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Radionuclide Adsorption Distribution Coefficients Measured in Hanford Sediments for the Low Level Waste Performance Assessment Project

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Pacific Northwest National Laboratory
Richland, Washington 99352

(a) Washington State University Tri-Cities, Richland, Washington 99352.

Abstract

Preliminary modeling efforts for the Hanford Site's Low Level Waste-Performance Assessment (LLW PA) identified ^{129}I, ^{237}Np, ^{79}Se, ^{99}Tc, and ^{234,235,238}U as posing the greatest potential health hazard. It was also determined that the outcome of these simulations was very sensitive to the parameter describing the extent to which radionuclides sorb to the subsurface matrix, i.e., the distribution coefficient (K_d). The distribution coefficient is a ratio of the radionuclide concentration associated with the solid phase to that in the liquid phase.

The objectives of this study were to 1) measure iodine, neptunium, technetium, and uranium K_d values using laboratory conditions similar to those expected at the LLW PA disposal site, and 2) evaluate the effect of selected environmental parameters, such as pH, ionic strength, moisture concentration, and radionuclide concentration, on K_d values of selected radionuclides. It is the intent of these studies to develop technically defensible K_d values for the PA. The approach taken throughout these studies was to measure the key radionuclide K_d values as a function of several environmental parameters likely to affect their values. Such an approach provides technical defensibility by identifying the mechanisms responsible for trends in K_d values. Additionally, such studies provide valuable guidance regarding the range of K_d values likely to be encountered in the proposed disposal site.

Important results concerning the K_d values for uranium (in the chemical form of uranyl) include:

- Uranyl-K_d values increased with increased contact time with sediments. Extended sediment contact times are expected to occur at the proposed LLW disposal site and therefore larger K_d values are warranted for the PA than those determined from conventional batch experiments with 7- to 14-day contact times.

- Uranyl-K_d values remained constant between the uranyl solution concentrations of 3.3 and 100 µg/L. Since the K_d values remained constant, a more complicated sorption model, such as the Langmuir Model or uranyl-concentration-dependent K_d Model, is not warranted for the PA over this uranyl concentration range.

- Uranyl-K_d values doubled from 1.07 to 2.22 mL/g as the pH of the system increased from pH 8 (ambient levels) to pH 10. Above a pH ~10, heterogeneous precipitation of uranium occurred resulting in apparent K_d values as high as 500 mL/g. Precipitation did not occur unless a sediment was present. Should high pH conditions exist in the study site, as may happen in a near-field containing a grout or glass waste form, elevated uranyl-K_d values may be warranted for the PA.

- Uranyl-K_d values varied as a function of moisture content. However, the trend was not consistent. In a coarse-grained sediment, the K_d values increased with increasing moisture saturation. In a more fine-grained sediment, the K_d values decreased with increasing moisture saturation. A unifying conceptual model was proposed to explain these differences based on the hydraulic conductivity within the fine pore spaces. Since most of the subsurface system being modeled by the PA contains coarse-grained sediments, a lower K_d value than that measured by conventional batch K_d methods may be warranted for the PA.

Important results concerning the K_d values of technetium (in the chemical form of pertechnetate) include:

- A small degree of anion exclusion of pertechnetate may have occurred in these studies. If this is the case, a slightly negative K_d value, about -0.1 mL/g, may constitute the lower limit of possible K_d values for the PA. Column studies would have to be conducted to validate the occurrence of this phenomenon.

- Pertechnetate-K_d values were very low and may have increased with increased contact time. For the PA, a very long contact time is expected. Based on these and other researchers' results, the best K_d estimate for the PA is approximately 0 ± 0.1 mL/g.

Important results concerning the K_d values of iodine (in the chemical form of iodide) include:

- The average iodide-K_d value in this study was 3 mL/g. This average is identical to that previously reported for Hanford sediments. Based on these studies, an iodide-K_d value greater than 0 mL/g is warranted for the PA.

- Iodide-K_d values increase with increased contact time with sediments. Extended sediment contact times are expected for the PA and therefore larger K_d values than those derived from conventional 30-d contact time experiments may be warranted for the PA.

Important results concerning the K_d values of neptunium (in the chemical form of NpO_2^{2+}) include:

- Neptunium K_d values generally increased with time.

- Neptunium K_d values were clearly greater than 0 mL/g indicating that the most conservative K_d estimate of 0 mL/g is not warranted for the PA. The lowest K_d value was 2.17 ± 0.35 mL/g and the highest value was 19.86 ± 0.45 mL/g.

These studies were conducted with sediments collected from the Hanford Site, primarily from the 200 Areas. They provided important insight as to the types of measurements that will be required once the site-specific sediments from bore holes become available. These studies also improved present understanding of the sorption behavior of these radionuclides and provided important quantitative descriptions of the effects of several variables on sorption behavior.

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Acronyms

K_d	distribution coefficient
LLW	low-level waste
PA	performance assessment
UFA	Unsaturated Flow Apparatus

1.0 Introduction

1.1 Background

A performance assessment (PA) is underway to evaluate the suitability of the unsaturated zone of the Hanford Site for the long-term disposal of radioactive low-level waste (LLW). These assessments [referred to as risk assessments by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)] are analyses that predict the transport of radionuclides and/or contaminants from a source to a receiptor 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 (DOE 1987, Kincaid et al. 1995, Wood et al. 1994, Mann et al. 1996).

Preliminary modeling efforts for the Hanford Site LLW PA were conducted to evaluate the potential health risk of a number of radionuclides, including Ac, Am, C, Ce, Cm, Co, Cs, Eu, I, Nb, Ni, Np, Pa, Pb, Pu, Ra, Ru, Se, Sn, Sr, Tc, Th, U, and Zr (Mann et al. 1996). The radionuclides, ^{129}I, ^{237}Np, ^{79}Se, ^{99}Tc, and ^{234,235,238}U, were identified as posing the greatest potential health hazard. The geochemical factors affecting the transport of these radionuclides in the Hanford Site subsurface environment were described by Kaplan et al. (1995). It was also determined that the outcome of these simulations were very sensitive to the parameter describing the extent to which radionuclides sorbed to the subsurface matrix, described as a distribution coefficient (K_d). The distribution coefficient is the ratio of the radionuclide concentration associated with the solid phase to that in the liquid phase. The literature-derived K_d values used in these simulations were likely, in some cases, to be overly conservative (i.e., lowest values within the range of reasonable values) because technically defensible, less conservative values were not available. Thus, these preliminary modeling results reflect a conservative estimate rather than a best estimate of the modelled scenario. The potential problem with providing an overly conservative estimate of health risk is that it may mislead us into directing resources to resolve nonexisting problems.

The most technically defensible approach to identifying K_d values for a PA is to measure K_d values in well-designed and carefully conducted laboratory studies that use sediments, groundwater, and radionuclide conditions similar to those at the study site. Using laboratory conditions similar or identical to the study site is important because there are a large number of liquid and solid phase properties that can influence K_d values (Kaplan et al. 1995). Additional complexity exists in the selection of K_d values for the PA because environmental conditions vary greatly between the near- and far-field. Consequently, any thorough study used to select K_d values for the PA needs to investigate a range of conditions. Some possibly important environmental conditions that will vary in the study site include, sediment type, pH, moisture concentration, ionic strength, and radionuclide concentration.

1.2 Objectives

The objectives of this study were:

1) to measure iodine, neptunium, technetium, and uranium K_d values using laboratory conditions similar to those expected in the LLW PA disposal site, and

2) to evaluate the effect of selected environmental parameters, such as pH, ionic strength, moisture concentration, and radionuclide concentration, on K_d values of selected radionuclides.

It is the intent of these studies to provide provisional K_d values for the PA. The approach taken throughout these studies was to measure the key radionuclide K_d values as a function of a number of environmental parameters likely to affect their values. Such an approach provides technical defensibility by identifying the mechanisms responsible for trends in K_d values. Additionally, such studies provide valuable guidance regarding the range of K_d values likely to be encountered in the proposed disposal site.

1.3 Scope

The radionuclides used in these studies were iodine, neptunium, technetium, and uranium. These radionuclides were among those in the LLW disposal site identified as most likely to pose a health risk (Mann et al. 1996).

The experiments were conducted with sediments collected from the Hanford Site, most of them from the 200 Areas. The experiments had to be conducted with non-site-specific sediments since site-specific sediments were not available at the start of the study. It is anticipated that the data collected from these studies will provide important guidance for judiciously using the site-specific sediment. The site-specific sediment collected from bore holes will be available in small quantities, one or two kilograms per sample. The sediments used in these studies were selected based on three criteria. First, they had to be from the Hanford Site and representative of the sediments in the Hanford Site 200 Areas. Secondly, the sediments had to be reasonably well characterized. This would save the project resources. Third, >5 kilograms of material had to be available.

2.0 Materials and Methods

2.1 Experimental Methods of Adsorption Experiments

Over thirty different experiments are described in this report. A generalized description of these experiments is provided below. The specific experimental conditions are described at the start of the appropriate Results and Discussion subsections (Section 3.0). There were three types of experiments conducted, saturated batch experiments (Section 2.1.1), unsaturated batch experiments (Section 2.1.2), and unsaturated column experiments (Section 2.1.3).

2.1.1 Saturated Batch Adsorption Experiments

The batch-K_d procedure used in these studies was unusually rigorous and included several steps that are commonly omitted. The additional rigor in these procedures was deemed necessary because the project required the measurement of very low K_d values with a high degree of accuracy (plus or minus 1 mL/g). Less complicated procedures have been used in other projects, but our experience is that they provide K_d values with variances too large for the application needed by the PA. Briefly, the sediment (described in Section 2.2) was first preequilibrated with uncontaminated Hanford groundwater (described in Section 2.2). This was accomplished by adding groundwater to the sediments, shaking the suspensions overnight, centrifuging, measuring the pH, and then pouring out the supernatant. This was repeated, typically about three times, until the pH of the groundwater wash solutions did not change before and after contact. The purpose of this preequilibration step, which is frequently omitted in batch-K_d experiments, was to isolate the radionuclide adsorption reaction from the large number of reactions that may occur while sediments and aqueous solution equilibrate. This has been shown to be a critical step in accurately measuring K_d values and results in minimizing the extent to which the radionuclide is removed from the aqueous phase via (co)precipitation. The preequilibration step maximizes the chance that adsorption is the dominant mechanism controlling the fate of the contaminant.

After preequilibrating the sediment with the groundwater, a radionuclide tracer was added to the groundwater. Then 20-mL of the spiked groundwater was added to 10-g sediment. The spiked solutions were placed on a slow moving platform shaker for different lengths of time, generally about a month. The suspension were then centrifuged and the supernate was passed through a 0.45-µm filter. After the pH was measured, the filtrate was analyzed for radionuclide concentration. Liquid scintillation counting was used to measure ^{99}Tc, ^{125}I, and ^{237}Np activity, and laser-phosphorimetry was used to measure UO_2^{2+} concentrations (Chemchek Instruments Inc., Richland, Washington). The K_d values were calculated using Equation 1:

$$K_d = \frac{(C_{blank} \text{ x } V_{spike}) - C_{effluent}(V_{spike} + V_{excess})}{C_{effluent} \text{ x } M_{sed}} \qquad (1)$$

where V_{excess}, (mL) is excess solution left from the third cold wash (weight of excess solution divided by solution density), M_{sed} is the mass of solid aquifer material (g), V_{spike} is the volume of ground water with radioactive tracer added(mL), $C_{effluent}$ is the activity or concentration of tracer in the effluent solution (dpm/mL), and C_{blank} is the tracer activity or concentration in the control (dpm/mL; spiked groundwater/no sediment).

The ratio of sediment to solution used in these K_d tests, 1:2, was much greater than the common ratio of 1:30. The higher ratio was selected to improve K_d measurement accuracy. As can be seen from Equation 2, the concentration of adsorbed radionuclide is determined by subtracting the concentration of the radionuclide in solution before, C_{spike}, and after, $C_{effluent}$, the radionuclide is put in contact with the sediment and then dividing by the mass of the sediment, M_{sed}. If little adsorption takes place, then the difference between C_{spike} and $C_{effluent}$ will be small. Compounding this problem is that liquid scintillation counting statistics improve at higher concentration. Thus, one of the difficulties in determining low K_d values is that two large numbers must be subtracted from each other to determine a small value, a poorly poised mathematical situation. To get a greater difference between C_{spike} and $C_{effluent}$, the ratio of sediment to solution was increased in these tests.

Three replicates of each treatment were generally conducted. Two types of control treatments were carried through all batch-K_d tests. A no-sediment control was included to account for decay and the extent to which radionuclides adsorbed to the surface of the labware. A no-spike control was included to correct for any background radioactivity or detection interferences. Thus for one K_d value (the mean of three replicates) a total of nine tests were conducted: 3 spiked-sediment K_d tests, 3 no-spike controls, and 3 no-sediment controls.

