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SELENITE TRANSPORT IN UNSATURATED TUFF FROM YUCCA MOUNTAIN

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ABSTRACT

Direct measurements of unsaturated selenite retardation coefficients and unsaturated hydraulic conductivity were obtained on two tuff samples from Yucca Mountain using the UFA™ technology. The retardation factor for the selenite species was only 2.5 in both Yucca Mountain vitric member at 62.6% saturation and zeolitized nonwelded tuff from G-tunnel at 52.8% saturation with respect to J-13 well water from the Nevada Test Site contaminated with selenium at 1.31 mg/l (ppm). In batch tests on the same material using 1.2 mg/l (ppm), the average K_d was determined to be 13, giving retardation factors higher than the UFA column breakthrough tests by an order of magnitude. The difference could result from preferential flow paths in the UFA column as might occur in the field or differences in residence times between the two types of tests. The unsaturated hydraulic conductivities during the experiments were 2.49×10^{-8} cm/s for the Yucca Mountain vitric member and 1.16×10^{-8} cm/s for the zeolitized nonwelded tuff.

I. INTRODUCTION

Direct measurements of transport parameters in actual subsurface materials under actual 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 transport parameters that are poorly known for real systems but that are key input parameters to existing and developing contaminant release models. This paper reports experimentally determined unsaturated R_f and K for cores of Yucca Mountain vitric member tuff and nonwelded zeolitized tuff from G-Tunnel Bed 5 with respect to J-13 well water contaminated with selenium at 1.31 mg/l (ppm) as the selenite species at 23° C. The purpose of this study was to demonstrate that the UFA method could rapidly and directly measure R_f and K in whole rock tuff cores, and to compare these directly measured unsaturated R_f values with those calculated from K_ds obtained through traditional batch tests on the same materials.

II. METHODOLOGY

A. 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[1]

$$R_f = V_{gw}/V_{sp} = 1 + \rho K_d/n \qquad (1)$$

where V_{gw} is the velocity of carrier fluid, V_{sp} is the velocity of the species, ρ is the dry bulk density and n is the porosity. K_d is defined as the moles of the species per gram of solid divided by the moles of the species per ml 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 $C/C_0 = 0.5$. It is now generally assumed that for unsaturated systems $n = \theta$ where θ is the volumetric water content.[1,2] This study experimentally addresses this concern under unsaturated conditions in whole rock, and

evaluates the use of batch experiment data in determining Rf in whole rock.

The solutions used were J-13 well water spiked with selenite to 1.31 ppm selenium. Selenium concentrations were determined using a Jarrell-Ash Model 976 Plasma Atomcomp inductively coupled argon plasma atomic emission spectrometer. A Dionex Series 4000i Ion Chromatograph was used to speciate the selenium. All selenium in the starting solutions and in all effluent solutions was found to be as the selenite species.

B. Hydraulic Conductivity

A new technology, the UFA™, was used to control hydraulic steady-state, temperature, degree of saturation, and flow rates in all retardation experiments and to measure the hydraulic conductivity. There are specific advantages to using a centripetal acceleration as a fluid driving force. It is a whole-body force similar to gravity, and so acts simultaneously over the entire system and independently of other driving forces, e.g., gravity or matric suction. It has been shown that capillary bundle theory holds in the UFA.[2,3] The UFA instrument consists of an ultracentrifuge with a constant, ultralow flow-rate pump which provides fluid to the sample surface through a rotating seal assembly and microdispersal system (Figure 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. There are now two different rotor sizes holding up to 50 cm^3 and 100 cm^3 of sample, respectively, and three different rotating seal assemblies for various applications and contaminant compatibilities; a face seal, a mechanical seal and a paramagnetic seal. Figure 1 shows the large sample option with the paramagnetic seal which is optimal for adsorption and retardation studies. Numerous studies comparing the UFA to traditional methods in soils and clays have been performed and the agreement is excellent.[3,4] Good agreement is expected since the choice of driving force does not matter provided the system is Darcian and the sample is not adversely affected by a moderately high driving force (≤1000 g for all samples run in these experiments), both of which hold for most geologic systems. Additionally, it has been recognized for some time that all $K(\theta)$ estimation techniques are extremely sensitive to the choice of the rock or soil residual water content, θ_r, and the saturated hydraulic conductivity, K_s, and that minor variations in θ_r or K_s produce order of magnitude changes in $K(\theta)$.[5] The direct $K(\theta)$ measurements of the UFA method are not sensitive or dependent in any way upon θ_r or K_s or even each other.

