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Uranium(VI) Sorption and Transport in Unsaturated, Subsurface Hanford Site Sediments - Effect of Moisture Content and Sediment Texture: Final Report for Subtask 2b

A. P. Gamerdinger
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**Uranium(VI) Sorption and Transport in Unsaturated,
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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

A series of experiments were conducted in fiscal year 1998 at the Pacific Northwest National Laboratory¹ as part of the Immobilized Low-Activity Waste-Performance Assessment. These experiments evaluated the sorption and transport of uranium, U(VI), under conditions of partial moisture saturation that are relevant to arid region burial sites and vadose-zone far-field conditions at the Hanford Site. The focus was on measuring breakthrough curves (from which distribution coefficient [K_d] values can be calculated) for U(VI) in three Hanford Site sediments that represent different texture classes in two unsaturated moisture conditions. Previous research showed that K_d values measured during transport in unsaturated sediments varied with moisture saturation.

For the current work in unsaturated sediments, the U(VI) K_d values decreased as the moisture content decreased in all three sediments evaluated, irrespective of their texture. In the medium-coarse sand, the K_d values decreased from 0.48 to 0.16 mL/g (67%) as the moisture saturation decreased from 30% to 12%. In the fine-sand sediment, the K_d value decreased from 1.42 to 0.39 mL/g (73%) as the moisture saturation decreased from 66% to 22%. In the silt loam, the K_d value decreased from 4.05 to 1.81 mL/g (55%) as the moisture saturation decreased from 83% to 41% (noting incomplete recovery of U(VI) in this experiment). The cause for this trend between moisture content and K_d values is not known. It appears likely that, as sediments were desaturated, the U(VI) contacted fewer sorption sites. In a sense, as the moisture content decreased, the effective exchange or sorption capacity of the sediment also decreased because solutes did not contact the total surface area.

In addition, both conservative (nonsorbing) tracer and U(VI) breakthrough curves exhibited nonequilibrium characteristics, particularly at the lowest moisture condition for each sediment. At decreasing moisture saturation, the proportion of immobile water increased in unsaturated coarse sand, fine sand, and silt loam. An approach for assessing mobile and immobile water domains was applied, and the data were well-described with a two-region transport model. More important, the parameters for dispersion, fraction of mobile water, and rate-limited mass transfer between mobile and immobile water regions were applied to predict U(VI) transport with reasonable success.

¹ Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

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1.0 Introduction

A performance assessment is under way to evaluate the suitability of the unsaturated zone of the Hanford Site for the long-term disposal of vitrified (glassified) low-activity waste. These assessments are analyses that predict the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. Previous analyses for proposed disposal actions on the Hanford Site show that groundwater transport presents the greatest potential for long-term dose uptake by humans (Mann et al. 1998). Further, the previous analyses showed that the key risk drivers at the proposed disposal site include ^{79}Se , ^{99}Tc , ^{129}I , $^{233,235,238}\text{U}$, and ^{237}Np .

The major pathway for transport of radionuclides from the Hanford Site's arid zone burial grounds is through the unsaturated sediments. The average moisture content of Hanford Site vadose-zone sediments ranges from 4% to 7% (v/v), which is equivalent to 10% to 20% saturation (Gee and Heller 1985, Schalla et al. 1988). Although considerable effort has been expended over the past few years to quantify the mobility of nuclear wastes and determine factors that influence radionuclide mobility (Ames et al. 1976, Serne et al. 1977, Wolfsberg 1978, Relyea and Serne 1979, and Serne et al. 1993), little work has been done to investigate the transport of radionuclides under conditions of partial saturation, which is most commonly found at arid region burial sites.

1.1 Objective

The objective of this investigation was to determine the effects of sediment moisture content on uranium(VI) transport and sorption in Hanford Site sediments. More specifically, the dependence of the change in distribution coefficient (K_d) with water saturation on particle size and mineral distribution was evaluated.

1.2 Scope

Three sediments were evaluated to determine whether moisture content affects the measured K_d values for U(VI): coarse sand, fine sand, and silt loam. These sediments were selected to augment the existing data for one coarse and two fine-grained sediments.