Among the variables investigated were sediment type, spike solution/sediment contact time, pH, ionic strength, and radionuclide concentration. In each case, the general procedure described above was followed with slight modifications to create the treatment of interest. A description of these treatments and procedure modifications are included in the appropriate Results and Discussion sections (Section 3.0).

2.1.2 Unsaturated Batch Adsorption Experiments

The procedure followed for the unsaturated batch K_d experiments was based on the saturated batch K_d experiments described in Section 2.1.1. About 1.5 kg of sediment Trench 8b and Trench 94 (described in Section 2.2) were preequilibrated with filtered (0.45-μm pore size) Hanford groundwater. After the third overnight preequilibration wash, a final 5-min rinse with deionized water was conducted and the sediments were placed in a 105^{0} C over to dry. The intent of the deionized water rinse was to replace the interstitial groundwater with a water containing fewer salts so that once the sediment were dried, a minimal amount of evaporite (residual salts) would accumulate on the sediment surface. Such residues would create an experimental artifact.

The dried preequilibrated sediments were then spread out on a large plastic sheet and iodine and uranium spiked groundwater was added to obtain the desired moisture content. The spiked solution was added in microliter aliquots to the sediment to ensure an even distribution of the radionuclide in the sediment. The spiked sediments were then transferred to zip-lock bags where they were exhaustively mixed by kneading by hand. The sediments were kneaded for about 15 minutes each. The samples were tamped down to approximately the same bulk density and then left in the dark at room temperature for about 1-mo. Occasionally during the 1-mo equilibration period, the bags were weighed to determine the amount of moisture and they were reopen to minimize that creation of a reducing environment within the closed system.

After the 1-mo equilibration period, the amount of moisture in the sediment was again gravimetrically determined. The sediment solution was recovered by centrifugation and then the uranium concentration in the recovered solutions was determined by laser-phosphorimetry (Chemchek Instruments Inc., Richland, Washington).

2.1.3 Unsaturated Column Adsorption Experiments

2.1.3.1 Theory Underlying the Unsaturated Flow Apparatus (UFA)

Retardation factors, R_f, can be determined in flow experiments where R_f for a particular species is the ratio of the groundwater velocity to the contaminant velocity. The retardation factor for the contaminant species is given by (Bouwer 1991)

$$R_f = V_{gw}/V_{sp} = 1 + \rho K_d/n \tag{2}$$

where V_{gw} is the velocity of the groundwater, V_{sp} is the velocity of the contaminant species, ρ is the bulk density and n is the porosity. It is generally accepted that for unsaturated systems $n = \theta$ where θ is the volumetric water content (Bouwer 1991). 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 and the contaminant travels along with the water at the groundwater flow rate. When the K_d value is large, as for plutonium ($K_d > 10^4$ in most soils), the contaminant may take several millennia to migrate only 100 m. Most often, batch experiments are performed to measure the K_d where one part of solid is placed into 30 parts of solution and shaken for 24 or 48 hours to observe the amount that is sorbed onto the solid. But for most subsurface conditions, batch experiments do not reproduce behavior in the field and can overestimate the retardation of soils and rocks. It is better to perform column experiments using the actual soil, groundwater and contaminants under field conditions. In column experiments, contaminated groundwater is pumped into a column of soil packed to field density. The effluent from the column is monitored for the contaminant of interest. A breakthrough curve is obtained for the particular contaminant and R_f is determined as the pore volume at which $C/C_o = 0.5$.

The unsaturated flow apparatus (UFA) achieves hydraulic steady state in a few hours for most geologic materials, even those with very low water contents (Wright et al. 1994). 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 matrix potential. The application of a centripetal acceleration (or its inertial effect, the centrifugal force) to geologic problems is as old as centrifugation itself (Russell and Richards 1938). However, the use of steady-state centrifugation to measure steady-state hydraulic conductivities has only recently been demonstrated (Nimmo et al. 1987; Conca and Wright 1992; Wright et al. 1994).

The UFA instrument consists of an ultracentrifuge with a constant, ultra-low flow pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system (Figure 1). The ultracentrifuge can reach accelerations of up to 20,000 g (coarse-grained sediments, such as Hanford sediments, are generally run only up to 1,000 g), temperatures can be adjusted from -20° to 150°C, and constant flow rates can be set as low as 0.001 mL/h. Effluent from the sample is collected in a transparent, volumetrically-calibrated chamber at the bottom of the sample assembly. Using a strobe light, an observer can check the chamber while the sample is being centrifuged. Materials can be run in the UFA as recomposited samples, or in situ samples can be subcored directly into the sample UFA chamber. Whole rock cores and cores of ceramics, grouts, and other solids are cast in an appropriate epoxy sleeve for use in the UFA. For this study a sample size of 42 cm^3 was used for recomposited sediment samples.

The UFA method is effective because it allows the operator to set the variables in Darcy's Law. Darcy's Law states that the fluid flux equals the hydraulic conductivity times the fluid driving force. Under a centripetal acceleration in which water is driven by both the matrix potential gradient and the centrifugal force per unit volume, Darcy's Law is given by

$$q = -K(\psi)\ [d\psi/dr - \rho\omega^2 r] \qquad (3)$$

where q is the flux density into the sample, K is the hydraulic conductivity, ψ is the matrix potential, $d\psi/dr$ is the matrix gradient, $\rho\omega^2 r$ is the centrifugal force per unit volume, r is the radius from the axis of rotation, ρ is the fluid density, and ω is the rotation speed in radians per second.

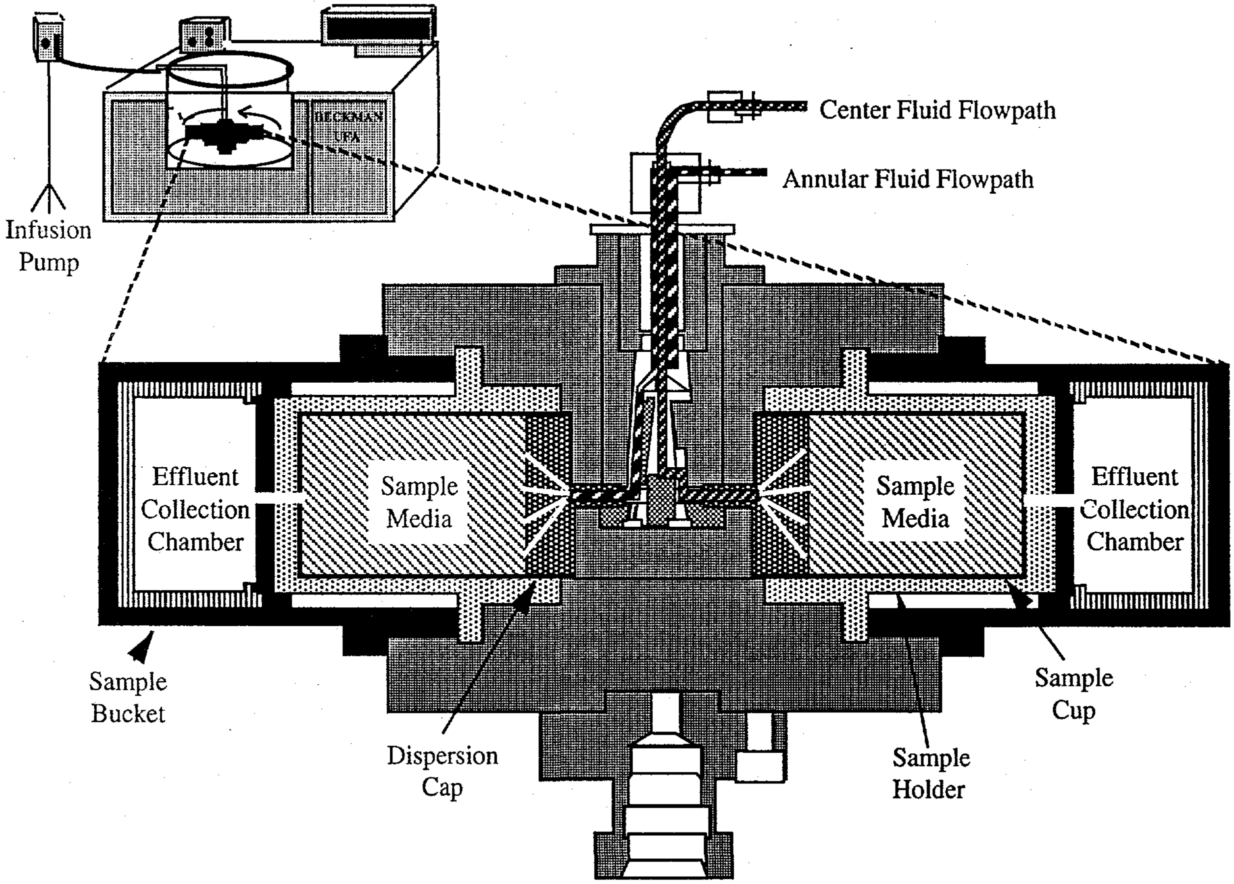

Figure 2.1. UFA Rotor and Seal Assembly

Hydraulic conductivity is a function of either the matrix potential or the volumetric water content within the UFA. Above speeds of about 300 rpm, provided that sufficient flux density exists, the matrix potential is much less than the centrifugal acceleration, $d\psi/dr \ll \rho\omega^2 r$. 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 volumetric water content, θ, Darcy's Law becomes

$$K(\theta) = q/\rho\omega^2 r. \tag{4}$$

2.1.3.2 UFA Experimental Methods

Three sediments, Trench 8, Trench AE-3, and McGee Ranch (described in Section 2.2), were uniformly packed into 42-cm^3 columns as dried samples. Gas in the sediments was then forced out of the column by slowly introducing unspiked groundwater through the bottom of the column. Once the sediment sample was degassed, groundwater was introduced at a rate of 0.01 mL/hr into the top of the column for 1 wk. Once the sediment and groundwater were brought into chemical and hydrological equilibrium, the saturated columns were placed into the UFA. Unsaturated hydraulic equilibrium was then established, generally requiring about 3 days. Column experiments were conducted at various volumetric water contents.

Once the column was brought to hydraulic equilibrium, hydraulic conductivity was determined using the UFA by standard methods (PNNL Method UFA-SK-01). Uranium retardation studies conducted under unsaturated conditions were then conducted. Columns were brought to the desired hydraulic equilibrium, which typically required about 3 days, and then Hanford groundwater spiked with 50-µg/L uranyl (UO_2^{2+}) was introduced into the column. The degree of sediment moisture saturation was determined gravimetrically on a daily basis during the course of the UFA experiments. Sample collection frequency for uranium analyses and duration of experiments vary with the objective of experiment. Laser phosphorimetry (Chemchek Instruments, Inc.) was used to measure total uranyl concentration. Column experiments with tritium were also conducted at various saturations to evaluate the flow of water.

2.2 Sediments and Groundwater Characterization

The groundwater used throughout these studies was collected from a well located in an uncontaminated portion of the Hanford Site: Well S3-25. The chemistry of this water is presented in Table 2.1.

There were four sediments used in these studies: Trench-8, Trench AE-3, TBS-1, and Trench-94. These sediments were collected from the 200 Areas on the Hanford Site (Table 2.2). Trench-8 and TBS-1 sediments were characterized by Serne et al. (1993) and Trench-94 was characterized by Rhoads et al. (1994). Selected properties of these sediments are presented in Table 2.3.

Table 2.1. Chemical Composition of Uncontaminated Groundwater (<0.45-µm Filter) Used in These Studies

Constituent	Concentration (mg/L)
pH	8.46 (unitless)
Cl^-	22
NO_3^-	1.7
SO_4^{-2}	108
Total Organic C	0.73
Total Alkalinity (as CO_3^{2-})	67.5
Al	0.14
B	0.05
Ba	0.069
Ca	67.5
Fe	3
K	3
Mg	16.4
Mn	0.046
Na	27.6
Si	16.2
Sr	0.28
^{99}Tc (µCi/L)	0.004 µCi/L
UO_2^{2+}	0.005

Table 2.2. Sediment Descriptions and Sample Locations

Sample Designation	Sample Texture	Sample Location
TBS-1	Touchet Bed Sand	Army Loop Road (S of 200-W)
Trench AE-3	Silty Loam	AE-3 Burial Ground Side Wall (200 W)
Trench-8	Medium Coarse Sand	W-5 Burial Ground Side Wall (200 W)
Trench-94	Very Coarse Sand	218-E-12B Burial Ground Side Wall (200 E)

Table 2.3. Selected Properties of the Sediments Used in These Studies

Constituent	TBS-1[(a)]	Trench AE-3[(b)]	Trench-8[(a)]	Trench-94[(c)]
pH	8.2	8.3	7.9	8.2
CEC (meq/100 g)	6	6.4	5.2	5.3
Surface Area (m^2/g)	6.3	14.8	6.1	6.3
In-situ Gravel (%)[(d)]	<1	<1	9.7	32.7
In-situ Sand (%)	79.2	41	78.6	67
In-situ Silt (%)	14.8	50	6.3	0.26
In-situ Clay (%)	5	9	5.4	0.04
<2-mm Sand (%)[(e)]	80	41	87	99.55
<2-mm Silt (%)	15	50	7	0.39
<2-mm Clay (%)	5	9	6	0.06
Particle Density (g/cm^3)	2.72	2.74	2.70	2.84
Saturated Hydraulic Conductivity (cm/s)	7e-4	6e-6	4.6e-2	---
Dominant Mineral in Clay Fraction	Smectite (84%) Illite (5%) Vermic. (5%)	Smectite (57%) Illite (19%) Vermic. (14%)	Smectite (57%) Illite (19%) Vermic. (18%)	Smectite (38%) Plagioclase (26%) Illite (13%)

(a) TBS-1 and Trench-8 sediment data is from Serne et al. (1993).