The UFA technology is so effective because it allows the operator to set the variables in Darcy's Law. Darcy's Law can then be used to determine hydraulic conductivity as follows. 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

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

where q is the flux density into the sample; K is the hydraulic conductivity, which 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. With multicomponent and multiphase systems in the UFA, 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, $d\psi/dr << \rho\omega^2 r$. Therefore, 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:

$$K(\theta) = q/\rho\omega^2 r \qquad (3)$$

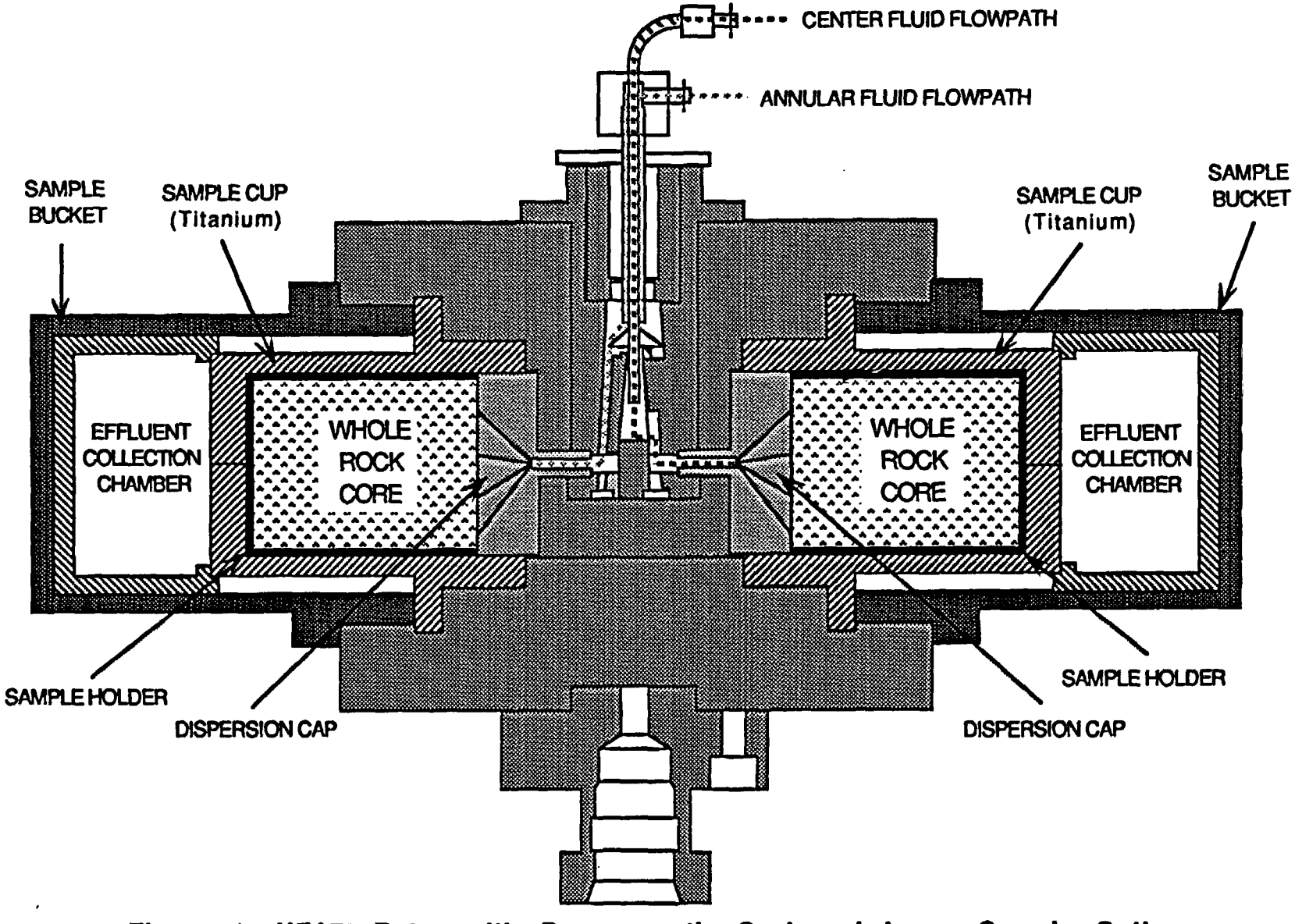

Figure 1. UFA™ Rotor with Paramagnetic Seal and Large Sample Options

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 an hydraulic conductivity of 8.28 x 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[2,4] and several comparisons between the UFA and other techniques have shown excellent agreement.[2,3] Because the UFA can control the hydraulic conductivity, fluid content, temperature and flow rates, directly and rapidly, other transport properties can then be measured as a function of fluid content by associated methods either inside or outside the UFA 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.[2,3,4,6,7] These studies have shown that: 1) compaction from acceleration is negligible for subsurface soils at or near their field densities. Bulk density in all samples run remain constant because a whole-body acceleration does not produce high point pressures. The notable exceptions are surface soils which can have unusually low bulk densities and special arrangements must be made to preserve their densities. Whole rock cores are completely unaffected, 2) 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 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 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 $d\psi/dr = 0$.