Unsaturated column transport experiments were conducted using the unsaturated flow apparatus (UFATM) method at two unsaturated moisture contents for each of the three sediments (UFA is a trademark of UFA Ventures, Richland, Washington). For each moisture condition, bromide was used as a conservative, noninteractive tracer. In this investigation, a mechanistic approach was used to evaluate tracer breakthrough in an effort to evaluate hydrodynamic properties, including solute dispersion and the effective water-filled porosity (immobile versus mobile water domains). U(VI) was applied as uranyl

(UO_2^{+2}) in uncontaminated Hanford Site groundwater. The entire breakthrough curve (both the leading edge and trailing edge of a pulse input) was attained to permit more detailed evaluation of the curves for determining the retardation factor and K_d .

Saturated column experiments were conducted with U(VI) on the fine sand and silt loam; penta-fluorobenzoic acid (PFBA) was used as the conservative, noninteractive tracer. Breakthrough curves, depicting the relative effluent concentration (C/C_0) versus dimensionless time (cumulative pore volumes of water passed through the column), were constructed from the experimental data for further analysis.

1.3 Background

Because contaminant transport requires that a liquid move the radionuclides either physically, as dispersed colloids, or as dissolved constituents in solution, the hydraulic conductivity of the sediment is important. Hydraulic conductivity is the ratio of the flux density (the volume of water flowing through a cross-sectional area per unit time) to the hydraulic gradient (the head drop per unit distance in the flow direction). If the sediment water does not move, then the radionuclides in groundwater do not move except by diffusion, which is a relatively slow process (Rancon 1973). When the sediment is saturated, nearly all pores are filled, and hydraulic conductivity is at a maximum. As the sediment becomes unsaturated, some of the pores become air filled, and the conductive cross-sectional area is decreased. In addition, the first pores to empty under tension are the largest and most conductive, and tortuosity is increased by emptying these pores. In unsorted sediments, the large pores that result in high conductivity at saturation become barriers to liquid flow between smaller pores during unsaturated flow. Hence, the transition from saturated to unsaturated flow may result in a steep drop in hydraulic conductivity of several orders of magnitude as the tension increases from 0 to 1 bar. At higher tensions, conductivity may be so low that steep negative pressure gradients are required for any appreciable sediment water flow to occur. An interesting corollary of the pore size-conductivity relationship is that at, or near, saturation, a sandy sediment conducts water more rapidly than a fine-textured sediment (silt clay) with many micropores. When the sediments are unsaturated, however, a greater percent of the pores in the silt clay sediments remain filled, and consequently, the hydraulic conductivity in these sediments does not decrease nearly as sharply as it does in sandy sediment under the same tension.

In modeling contaminant transport in unsaturated conditions, the retardation factor (R_f) is typically defined as:

$$R_f = 1 + \left(\frac{\rho_b}{\theta} \right) K_d \quad (1)$$

where ρ_b is the bulk density and θ is the volumetric water content of the sediment. The extent to which contaminants sorb to sediments is reflected in the K_d value. Equation (1) assumes a constant ratio between the sorbed and solution concentration (linear sorption isotherm) and that K_d is constant as a function of the volumetric water content. This relationship is convenient for modeling; however, its validity is not known. There have been experiments to test this assumption, and the results have been

mixed (Knoll 1960; Nielsen and Biggar 1961, 1962; Baetsle et al. 1966; Routson and Serne 1972; Gee and Campbell 1980; Lindenmeier et al. 1995; Kaplan et al. 1996).

There are theoretical reasons for believing that K_d values may vary as a function of volumetric water content. The first is based on changes in water distribution and flow, which affect the surface exposed to mobile solutes. Under saturated conditions, all of the pores are water filled, and water comes in contact with essentially all of the matrix surfaces. Immobile regions, where water is held tightly by the matrix, can exist and are known to occur in sediments containing clays and aggregates. In this situation, the transport of solutes to the immobile water domain is limited by diffusion. As sediments become increasingly unsaturated, water flows through a smaller fraction of the available pore space and can move as thin films along the surface of larger pores. In very dry sediments, there may be an increase in the immobile water domain, and a smaller percentage of the total exchange sites will contact the mobile aqueous phase. Thus, solutes undergoing advective transport with flowing water will not be exposed to the sediment surfaces of the immobile water domain; solute transfer to these interstitial regions and surfaces is limited by diffusion from the mobile to immobile water.