(b) Analysis for Trench AE-3 conducted for this project. It has not been previously reported.

(c) Trench-94 sediment data is from Rhoads et al. (1994). It is referred to by Rhoads et al. (1994) as sediment from the 218-E-12B burial ground.

(d) In-situ compositions refer to the total sediment as it exists in the ground. This sediment was not used in the adsorption experiments.

(e) The <2-mm fraction was used in the adsorption experiments.

3.0 Results and Discussion

3.1 Uranium

3.1.1 Uranium-K_d Values: Effect of Contact Time

The K_d values of uranium, as uranyl (UO_2^{2+}), were measured on three sediments as a function of contact time. Contact time was considered an important variable because of the exceptionally long contact time between the radionuclides and sediments in the LLW disposal site. Furthermore, researchers in our lab have recently shown that the assumption of instantaneous uranyl adsorption to Hanford sediments is incorrect (Lindenmeier et al. 1995). For this study, batch experiments were sampled 7, 266, 328, and 398 days after an uranyl-spiked Hanford groundwater was put in contact with three sediments. Separate tubes containing were used for each sampling period. The groundwater is described in Table 2.1 and the sediments used in these tests are described in Tables 2.2 and 2.3. The uranyl concentrations spiked into the groundwater was 350 µg/L.

For all three sediments, the K_d values consistently increased over the 13 month duration of this experiment (Figure 3.1). The U-K_d values increased 149% for the Trench AE-3 sediment, 115% for the Trench 94 sediment, and 71% for the TSB-1 sediment. Neither the magnitude nor the percent change were positively correlated to pH or cation exchange capacity of the sediment (Figure 3.1 and Table 2.3). The K_d values associated with Trench AE-3 sediment appear to increase linearly with time. Those associated with the other two sediments, appear to level off with time. Based on simple linear regression analysis (no conceptual model is meant to be implied by these analyses), this trend is highly significant. The regression coefficient values, r, ranged from 0.94 for the TSB-1 sediment to 0.98 for the Trench 94 sediment.

The cause for this consistent and significant trend is not known. Some possible explanations include: 1) as the sediment aged, calcite recrystallizes on the sediment surface, thereby burying sorbed uranium and creating new sorption sites, 2) the uranium adsorption reaction is diffusion limited and with time, the uranyl molecules came into contact with more and more adsorption sites, 3) the shaking process caused the particles or aggregates of the particles to break apart thereby creating more surface area for sorption to occur, and 4) microbial population in the sediment suspension may have increased during the extended contact time, resulting in the generation of additional uranyl adsorption sites. We anticipate evaluating the third possibility by comparing the clay-size particle concentrations in the sediments before and after the experiment.

The results of this experiment were unexpected. The initial design for this study called for three sampling periods with four replicates. After measuring the K_d values of the first two sampling periods, the experimental design was changed. The revised experimental design increased the number of sampling dates to five and decreased the number of replicates for the remaining three sampling periods. The last sampling for this experiment will be conducted next year, 1997.

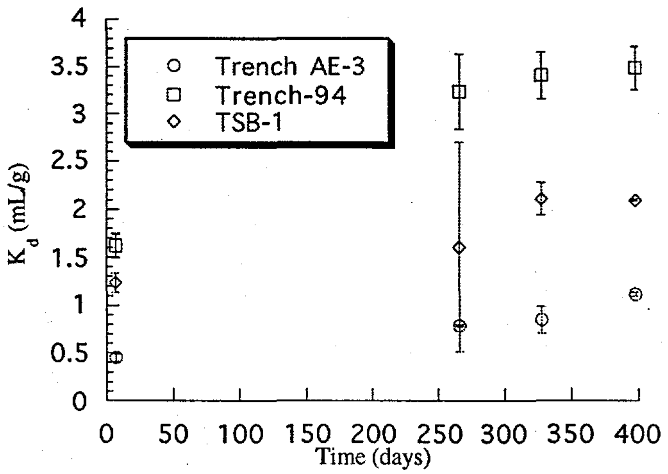

Figure 3.1. Uranyl K_d Values as a Function of Contact Time With Three Sediments (UO_2^{2+} Spike Concentration = 350.37 µg/L; Solid:Solution = 1:2; Background Solution = Hanford Groundwater)

3.1.2 Uranium-K_d Values: Effect of Uranium Solution Concentration

Uranium-K_d values were measured as a function of uranyl concentration in solution. The reason for this study is that the degree to which many radionuclides adsorb to mineral surfaces has been shown to be solution-concentration dependent (Sposito 1984). Typically, as the concentration increases, the degree of adsorption either levels off or decreases. The explanation for this phenomena is that the number of adsorption sites on the mineral becomes limiting. Also, the presence of an absorbate on the surface of a mineral may electrostatically or sterically interfere with the adsorption of subsequent adsorbates. The initial solution uranyl concentration in solutions ranged from 3.3 to 100 µg/L. The uranyl was added to uncontaminated Hanford groundwater (Table 2.1) and the resulting spiked solution was put in contact with two sediments, Trench 94 and Trench AE-3 (Tables 2.2 and 2.3). The uranyl spiked solutions and sediment suspension were placed on a platform shaker for 30 d before the solution uranyl concentrations were determined by laser-phosphorimetry (Chemchek Instruments Inc., Richland, Washington).

The uranyl-K_d values remained quite similar throughout the range of solution uranyl concentrations investigated (Figure 3.2). The average K_d for the Trench 94 sediment was 0.14 ± 0.07 mL/g and for the Trench AE-3 sediment was 0.45 ± 0.14 mL/g. The Trench AE-3 average is consistent with the 7-day data presented in Figure 3.1. However, the Trench 94 data is lower than the 7-day data presented in Figure 3.1. The cause for this is not known. The implication of this data set for the PA is that a single K_d value can be used throughout this solution uranyl concentration range. Stated in surface chemistry terms, the adsorption isotherm is linear in the range evaluated; thus, the K_d model is appropriate for describing uranyl adsorption in this system. This is not altogether surprising considering that the number of uranyl adsorption sites in these sediments likely far exceeds the low range of uranyl concentrations used in these studies.

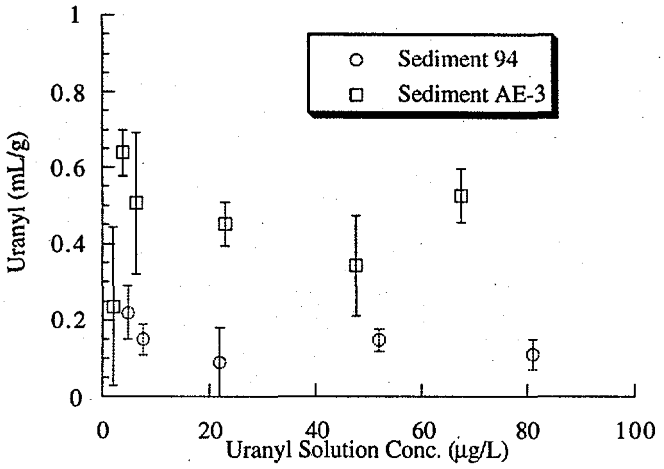

Figure 3.2 Uranyl-K_d Values for Two Sediments as a Function of Solution Uranyl Concentrations (Contact Time = 30 d; Sediment:Solution = 1:2; Solution = Uncontaminated Hanford Groundwater)

3.1.3 Uranium-K_d Values: Effect of Solution Ionic Strength

It is likely that a plume emanating from the LLW-PA disposal site will have an ionic strength gradient. Ionic strength(a) is a measure of the sum of ions in a system and has been shown to have significant effects on sorption processes (Stumm and Morgan 1981; Sposito 1984; Serne et al. 1993). Generally, as the ionic strength increases, adsorption of contaminants decreases because there is greater competition for adsorption sites. However, high ionic strengths can occasionally have the opposite effect, that is, as the ionic strength increases, the extent to which solutes are removed from solution increases (Stumm and Morgan 1981). The cause for this has been attributed to (co)precipitation (Stumm and Morgan 1981). In this latter situation, as the ionic strength increases, a greater concentration of the ligand is introduced into the system, causing more precipitation of the contaminant .

A solubility and batch K_d study was conducted such that the solubility and K_d values of UO_2^{2+} were measured as a function of ionic strength. In this study, the ionic strength of Hanford groundwater (Table 2.1) was adjusted by adding fixed amounts of sodium perchlorate, $NaClO_4$. Sodium perchlorate was selected as the salt to control ionic strength because sodium will likely be the dominant cation emanating from the waste forms and the perchlorate anion, ClO_4^-, is a non-complexing ligand. Thus, the perchlorate anion will increase the ionic strength without greatly affecting the chemical speciation. The sodium perchlorate/groundwater solutions were placed on a platform shaker to equilibrate for one week. A uranium nitrate solution was added to the sodium perchlorate/groundwater solutions to make a final concentration of ~200 µg/L uranyl. The uranyl

---

(a) Ionic strength (I) is defined as:

$$I = 0.5\Sigma(m_i z_i^2)$$

where m_i is the molar concentration of species i and z_i is the valance of species i.

groundwater solution was permitted to equilibrate for another week, after which the solution pH was measured. The solutions were passed through a 0.007-µm filter and the electrical conductivity and uranyl concentration were measured in the filtrate. The dissolved uranyl concentration was operationally defined as the fraction of uranyl that could pass through the 0.007-µm filter. The uranyl solubility ratio was defined as:

$$\text{Solubility Ratio} = \frac{C_{\text{final}}}{C_{\text{initial}}} \tag{5}$$

where C_{final} is the uranyl concentration in the <0.007-µm filtrate and C_{initial} is the uranyl concentration added to the groundwater. No sediment was added to the tests used to calculate the solubility ratios. The <0.007-µm filtrates were later used in batch-K_d experiments. All test were conducted in triplicate. Triplicate negative controls (no uranyl spike + sediment) and positive controls (uranyl spike + no sediment) were carried through all analyses.

Electrical conductivity is a measure of the ion activity (concentration) in water. The electrical conductivity increased linearly with amount of sodium perchlorate added to the groundwater solution (Table 3.1). This suggests that the Na^+ and ClO_4^- ions went into solution and did not form neutral complex species. The percent of uranyl remaining in solutions after filtration as a function of added sodium perchlorate is also shown in Table 3.1. The sodium perchlorate had no significant effect on the concentration of uranyl in solution, as suggested by the overlapping standard deviation values of the solubility ratios (Table 3.1). Uranyl concentrations in the six spiked solutions ranged from 191 to 200 µg/L with overlapping error bars.

The uranyl solutions described in Table 3.1 were used in batch-K_d experiments. Although there was a very slight increase in the uranyl-K_d values with increased additions of sodium perchlorate, the trend was not statistically significant ($P \geq 0.05$) (Table 3.2). It is important to note that the final pH values after the 14-d contact time were essentially identical, indicating that ionic strength was increased in these experiments independent of pH. These results have ramifications for the PA in that separate uranyl-K_d values will likely not have to be selected to describe uranyl adsorption to systems with different ionic strengths.

3.1.4 Uranium-K_d Values: Effect of pH

The pH of the plume emanating from the proposed burial site is very likely to encounter a pH gradient. If cement is used as a burial material, the pH in the plume may vary from about 12.5 in the near field to about 8.0 in the far field. The pH of a system has been shown to have a rather large effect on adsorption tendencies to pure mineral phases (Giblin 1980, Salter et al. 1981, Anderson et al. 1982, Zachara and McKinley 1993) and natural sediments (Koss 1988, Eridson et al. 1993, Zachara et al. 1992, Puls et al. 1982, Johnson et al. 1995). The most common trend observed is that uranyl adsorption increases from pH 3.5 to about 8 and then it plateaus until about pH 10, where it starts to decrease. The cause for the initial increase in adsorption with increased pH is due to the overall increase in the number of adsorption sites (specifically, increases in the cation exchange capacity and the magnitude of the negative charge on the variable charged clays). The decline in uranyl adsorption as the pH increases above 10 is often attributed to the formation of anionic carbonate and hydroxyl complexes in solution, such as $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, and $UO_2(OH)_3^-$. These anionic uranyl-baring species do not adsorb strongly, thus K_d values drop.

