curve. The photodiode sensor provided a linear response ($r^2 = 0.991$) to CuSO_4 concentrations over a range of 0.0–0.4 mol/L (Figure 2).

Results

Results of a representative laboratory diffusion experiment with CuSO_4 (Figure 3) show diffusion of 0.4 M CuSO_4 into deionized water. Profiles taken over 10 hours show the advance of the CuSO_4 diffusion front profile with time. In contrast to symmetrical Fickian diffusion (Figure 4a), the profiles are skewed. They show more tailing of the profile at low CuSO_4 concentrations, where the diffusion coefficients are the highest. The hinge point of the profiles (location at which the profiles cross) is located at 0.23 mol/L. Owing to experimental design limitations, the profiles from the experiment (Figure 3) are not perfectly synoptic. The experimental apparatus required approximately 40 min to collect one profile. Since the data are not collected instantaneously throughout a profile, a small amount of temporal skew is introduced as an experimental artifact. Model predictions made with each point on a profile, predicted at the same time the measurements were made,

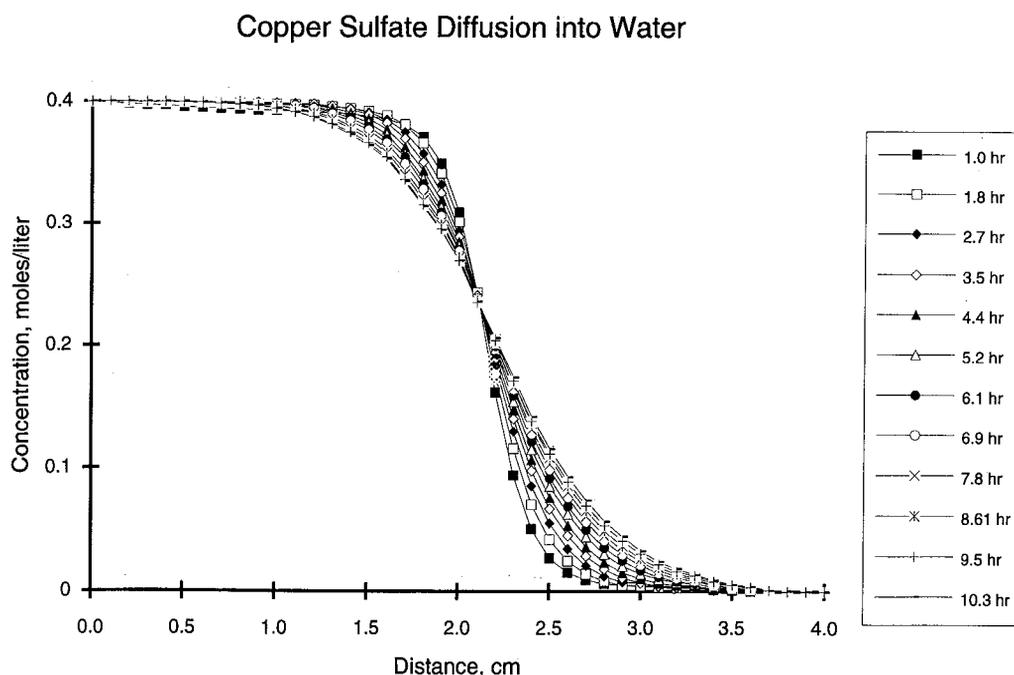


Figure 3. Profiles of 0.4 M CuSO_4 diffusing into deionized water. Each point is the average of 50 measurements. The standard deviation among the measurements is smaller than the thickness of the line used to connect the points. The times in the legend are the times at which the midpoint of each profile was measured.

