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Yucca Mountain Site Characterization Program
Milestone 3415

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VALIDITY OF BATCH SORPTION DATA TO DESCRIBE SELENIUM TRANSPORT THROUGH UNSATURATED TUFF

Yucca Mountain Site Characterization Program Milestone 3415

by

James L. Conca and Inés R. Triay

ABSTRACT

As part of the project to characterize Yucca Mountain as a potential site for a high-level nuclear waste repository, we used UFA™ technology (centrifuge-induced flow) to directly measure selenite retardation coefficients and hydraulic conductivity under unsaturated conditions on two tuff samples from Yucca Mountain. The retardation factor for the selenite species was 2.5 in both Yucca Mountain vitric tuff at 62.6% saturation and zeolitic nonwelded tuff from G-tunnel at 52.8% saturation. For these column experiments, we prepared a solution, using J-13 well water from the Nevada Test Site, with a selenium concentration of 1.31 mg/L (ppm). The retardation factor of 2.5 measured for both tuffs translates into a sorption distribution coefficient, K_d, of 0.9 mL/g for the vitric tuff and 0.8 mL/g for the zeolitic tuff. For batch sorption experiments, using the same zeolitic tuff as for the column experiments and solutions of J-13 well water with a selenium concentration of 1.1 mg/L (ppm), the average K_d was determined to be 0.1 $\pm$ 0.2 mL/g. Given the small K_d values for selenium sorption, general agreement between the batch and column measurements (obtained under unsaturated conditions) was observed. The unsaturated hydraulic conductivities during the experiments were 2.5×10^{-8} cm/s for the Yucca Mountain vitric tuff and 1.2×10^{-8} cm/s for the zeolitic nonwelded tuff from G-tunnel.

INTRODUCTION

Direct measurements of transport parameters in actual subsurface materials under subsurface conditions are necessary for defensible modeling of contaminant transport in host rocks and engineered barriers surrounding nuclear and hazardous waste repositories. The hydraulic conductivity, K, and the retardation factor, R_f, along with the associated distribution coefficient, K_d, are poorly known transport parameters for real systems but are key input parameters to existing and developing contaminant release models. We experimentally determined unsaturated R_f and K for cores of Yucca Mountain vitric-member tuff and zeolitic nonwelded tuff from G-Tunnel, Bed 5, with respect to J-13 well water with a selenium concentration (as selenite) of 1.31 mg/L (ppm) at 23°C. Our intent was to demonstrate that a method in which flow is induced with an ultracentrifuge (the UFA™ method) could rapidly and directly measure R_f and K in whole rock tuff cores and then to compare these directly measured unsaturated R_f values with those calculated from K_d values obtained through traditional batch tests on the same materials.

METHODOLOGY

Retardation

Retardation factors can be determined in flow experiments where R_f for a particular species is the ratio of the solution velocity to the species velocity. The retardation factor for that species is given by:

$$R_f = \frac{V_{gw}}{V_{sp}} = 1 + \rho_d \frac{K_d}{\varepsilon} \quad , \qquad [1]$$

where V_{gw} is the velocity of carrier fluid, V_{sp} is the velocity of the species, ρ_d is the dry bulk density, ε is the porosity, and K_d is defined as the moles of the species per gram of solid divided by the moles of the species per milliliter of solution. If none of a particular species is lost to the solid phase, then $K_d = 0$ and $R_f = 1$ for that species. In column experiments, a breakthrough curve is obtained for the particular species and R_f is determined as the pore volume at which the concentration of the species in the solution that has passed through the column is 50% of the intial concentration (C/C_o = 0.5). It is now generally assumed that for unsaturated systems $\varepsilon = \theta$, where θ is the volumetric water content (Bouwer 1991; Conca and Wright 1992a). This study experimentally addresses this concern under unsaturated conditions in whole rock and evaluates the use of data from batch experiments in determining R_f in whole rock.