These physical changes in water distribution and the mobile water domain may affect sorption to the solid phase. As a smaller fraction of the mineral surface is exposed to the mobile aqueous phase, the effective exchange capacity of the sediment will change. These effects will be highly dependent on the sediment texture. For example, the clay fraction of the sediment constitutes the largest exchange capacity and the smallest pore sizes and is often associated with the immobile water domain. Solutes moving through an unsaturated sandy sediment with a small clay fraction may not be exposed to the clay surfaces during transport, thus reducing the effective exchange capacity. However, in unsaturated, fine-textured sediments, there may be little measurable effect on sorption because a greater percentage of micropores remain filled and water continues to flow through the matrix.

Another reason for believing that K_d values would vary with the degree of saturation is because the aqueous phase, moving as film flow in the unsaturated systems, is in closer contact with the sediment surfaces. The ionic strength of the aqueous phase tends to increase closer to the clay surfaces. Thus, as a sediment dehydrates, the system tends to have a higher ionic strength. The K_d values for many cations tend to decrease with increases in ionic strength because of the increased presence of competing cations.

Knoll (1960) evaluated whether sediment sorption of radionuclides was a function of saturation. Small columns of a fairly uniform very fine sand at constant temperature were used with an influent solution containing 1 g/L Ca, 0.1 mg/L Sr, and 2×10^{-2} $\mu\text{Ci/mL}$ ^{90}Sr . There was no apparent difference in Sr retention capacity between saturated and unsaturated sediments. However, it is worth noting that flow-rate differences between 100% saturation and 36% saturation were less than a factor of 100. With use of a natural sediment of less-uniform pore size, flow-rate (hydraulic conductivity) differences would have been much greater and the volume of sediment contacted by the aqueous phase under unsaturated flow conditions could have been much smaller. This would have resulted in the flowing water coming into contact with portions of the sediment with appreciably different cation-exchange capacities. Routson and Serne (1972), in a study involving experimental verification of their one-dimensional PERCOL model, determined the breakthrough curves and ^{85}Sr capacity for unsaturated sandy loam sediment columns at 96%, 75%, 63%, and 45% of saturation. They reported no apparent change of Sr retention capacity as a

function of moisture saturation. These experiments were not replicated. However, based on the wide range of Sr retardation factors and the high variability associated with the ^3H tracer experiments, it is likely that a large number of replicates would have been required for the researchers to have observed a trend. Gee and Campbell (1980) also reported that changes in water saturation percentage of the sediment, from 56% to 31%, had little to no effect on ^3H , Co-EDTA (ethylene diamine tetraacetic acid) complex, Tc, and I sorption (K_d values). Each of these tracers has a very low K_d value; therefore, measuring retardation factor differences from any treatment, including moisture, would be difficult because the range of possible values would be very small.

Contrary to the above work, Nielsen and Biggar (1961, 1962) showed that the drier the sediment, the higher the retardation factor. They attributed this trend to desaturation that eliminated the larger flow channels, resulting in increasing volumes of immobile water that are difficult to displace. In an eolian sand column of 100%, 45%, and 30% saturation, Baetsle et al. (1966) observed that ^{85}Sr leachate came out in concentration pulses, leading them to conclude that solutions in nonsaturated columns percolated through channels of varying capacity to retard Sr mobility.

Previous work conducted for this project (Kaplan et al. 1996) showed that U(VI) K_d values varied as a function of moisture content. However, the trend was not consistent between sediment types. In a coarse-grained sediment, the K_d values increased with increasing moisture saturation. In two fine-grained sediments, the K_d values decreased with increasing moisture saturation. A unifying conceptual model was proposed to explain these differences based on the mineral distribution and the extent to which fine particles form hydraulically continuous pores. On desaturating the coarse-grained sediment, the water may have "bypassed" the smaller pores because they were not continuous throughout the length of the entire column. These smaller pores are created from smaller clay materials that have high densities of adsorption sites. In the finer-grained sediment, the K_d values increased on desaturation because a greater percentage of the water, on desaturation, traveled through the smaller pores that were continuous through the entire column. These results, as well as those of Nielsen and Biggar (1961, 1962) and Baetsle et al. (1966), contradict the assumption that the degree of adsorption remains constant as a function of saturation.