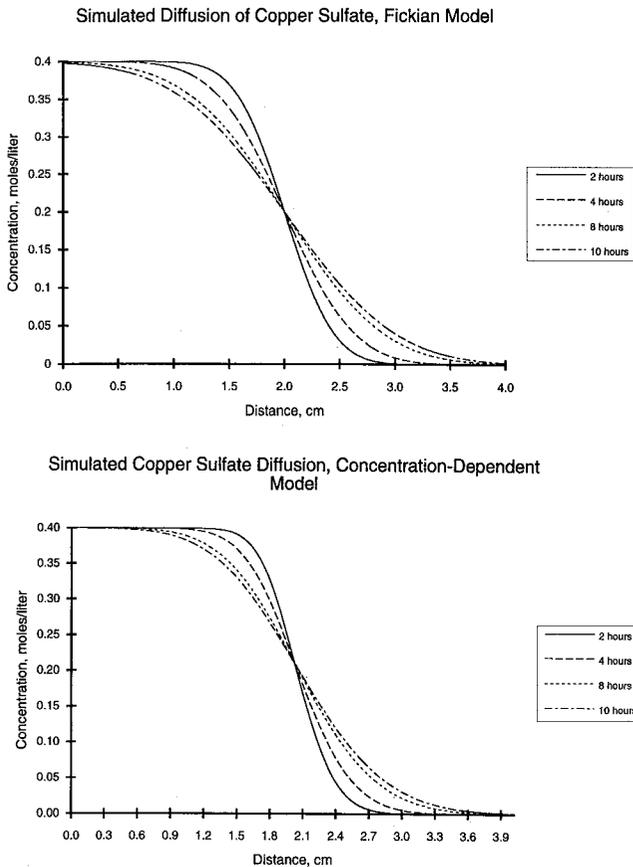


Figure 4. Simulated diffusion of CuSO_4 using (a) a simple Fickian model and (b) the concentration-dependent diffusion coefficient model. The simulated Fickian data were calculated with the error function solution to the diffusion equation (3). The concentration-dependent data were calculated numerically (2).

show that the temporal skew contributes less than 10% of the total skew.

Simulated diffusion profiles of CuSO_4 (Figure 4b) using concentration-dependent diffusion coefficients are very similar to the measured data. Like the measured data, the simulated data show considerable skew in the profiles, and the hinge point is slightly above $0.50 C_0$, at $0.52 C_0$, (0.21 mol/L).

Discussion

A method used by *Bear* [1961] to determine dispersion coefficients in one-dimensional column experiments can be used to determine diffusion coefficients from the experimental data. The temporal growth rate of the transition zone provides a way to explore the differences between the models or to compare the models to the experiments. The slope of the curve is used to obtain an apparent diffusion coefficient. Plotting the width of half the transition zone (from $C/C_0 = 0.50$ to $\pm 0.40 C/C_0$) against the square root of time, allows calculating the effective diffusion coefficients from the slopes of the best fit lines, when the error function solution to the diffusion equation is expressed in the form

$$x = \left[2 \operatorname{erfc}^{-1}(2C) \sqrt{D} \right] \sqrt{t}. \quad (4)$$

All terms in this equation are known except for the diffusion coefficient, which is proportional to the slope of the best fit line.

We have used this method to analyze our simulated data (Figure 5a). The open squares are the data from the growth of the transition zone between 0.04 and 0.2 mol/L; the open triangles are data from the growth of the transition zone between 0.2 and 0.36 mol/L. The closed circles are the data from the Fickian model, using the constant, infinite dilution diffusion coefficient of $8.58 \times 10^{-6} \text{ cm}^2/\text{s}$ [Miller *et al.*, 1980]. With this analysis the Fickian model data (Figure 4a) simulated with the constant, infinite dilution diffusion coefficient of $8.58 \times 10^{-6} \text{ cm}^2/\text{s}$ yielded an apparent diffusion coefficient, $D = 8.49 \times 10^{-6} \text{ cm}^2/\text{s}$ (Figure 5a). This apparent value is very close to the true value used to make the predictions.