We prepared solutions using J-13 well water with a selenite concentration of 1.31 ppm and determined the selenium concentrations with an inductively coupled, argon plasma, atomic emission spectrometer (Jarrell-Ash Model 976 Plasma Atomcomp). We used an ion chromatograph (Dionex Series 4000i) to determine the speciation of selenium in solution. All selenium in the starting solutions and in all effluent solutions was found to exist as selenite.

Hydraulic Conductivity

One way to drive fluid through rock is to use centripetal acceleration as the driving force. We used this approach with a new technology (UFA) to produce hydraulic steady-state, to control temperature, degree of saturation, and flow rates in all retardation experiments, and to measure the hydraulic conductivity. A specific advantage of this approach is that centripetal acceleration is a whole-body force similar to gravity that acts simultaneously over the entire system and independently of other driving forces, such as gravity or matric suction. It has been shown that capillary bundle theory holds in the UFA method (Conca and Wright 1992a and 1992b).

The UFA instrument consists of an ultracentrifuge with a constant, ultralow flow-rate pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system (Fig. 1). Accelerations up to 20,000 g are attainable at temperatures from −20° to 150°C and flow rates as low as 0.001 mL/hr. The effluent is collected in a transparent, volumetrically calibrated container at the bottom of the sample assembly. The effluent collection chamber can be observed during centrifugation using a strobe light.

The current instrument has two different rotor sizes that hold up to 50 and 100 cm^3 of sample, respectively. Three different rotating seal assemblies facilitate various applications and contaminant compatibilities; they are a face seal, a mechanical seal, and a paramagnetic seal. Figure 1 shows the large-sample option with the paramagnetic seal, a configuration that is optimal for adsorption and retardation studies.

Numerous studies have compared use of the UFA approach with traditional methods of doing this type of analysis in soils and clays, and the agreement is excellent (Conca and Wright 1992b; Nimmo et al. 1987). Good agreement is expected because the choice of driving force does not matter provided the system is Darcian (see next paragraph) and the sample is not adversely affected by a moderately high driving force ($\leq$ 1000 g for all samples run in these experiments); both of these provisions hold for most geologic systems. Additionally, all techniques for estimating $K(\theta)$ are