1.4 Document Outline

This report is composed of several chapters in addition to this introduction. The materials and methods are given in Chapter 2.0. Chapter 3.0 describes the results and gives the discussion for those results. The conclusions gained from these sediment studies are given in Chapter 4.0, followed by the references cited in the text (Chapter 5.0).

2.0 Materials and Methods

2.1 Aqueous Solution and Sediment Properties

Uncontaminated Hanford Site groundwater was filtered (0.45 μm) and used as the aqueous solution matrix in all transport experiments. Chemical properties of Hanford Site groundwater are listed in Table 1. The initial concentration of U(VI) as UO_2^{+2} was $\sim 470 \mu\text{g L}^{-1}$ in all of the transport experiments. UO_2^{+2} is predicted to form carbonate complexes in this system, predominately $\text{UO}_2(\text{CO}_2)_2^{-2}$ and $\text{UO}_2(\text{CO}_2)_3^{-4}$ (Kaplan et al. 1996). The initial concentration of bromide, prepared from KBr, was $\sim 2,000$ ppm. The pH of the column effluent was determined for selected samples during transport experiments.

Three sediments were selected based on differences in particle-size distribution and included a coarse sand, a fine sand, and a silt loam. The <2 -mm fraction was used, and the particle-size distribution is summarized in Table 2.

Table 1. Chemical Composition of Uncontaminated Hanford Site Groundwater ($<0.45 \mu\text{m}$ filtered)

Constituent	Concentration (mg/L)
pH	8.4 (unitless)
Cl^-	24
NO_3^-	1.7
SO_4^{-2}	109
Total organic carbon	0.73
Total alkalinity (as CO_3^{-2})	160
Al	0.14
B	0.05
Ba	0.069
Ca	58
Fe	0.14
K	14
Mg	16
Mn	0.046
Na	30
Si	16.2

Table 2. Particle-Size Distribution (<2-mm fraction) Based on Percent by Weight

Sediment	Sand (%)	Silt (%)	Clay (%)
Medium coarse sand	98	<1	2
Touchet Bed sand	80	15	5
Warden silt loam	47	53 ^(a)	ND ^(b)
(a) Includes clay.			
(b) Not determined.			

2.2 Unsaturated Column Experiments

Unsaturated column experiments were conducted with a UFA by adapting the standard Pacific Northwest National Laboratory procedures for miscible displacement of the solute. Columns (5.9 cm length, 2.2 cm radius) were packed to a uniform bulk density, saturated with groundwater, and then placed in the UFA. Columns were equilibrated to steady-state moisture and flow rate prior to initiating transport experiments. The UFA rotational speed and solution flow rate determine the volumetric water content. Parameter values for each column are reported with the results section.

At each moisture condition, separate experiments were conducted first with the bromide tracer, then with U(VI). The length of the pulse injection (t_0), expressed as pore volumes, is indicated on the breakthrough curves and tables in the next section. The degree of moisture saturation was determined gravimetrically at each sampling point over the course of the experiment. Moisture saturation is expressed as the percent of the total porosity (v/v) that is water filled; 100% saturation indicates that the void space is completely occupied by water. Bromide was analyzed using an ion-selective electrode, and U(VI) was determined by laser phosphorimetry.

2.3 Saturated Column Experiments

Saturated columns were packed in the same manner as unsaturated columns, saturated with groundwater, and equilibrated to a stable water content prior to initiating the transport experiments. The Touchet Bed sand column was 10 cm long; the Warden silt loam column was 5 cm long; the radius for both was 2.5 cm. The water content was determined gravimetrically and compared with the theoretical value (based on sediment bulk density and particle density). Separate experiments were conducted first with the PFBA tracer, followed by U(VI), on the same sediment column. Column effluents for the PFBA tracer experiments were analyzed directly on-line by flow-through ultraviolet detection, and U(VI) was analyzed by laser phosphorimetry. Preliminary experiments showed identical results using Br⁻ or PFBA. Because of the ease of measuring PFBA on-line, in contrast to the more time-consuming method for Br⁻ analysis by ion-selective electrode, PFBA will be used whenever possible (typically limited to saturated experiments using the UFA sampling method).