A similar analysis of the concentration-dependent model does not yield a true diffusion coefficient but rather an effective diffusion coefficient (D_{eff}) which integrates over the diffusion coefficients which change with concentration. While we are not suggesting this analysis as a method for determining diffusion coefficients for this system, or any other high-ionic strength system, it does yield an effective diffusion coefficient for the particular conditions studied. This effective diffusion coefficient is a good way to compare the experimental data to the simulated data. In this manner we have analyzed the data of our concentration dependent model profiles (Figure 4b) to

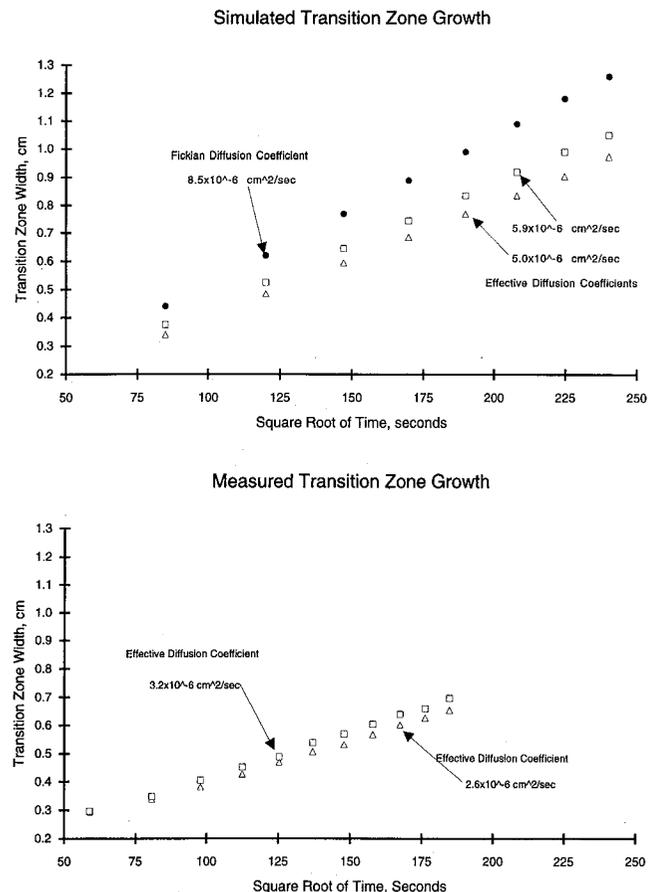


Figure 5. Transition zone growth using simulated data (a) from a Fickian model and the concentration-dependent model and (b) from the experimental data. Effective diffusion coefficients were calculated from the slopes of the best fit lines (calculated by linear regression) and (4).

calculate D_{eff} (Figure 5a) for the simulated condition of 0.4 M CuSO_4 diffusing into deionized water. The transition zone growth at the low concentration half of the profile, from 0.04 to 0.20 mol/L ($C/C_0 = 0.10\text{--}0.50$), yielded an effective diffusion coefficient of $5.9 \times 10^{-6} \text{ cm}^2/\text{s}$. The high-concentration side of the profile (from 0.20 to 0.36 mol/L) yielded an effective diffusion coefficient of $5.0 \times 10^{-6} \text{ cm}^2/\text{s}$. These effective diffusion coefficients are significantly different from each other at the 95% confidence level. Both of these effective diffusion coefficients are significantly less than the apparent coefficient from this same analysis of the data simulated with a Fickian model and the infinite dilution diffusion coefficient. For the conditions of this experiment the effective diffusion coefficient for the low concentration half of the diffusion front profiles is 31.2% less than the infinite dilution diffusion coefficient, and the effective diffusion coefficient for the high-concentration half of the measured diffusion front profiles is 41.7% less.

For our experimental data (Figure 3) the transition zone growth at the low concentration half of the profile from 0.04 to 0.20 mol/L (C/C_0 from 0.10 to 0.50), yielded an effective diffusion coefficient of $3.2 \times 10^{-6} \text{ cm}^2/\text{s}$ (Figure 5b). This effective coefficient is significantly greater than the effective diffusion coefficient for the high-concentration side of the profile, from 0.20 to 0.36 mol/L (C/C_0 from 0.50 to 0.90) of $2.6 \times 10^{-6} \text{ cm}^2/\text{s}$. These effective diffusion coefficients are significantly different from each other and are 62.7% and 69.7%, respectively, less than the infinite dilution diffusion coefficient of $8.58 \times 10^{-6} \text{ cm}^2/\text{s}$.