Table 3.1. Uranyl Solubility Ratios of Hanford Groundwater Treated with Varying Concentrations of Sodium Perchlorate[(a)]

Final Concentration of $NaClO_4$ Added (mM)	Electrical Conductivity (µS/cm)	Average Final Uranyl in <0.007-µm filtrate (µg/L)	Average Solubility Ratio
0	565 ± 0	192 ± 7	1.00 ± 0.04
0.3	594 ± 0	195 ± 2	1.02 ± 0.01
1.0	661 ± 0	197 ± 2	1.03 ± 0.01
1.7	742 ± 0	194 ± 4	1.01 ± 0.02
4.1	967 ± 0	201 ± 4	1.05 ± 0.02
14.0	1984 ± 0	197 ± 4	1.02 ± 0.02

(a) Means followed by standard deviation of three observations; Trench AE-3 sediment; initial uranyl concentration ~192 µg/L; equilibration period for $NaClO_4$ adjustment = 2 wks; equilibration period for subsequent uranyl spike = 2 wks.

Table 3.2. Effects of Sodium Perchlorate Additions on Uranyl-K_d Values[(a)]

$NaClO_4$ Added (mM)	Suspension pH After 1 hr Contact Time	Final Suspension pH After 2-wk Contact Time	Average K_d (mL/g)
0	8.31 ± 0.00	7.92 ± 0.02	1.99 ± 0.10
0.3	8.37 ± 0.01	8.05 ± 0.01	1.92 ± 0.13
1.0	8.30 ± 0.01	7.99 ± 0.00	1.91 ± 0.17
1.7	8.32 ± 0.03	7.99 ± 0.01	2.10 ± 0.22
4.1	8.26 ± 0.01	7.98 ± 0.00	2.25 ± 0.15
14.0	8.27 ± 0.01	7.97 ± 0.01	2.44 ± 0.44

(a) Mean and standard deviation of three observations. Trench AE-3 sediment; Hanford groundwater spiked with ~192 µg/L.

3.1.4.1 First pH/Uranyl Trial

Two studies were conducted in which sodium hydroxide (NaOH) was used to vary the pH of suspensions of Trench AE-3 sediment in Hanford groundwater. Although it is more difficult to stabilize elevated aqueous pH system, we elected not to conduct these experiments in a CO_2-free environment chamber. The reason for this is because CO_2 would exist in the Hanford subsurface environment. Sodium hydroxide was selected for these studies because the Na^+ cation and OH^- anion are the dominant ions released from several types of glass. In the first experiment, a set amount of sodium hydroxide was added to the system and the sediments were purposely not preequilibrated with the sodium hydroxide solutions. The intent of not preequilibrating the sediments was to simulate the effect, if any, the edge of the contaminant plume would have on uranyl-K_d values. The molar concentrations of sodium hydroxide added was identical to the amount of sodium perchlorate added to the experiment described in Section 3.1.3. After equilibrating the sodium hydroxide solutions for one week, the solutions were spiked with ~200 µg/L uranyl, permitted to equilibrate for another week, passed through a 0.007-µm filter, and finally the pH and uranyl concentrations of the filtrates were determined. Solubility ratios were calculated using Equation 5. These solutions were then used in batch-K_d experiments in which the sediment to solution ratio was 1:2. This experiment will be referred to as the First pH/Uranyl Trial.

The pH of the sodium hydroxide-amended Hanford groundwater solutions in the First pH/Uranyl Trial ranged from 8.4 to 11.9 (Table 3.3). The solubility ratios decreased consistently and significantly ($P \leq 0.05$) from 1.00 to 0.92, i.e., about 8% of the uranyl in the highest pH solution could not pass through the 0.007-µm filter and all of the uranyl in the lowest pH solution passed through the 0.007-µm filter. The electrical conductivity values of the solutions increased concomitantly with pH and the amount of sodium hydroxide added. Taking into consideration the results from the sodium perchlorate study (Section 3.1.3), it appears that the decrease in solubility can be attributed primarily to the increase in pH and not the increase in electrolyte concentrations.

The uranyl solutions described in Table 3.3 were used in batch-K_d experiments. Increasing sodium hydroxide additions to the uranyl-spiked Hanford groundwater increased the 1-hr pH values of only the three highest NaOH treatments, the treatments receiving 1.7-, 4.06- and 14-mM NaOH (Table 3.4). By the end of the two week equilibration period the pH had decreased between 0.1 and 0.5 pH units, indicating that equilibrium conditions had not been achieved. This was not surprising since these sediments were not preequilibrated with the appropriate pH-adjusted background solutions. The uranyl-K_d values gradually increased as the amount of sodium hydroxide added increased between 0 and 4.1 mM. This trend is likely due to an increase in the number of adsorption sites (an increase in surface hydroxyl groups) as the pH increases. The uranyl-K_d value for the 14-mM sodium hydroxide treatment increased dramatically. When considered with the rest of the K_d data presented in Table 3.3, the sorption phenomena can be attributed predominantly to precipitation and not to adsorption. What is important to note here, is that the precipitation did not occur until the sediment was added to the system (Tables 3.3 and 3.4). This type of precipitation, referred to as heterogeneous precipitation (heterogeneous with respect to the types of phases in the system) and has been attributed to the solid phase providing a seed for precipitation to occur (Stumm and Morgan 1981; Stumm 1992). The possible phases that may have precipitated will be discussed in Section 3.1.4.2.

The addition of sodium hydroxide increased the ionic strength as well as the pH of the solutions. In an attempt to evaluate whether the observed differences in uranyl-K_d values were attributed to pH or ionic strength changes, a separate experiment was set up with molar additions of sodium perchlorate (Table 3.2) identical to the sodium hydroxide additional of this experiment (Table 3.4). In the sodium perchlorate experiment, the pH remained essentially constant, while the ionic strength increased (Tables 3.1 and 3.2). The results of this study showed that the uranyl-K_d remained quite similar throughout the entire ionic strength ranged investigated. Thus, the differences in the First pH/Uranyl Trial can be attributed to NaOH changes on the pH of the system and not to the concomitant increase in ionic strength.

Table 3.3. Uranyl Solubility Ratios of Hanford Groundwater Treated with Varying Concentrations of Sodium Hydroxide: First pH/Uranyl Trial(a)

Final Concentration of NaOH Added (mM)	pH	Electrical Conductivity (µS/cm)	Final Uranyl in <0.007-µm filtrate (µg/L)	Solubility Ratio(b)
0	8.59	533 ± 0	195 ± 4	1.00 ± 0.019
0.3	8.54	504 ± 0	188 ± 4	0.96 ± 0.021
1.0	8.64	479 ± 0	185 ± 4	0.95 ± 0.021
1.7	9.52	480 ± 0	182 ± 5	0.93 ± 0.025
4.1	10.41	623 ± 0	184 ± 3	0.94 ± 0.013
14.0	11.88	2740 ± 0	179 ± 7	0.92 ± 0.035

(a) Trench AE-3 sediment; equilibration period for NaOH adjustment = 2 wks; equilibration period for subsequent uranyl spike = 1 wk.
(b) The solubility ratio is defined in Equation 5.

Table 3.4. Effect of Sodium Hydroxide Additions on Uranyl-K_d Values: First pH/Uranyl Trial(a)

NaOH Added (mM)	Suspension pH After 1 hr Contact Time	Final Suspension pH After 2-wk Contact Time	K_d (mL/g)	Apparent-K_d(b)
0	8.13 ± 0.05	7.97 ± 0.00	1.26 ± 0.12	1.26 ± 0.16
0.3	8.15 ± 0.01	7.95 ± 0.03	1.27 ± 0.55	1.42 ± 0.59
1.0	8.17 ± 0.01	7.96 ± 0.02	2.86 ± 0.53	3.15 ± 0.42
1.7	8.38 ± 0.01	7.98 ± 0.071	3.09 ± 0.25	3.52 ± 0.12
4.1	9.34 ± 0.01	8.21 ± 0.07	3.51 ± 0.26	3.90 ± 0.37
14.0	11.56 ± 0.00	10.97 ± 0.07	545.7 ± 70.4	882.5 ± 33.8

(a) Mean and standard deviation of three observations; Trench AE-3 sediment; Hanford groundwater spiked with ~200 µg/L.
(b) Apparent-K_d values account for the total amount of uranium removed from solution by precipitation, as estimated in Table 3.2, and that removed by the sediment (as reported in column 4 of this table).

Since contaminant transport modelers are interested in the total amount of contaminant partitioned from the aqueous to the solid phase, whether it be via adsorption or precipitation, an apparent-K_d value was calculated (Table 3.4). This value accounts for the total amount of uranyl removed from solution, whether it be via precipitation, as estimated by the solubility ratios in Table 3.3, or removed by the sediment (as reported in column 4 of Table 3.4). The apparent-K_d values are generally slightly larger than the K_d values, except in the case of the 14-mM NaOH treatment in which the apparently-K_d value is 62% greater than the K_d value.

3.1.4.2 Second pH/Uranyl Trial

In the Second pH/Uranyl Trial, the pH of six groundwater suspensions was adjusted to pH values ranging from 8.2 to 11.8 with sodium hydroxide. These pH values were carefully maintained at the desired values for a period of two weeks. Once the pH values stabilized, the solutions were spiked with ~200 µg/L uranyl and then permitted to return to equilibrium for another week. The solutions were then passed through a 0.007-µm filter and the pH and uranyl concentrations of the filtrate were determined. The uranyl solubility ratio was calculated directly from this data using Equation 5. A portion of the non-spiked, pH-adjusted groundwater was used to preequilibrate the sediments prior to conducting batch-K_d experiments. The sediments were washed three times with the pH-adjusted solutions, each for 24-hr periods. The spiked groundwater solutions used to calculate solubility ratios were brought into contact with the preequilibrated sediments to a final sediment:solution mass ratio of 1:2. After two weeks, the solution and solid phases were separated by centrifugation and filtration and the solution phase was analyzed for pH, uranyl concentration, carbonate concentration, and major cation and anion concentrations.

The solubility ratios of the Second pH/Uranyl Study are reported in Table 3.5. These solubility ratios are generally slightly higher than those of the First pH/Uranyl Study (Table 3.3). They indicate that essentially no uranyl precipitation occurred during this portion of the experiment (except for Treatment 5). In the first study, the uranyl solubility slightly decreased as the solution pH increased. The cause for this difference is not known.

Table 3.5. Uranyl Solubility Ratios of Hanford Groundwater Treated with Varying Concentrations of Sodium Hydroxide: Second pH/Uranyl Trial[a]

Treatment	$pH_{Solution}$[b]	Final Uranyl in <0.007-µm filtrate (µg/L)	Solubility Ratio[c]
1	8.29 ± 0.03	179 ± 3	1.03 ± 0.02
2	9.00 ± 0.01	176 ± 3	0.98 ± 0.02
3	9.5 ± 0.02	176 ± 2	0.98 ± 0.01
4	10.02 ± 0.02	176 ± 4	0.98 ± 0.02
5	11.00 ± 0.02	161 ± 4	0.90 ± 0.02
6	12.01 ± 0.01	180 ± 3	1.00 ± 0.02
(-) Control: no soil + no uranyl spike	8.32 ± 0.07	6 ± 1	--

(a) Trench AE-3 sediment; equilibration period for sodium hydroxide adjustment = 2 wks; equilibration period for subsequent uranyl spike = 1 wk.
(b) pH of solution, without sediment, taken at the end of the experiment.
(c) The solubility ratio is defined in Equation 5.

Effects of the sodium hydroxide additions on uranyl-K_d values for the Second pH/Uranyl Trial are described in Table 3.6. The uranyl-K_d values increase slightly between the final pH values of 8 and 9, between Treatments 1 and 4 (Table 3.6). This trend can be attributed to an increase in the number of adsorption sites induced by elevating the pH. The uranyl-K_d value for the two highest pH treatments, Treatments 5 and 6, increased dramatically. When considered with the rest of the K_d data presented in Table 3.6, the sorption phenomena for these two treatments can be attributed primarily to precipitation and not to adsorption.