3.0 Results and Discussion

3.1 Unsaturated Column Experiments

The results of the U transport experiments on unsaturated coarse sand, fine sand, and silt loam are shown in Figures 1 through 4 and Table 3 for two moisture conditions. The retardation factor was determined by mathematical moment analysis (Valocchi 1985); the K_d value was calculated with Equation (1). These values are reported in Table 3, along with experimental parameters for each column. The pulse injection (t_0) is also indicated by an arrow(s) on the figures.

The method used to determine the retardation factor (R) is based on the center-of-mass of the experimental breakthrough curve. Because of the incomplete curve for the Warden silt loam at 83% saturation (see Figure 3), the distal portion, or "tail," of the curve was extrapolated to background (5 to 7 ppb U[VI], or $C/C_0 = 0.01$) to calculate R . Although the U(VI) curve at 41% moisture was complete (effluent concentration reached background), mass recovery of U(VI) was <70%, indicating that 30% of the U(VI) was retained in the sediment matrix. In this case, R was determined for eluted U(VI) without correction. The corresponding K_d value at 41% moisture represents the K_d for reversible sorption but does not account for apparently strong, or irreversibly sorbed, U(VI) in the column. Looking at the overall trend shown in Figure 5 for each of the three sediments, the K_d determined in unsaturated transport experiments

Figure 1. Uranium(VI) Transport in Coarse Sand at 30% and 12% Saturation (arrows indicate spike injection stoppage)

Figure 2. Uranium(VI) Transport in Fine Sand at 66% and 22% Saturation (arrows indicate spike injection stoppage)

Figure 3. Uranium(VI) Transport in Silt Loam at 83% and 41% Saturation (arrows indicate spike injection stoppage)

Figure 4. Uranium(VI) Transport in Silt Loam at 42% Saturation: Replicates (arrow indicates spike injection stoppage)

Table 3. Unsaturated Column and Sorption Parameters for Uranium(VI)

Moisture Saturation (%)	Pore Volume (cm ³)	Bulk Density, ρ (g/cm ³)	Volumetric Moisture, θ	Pore Velocity, v (cm/h)	Pulse Injection, t_0 (h)	Recovery (%)	Retardation Factor, R	K_d (mL/g)
Medium Coarse Sand								
29.8	11.2	1.71	0.118	44.6	27.16	99.9	8.01	0.48
12.4	4.67	1.71	0.049	67.1	38.85	97.7	6.46	0.16
Touchet Bed Sand								
66.2	27.5	1.59	0.289	18.2	10.83	94.4	8.81	1.42
22.3	9.30	1.59	0.097	33.9	19.57	96.0	7.42	0.39
Warden Silt Loam								
83.0	36.4	1.43	0.381	15.5	11.24	97.2 ^(a)	16.25 ^(a)	4.05 ^(a)
41.4	18.16	1.43	0.190	17.3	21.33	68.6	14.64 ^(b)	1.81 ^(b)
(a) Based on extrapolating tail of breakthrough curve to zero; actual recovery was 81.6%.								
(b) Not adjusted for U(VI) retained in the column.

Figure 5. Dependency of Uranium(VI) K_d Values on Moisture Saturation for Three Sediment Types

decreased with decreasing moisture saturation: 67%, 73%, and 55% for the coarse sand, fine sand, and silt loam, respectively. It is important to recognize the trend for the silt loam might reverse if a K_d for the noneluted U(VI) was determined.

For a system at equilibrium, the breakthrough curve has a symmetrical, sigmoidal shape at the leading and tailing edges. The U(VI) curves in these experiments exhibit early breakthrough (shifted left) and tailing, characterized by a delayed approach of the front to $C/C_0 = 1$, and a slow approach to zero on the tailing edge. This shape is characteristic of physical and/or chemical nonequilibrium processes. The effect is most pronounced for the lowest moisture condition. Rate-limited mass transfer of the solute between mobile and immobile water regions is one type of flow heterogeneity that results in physical nonequilibrium. Both sorptive and nonsorptive solutes are subject to physical nonequilibrium, while only sorptive solutes are subject to chemical nonequilibrium. Mechanistic analysis of tracer curves can be used to distinguish physical and chemical nonequilibrium processes.