III. RESULTS

A. Column Breakthrough Test Results

For these experiments, the UFA rotation speed was set at 2000 rpm with a flow rate of 0.2 ml/hr into each sample. The experiment was run for 9 days. Figure 2 shows the breakthrough curves for selenite in the Yucca Mountain vitric member at 62.6% saturation, and in the zeolitized nonwelded tuff at 52.8% saturation. The experiment was stopped before full breakthrough in the zeolitized nonwelded tuff, but the $C/C_0 = 0.5$ point was reached. The retardation factor for each tuff sample is only 2.5, giving a K_d of 0.94 for the Yucca Mountain vitric member and 0.79 for the zeolitized nonwelded tuff.

The unsaturated hydraulic conductivity during these experiments for each sample at these water contents was 2.49 x 10^{-8} cm/s for the Yucca Mountain vitric member and 1.16 x 10^{-8} cm/s for the zeolitized nonwelded tuff. Figure 3 gives the characteristic curves, $K(\theta)$, for Yucca Mountain vitric member and nonwelded zeolitized tuff determined in separate experiments as well as measurements for other tuffs and materials for comparison. As in most whole rock cores studied[2,3] 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.

B. Batch Test Results

Batch adsorption tests were conducted using the same J-13 well water spiked with selenite to 1.2 ppm selenium concentrations and the same nonwelded zeolitized tuff from G-Tunnel Bed 5 as in the UFA column breakthrough test. The batch adsorption tests consist of crushing and sieving the tuff, placing the selenium-contaminated solution in contact with the tuff, separating the phases by normal centrifugation, and determining the amount of selenium in each phase by Inductively Coupled Plasma - Mass Spectrometry. Control samples were utilized to determine the sorption of selenium onto the walls of the sorption containers. The control samples consisted of following the described