Table 3.6. Effects of Sodium Hydroxide Additions on Uranyl-K_d Values: Second pH/Uranyl Trial(a)

Treatment	Suspension pH After 5-day Contact Time	Suspension pH After 2-wk Contact Time	K_d (mL/g)	Apparent-K_d $^{(b)}$
1	8.17 ± 0.14	8.48 ± 0.06	1.07 ± 0.19	1.07 ± 0.19
2	8.40 ± 0.07	8.26 ± 0.04	1.46 ± 0.14	1.55 ± 0.10
3	8.72 ± 0.03	8.44 ± 0.03	1.37 ± 0.03	1.44 ± 0.07
4	9.31 ± 0.03	9.12 ± 0.01	2.12 ± 0.16	2.22 ± 0.15
5	10.34 ± 0.14	10.27 ± 0.14	29.39 ± 18.04	32.90 ± 19.96
6	11.78 ± 0.08	11.82 ± 0.07	496.6 ± 8.8	496.6 ± 8.8
(+) Control: no sediment + uranyl spike	8.71 ± 0.57	8.65 ± 0.15	--	--
(-) Control: no sediment + no uranyl spike	8.32 ± 0.07	8.29 ± 0.16	--	--

(a) Mean and standard deviation of three observations; Trench AE-3 sediment; Hanford groundwater spiked with ~200 µg/L.

(b) Apparent-K_d values account for the total amount of uranium removed from solution by precipitation, as estimated in Table 3.5, and that removed by the sediment (as reported in column 4 of this table). Since solubility values can not theoretically be greater than one, those ratios that were experimentally determined to be greater than one (Treatments 1 and 6) were reassigned values of one.

Apparent-K_d values (Table 3.6) represent the amount of uranium removed from solution by aqueous precipitation, as estimated in Table 3.5, and that removed by the sediment (as reported in column 4 of Table 3.6). The apparent-K_d values were equal to or slightly larger than the K_d values.

3.1.4.3 Heterogeneous Uranyl Precipitation Induced by Increased pH

It is important to note that uranyl precipitation in Treatments 5 and 6 in the Second pH/Uranyl Trial did not occur until the solutions were combined with the sediments. In Table 3.5, the solubility ratio of Treatments 5 and 6 were >0.9, indicating that little precipitation of uranyl occurred in solution. However, once sediments were added to these solutions, uranyl precipitation was apparent (Table 3.6). This type of precipitation, referred to as heterogeneous precipitation or heterogeneous nucleation (heterogeneous with respect to the types of phases in the system), is rarely reported in adsorption isotherm experiments but is frequently observed in precipitation experiments (Stumm 1992). It has been attributed to the solid phase providing a seed for precipitation to occur or to the higher concentration of solutes near or on the solid surfaces (Steefel and Van Cappellen 1990; Stumm 1992).

Heterogeneous precipitation is in many cases the predominant formation process for crystals in natural waters. In a similar way as catalyst reduces the activation energy of a chemical reaction, foreign solids may catalyze the nucleation process by reducing the energy barrier. Qualitatively, if the surface of the solid substrate matches that of the crystal, the interfacial energy between the two solids is smaller than the interfacial energy between the crystal and the solution, and nucleation may take place at a lower saturation index on a solid substrate surface than in solution. For this reason, phase changes in natural waters are almost invariably initiated by heterogeneous solid substrates (Stumm 1992).

The aqueous chemical composition of the solution in the Second pH/Uranyl Trial are presented in Table 3.7. The solution pH after making contact with the sediments ranged from 8.3 to 11.8. As expected, the concentrations of sodium and carbonates increased with pH. The large increase in silicate at pH >10 can be attributed to the dissolution of minerals containing silicon. There were rather large decreases in calcium and magnesium concentration as the pH was increased. As mentioned above, Treatments 5 and 6 showed evidence of precipitation. In comparing the solution chemistries of these treatments before and after contact with the sediment, it can be seen that uranyl, calcium, potassium, and magnesium concentrations decreased and silicate concentration increased.

Uranyl speciation in these solutions was calculated using the uranyl thermodynamic constants of Wanner and Forest (1992) and the thermodynamic MINTEQA2 code (Version 3.10, Allison et al. 1991). The results of these calculations are presented in Table 3.8. Importantly, all uranyl species in solution were calculated to exist as neutral or anionic species. Instead, all the uranyl existed as anionic complexes. In the five lower pH treatments, the carbonate-uranyl complexes dominated the system. In the highest pH solutions, all the uranyl existed as hydroxide-uranyl complexes. This change in speciation occurred because, as the pH increased, the number of moles of hydroxides also increased and these hydroxides were able to out compete the carbonate molecules to form uranyl complexes. The uranyl speciation before and after equilibration with the sediment did not change greatly for Treatment 1 (pH 8.3) and Treatment 6 (pH 11.8). For Treatment 5 (pH 10.3), more carbonate-uranyl species were observed after equilibration with the sediment. This may be attributed partially to the slight decrease in pH from 11.0 to 10.3 during the sediment equilibration period.

Saturation indices for these solutions were also calculated using the MINTEQA2 code. A saturation index is a measure of the tendency of a solid phase to precipitate from solution; values greater than 0 indicate that a solid phase is saturated and therefore, it is thermodynamically possible for it to precipitate. Saturation indices of selected mineral phases are presented in Figures 3.3 and 3.4. The chemical composition of the mineral phases included in Figures 3.3 and 3.4 are:

Aragonite:	$CaCO_3$ (orthorhombic crystal structure)
Calcite:	$CaCO_3$ (hex/rhombo crystal structure)
Haiweeite:	$Ca(UO_2)_2Si_6O_{15}{\bullet}5H_2O$
Schoepite 2.00:	$UO_3{\bullet}2.00H_2O$
Sklokowskite:	$Mg(UO_2)_2Si_2O_7{\bullet}4H_2O$
Soddyite:	$(UO_2)_5Si_2O_9{\bullet}6H_2O$.

Table 3.7. Aqueous Chemical Composition (mg/L) of Hanford Groundwater Solutions Spiked with Uranyl Before and After Equilibration with Trench AE-3 Sediment: Second pH/Uranyl Trial

	Sol'n Chemistry After Sediment Contact					
	Treatment[a] 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5	Treatment 6
$pH_{initial}$[b]	8.3	9.0	9.5	10.0	11.0	12.0
pH_{final}[b]	8.5	8.3	8.4	9.1	10.3	11.8
UO_2^{2+}	0.117	0.102	0.104	0.088	0.017	0.0009
Cl^-	51	58	45	40	43	40
SO_4^{2-}	110	128	114	115	114	115
PO_4^{3-}	0.7	0.9	0.9	0.9	1.3	1.2
CO_3^{2-}	122	107	123	144	194	358
Ca	76	37	20	6	2	4
K	21	28	16	9	5	7
Mg	14.7	8.9	4.8	1.1	0.1	<0.1
Na	35	93	126	160	205	539
H_4SiO_4	71	71	67	61	100	449

	Sol'n Chemistry After Sediment Contact		Sol'n Chemistry Before Sediment Contact		
	(+) Control[c]	(-) Control[c]	Treatment 1	Treatment 5	Treatment 6
$pH_{initial}$	8.4	8.3	8.3	11.0	12.0
pH_{final}	8.6	8.3	NA	NA	NA
UO_2^{2+}	0.191	0.006	0.185	0.161	0.180
Cl^-	31	34	24	30	29
SO_4^{2-}	75	109	109	107	108
PO_4^{3-}	0.7	0.8	1.9	1.3	1.3
CO_3^{2-}	82	123	160	192	376
Ca	59	74	58	2.3	1.3
K	37	13	14	20	16
Mg	17	14	16	2.0	0.1
Na	31	34	30	158	423
H_4SiO_4	57	73	54	26	29

(a) Treatments are numbered in order of the increasing amounts of sodium hydroxide added to the Hanford groundwater. Treatment Number 1 received no sodium hydroxide.

(b) $pH_{initial}$ = pH prior to adding solution to sediment. pH_{final} = pH at the end of the equilibration period with sediment.

(c) (+) Control = no sediment + ~200 µg/L uranyl spike; (-) Control = no spike + no sediment.

Table 3.8. Results of Thermodynamic Calculations of the Uranyl Speciation in a Hanford Groundwater Before and After Equilibration with Trench AE-3 Sediment: Second pH/Uranyl Trial[(a)]

	pH	$UO_2(CO_2)^{2-}$ (%)	$UO_2(CO_2)_3^{4-}$(%)	$UO_2(OH)_2^0$ (%)	$UO_2(OH)_3^{1-}$(%)	$UO_2(OH)_4^{2-}$(%)
Trt. 1 After Sediment	8.5	23	75	1		
Trt. 2 After Sediment	8.3	35	62	2		
Trt. 3 After Sediment	8.4	28	70	2		
Trt. 4 After Sediment	9.1	7	93			
Trt. 5 After Sediment	10.3		98		2	
Trt. 6 After Sediment	11.8			4	94	2
(+) Control	8.6	27	68	3	2	
(-) Control	8.3	32	66	2		
Trt. 1 Before Sediment	8.3	28	71			
Trt. 5 Before Sediment	11		60		40	
Trt. 6 Before Sediment	12		2		96	2

(a) Solution chemistry used in these calculation are presented in Table 3.7. Treatments are numbered in order of the increasing amounts of sodium hydroxide added to the Hanford groundwater. Treatment Number 1 received no sodium hydroxide.Uranyl thermodynamic constants from Wanner and Forest (1992); MINTEQA2 software used to make thermodynamic calculations (Version 3.10, Allison et al. 1991).

Some phases determined to have saturation indices greater than zero are not included in Figures 3.3 and 3.4 because they are either high temperature phases (such as $CaUO_4$) or are known to be kinetically limited (Wollastonite, $CaSiO_3$).

Based on the data in these two figures, there appears to be at least two possible mechanisms for the precipitation of uranyl from the high pH treatments in the Second pH/Uranyl Trial: 1) coprecipitation with calcite and aragonite, and 2) precipitation as a uranium phase. The phases with saturation indices greater than zero for Treatments 5 (pH 10.3) and 6 (pH 11.8) were aragonite, calcite, haiweeite, and sklodowskite. Based on comparisons of the ionic radius of calcium and uranium with a coordination number of six, it is possible for a uranium ion (0.81e-10 m) to substitute for the calcium ion (1.00e-10 m) in aragonite and calcite. Cations with ionic radii within 20% can substitute for one another in solid phases (Shannon 1976). Coprecipitation of metals into aragonite and calcite has been reported frequently (reviewed by Reeder 1983). At pH 11.8, haiweeite had the highest saturation index. Even though the other uranium phases have saturation indices below zero, they too must be considered as possible precipitated phases in the pH 11.8 solution.

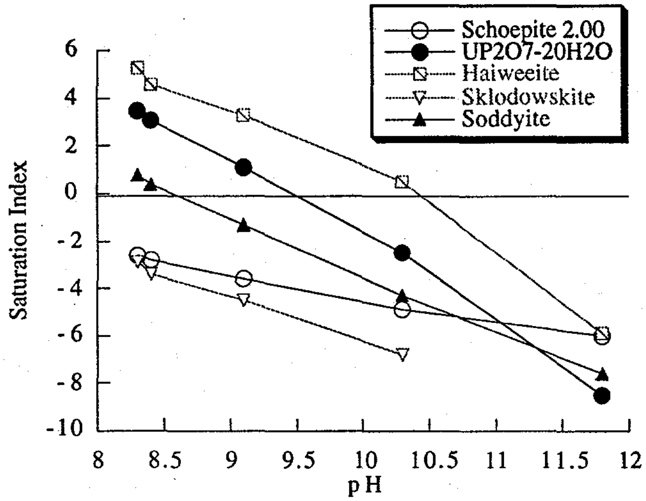

Figure 3.3. Uranyl Saturation Indices From the Second pH/Uranyl Trial

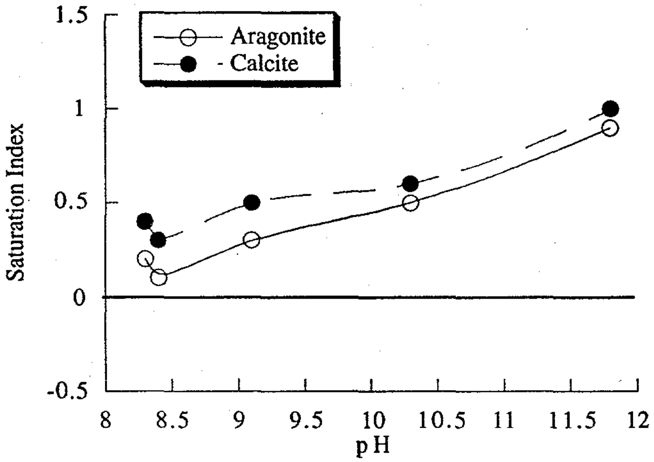

Figure 3.4. Saturation Indices of Calcite and Aragonite From the Second pH/Uranyl Trial

3.1.5 Uranium-K_d Values: Effect of Unsaturated Moisture Conditions

3.1.5.1 Introduction

The major pathway for transport of radionuclides from the Hanford Site's arid zone burial grounds is through unsaturated sediments. The average moisture content of Hanford vadose zone sediments range 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.