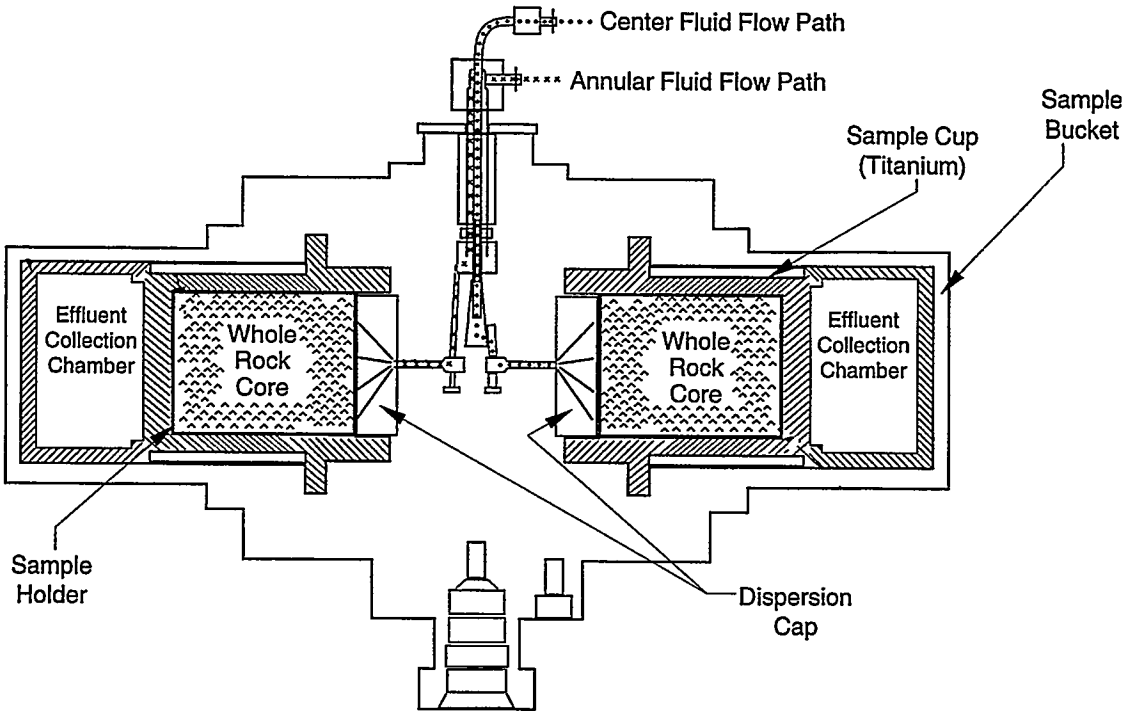

Figure 1. The UFA Method. Schematic of the UFA rotor shown with paramagnetic seal and the large-sample options, a configuration that is optimal for adsorption and retardation studies.

extremely sensitive to the choice of the rock or soil residual water content, θ_r, and to the saturated hydraulic conductivity, K_s; minor variations in θ_r or K_s produce order of magnitude changes in $K(\theta)$ (Stephens and Rehfeldt 1985).

The UFA technology is effective because it allows the operator to set the variables in Darcy's Law, which can then be used to determine hydraulic conductivity. Under a centripetal acceleration in which water is driven by both the potential gradient, $d\psi/dr$, and the centrifugal force per unit volume, $\rho\omega^2 r$, Darcy's Law is

$$q = -K(\psi)[\frac{d\psi}{dr} - \rho\omega^2 r] \quad , \qquad [2]$$

where q is the flux density into the sample; K, the hydraulic conductivity, is a function of the matric suction (ψ) and therefore of water content (θ); r is the radius from the axis of rotation; ρ is the fluid density; and ω is the rotation speed. When multi-component and multiphase systems are present in the UFA instrument, each component reaches its own steady-state with respect to each phase, as occurs in the field. Appropriate values of rotation speed and flow rate into the sample are chosen to obtain desired values of flux density, water content, and hydraulic conductivity in the sample. Above speeds of about 300 rpm, depending upon the material and providing that sufficient flux density exists, $d\psi/dr << \rho\omega^2 r$. Under these conditions, Darcy's Law is given by $q = -K(\psi)\,[-\rho\omega^2 r]$. Rearranging the equation and expressing hydraulic conductivity as a function of water content, Darcy's Law becomes:

$$K(\theta) = \frac{q}{\rho\omega^2 r} \quad . \qquad [3]$$

As an example, a whole rock core of Topopah Spring Member tuff accelerated to 7500 rpm with a flow rate into the core of 2 mL/hr achieved hydraulic steady-state in 30 hours with a hydraulic

conductivity of 8.3×10^{-9} cm/sec at a volumetric water content of 7.0%. Previous studies have verified the linear dependence of K on flux and the second-order dependence on rotation speed (Conca and Wright 1992a; Nimmo et al. 1987) and several comparisons between the UFA method and other techniques have shown excellent agreement (Conca and Wright 1992a and 1992b). Because the UFA method can directly and rapidly control the hydraulic conductivity, fluid content, temperature and flow rates, other transport properties can then be measured as a function of fluid content by associated methods either inside or outside the UFA instrument during the overall run.

Fundamental physics issues involving flow in an acceleration field have been raised and successfully addressed by previous research and in numerous forums (Conca and Wright 1992a and 1992b; Nimmo et al. 1987; Nimmo and Akstin 1988; Nimmo and Mello 1991). These studies have shown, first, that compaction from acceleration is negligible for subsurface soils at or near their field densities. Bulk density in all samples remain constant because a whole-body acceleration does not produce high point pressures. A notable exception is surface soils, which can have unusually low bulk densities; special arrangements must be made to preserve their densities. Whole rock cores are completely unaffected.