The effective diffusion coefficients for the concentration-dependent model and the experimental data illustrate the differences in the growth rate of the transition zones. For high-ionic strength solutions a Fickian model with an infinite dilution diffusion coefficient will always predict greater diffusion of electrolytes than a physico-chemically based model which allows the diffusion coefficients to vary with concentration. However, at very low concentrations they will predict nearly the same results. A Fickian model and the infinite dilution diffusion coefficient will also predict a wider transition zone between a high-ionic strength fluid (like seawater) and fresh water than will our concentration-dependent model which considers the effects of ionic strength or concentration on diffusion.

Most models of salt water intrusion have predicted wide, brackish transition zones between the fresh water of the coastal aquifer and the intruding seawater. Henry [1964a, b] states that his analytical model is only appropriate for wide transition zones. He uses a large, constant coefficient of diffusion for NaCl which is about 4 orders of magnitude greater than either the infinite dilution diffusion coefficient for NaCl or the NaCl diffusion coefficient appropriate for seawater. Subsequent numerical simulations of this problem [e.g., Pinder and Cooper, 1970; Lee and Cheng, 1974; Segol and Pinder, 1976; Voss, 1984] have followed Henry's lead in predicting wide transition zones. This may be primarily a result of the large dispersion coefficients necessary to minimize numerical dispersion and oscillation problems inherent in the numerical algorithms.

More recently, Herbert *et al.* [1988] simulated brine transport as part of the international HYDROCOIN project. To avoid convergence problems, they used a method called parameter stepping in which they varied the diffusion coefficient during the course of a simulation. Their simulations showed qualitative agreement with the HYDROCOIN test case, but their

method was slow to converge in low-velocity regions. In low velocity-regions the importance of diffusion in controlling solute transport is likely to be equivalent to that of transverse dispersion. Low-velocity regions are those areas in which an accurate representation of the ionic diffusion coefficient will be most important. Herbert *et al.* [1988, p. 1792] comment, "Whilst much has been learnt, it would be fruitful to study simpler systems." Our simple one-dimensional experiments and simulations have shown that use of concentration dependent diffusion coefficients provide a far better means of simulating diffusion in brines than does a Fickian model with a constant diffusion coefficient.

Oldenburg and Pruess [1995] discuss the importance of the diffusion coefficient in simulating brine transport, but they still employ a coefficient at least an order of magnitude larger than is physically chemically realistic. Their numerical simulator was validated by comparison not only with the Henry problem but also with the Elder [1967] problem, as recommended by Voss and Souza [1987]. The Elder problem is for buoyant thermal convection, an entirely different process than convection due to high-salt concentration. Without any chemical basis to their arguments, Oldenburg and Pruess [1995] showed the strong dependence of their density-coupled transport equations to the diffusion coefficient in simulating brine flow. They also showed the sensitivity of the system dynamics to the value of the diffusion coefficient. We have endeavored in our experiments to show not only the importance of diffusion in electrolyte transport in high ionic strength systems but also to consider the effects of solute concentration on the diffusion coefficient.

It is likely that there are unmodeled processes responsible for our observed discrepancy between theory and experiment. Any effect of solution viscosity or density on diffusion ought to be accounted for in the diffusion coefficients which Miller *et al.* [1980] measured at a series of CuSO_4 concentrations. Their published coefficients include the variation of viscosity and density with concentration and thus account for the effects of these on diffusion. Any explanations related to experimental error and design would cause increased diffusion, yet the observed discrepancy is reduced diffusion in the experiments, compared to our theory. Such processes related to experimental design include the detector response function and an initially diffuse interface between the CuSO_4 solution and the water. Deconvolution of our detector response function showed that the only effect of the detector response function on our measured profiles is to increase the apparent diffusion. An initially diffuse "interface" would also result in apparently increased diffusion. These are all processes which increase diffusion and can therefore be dismissed as reasons explaining the discrepancy between our model and the experiments.