Because radionuclide migration requires that a liquid move the radionuclides either physically, as dispersed colloids, or as dissolved constituents in solution, hydraulic conductivity 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 soil 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 soil is saturated, nearly all pores are filled and hydraulic conductivity is at a maximum. As the soil 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 soil water flow to occur. An interesting corollary of the pore size-conductivity relationship is that at, or near, saturation, a sandy soil conducts water more rapidly than a clay soil with many micropores. When the soils are unsaturated, however, many of the micropores in the clay soil remain filled, and consequently, the hydraulic conductivity in the clay soil does not decrease nearly as sharply as it does in sandy soil under the same tension.

In modeling contaminant transport in unsaturated conditions, the definition of the retardation factor (R_F; Equation 2) takes on a new form:

$$R_F = 1 + \frac{\rho_b}{\theta} K_d \qquad (6)$$

where θ, the volumetric water content of the sediment, replaces ϕ, sediment porosity, in Equation 2. Equation 6 explicitly assumes that the extent to which contaminants sorb to sediments, the K_d value, is constant as a function of the volumetric water content. This relationship is convenient for modeling; however, its validity is not certain. There have been experiments to test this assumption, and the results have been mixed (Knoll 1960, Nielsen and Biggar 1961, Nielsen and Biggar 1962, Baetsle et al. 1966, Routson and Serne 1972, Gee and Campbell 1980, Lindenmeier et al. 1995).

There are theoretical reasons for believing that K_d values vary as a function of volumetric water content. First, as the sediment becomes increasingly unsaturated there will be a smaller percentage of the total exchange sites in contact with the aqueous phase. For example, if only half of the exchange sites of a sediment come into contact with the aqueous phase, then the effective exchange capacity of the sediment is decreased by half. Therefore, as less mineral surface is exposed to the aqueous phase, the lower the effective exchange capacity becomes because less of the surface is exposed to the solute of interest. On the other hand, the clay fraction of the soil constitutes the largest exchange capacity and smallest pore sizes. Since increasingly smaller pores are involved in increasingly less saturated sediments, there may be little measurable effect on the exchange capacity of the soil in unsaturated conditions.

Another reason for believing that K_d values would vary with degree of saturation is because in the unsaturated systems the aqueous phase moving as film flow is in closer contact with the sediment surfaces. Solutes in the middle of large pores have less interaction with sediment surfaces than solutes nearer to the sediment surfaces. In unsaturated conditions, the middle of large pores tend to be empty, resulting in a greater percentage of pore water coming in close contact with the sediment surface. Finally, 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 value for many cations tends to decrease with increases in ionic strength.

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^{2+}, 0.1 mg/L Sr^{2+}, and 2 x 10^{-2} µCi/mL ^{90}Sr. There was no apparent difference in Sr retention capacity between saturated and unsaturated soils. However, it is worth noting that column flow rate differences between 100% saturation and 36% saturation were less than a factor of 100. With use of an aggregate of less uniform pore size, flow rate (hydraulic conductivity) differences could have been much greater, the volume of soil contacted by the aqueous phase under unsaturated flow conditions much smaller, and hence the cation exchange capacity of soil might have differed considerably between saturated and unsaturated flow conditions. 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 Tank Farm sandy loam soil 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 tritium tracer experiments, it is likely that in order for the researchers to have observed a trend, a large number of replicates would have been required. 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 tritium, cobalt-EDTA complex, technetium, and iodine sorption (K_d values). Each of these tracers have very low K_d values and therefore, measuring retardation factor differences due to 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 soil, the higher the retardation factor. They attributed this trend to desaturation eliminating the larger flow channels resulting in increasing volumes of stagnant water, which 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 preferred channels.

To date, Lindenmeier et al. (1995) have reported the most extensive data set comparing degree of moisture saturation with K_d values. They investigated ^{85}Sr and uranyl transport through Trench 8 sediment (Table 2.2) using the UFA (Section 2.1.3). Uranyl-K_d values decreased from 2.35 mL/g at 100% saturation to 0.6 mL/g at 29% saturation. Similarly, ^{85}Sr-K_d values decreased from 1.6 mL/g at 100% saturated to 0.75 at 26% saturation. They offered a number of possible explanations including that as the system became increasingly unsaturated, the radionuclides were put into contact with proportionally fewer adsorption sites. These studies were conducted well, providing replicate column results and tritium transport data in support of their interpretation of the results. Additional discussion of this data is provided below.

3.1.5.2 Unsaturated Batch K_d Values

Three sediments, Trench AE-3, Trench 94, and TSB-1 (described in Table 2.2) were used to determined batch uranyl-K_d values as a function of degree of saturation (Figure 3.5). These K_d values did not vary in a consistent manner with moisture saturation. The variability did not increase with decreasing saturation, as one would expect if mixing of the sediment and spiked groundwater was not thorough (it is easier to obtain more uniform mixing in high moisture conditions). Instead, it appears that this variability is real and reflects the actual heterogeneity in the samples. The average K_d values over all the saturations measured for each sediment are:

1.19 ± 0.28 mL/g for TSB-1 sediment,
1.44 ± 0.39 mL/g for Trench 94 sediment, and
0.97 ± 0.14 mL/g for Trench AE-3 sediment.

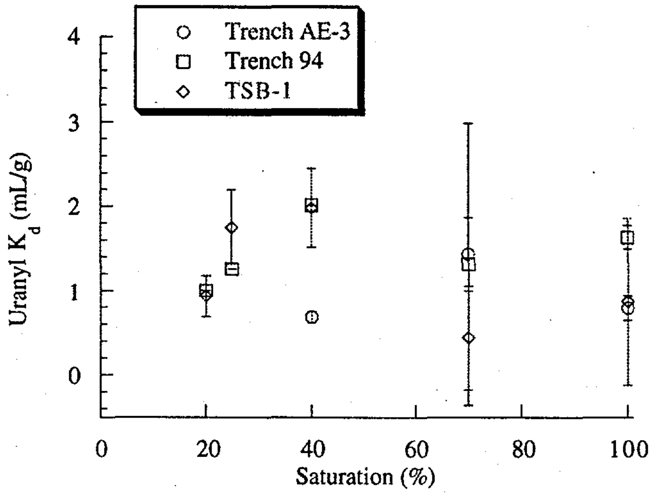

Figure 3.5. Uranyl-K_d Values of Three Sediments Measured by Unsaturated-Batch Methods

These values are remarkably similar to those generated for the uranyl-K_d values presented in Figure 3.1 for the 7-day contact time (the batch experiments used a solution to sediment ratio of 2:1, or >500 percent saturation). The uranyl K_d values presented in Figure 3.1 at 7-day are:

1.23 ± 0.10 mL/g for TSB-1,
1.62 ± 0.13 mL/g for Trench 94, and
0.45 ± 0.04 mL/g for Trench AE-3.

The contact time for the unsaturated batch K_d values was 30 days.

3.1.5.3 Unsaturated Column K_d Values

The first set of experiments conducted with the UFA were designed to evaluate the trend reported by Lindenmeier et al. (1995), namely that uranyl-K_d values decrease with decreasing saturation. The same experimental procedures and sediment, Trench 8 (Table 2.3), that Lindenmeier et al. (1995) used were used in these experiments. The breakthrough curves and a summary of these two experiments are presented in Figures 3.6 and 3.7.

The data in Table 3.9 has been superimposed on the data of Lindenmeier et al. (1995) (Figure 3.8). These data are consistent in magnitude with those of Lindenmeier et al. (1995) and, more importantly, they follow the general trend of the other data. (Two additional UFA experiments at ~60% and 100% saturations were conducted, but their results are suspect due to repeated pump failure). The consistency of the new data with that previously reported further substantiates the conclusion that increases in moisture saturation of Trench 8 sediments results in increases in uranyl-K_d values.

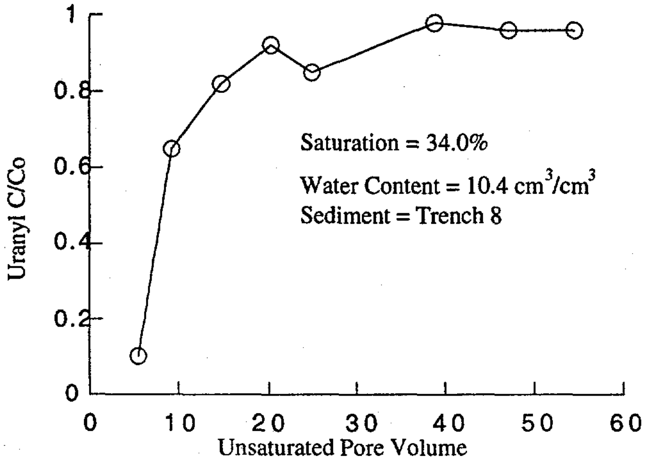

Figure 3.6. Uranyl-Breakthrough Curve in Trench 8 Sediment at 34% Moisture Saturation Using an Unsaturated Flow Apparatus (C = Effluent Uranyl Concentration and C_0= Initial Uranyl Concentration)

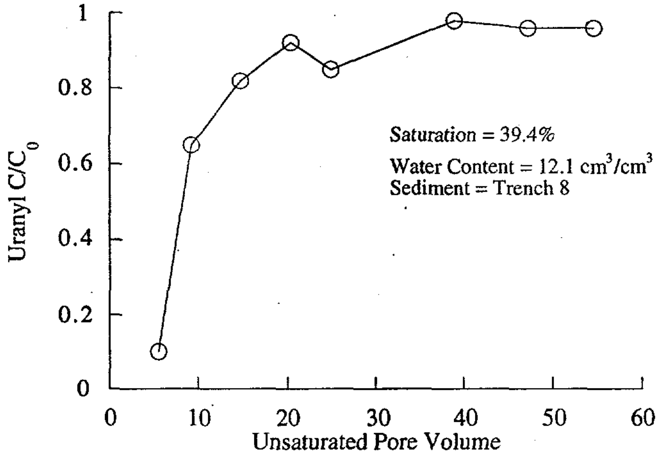

Figure 3.7. Uranyl-Breakthrough Curve in Trench 8 Sediment at 39% Moisture Saturation Using an Unsaturated Flow Apparatus (C = Effluent Uranyl Concentration and C_0= Initial Uranyl Concentration)

Table 3.9. Summary of Uranyl-K_d Values in Trench 8 Sediment Measured by the UFA

Column Number	Residence Time (hr)	Pore Water Velocity (cm/hr)	Water Content (%, v/v)	Saturation (%)	R_F (m/hr)/(m/hr)	K_d (mL/g)
1	19.0	0.31	10.44	34.0	7.9	0.42
2	22.0	0.27	7.09	39.4	8.2	0.51

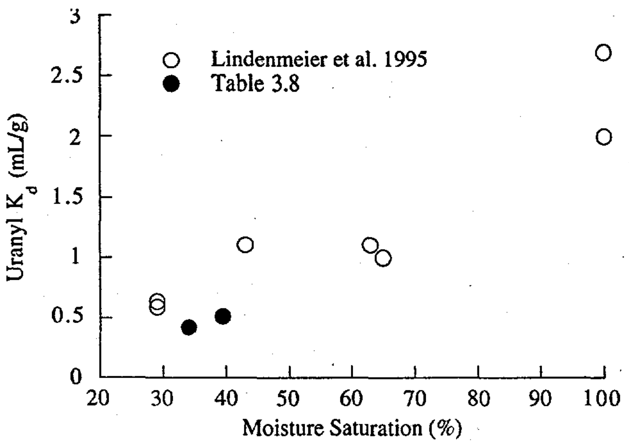

Figure 3.8. Uranyl-K_d Values in Trench 8 Sediment Versus Percent Moisture Saturation in Trench 8 Sediment [Data Presented In Table 3.9 and Reported by Lindenmeier et al. (1995)].

A second suite of experiments were conducted with Trench AE-3 and McGee sediments. These sediments were selected because they contain appreciably more fine-grained materials and vastly different flow properties than the Trench 8 sediment. The particle size distribution for the three sediments are:

Trench AE-3: sand = 41%, silt = 50%, and clay = 9%
McGee: sand = 34%, silt = 49%, and clay = 17%, and
Trench 8: sand = 87%, silt = 7%, and clay = 6%.

The differences in particle size distribution result in appreciably different unsaturated hydraulic conductivities (Figure 3.9). The Trench 8, the more coarse textured sediment, has greater hydraulic conductivities at a given volumetric water content than the other two more fine-textured sediments. Based on this data it was anticipated that the flow patterns as a function of saturation would be appreciably different between these sediments and the Trench 8 sediment.