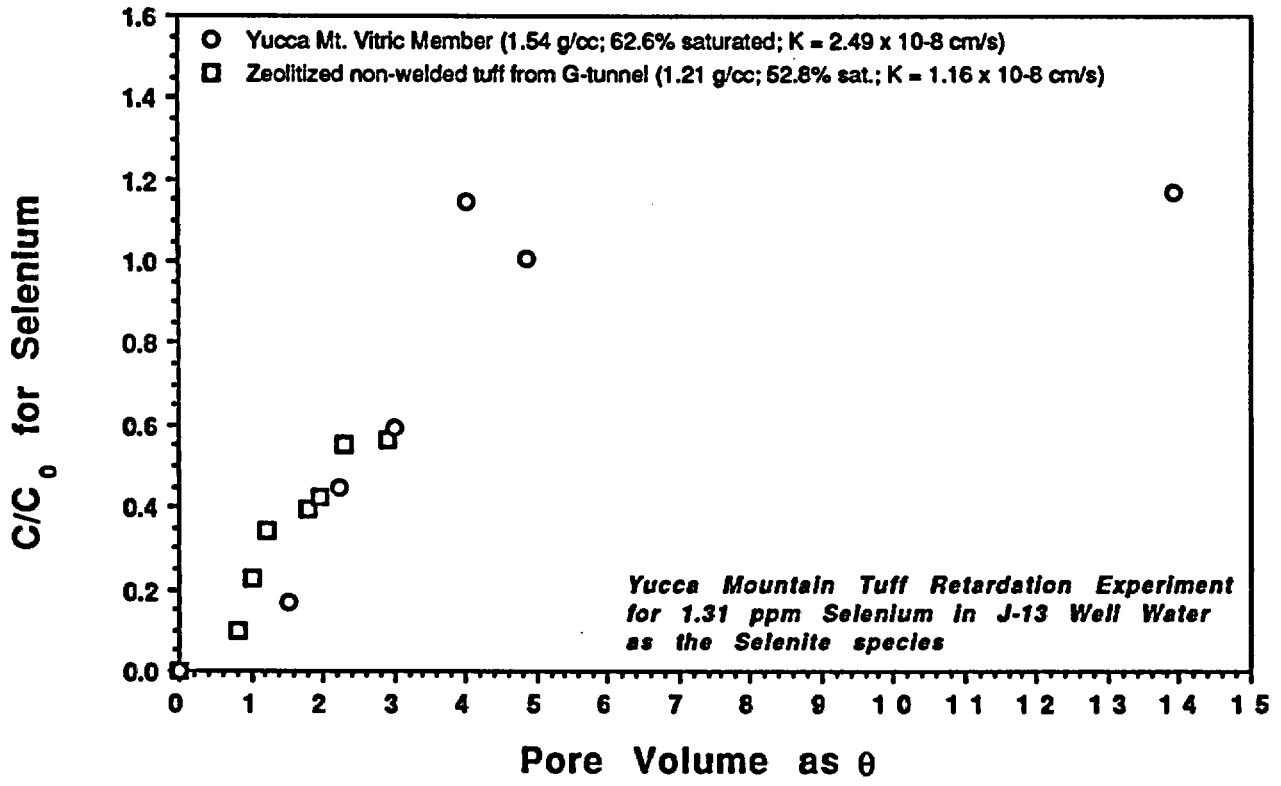

Figure 2. UFA column Breakthrough Curves for Selenite

batch sorption procedure with a sample containing the selenium solution only, 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 coef-ficients obtained using dry- and wet-sieved tuff are given in Table 1.

Selected sorption distribution coefficients for selenium in zeolitic tuffs using J-13 well water presented by Thomas (1987) are summarized in Table 2.[8] The mineralogy of these tuff samples was determined by Chipera and Bish (1989) and is given in Table 3.[9] These mineralogies should be similar to those of the G-Tunnel Bed 5 nonwelded, zeolitized tuff used in this study.

TABLE 1. Data for Selenium Batch Adsorption Experiments on G-Tunnel Bed 5 Nonwelded, Zeolitized Tuff

Water Type	J-13 well water
Tuff Particle Size	75-500 μm
Temperature	20°C
Length of Sorption	26 days
Initial Se Concentration	1.2 ppm
Solution pH after Sorption	8.1

Dry-Sieved Tuff K_ds (ml/g)

Trial #1	Trial #2	Trial #3	Trial #4
15	16	13	13

Wet-Sieved Tuff K_ds (ml/g)