Results of tracer transport experiments on the same three sediments and moisture conditions are shown in Figures 6, 7, and 8. Once again, the shape of the breakthrough curves suggests nonequilibrium, and again, the effect is most pronounced for the low-moisture condition. Retardation factors were determined by mathematical moment analysis (Valocchi 1985). These values, along with experimental parameters for each column, are reported in Table 4.

The retardation factor for a nonsorbing tracer should equal unity. Values for the lowest moisture condition on each of the three sediments are <1 . This could be the result of solute "exclusion" from a fraction of the pore spaces because of an anion exclusion mechanism or this could reflect a reduction in the effective pore volume because of an immobile water domain.

Figure 6. Bromide Transport in Coarse Sand at 32% and 14% Saturation (arrows indicate spike injection stoppage)

Figure 7. Bromide Transport in Fine Sand at 68% and 23% Saturation (arrows indicate spike injection stoppage)

Figure 8. Bromide Transport in Silt Loam at 84% and 42% Saturation (arrows indicate spike injection stoppage)

Table 4. Unsaturated Column and Sorption Parameters for Bromide

Moisture Saturation (%)	Pore Volume (cm^3)	Bulk Density, ρ (g/cm^3)	Volumetric Water Content, θ	Pulse Injection, t_0 (h)	Pore Velocity, v (cm/h)	Recovery (%)	Retardation Factor, R
Medium Coarse Sand							
31.8	12.0	1.71	0.125	15.36	42.1	99.0	1.07
14.4	5.43	1.71	0.057	11.01	57.7	99.8	0.77
Touchet Bed Sand							
67.8	28.23	1.59	0.296	6.04	17.8	99.0	1.02
22.9	9.54	1.59	0.100	6.09	32.9	95.7	0.73
Warden Silt Loam							
83.7	36.7	1.43	0.385	4.94	15.4	98.8	1.07
41.8	18.3	1.43	0.192	4.42	17.1	97.1	0.98

An approach for detailed analysis and modeling of tracer breakthrough curve data to distinguish mobile and immobile water domains is described in the next section. The approach is demonstrated for the fine sand at 23% moisture.

3.2 Theory, Analysis, and Modeling of Breakthrough Curve Data

The above results and previous research (Kaplan et al. 1996) suggest a change in U(VI) sorption, as indicated by the K_d value, with changes in moisture saturation during unsaturated transport experiments. One possible explanation is a change in water distribution and water flow with progressive desaturation, with subsequent effects on solute transport, and finally, on sorption sites to which the solute is exposed during transport. Understanding the change in U(VI) sorption requires a quantitative approach for determining the mobile-immobile water regime. This is accomplished by a mechanistic evaluation of tracer breakthrough curves to determine hydraulic parameters.

So-called "two-region" or "two-site" models have been described in several places (van Genuchten and Wierenga 1976, Selim et al. 1976, Cameron and Klute 1977), with solutions provided by van Genuchten (1981). The equations are summarized here and use the notations of van Genuchten and Parker (1984).

The liquid phase is partitioned into mobile (macroporosity) regions and immobile (microporosity) regions. Advective solute transport is limited to the mobile water phase. Transport in and out of the immobile water domain is diffusion limited. The governing equations for the two-region model are:

$$(\theta_m + f\rho K_d) \frac{\partial c_m}{\partial t} + [\theta_{im} + (1-f)\rho K_d] \frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - q \frac{\partial c_m}{\partial x} \quad (2)$$

$$[\theta_{im} + (1-f)\rho K_d] \frac{\partial c_{im}}{\partial t} = \alpha^* (c_m - c_{im}) \quad (3)$$

where θ is volumetric water content; subscripts m and im are mobile and immobile phases, respectively; f is fraction of sorption sites that equilibrates with the mobile liquid phase; ρ is sediment bulk density; c is solute concentration; D is dispersion coefficient; q is Darcy velocity; and α^* is first-order rate constant that governs the rate of solute exchange between the mobile and immobile regions.

The dimensionless variables P , β , and ω are introduced:

$$P = \frac{v_m L}{D_m} \quad (4)$$

$$\beta = \frac{\theta_m + f\rho K_d}{\theta + \rho K_d} \quad (5)$$

$$\omega = \frac{\alpha^* L}{q} \quad (6)$$

where

$$v_m = \frac{q}{\theta_m}$$

$$D = \frac{D_m \theta_m}{\theta}$$

v is average pore water velocity and L is column length (sediment bed length).