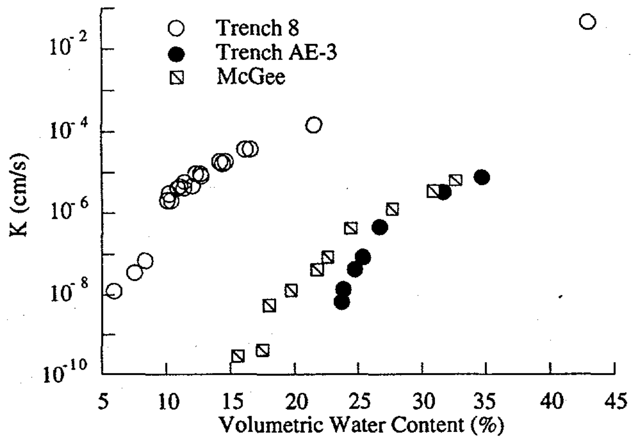

Figure 3.9. Unsaturated Hydraulic Conductivity Values (K) for Trench 8, Trench AE-3, and McGee Sediments

Prior to introducing the uranyl-spiked groundwater, a tritium spike was introduced into three of the columns. Qualitative and quantitative information about the flow patterns of water through a sediment can be obtained from tritium experiments (Bear 1969, Hillel 1980). Perhaps the most important information for how the data has been handled in this study is where the tritium breakthrough occurs, i.e., where $C/C_0 = 0.5$ (C = effluent uranyl concentration and C_0 = initial uranyl concentration). Other important information that can be obtained from tritium breakthrough experiments is the shape of the curve, the symmetry around the inflection point, and symmetry of the leading and trailing edge of a spike plume. In a ideal porous media, tritium has a relative concentration of 0.5 ($C/C_0 = 0.5$,) at one pore volume. For the Trench AE-3 sediment, the tritium breakthrough occurred at 1.10, 1.00 and 1.08 pore volumes (Table 3.10 and Figures 3.10). This variability is not acceptable. Certainly part of the variability can be attributed to experimental procedure. More tritium concentration data points should have been collected near the critical point of 1-pore volume.

Table 3.10. Summary of Tritium Breakthrough Experiments in Trench AE-3 Sediments (Breakthrough Curve Data Presented in Figure 3.8)

Column Number	Sediment	Saturation (%)	Water Content (%, v/v)	Residence Time (hr)	Pore Volume at $C/C_0 = 0.5$
9	AE-3	63	19	57	1.10
10	AE-3	62	19	59	1.00
11	AE-3	63	19	59	1.08

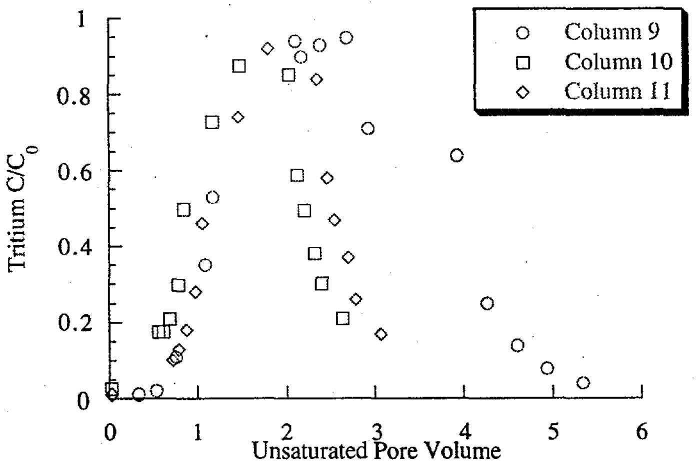

Figure 3.10. Tritium Breakthrough Curves for UFA Columns Containing Trench AE-3 Sediments at ~62% Saturation (Columns Described in Table 3.10, (C = Effluent Uranyl Concentration and C_0 = Initial Uranyl Concentration)

A summary of the uranyl-breakthrough curves conducted with the Trench AE-3 and McGee sediments are presented in Table 3.11. The experiments with the Trench AE-3 columns were conducted first and showed that as the percent moisture saturation increased from 52% to 100%, the uranyl-K_d value decreased from 2.48 mL/g to 0.91 mL/g (Figure 3.11). This is precisely the opposite trend observed with the Trench 8 sediment (Figure 3.8).

Table 3.11. Summary of Uranyl-K_d Values in Trench AE-3 and McGee Sediments Measured at Various Moisture Contents

Column Number	Sediment	Saturation (%)	Water Content (%, v/v)	Residence Time (hr)	R_F (m/hr)/(m/hr)	K_d (mL/g)
3	AE-3	52	20	59	23.2	2.48
4	AE-3	63	20	59	18	1.96
5	AE-3	81	29	59	7.8	1.24
6	AE-3	100	36	--	5.7	0.91
7	McGee	60	22	59	35	4.6
8	McGee	100	37	--	8	1.58

Instead of adding more data points to the Trench AE-3 data set, a third sediment, the McGee sediment, was selected to evaluate further the role that different sediment played in the moisture dependency of K_d values. As mentioned above, the physical properties of the McGee sediment is more similar to those of the Trench AE-3 than to the Trench 8 sediment. To date, only two UFA column experiments have been conducted with the McGee sediment, at 60 % and 100% saturation (Figure 3.11). These results, although not conclusive by any means, support the trend observed with the Trench AE-3 sediment, namely, that as the moisture increases, the uranyl-K_d values decrease.

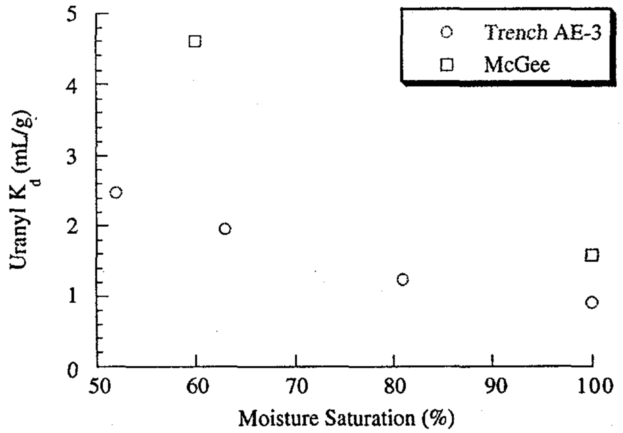

Figure 3.11. Uranyl-K_d Values Versus Percent Moisture Saturation in Trench AE-3 and McGee Sediments (Data Presented in Table 3.11).

Column Number 5 described in Table 3.11 was used in an extended study to evaluate whether steady state conditions in regards to uranyl sorption existed under the flow conditions of these experiments. During the extended duration of this experiment, the flow of the infused uranyl-spiked groundwater was stopped twice for 4-day periods (Figure 3.12). The net effect of stopping the flow during these two periods was to create a longer residence time. The two stop-flow periods are indicated with arrows in Figure 3.12. The residence time during routine flow periods was 59 hr; the residence time during the stop-flow period was 155 hr. After the first stop-flow period, which occurred at about 12 pore volumes, the effluent uranyl concentrations decreased sharply by 43%. This indicates that the uranyl did not have enough time during the 59-hr residence time to adsorb to the sediments, i.e., uranyl adsorption was kinetically limited. A second stop-flow event occurred at about 14 pore volumes. A much smaller decrease in effluent uranyl concentrations resulted. The cause for the difference in response to the two stop-flow events is not known. One possible explanation is that most of the uranyl adsorption sites on the sediment at the time of the second stop-flow event had been occupied. The fact that the uranyl adsorption was kinetically inhibited did not make as much a difference as when fewer of the uranyl adsorption sites were occupied.

This study indicates that the K_d values measured by the column method are likely to be less than those that are measured using batch techniques. The reason for this is that the contact time between the uranyl solution and sediment is much greater in batch studies. In fact, according to Figure 3.1, uranyl sorption continues to increases with contact times equal to at least one year.

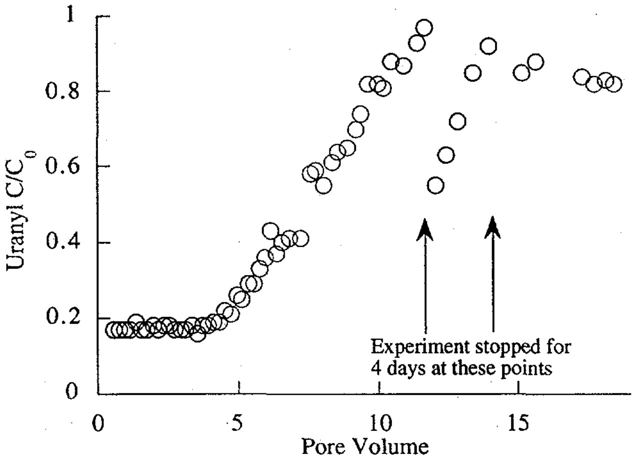

Figure 3.12. Stop-Flow UFA Experiment at 81% Saturation Using Trench AE-3 Sediment and a Flow Residence Time of 59 Hours (C = Effluent Uranyl Concentration and C_0 = Initial Uranyl Concentration)

3.1.5.4 Conclusions on Moisture Dependency of K_d Values

There are at least three explanations to account for the differences in the trends observed between uranyl-K_d values and moisture content: 1) there is no trend, 2) the trend can be attributed to differences in how the background and uranyl aqueous chemistry changed during desaturation, or

3) the trend can be attributed to sediment physical properties. Regarding the first explanation, each of the opposing trends are statistically significant at a confidence level of >99%. The regression equation for the Trench 8 sediment data in Figure 3.8 is:

$$(UO_2^{2+}\text{-}K_d) = -0.28 + 0.025\ (\%\ \text{Saturation}) \qquad R^2 = 0.86,\ n = 9 \tag{7}$$

and for the Trench AE-3 sediment data in Figure 3.11:

$$(UO_2^{2+}\text{-}K_d) = 4.1 - 0.033\ (\%\ \text{Saturation}) \qquad R^2 = 0.96,\ n = 4 \tag{8}$$

Regarding the second explanation, the columns were brought not only into hydrological equilibrium, but also into chemical equilibrium prior to introducing the uranyl spike. This was accomplished by flushing unspiked Hanford groundwater through the columns at the appropriate saturation for several days, for tens of pore volumes. Therefore, it is not likely that salt build-up is likely to have occurred upon dehydration (as is the likely situation in the unsaturated batch K_d trials described in Section 3.1.5.2). Furthermore, the sodium perchlorate experiment described in Section 3.1.4 indicates that ionic strength concentrations over a wide range have little effect on uranyl adsorption in these sediment/groundwater systems (Section 3.1.4).

The third explanation, regarding the sediment physical properties, is the most intellectually satisfying. Since trends have been measured on only two sediments, sufficient data is certainly lacking to definitively identify the mechanism responsible for these two opposing trends. Our working hypothesis is that moisture dependency of K_d values is attributed to at least two sediment characteristics: mineral distribution and the extent to which fine particles form hydraulically continuous pores. If the mineralogy is largely uniform, then the change in flow paths upon desaturation will not result in exposing the contaminants to surfaces with varying adsorption site densities (moles adsorption sites/m^2). If the mineralogy varies or perhaps more specifically, if the charge density of the minerals vary, than a greater moisture dependency of K_d values is possible.

The other important sediment parameter in this hypothesis is the extent to which fine particles form hydraulically continuous pores (Figure 3.13). In the coarse-grained sediment tested, Trench 8, the K_d decreased with desaturation. Based on this observation, it may be assumed that dissolved uranyl came into contact with fewer adsorption sites. One possible explanation for this would be that as the sediments desaturated, the flow path was rerouted away from the smaller pores that were not hydraulically continuous through the length of the column (Figure 3.13-A). In so doing, the water and the uranyl molecules by-passed the fine-sized particles. These fine-sized particles contain higher densities of adsorption sites than coarse-grained particles. In this conceptual model, film flow must be assumed at lower saturations. If water was assumed to flow only in saturated pores, then as the system desaturated, the large pores would drain first, leaving water to flow only in the small pores associated with small particles. Such a flow pattern would result in a higher K_d value upon desorption. Since 90% (w/w) of the Trench 8 sediment was sand (0.05 to 2 mm diameter particles), it is likely that a majority of the pores were large. The presence of a large number of large pores can also be inferred by the unsaturated hydraulic conductivity data presented in Figure 3.9. With so few clay and silt particles in this sediment it is not likely that the small pores were continuous through the entire column. The discontinuity of small pores would create clusters or islands of small pores in which little hydraulic continuity would occur.

In the finer-grained Trench AE-3 sediment, only 41% of the particles were the size of sand, indicating it had fewer large pores and more smaller pores than the Trench 8 sediment. The increased number of smaller particles in the Trench AE-3 sediment also suggests that there was greater likelihood that the small pores were hydraulically continuous (Figure 3.13-B). This in turn would reduce the likelihood of creating hydraulically isolated zones of fine pores. As can be inferred from Figure 3.9, flow through the Trench AE-3 sediment occurred predominantly in the larger pores under saturated conditions and in increasingly smaller pores as the system became increasingly unsaturated. Since the fine-grained particles that form smaller pores have greater densities of adsorption sites than the coarse-grained particles, an increase in K_d would be expected upon desaturation in this second system. It is possible to experimentally distinguish between the types of flow patterns described in Figure 3.13 by conducting detailed tritium breakthrough experiments at varying saturation. Detailed moisture retention curves (moisture content versus vacuum pressure) or moisture versus unsaturated hydraulic conductivity data (such as Figure 3.9) may also provide important insight into differentiating the different flow patterns in sediments.

