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Introduction

The fate of radionuclides in the subsurface is of critical importance to the planning, siting, and evaluation of repositories for radioactive wastes. Mathematical models are an integral component of this process. An accurate understanding of radionuclide transport is required to successfully formulate and use these models. It is well-known that the subsurface is both physically and chemically heterogeneous. Recent research has shown that the resultant spatial variability of hydraulic conductivity and of sorption capacity can significantly affect solute transport in the subsurface. The impact of hydraulic conductivity variability and sorption capacity variability on the transport of radionuclides is, therefore, of great interest. Very few well-controlled, experimentally based laboratory investigations of the transport of radionuclides in physically and chemically heterogeneous porous media have been reported in the literature. The purpose of this paper is to report the preliminary results of such an investigation. We present results obtained for transport of Co^{2+} in a column packed with two media of differing hydraulic conductivities and sorption capacities. In addition to being influenced by these heterogeneities, transport of the Co^{2+} is also influenced by rate-limited diffusive mass transfer and nonequilibrium sorption.

Experimental Section

The miscible displacement technique was used to obtain breakthrough curves for the transport of a nonreactive tracer (^3H_2O) and Co^{2+} in a column packed with two media of differing hydraulic conductivities and sorption capacities. A stainless steel column (7.6 cm diameter, 30.5 cm length) was packed sequentially with the two media. First, a central core of no. 70-mesh fine sand, coated with poorly crystalline iron oxide (1.2% by mass), was emplaced; the diameter of the core was 4.1 cm. Second, the volume between the core and the column wall was filled with a no. 20-mesh uncoated sand. The mass of no. 20 sand represented 74% of the total mass of solids packed in the column. The gravimetrically measured bulk density and porosity of the packed column were 1.44 g cm⁻³ and 0.49, respectively. The pore volume of the column was 680 cm³, and the dead volume was less than 2 cm³.

After packing and prior to the transport experiment, the column was flushed with approximately 10 pore volumes of an electrolyte solution [10^{-3} M $Ca(ClO_4)_2$] of pH 6.5. A piston-driven high-performance liquid chromatography pump (SSI Model 300) was used to generate constant flow. The transport experiment was performed by injecting into the column a step input of solution containing the solutes at constant concentration, C_0 [^3H_2O,

31 000 CPM cm⁻³; Co^{2+}, 0.59 mg L⁻¹ with 30 000 CPM cm⁻³ as ^{57}Co]. The effluent was directed to a fraction collector (ISCO Retriever), and selected fractions were analyzed by liquid scintillation (Packard Tricarb). The flow rate at which the experiment was performed was equivalent to an average linear porewater velocity (v) of approximately 8 cm h⁻¹.

Models based on the dual-porosity concept were used to analyze the breakthrough curves. With the dual-porosity approach, the porous medium is assumed to consist of two domains: one with a relatively large hydraulic conductivity such that advective–dispersive transport occurs and another with a relatively low hydraulic conductivity such that there is minimal advective–dispersive transport. Exchange of solute mass between the two domains is represented by the use of a first-order mass transfer equation. A model developed for nonsorbing solutes (1) was used to analyze the ^3H_2O breakthrough curve. This model has the following four parameters: P, the Peclet Number; ϕ, the fraction of porosity that is associated with the advective domain; ω, the ratio of hydraulic residence time to mass transfer time; and the input pulse, T. For the stratified-media column, the no. 20-mesh sand will be assumed to comprise the advective domain, whereas the no. 70-mesh sand will be assumed to comprise the nonadvective domain. With the mass of the no. 20 sand representing 74% of the total mass of solids, the foregoing assumption results in a value of 0.74 for ϕ. The input pulse is known from the experiment. A value for P (100) was obtained from an experiment performed with a homogeneously packed column. This leaves ω as the only unknown. The optimized value was found by use of a nonlinear least-squares optimization program (2).