A numerical solution to the two-region model (CFITIM3, University of Florida), based on the solution of van Genuchten (1981), was applied to illustrate the approach for determining mobile-immobile water regions. This approach will be refined and subsequently applied to all of the breakthrough curve data collected in this subtask.

First, the breakthrough curve data for the nonsorbing tracer is modeled to determine dispersion (from P), the fraction of mobile water (from β), and the rate coefficient for mass transfer between the mobile and immobile water regions (from ω); a nonlinear least-squares curve-fitting routine is used. Fixed values for these parameters are then applied with the model to describe $U(VI)$ data. The retardation factor for the nonsorbing tracer was fixed at 1.0. When this model was applied to fit all three parameters (P , β , ω), the confidence intervals for the fitted parameters were extremely wide. The Peclet number, P , was therefore constrained and fixed to a value of 2 (reasonable for a system with high-effective dispersion). The results of curve fitting with the two-region model are summarized in Table 5, where the 95% confidence interval for the fitted parameter is in parentheses.

Table 5. Curve-Fitting Results for Nonsorbing Tracer Breakthrough Curve with the Two-Region Model^(a)

Moisture Saturation (%)	Retardation Factor	P	β	ω
Touchet Bed Sand				
23	1.0	2	0.338 (0.255 - 0.422)	0.250 (0.136 - 0.365)
(a) Values for R and P were fixed at 1.0 and 2, respectively.				

The above parameters for P , β , and ω characterize the mobile-immobile water regime for the fine sand at 23% moisture saturation. These results, combined with the retardation value for $U(VI)$ transport (determined by moment analysis), were applied to predict $U(VI)$ breakthrough at the same moisture condition. The results are presented in Figure 9.

Figure 9. Simulated Uranium(VI) Transport in Fine Sand at 22% Saturation (arrow indicates spike injection stoppage)

The reasonable agreement between the two-region model prediction and the experimental data indicates that the early U(VI) breakthrough and tailing can be explained by the mobile-immobile water domains and the rate-limited mass transfer of U(VI) between these domains.

3.3 Saturated Column Experiments

Results of the saturated column experiments on fine sand and silt loam are illustrated in Figure 10 and summarized in Table 6.

The trend of increased sorption on the fine-textured silt loam is as expected, and mass balance indicates that the experimental error was relatively small. The K_d values for the saturated sediments are inconsistent with the general trend indicated for the unsaturated columns. Interestingly, the values for 100% moisture saturation fall between the values obtained for the unsaturated moisture conditions. Because of the difference in methodologies for determining unsaturated versus saturated transport, the systematic differences will be evaluated further with replication. A primary difference is that flow is briefly interrupted when each effluent-sampling event is performed in the unsaturated experiments (each point on the breakthrough curves), while flow during the saturated experiment is continuous. The flow interruptions in the UFA experiments may have resulted in increased time for diffusion of U(VI) within the sediment matrix, thereby increasing the extent of U(VI) sorption (provided the U(VI) sorption is kinetically hindered).

Figure 10. Simulated Uranium(VI) Transport at 100% Moisture Saturation

Table 6. Saturated Column and Sorption Parameters for Uranium(VI)

Moisture Saturation (%)	Pore Volume (cm ³)	Bulk Density, ρ (g/cm ³)	Volumetric Moisture, θ	Pulse Injection, t_0 (h)	Pore Velocity, v (cm/h)	Recovery (%)	Retardation Factor, R	K_d (mL/g)
Touchet Bed Sand								
100	22.9	1.53	0.421	26.92	24.5	100.9	3.85	0.79
Warden Silt Loam								
100	12.2	1.40	0.427	43.24	25.9	101.2	7.02	1.83

Kaplan et al. (1996) reported that, as moisture content decreased, U(VI) K_d values increased in fine-textured sediments and decreased in coarse-textured sediments. Results reported here are consistent with observations for the coarse-textured sediments but differ for the fine-textured sediments. The K_d trend on fine-textured sediments reported in Kaplan et al. (1996) was based on five observations for two sediments, where two of the five observations were for 100% saturation using traditional column methods and not a UFA. As mentioned above, the greater opportunity for diffusion with the UFA method may explain the observed increase in sorption for unsaturated, compared with saturated, conditions that was reported previously.