The studies have also shown that three-dimensional deviations of the driving force with position in the sample are less than a factor of 2, but moisture distribution is uniform to within 1% in homogeneous systems because water content depends only upon ψ, and unit gradient conditions are achieved in the UFA instrument in which $d\psi/dr = 0$. Hydraulic steady-state is not as sensitive to changes in rotation speed as to flux density. In heterogeneous samples or multicomponent systems such as rock, each component reaches its own hydraulic steady state and water content, as occurs for such materials under natural conditions in the field. This last effect cannot be reproduced with pressure-driven techniques, but only under a whole-body force field such as with gravity columns or centrifugal methods. The ratio of flux to rotation speed is always kept high enough to maintain the condition of $d\psi/dr = 0$.

RESULTS AND DISCUSSION

Column Breakthrough Test Results

For these experiments, the rotation speed was set at 2,000 rpm with a flow rate into each sample of 0.2 mL/hr. The experiment was run for 9 days with an initial selenium concentration of 1.31 ppm. Figure 2 shows the breakthrough curves for selenite in the Yucca Mountain vitric member at 62.6% saturation and in the zeolitic nonwelded tuff at 52.8% saturation. The experiment was stopped before full breakthrough in the zeolitic nonwelded tuff, but the $C/C_o = 0.5$ point was reached. The retardation factor for each tuff sample is only 2.5, giving a K_d of 0.9 mL/g for the Yucca Mountain vitric member and 0.8 mL/g for the zeolitic nonwelded tuff.

During these experiments, the unsaturated hydraulic conductivity, K, for each sample at these water contents was 2.5×10^{-8} cm/s for the Yucca Mountain vitric member tuff and 1.2×10^{-8} cm/s for the zeolitic nonwelded tuff. Figure 3 gives the characteristic curves, $K(\theta)$, for Yucca Mountain vitric member and zeolitic nonwelded tuff determined in separate experiments, as well as measurements for other tuffs and materials for comparison. As in most whole rock cores studied (Conca and Wright 1992a and 1992b), the characteristic curves for the tuffs are steep, almost linear functions of the volumetric water content and are displaced according to the degree of welding and alteration.

Batch Test Results

We conducted batch adsorption tests using the same J-13 well water with a slightly lower selenium concentration of 1.1 ppm and the same zeolitic nonwelded tuff from G-Tunnel, Bed 5, as in the UFA column breakthrough test. The batch adsorption tests consist of crushing and wet-sieving the tuff, pretreating the tuff with J-13 water, placing