A model that accounts for spatially variable hydraulic conductivity, spatially variable sorption capacity (dual-porosity approach), rate-limited mass transfer, and rate-limited sorption/desorption (two-compartment approach) (3) was used to analyze the breakthrough curve obtained for Co^{2+}. In addition to P, ϕ, and ω, values for which were reported above, this model has the following parameters: f, mass fraction of sorbent comprising the advective domain; K_a and K_n, the equilibrium sorption constants for the advective (a) and nonadvective (n) domains; R, the global retardation factor; F, the fraction of sorbent for which sorption is instantaneous; and k_2, the reverse sorption rate coefficient. With the assumption that the no. 20-mesh sand comprises the advective domain, f is calculated to be 0.74. Values for K_a and K_n were obtained from batch sorption experiments. Isotherms were measured for both media following the typical batch procedure, with each isotherm consisting of five different initial concentrations and with four replicates for each concentration. A value for R was calculated by using the measured
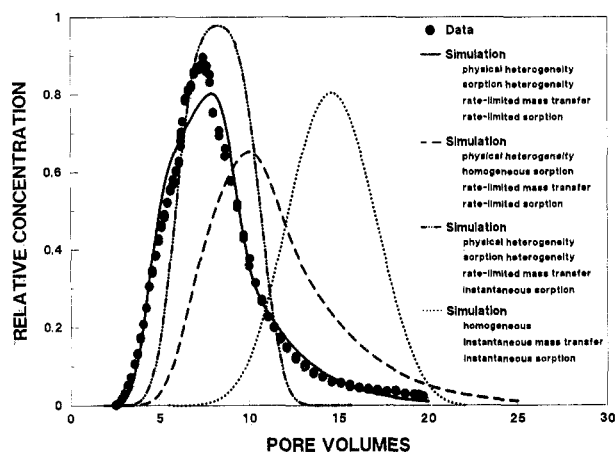
Figure 1. Experimental and simulated breakthrough curves for transport of Co^{2+} through a column packed with two porous media of differing hydraulic conductivities and sorption capacities.

K_a and K_n values. Values for F and k_2 will be obtained by optimization of the Co^{2+} breakthrough curve.

Results and Discussion

The two sorption isotherms were well-fitted by the Freundlich equation $[S = K_f C^n]$, with $K_f = 2.05$, $n = 0.71$ for the no. 20 sand and $K_f = 6.86$, $n = 0.72$ for the no. 70/FeOx sand. The sorption capacities of the two media, therefore, differ by about a factor of 3. Sorption was reversible for both sorbents, and neither material contained strong oxidants such as manganese oxides that may catalyze transformation of Co(II) to Co(III) (cf. refs 4 and 5). The sorption of Co^{2+} was dominated by surface coordination reactions with iron-oxides and silica, with a small contribution of selective ion exchange to the micaceous mineral fraction.

The breakthrough curve for ^3H_2O (not shown) was asymmetrical and exhibited a delayed approach to relative concentrations of 1 and 0 (i.e., tailing). The optimized (one parameter) simulation produced with the dual-porosity model matched the data quite well. The retardation factor was 1, demonstrating the absence of sorptive interactions. The asymmetrical and tailed breakthrough curve for ^3H_2O, a nonreactive and nonsorbing solute, indicates the effect of hydraulic conductivity variability on solute transport. It is expected that the hydraulic conductivity variability will also influence the transport of Co^{2+}. Based on the results of the ^3H_2O transport experiment and the sorption isotherm experiment, it is evident that the column does indeed consist of two media with differing hydraulic conductivities and sorption capacities.

The breakthrough curve obtained for the transport of Co^{2+} through the column is presented in Figure 1. A simulated curve produced for the case of a homogeneous porous medium and instantaneous sorption is also presented in Figure 1. The Co^{2+} breakthrough curve is shifted to the left of the curve obtained for ideal conditions. In addition, the Co^{2+} breakthrough curve exhibits a delayed approach to relative concentration of 0. The comparison reveals that transport of Co^{2+} through the heterogeneous porous medium is significantly nonideal.

The result obtained from analyzing the ^3H_2O breakthrough curve with a dual-porosity-based model is used to provide a value for ω (0.02), the parameter that

represents the effect of physical heterogeneity on the transport of Co^{2+}. Note that the ω value obtained for ^3H_2O is modified to account for the difference in diffusivities between ^3H_2O and ^{57}Co (3). The results from the sorption isotherm experiments are linearized $[K_l = K_f C_0^{n-1}]$ (6) to provide values for K_a (2.38) and K_n (7.92). Using these data, the global retardation factor $[R = 1 + (\rho/\theta)(fK_a + (1 - f)K_n)]$ is calculated to be 12.2.