Trial #1	Trial #2	Trial #3	Trial #4
14	15	10	13

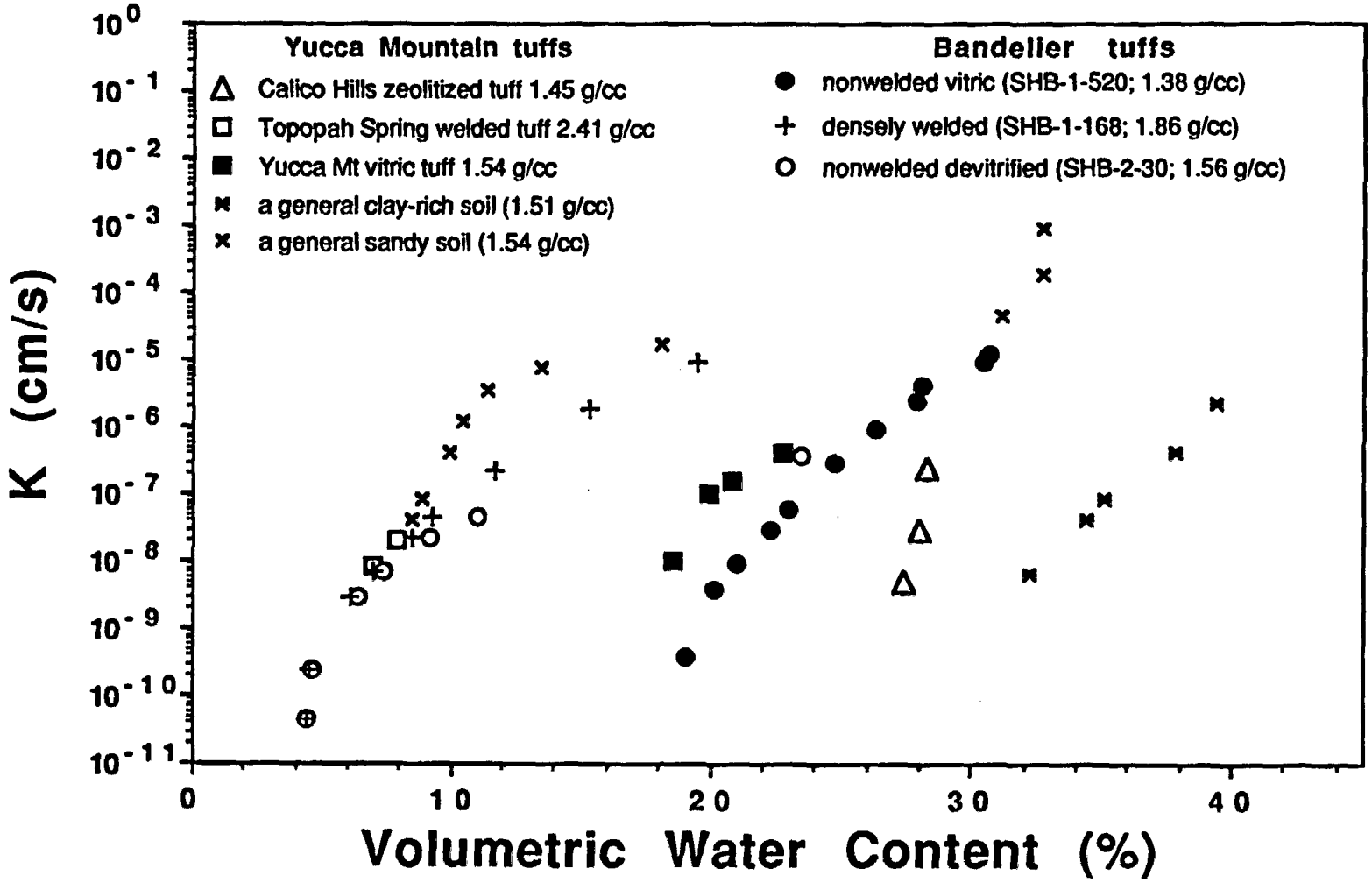

Figure 3. Unsaturated hydraulic conductivity of various media

TABLE 2. Data for Selenium Batch Adsorption Experiments on Zeolitic Tuffs Presented by Thomas (1987)