A possible process retarding transport is an effective interfacial tension between the "two" fluids, the 0.4 M CuSO_4 solution and the water, even though both fluids are aqueous. Another possibility is that the diffusion coefficients used to make the predictions were wrong. The coefficients were carefully measured by competent researchers. However, their diffusion coefficient determinations [Miller *et al.*, 1980] were made across very small concentration gradients (ΔC), unlike the initial condition of our experiments. For their measurement of the CuSO_4 diffusion coefficient for 0.41480 mol/L (the measurement made at the concentration closest to our experimental initial concentration of 0.40 mol/L) the ΔC in the experiment was 0.03131 mol/L. This small ΔC is necessary in their diffusion coefficient determinations so that the diffusion coef-

ficients do not change during the measurement. Our experiments had an initial ΔC of 0.40 mol/L.

Experiments to verify the model show even less diffusive transport than our theory predicts. Since we have eliminated calibration problems and other experimental artifacts as possible causes, the most probable reason for the differences between the model predictions and the experiments is that there are additional processes causing reduced diffusion that we have not included in the model.

Conclusions

Theories which do not allow ionic diffusion coefficients to change with concentration are neglecting an important part of the solute chemistry in their approximation of the dispersion coefficient. Application of nonequilibrium thermodynamics and electrolyte physical chemistry provides the basis for a new model of electrolyte transport in high-ionic strength groundwater. Our experiments have shown that current theoretical models which include nonequilibrium thermodynamics and electrolyte physical chemistry are still overpredicting diffusive transport. Therefore more work is needed to identify and quantify the processes that are controlling diffusion in high-ionic strength solutions.

Acknowledgments. We thank Jon Woodruff for his assistance with the experimental work. Berry Lyons read the manuscript critically; he, David Benson, and Scott Tyler engaged in helpful discussions on the experiments. Major funding was provided by the National Science Foundation Program in Hydrologic Sciences grant EAR-9218582. Additional support to AEC was provided by a Department of Energy EPSCoR Traineeship and a graduate student research grant from the Geological Society of America.