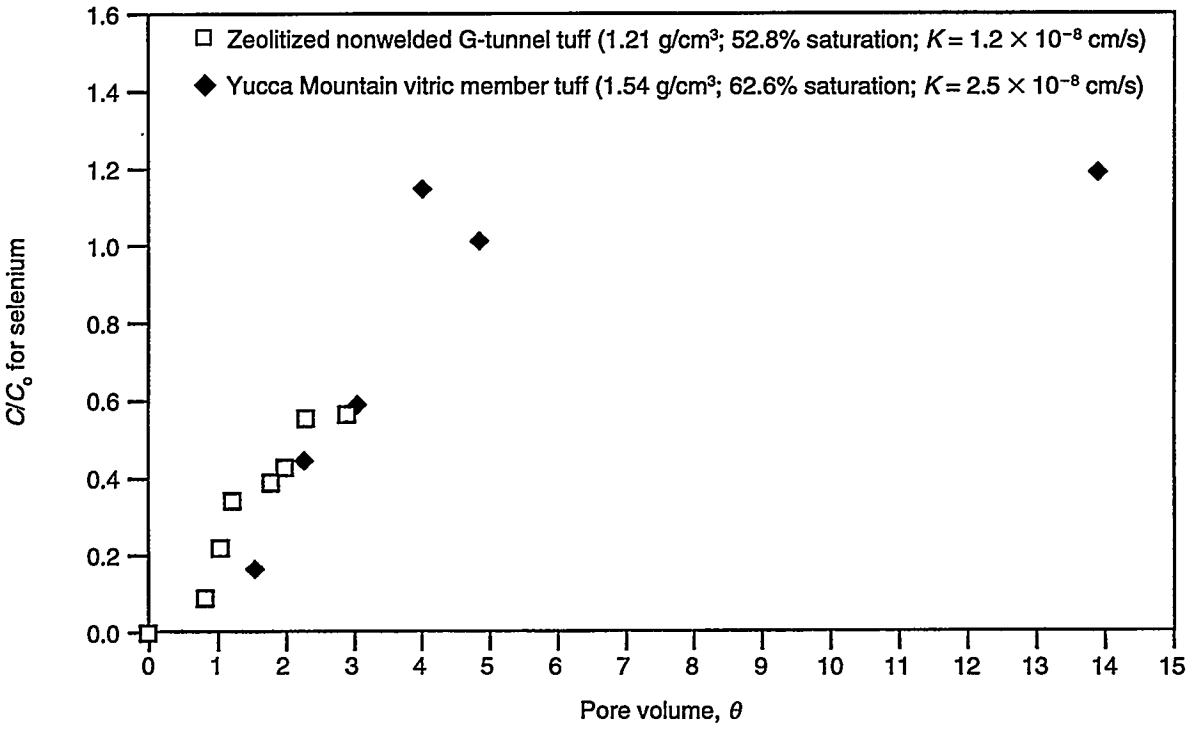

Figure 2. Breakthrough Curves. UFA column data for a Yucca Mountain tuff retardation experiment that show the breakthrough curves for selenium. The initial concentration, C_o, of selenium (as selenite) was 1.31 ppm in J-13 well water.

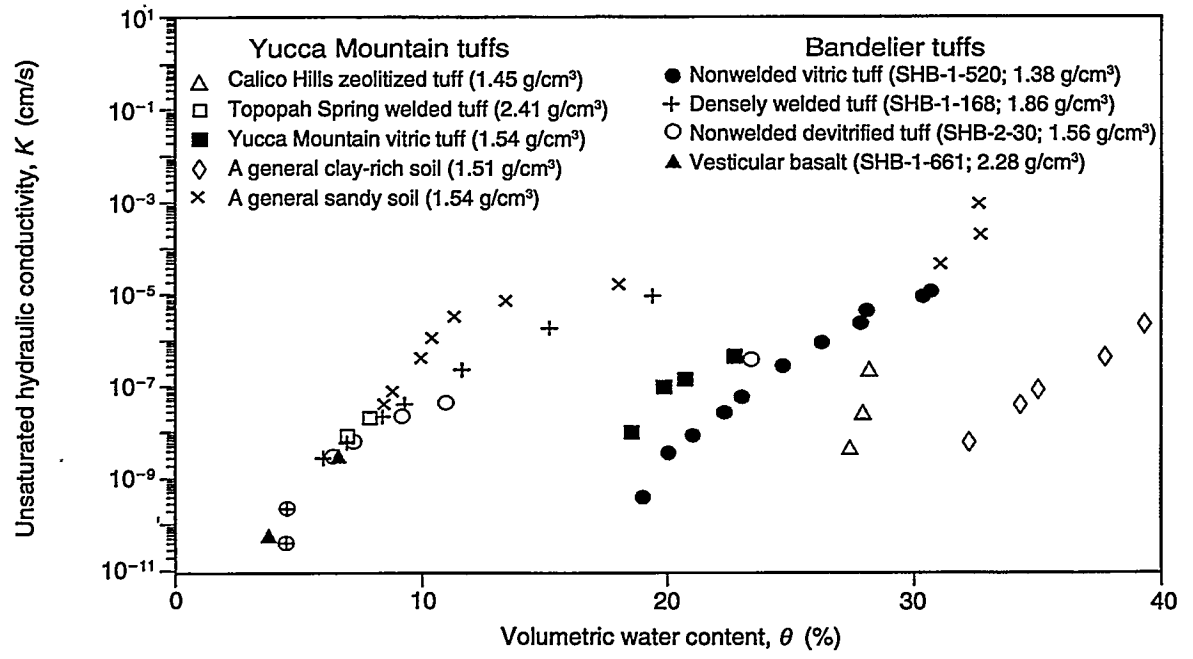

Figure 3. Unsaturated Hydraulic Conductivity. UFA column data for various Yucca Mountain and Bandelier tuffs and other soil samples that show the unsaturated hydraulic conductivity, K, as a function of volumetric water content, θ. The name and the density of each tuff is given in the legend.