4.0 Conclusions

A series of experiments were conducted to evaluate the sorption and transport of U(VI) under conditions of partial moisture saturation that are relevant to arid region burial sites and far-field conditions at the Hanford Site. The focus was on measuring K_d values for U(VI) in a series of Hanford Site sediments, representing different texture classes at two unsaturated moisture conditions. Potential changes in the water-flow regime with decreasing moisture saturation, and the dependence of these changes on sediment particle-size distribution, were recognized at the outset. Particular attention was given to the use of non-sorbing tracers (bromide and PFBA) in an effort to characterize changes in water flow, notably, the proportion of mobile to immobile water. This is an important first step for determining if observed changes in U(VI) K_d values can be explained by changes in the mobile and immobile water-flow regime.

For unsaturated sediments, the U(VI) K_d values decreased as the moisture content decreased in all three sediments evaluated, irrespective of their texture. In the medium-coarse sand, the K_d values decreased from 0.48 to 0.16 mL/g (67%) as the moisture saturation decreased from 30% to 12%. In the fine sand, the K_d value decreased from 1.42 to 0.39 mL/g (73%) as the moisture saturation decreased from 66% to 22%. In the silt loam, the K_d value decreased from 4.05 to 1.81 mL/g (55%) as the moisture saturation decreased from 83% to 41% (noting incomplete recovery of U(VI) in this experiment). The cause for this trend between moisture content and K_d values is not known. It appears likely that, as sediments were desaturated, the U(VI) contacted fewer sorption sites. In a sense, as the moisture content decreased, the effective exchange or sorption capacity of the sediment also decreased because solutes did not contact the total surface area.

Although the breakthrough curves for U(VI) on the silt loam at 41% moisture saturation were complete, 30% of the applied mass was not recovered. While the eluted U(VI) was transported with an apparent decrease in sorption, the low recovery indicates that some of the U(VI) was retained in the sediment matrix. The reason for this is not known. It is possible that changes in solution or surface chemistry occurred at the low-moisture condition, causing a change in U(VI) speciation such that a different chemical species was retained in the column.

Breakthrough curves exhibited nonequilibrium characteristics, particularly at the lowest moisture condition for each sediment. An approach for assessing mobile-immobile water domains was applied for the fine sand at 23% moisture saturation. The data were well-described with a two-region transport model. More important, the parameters for dispersion, fraction of mobile water, and rate-limited mass transfer between mobile and immobile water regions were applied to predict U(VI) transport with reasonable success.

Important conclusions are summarized as follows.

- At decreasing moisture saturation, the proportion of immobile water increased in unsaturated coarse sand, fine sand, and silt loam sediments.
- U(VI) K_d values decreased with decreasing moisture saturation, irrespective of sediment texture.

Mass transfer of solutes, including U(VI), to regions of microporosity is limited when mobile-immobile water conditions develop. Immobile water domains are associated with regions of microporosity and fine-textured particles. Relationships among texture, surface area, and exchange or sorption capacity are well-established. An important implication of this research is that the effective exchange capacity of the sediment may be reduced for solutes undergoing transport in unsaturated, sandy sediments where immobile water domains develop. The observed decrease in K_d , particularly for the sandy sediments, is consistent with limited mass transfer to sorption sites in the immobile water region.

The flow rates in these experiments were faster than those expected in the unsaturated vadose zone of the site. The linear pore-water velocity in these experiments ranged from 15 to 70 cm h⁻¹, which may represent flow during rain events, but is certainly much faster than the average linear velocity. The UFA offers the only available method to study solute transport under unsaturated conditions at these low-moisture conditions, but cannot be used at flow rates that would more closely approximate expected average conditions in the field. The difference in flow rates may be important, and may compromise statements about the site vadose zone. Slower flow rates in the field would result in increased mass transfer by diffusion. Consequently, the observed nonequilibrium for water flow may be less apparent in expected vadose-zone conditions. Even so, flow heterogeneities such as mobile-immobile water domains are observed under field conditions. The results presented here demonstrate that accounting for these heterogeneities can explain observed differences in sorption and transport.

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