References

- Bear, J., Some experiments in dispersion, *J. Geophys. Res.*, 66(8), 2455–2467, 1961.
- Bradley, J. S., Safe disposal of toxic and radioactive liquid wastes, *Geology*, 13(5), 328–329, 1985.
- Bredehoeft, J. D., and T. Maini, Strategy for radioactive waste disposal in crystalline rocks, *Science*, 213(4505), 293–296, 1981.
- Crank, J., *The Mathematics of Diffusion*, 2nd ed., Oxford Univ. Press, New York, 1975.
- Duffy, C. J., and S. Al-Hassan, Groundwater circulation in a closed desert basin: Topographic scaling and climatic forcing, *Water Resour. Res.*, 24(10), 1675–1688, 1988.
- Elder, J. W., Transient convection in a porous medium, *J. Fluid Mech.*, 27(3), 609–623, 1967.
- Farber, D. L., Q. Williams, and F. J. Ryerson, Diffusion in Mg_2SiO_4 polymorphs and chemical heterogeneity in the mantle transition zone, *Nature*, 371(6499), 693–695, 1994.
- Felmy, A. R., and J. H. Weare, Calculation of multicomponent ionic diffusion from zero to high concentration, I, The system Na-K-Ca-Mg-Cl-SO₄-H₂O at 25°C, *Geochim. Cosmochim. Acta*, 55(1), 113–131, 1991.
- Frind, E. O., Simulation of long-term transient density-dependent transport in groundwater, *Adv. Water Resour.*, 5, 73–78, 1982.
- Henry, H. R., Interfaces between salt water and fresh water in coastal aquifers, in *Sea Water in Coastal Aquifers*, U.S. Geol. Surv. Water Supply Pap., 1613-C, 35–70, 1964a.
- Henry, H. R., Effects of dispersion on salt encroachment in coastal aquifers, in *Sea Water in Coastal Aquifers*, U.S. Geol. Surv. Water Supply Pap., 1613-C, 70–84, 1964b.
- Herbert, A. W., C. P. Jackson, and D. A. Lever, Coupled groundwater flow and solute transport with fluid density strongly dependent upon concentration, *Water Resour. Res.*, 24(10), 1781–1795, 1988.
- Huppert, H. H., and J. S. Turner, On melting icebergs, *Nature*, 271(5640), 46–48, 1978.
- Lau, L. S., Seawater encroachment in Hawaiian Ghyben-Herzberg Systems, *Proc. Symp. Ground-Water Hydrol.*, 259–271, Am. Water Resour. Assoc., San Francisco, Calif., 1967.
- Lee, C.-H., and R. T. Cheng, On seawater encroachment in coastal waters, *Water Resour. Res.*, 10(5), 1039–1043, 1974.
- Li, Y.-H., and S. Gregory, Diffusion of ions in sea water and in deep-sea sediments, *Geochim. Cosmochim. Acta*, 38(5), 703–714, 1974.
- Liang, Y., F. M. Richter, and E. B. Watson, Convection in multicomponent silicate melts driven by coupled diffusion, *Nature*, 369(6497), 390–392, 1994.
- Macumber, P. G., Hydrological processes in the Tyrrell Basin, south-eastern Australia, *Chem. Geol.*, 96(1/2), 1–18, 1992.
- McElwee, C. D., A model study of salt-water intrusion to a river using the sharp interface approximation, *Ground Water*, 23(4), 465–475, 1985.
- Miller, D. G., J. A. Rard, L. B. Eppstein, and R. A. Robinson, Mutual diffusion coefficients, electrical conductances, osmotic coefficients and ionic transport coefficients I_{ij} for aqueous CuSO₄ at 25°C, *J. Solution Chem.*, 9(7), 467–496, 1980.
- Motz, L. H., Salt-water upconing in an aquifer overlain by a leaky confining bed, *Ground Water*, 30(2), 192–198, 1992.
- Oldenburg, C. M., and K. Pruess, Dispersive transport dynamics in a strongly coupled groundwater-brine flow system, *Water Resour. Res.*, 31(2), 289–302, 1995.
- Pinder, G. F., and H. H. Cooper, A numerical technique for calculating the position of the saltwater front, *Water Resour. Res.*, 6(3), 875–882, 1970.
- Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes*, Cambridge Univ. Press, 1992.
- Segol, G., and G. F. Pinder, Transient simulation of saltwater intrusion in southeastern Florida, *Water Resour. Res.*, 12(1), 65–70, 1976.
- Voss, C. I., SUTRA: A finite-element simulation model for saturated-unsaturated fluid-density-dependent ground-water flow with energy transport or chemically-reactive single-species solute transport, U. S. Geol. Surv. Water Resour. Invest. Rep., 84-4369, 409 pp., 1984.
- Voss, C. I., and J. Andersson, Regional flow in the Baltic Shield during Holocene coastal regression, *Ground Water*, 31(6), 989–1006, 1993.
- Voss, C. I., and W. R. Souza, Variable density flow and solute transport simulation of regional aquifers containing a narrow freshwater-saltwater transition zone, *Water Resour. Res.*, 23(10), 1851–1866, 1987.
- Welty, C., and L. W. Gelhar, Simulation of large-scale transport of variable density and viscosity fluids using a stochastic mean model, *Water Resour. Res.*, 28(3), 815–827, 1992.
- Wheatcraft, S. W., and F. J. Peterson, Numerical modeling of liquid waste injection into a two-phase fluid system, *Tech. Rep.*, 125, Univ. of Hawaii Water Resour. Res. Cent., Honolulu, 1979.
- A. E. Carey, Hydrology/Hydrogeology Program, University of Nevada, Reno, NV 89557.
- R. J. Glass and J. P. O'Rourke, Geosciences Division, Sandia National Laboratory, Albuquerque, NM 87185.
- S. W. Wheatcraft, Department of Geological Sciences/172, University of Nevada, Reno, NV 89557.

(Received March 14, 1995; accepted May 24, 1995.)