Tuff G1-1436	
Initial Se Concentration	1×10^{-10} *M*
Length of Sorption	42 days
K_ds (ml/g)	
Trial #1	11
Trial #2	14
Tuff G1-2289	
Initial Se Concentration	8×10^{-10} *M*
Length of Sorption	28 days
K_ds (ml/g)	
Trial #1	10
Trial #2	12
Tuff G1-2289	
Initial Se Concentration	1×10^{-10} *M*
Length of Sorption	42 days
K_ds (ml/g)	
Trial #1	9
Trial #2	8
Tuff G4-1608	
Initial Se Concentration	2×10^{-9} *M*
Length of Sorption	42 days
K_ds (ml/g)	
Trial #1	15
Trial #2	16

TABLE 3. Mineralogy of Zeolitic Tuff by Chipera and Bish (1989)

Tuff	G1-1436	G1-2289	G4-1608
Clinoptilolite	73±5%	6±3%	54±4%
Mordenite		43±20	
Opal-CT	14±3	7±3	20±5
Alkali Feldspar	6±1	35±18	11±2
Smectite	Trace	2±1	5±2
Quartz	3±1	7±2	6±1

Comparison of the results in Table 1 with the previous results in Table 2 indicates good agreement, even though previous experiments were performed with solutions having an initial selenium concentration in the range of 10^{-9} to 10^{-10} *M*, four to five orders of magnitude lower than the selenium concentrations used for the unsaturated UFA column breakthrough tests and the sorption batch experiments reported in Table 1 and Figure 2 which are 1.5×10^{-5} *M*.

IV. DISCUSSION

The unsaturated K_ds for selenite measured in the UFA column breakthrough test are lower than those determined from the batch tests. The UFA results are also lower than those expected from batch studies on similar materials, but within an order of magnitude.[8] Studies by Zachara and Rai of selenite sorption on soils gave K_ds between 0.02 and 4.63 (John Zachara, 1994, personal communication; in press) which are also low, but consistently higher than selenate and sulfate K_ds in the same materials.

The lower unsaturated K_ds measured in UFA column breakthrough tests may result from preferential flow paths of the migrating solutions in whole rock. Alternatively, the low K_ds in the tuffs could result from non-linearity in the adsorption isotherm for selenite in this high of a concentration range. However, the batch test results of Table 2 suggest that the isotherm is fairly linear. Rogers and Meijer[10] showed that crushing to various particle sizes does not seem to affect sorption in tuff. In related experiments, UFA column breakthrough tests and batch tests were performed on the same soil from the Hanford Site with respect to uranium in Hanford groundwater.[2] These results gave a retardation factor of 2.3 for the UFA column breakthrough tests at two different degrees of saturation (77% saturated and 26% saturated) and a calculated retardation factor of between 4 and 9 from the measured K_ds of the batch tests. However, in these batch tests the variations appeared to be strongly dependant upon residence time and aqueous chemical effects (Clark Lindenmeier and Jeff Serne, 1994, personal communication). The batch tests compared best with the UFA column breakthrough tests when the residence times were close. Therefore, residence times could also have caused K_d differences between the UFA column tests and the batch tests for selenate. Further work with both soils and whole rock at various concentrations and residence times may resolve these issues. Even so, it appears that although UFA column breakthrough tests and batch tests may be significantly different depending upon the

material, the difference will probably not exceed an order of magnitude.

V. 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 at 62.6% saturation and zeolitized nonwelded tuff from G-tunnel at 52.8% saturation with respect to J-13 well water contaminated with selenium at 1.31 mg/l (ppm). In batch tests on the same material using 1.2 mg/l (ppm) the average K_d was determined to be 13, giving retardation factors higher than the UFA column breakthrough tests by an order of magnitude. The difference may result from preferential flow paths in the UFA column as might occur in the field or differences in residence times between the two types of tests. The unsaturated hydraulic conductivities during the experiments were 2.49×10^{-8} cm/s for the Yucca Mountain vitric member and 1.16×10^{-8} cm/s for the zeolitized nonwelded tuff.

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