The optimized curve obtained for the case of hydraulic conductivity variability, sorption capacity variability, rate-limited mass transfer between the two layers, and rate-limited sorption/desorption is shown in Figure 1. This curve matches the experimental data quite well. The values obtained for the two optimized parameters were $k_2 = 0.14$ h^{-1} and $F = 0.68$. These values are within the range of values obtained from batch sorption experiments performed with Co^{2+} and other radionuclides (7–9). A simulated curve produced for the case of hydraulic conductivity variability, sorption capacity variability, rate-limited mass transfer between the two layers, and instantaneous sorption/desorption is shown in Figure 1. This simulation does not describe the experimental data very well. The fact that nonequilibrium sorption terms are required to fully describe the experimental data and that the values of the nonequilibrium parameters are similar to published kinetic data supports the contention that the transport of Co^{2+} in our porous-media system was influenced by rate-limited sorption/desorption.

A simulated curve for the case of homogeneous sorption, hydraulic conductivity variability, and rate-limited mass transfer and sorption is also presented in Figure 1. Clearly, the influence of sorption variability must be considered to accurately simulate the transport of Co^{2+}. Based on the preceding results, it appears that the transport of Co^{2+} was influenced by several factors, including hydraulic conductivity variability, sorption capacity variability, rate-limited mass transfer between the two layers, and rate-limited sorption/desorption.

The retardation factor calculated by using data obtained from batch-isotherm experiments was very representative of the observed transport of Co^{2+} in the column. In addition, the mass transfer of Co^{2+} between the two layers appears to have been represented well by using the results obtained from analysis of the ^3H_2O breakthrough curve. This consistency between different experiments supports the contention that the nonideal transport exhibited by Co^{2+} was indeed caused by a combination of several discrete factors.

Conclusion

The impact of hydraulic conductivity variability and sorption capacity variability on the transport of radionuclides in porous media is critically important to an accurate understanding of the fate of radionuclides in the subsurface. The results of a well-controlled, experimentally based investigation of the transport of Co^{2+} in a physically and chemically heterogeneous porous medium have demonstrated that transport in heterogeneous porous media can be significantly nonideal. As such, transport of radionuclides in heterogeneous porous media should receive further attention. For the present case, rate-limited sorption of Co^{2+} by the porous media appeared to be important. It must be remembered, however, that other processes, such as oxidation by manganese oxides [Co(II)

→ Co(III)] with subsequent surface precipitation, may also be important for the transport of Co^{2+} in subsurface environments.

Literature Cited

(1) Coats, K. H.; Smith, B. D. *J. Soc. Pet. Eng.* **1964**, *4*, 73.
(2) van Genuchten, M. Th. *Non-equilibrium transport parameters from miscible displacement experiments*; Research Report 119; U.S. Salinity Laboratory, U.S. Department of Agriculture: Washington, DC, 1981.
(3) Brusseau, M. L.; Jessup, R. E.; Rao, P. S. C. Water Resour. Res. **1989**, *25*, 1971.
(4) Hem, J. D. *Chem. Geol.* **1978**, *21*, 199.
(5) Hem, J. D.; Roberson, C. E.; Lund, C. J. *Geochim. Cosmochim. Acta* **1985**, *49*, 801.
(6) Brusseau, M. L.; Rao, P. S. C. *CRC Crit. Rev. Environ. Control* **1989**, *19*, 33.
(7) Bencala, K. E.; Jackman, A. P.; Kennedy, V. C.; Avanzino, R. J.; Zellweger, G. W. *Water Resour. Res.* **1983**, *19*, 725.
(8) Lyon, K. E.; Patterson, R. J. *Water Pollut. Res. J. Can.* **1984**, *19*, 23.
(9) Fuentes, H. R.; Polzer, W. L.; Essington, E. H.; Roensch, F. R. In *Proceedings of Waste Management '85*, Waste Management Association: Tucson, AZ, Mar 24–28, 1985.