the selenium solution in contact with the tuff, separating the phases by centrifugation, and determining the amount of selenium in each phase by difference using inductively coupled plasma mass spectrometry. Control samples were used to determine the sorption of selenium onto the walls of the sorption containers. The control procedure consisted of following the described batch sorption procedure with a sample containing the selenium solution, except with no tuff added. The results of the control experiments indicate no loss of selenium due to precipitation or sorption onto the walls of the container during the batch sorption experiment. The sorption distribution coefficients we obtained are given in Table 1. The Eh of all solutions, measured after the sorption experiments, varied from 140 to 150 millivolts.

The data presented in Table 1 and Fig. 2 indicate agreement between the column and the batch-sorption experiments. At a selenium concentration of ~1 ppm, no sorption of the selenium by the tuff is observed for the zeolitic tuff used in batch experiments, and minimal sorption (K_d of 0.8 mL/g) is observed for the zeolitic tuff used in the unsaturated column experiments. The method we used for the batch-sorption experiments to determine K_d values (by difference) involves subtracting the selenium concentration in solution after equilibration with the solid phase from the initial selenium concentration in solution. This method yields large scatter in the data when the batch-sorption distribution coefficient is small because two large numbers are subtracted to get a small number. Inspection of Table 1 also suggests that the kinetics of selenium sorption onto tuff are fast.

TABLE 1. Selenium Batch Adsorption on Nonwelded Zeolitic Tuff*

Pretreatment period (days)	Sorption period (days)	K_d (mL/g)
6.9	0.04	−0.2
6.9	0.04	0.3
6.8	13.9	0.0
6.8	13.9	0.2

*Experimental conditions: J-13 water; 20°C; 75-500 μm tuff particle sizes; 1.1 ppm initial selenium concentration; solution pH after sorption of 8.4; and samples from the same location in G-Tunnel, Bed-5, as the tuff used in the column experiments.

In previous experiments (Conca and Triay 1994), tuff samples from the same vicinity (but not from the same location) as the tuff samples used for column experiments were used to compare results of the batch and column experiments. Agreement was not observed for the zeolitic tuff, which is why it was decided to repeat the batch sorption experiments here using zeolitic tuff from the exact same location as that used in the column experiments. The reason for the disagreement between the batch and the column results in the previous work is most likely due to a difference in the mineralogy of the samples.

CONCLUSIONS

This study demonstrated the feasibility of using the UFA technology to rapidly and directly measure retardation factors and hydraulic conductivities in whole rock cores of tuff under the unsaturated conditions that exist in the field. In UFA column breakthrough tests, the retardation factor for the selenite species was only 2.5 in both Yucca Mountain vitric member tuff at 62.6% saturation and zeolitic nonwelded tuff from G-tunnel at 52.8% saturation for a selenium concentration in J-13 water of 1.31 ppm. In batch tests on the same material with an initial selenium concentration of 1.1 ppm, the average K_d was 0.08 ± 0.2 mL/g, which gives retardation factors that are slightly lower than those from the UFA column breakthrough experiments. This finding suggests that using batch sorption coefficients to predict radionuclide transport through unsaturated tuff will yield conservative results.

Future experiments will use initial selenium concentrations smaller than the ones used in these experiments to further assess the validity of batch sorption distribution coefficients to predict transport under unsaturated conditions. The unsaturated hydraulic conductivities during the experiments were 2.5×10^{-8} cm/s for the Yucca Mountain vitric member tuff and 1.2×10^{-8} cm/s for the zeolitic nonwelded tuff.

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