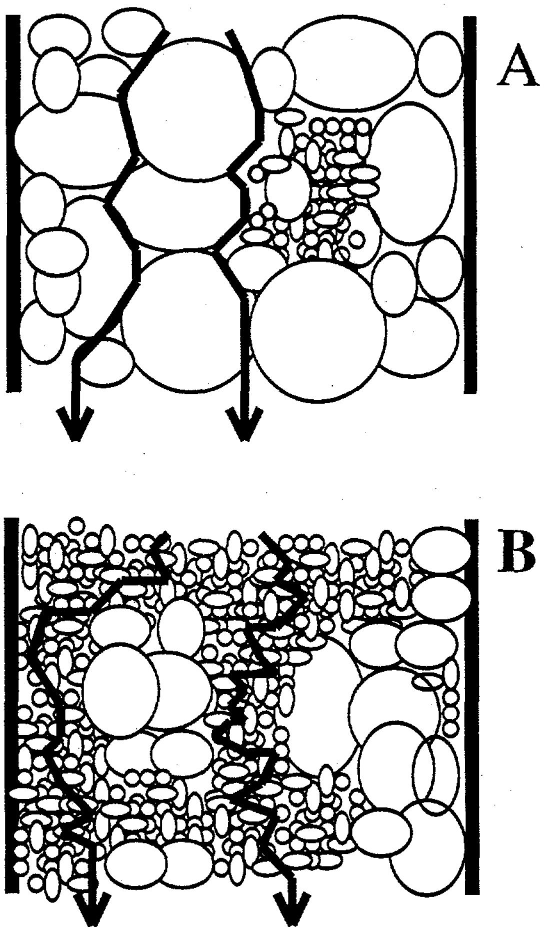

Figure 3.13. Schematic of the Proposed Flow Patterns in (A) A Sediment Containing Fine Particles That Do Not Form Hydrologically Continuous Pores and (B) A Sediment Containing Fines That Form Hydrologically Continuous Pores

Figure 3.14 provides a schematic of the overall trends this working hypothesis describes. For sediments with nearly uniform mineralogy and pore size distributions, little moisture dependency of K_d values would be expected (Figure 3.14, Line A). If a sediment with a heterogenous pore size distribution has a sufficient amount of fine-grained material to preclude hydraulic isolation of small pores upon desaturation, than an increase in K_d values would be expected upon desaturation (Figure 3.14, Line B). Conversely, if a sediment with a heterogenous pore size distribution does not have a sufficient amount of fine-grained materials to preclude hydraulic isolation of the small pores upon desaturation, then a decrease in K_d values would be expected upon desaturation (Figure 3.14, Line C). In the latter case, the unsaturated flow conditions would eventually produce film flow over the coarse-grained particles which have lower densities of adsorption sites than the finer-grained particles. As the mineralogy of the particles in the sediment become increasingly more similar, the slopes of lines B and C approach that of line A.

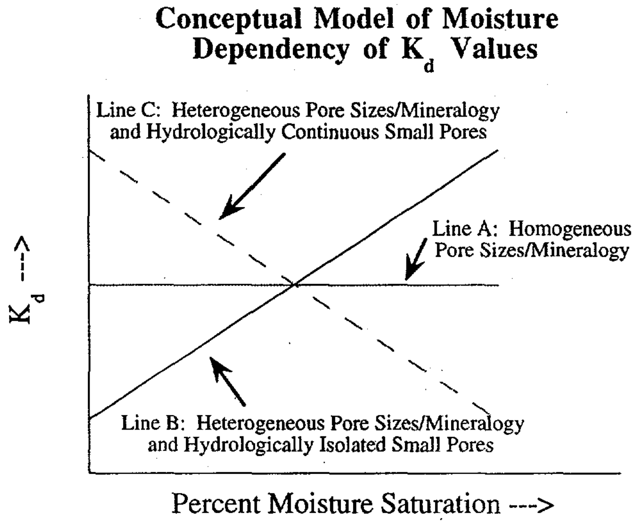

Figure 3.14. Conceptual Model Describing the Moisture Dependency of K_d Values Based on Sediment Small Pore Hydraulic Continuity and Heterogeneity of Mineralogy and Pore Sizes

3.1.6 Uranium-K_d Values: Conclusions and Implications for the PA

The K_d values reported in this section almost double the total number of uranyl-K_d data in Hanford sediments (as summarized in Kaplan and Serne 1995). Perhaps more importantly, these studies have quantified uranyl sorption in a wide range of environmental conditions and have improved our overall understanding of the important geochemical processes affecting uranyl sorption. Uranyl-K_d values reported in this section varied from 0.42 mL/g in a 39% moisture saturated Trench 8 sediment (Figure 3.8) to 545.7 mL/g in a pH 11.6 system dominated by sodium hydroxide (Table 3.4). The vast majority of K_d values existed in the range between 1.0 and 2.5 mL/g.

Important results concerning the K_d values for uranium (in the chemical form of uranyl) include:

- Uranyl-K_d values increased with increased contact time with sediments. Extended sediment contact times are expected to occur at the proposed LLW disposal site and therefore larger K_d values are warranted for the PA than those determined from conventional batch experiments with 7 to 14 day contact times.
- Uranyl-K_d values remained constant between the uranyl solution concentrations of 3.3 and 100 µg/L. Since the K_d values remained constant, a more complicated sorption model, such as the Langmuir Model, is not warranted for the PA over this uranyl concentration range.

- Uranyl-K_d values doubled from 1.07 to 2.22 mL/g as the pH of the system increased from ambient levels, pH 8, to pH 10. Above a pH ~10, heterogeneous precipitation of uranium occurred resulting in apparent K_d values as high as 500 mL/g. Precipitation did not occur unless a sediment was present. Should high pH conditions exist in the study site, as might be the case in the near-field, elevated uranyl-K_d values may be warranted for that portion of the PA.

- Uranyl-K_d values varied as a function of moisture content. However, the trend was not consistent. In a coarse-grained sediment, the K_d values increased with increasing moisture saturation. In a more fine-grained sediment, the K_d values decreased with increasing moisture saturation. A unifying conceptual model was proposed to explain these differences based on the hydraulic conductivity within the fine pore spaces. Since most of the subsurface system being modeled by the PA contains coarse-grained sediments, a lower K_d value than that measured by conventional batch K_d methods may be warranted for the PA.

- Uranyl-K_d values did not change as a function of ionic strength.

3.2 Technetium

3.2.1 Technetium-K_d Values: Effect of Technetium Solution Concentration

Technetium-K_d values were measured for two sediments as a function of solution technetium activities, i.e., isotherm experiments were conducted. The technetium specie added to the Hanford groundwater was the pertechnetate anion, TcO_4^-. Solution technetium activities at the start of the experiments varied about three orders of magnitude, 0.3 to 100 μCi/L ^{99}Tc. The contact time with the sediments, Trench 94 and Trench AE-3, was 30 days.

The pertechnetate-K_d values were very low for both sediments, ranging from 0.11 to -0.16 mL/g (Figure 3.15). The K_d values did not vary in a consistent trend with pertechnetate activity. The average K_d value across all equilibrium pertechnetate activities in the Trench 94 sediment was -0.02 ± 0.07 mL/g and in the Trench AE-3 sediment was -0.05 ± 0.05 mL/g.

3.2.2 Technetium-K_d Values: Effect of Contact Time

The effect of contact time on pertechnetate-K_d values were investigated. Three sediments, Trench 94, Trench AE-3, and TSB-1 (sediments characterized in Table 3.3) were mixed with Hanford groundwater (Table 3.1) spiked with approximately 100 μCi/L ^{99}Tc as pertechnetate (TcO_4^-). The solution to sediment ratio was 2:1 and the contact time varied from 7 to 398 days.

The K_d values were very low for all three sediments, ranging from -0.18 to +0.11 mL/g (Figure 3.16). For all three sediments the K_d values were slightly negative for short contact times and were positive for contact times greater than 300 days.

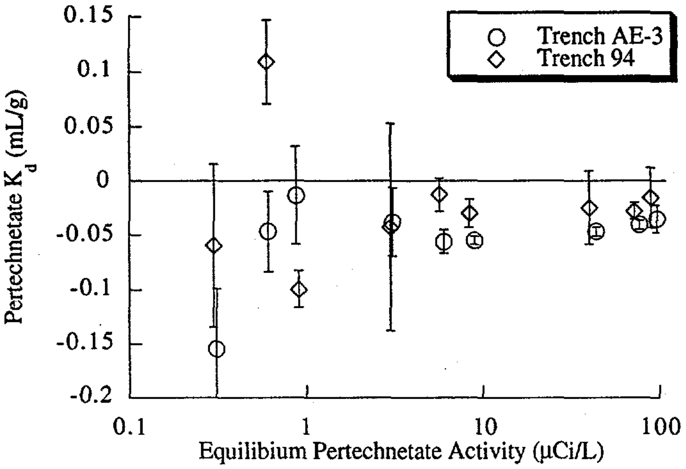

Figure 3.15. Pertechnetate-K_d Values of Two Sediments as a Function of Solution Pertechnetate Activity (Contact Time = 30 d; Sediment:Solution = 1:2; Background Solution = Hanford Groundwater)

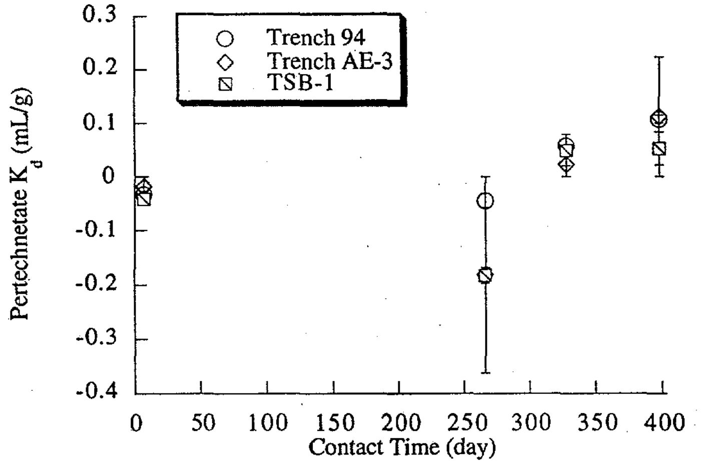

Figure 3.16. Pertechnetate-K_d Values as a Function of Contact Time with Three Sediments (Sediment:Solution = 1:2; Background Solution = Hanford Groundwater; Initial ^{99}Tc activity = 100 µCi/L)

3.2.3 Technetium-K_d Values: Conclusions and Implications for the PA

All the pertechnetate-K_d values were quite low. In fact, the majority of them had a negative value. Negative pertechnetate-K_d values have been frequently reported in the past and have always been treated as an experimental error (Routson et al. 1977, Gee and Campbell 1980, Serne et al. 1993). Furthermore, these negative K_d values have often been treated as equivalent to a K_d of 0 mL/g. Routson et al. (1977) measured pertechnetate-K_d values as a function of sodium bicarbonate concentrations and reported values ranging from -0.05 ± 0.01 to 0.02 ± 0.06 mL/g with an average of -0.014 mL/g (standard deviation was not reported); half of the reported values were negative and half were positive. Serne et al. (1993) reported both positive and negative pertechnetate-K_d values for three Hanford sediments. Of the 14 K_d values reported, 6 were negative. Gee and Campbell (1980) reported rather large negative K_d values in a system consisting of a high concentration salt solution and a Hanford sediment: -3 ± 2 and -1 ± 2 mL/g (Gee and Campbell 1980; Table 5). In a separate set of batch-K_d experiments in which ionic strength was varied, they measure 24-K_d values from two sediments. The K_d values ranged from -2.77 ± 0.23 to 1.27 ± 1.67 mL/g, with an overall average of -0.73 ± 1.07 and -0.08 ± 0.78 (Gee and Campbell 1980, Table 4). Fourteen of the 24 K_d measurements were negative. The mean plus or minus the standard deviations of the pertechnetate-K_d values reported by Serne et al. (1993) generally included 0 mL/g; those of Routson et al. (1977) and Gee and Campbell (1980) rarely included 0 mL/g.

Some of the reported negative pertechnetate-K_d values can in part be attributed to experimental error originating from trying to measure little or no pertechnetate adsorption. For just this reason, we elected to use a rather large sediment to solution ratio (1:2) to improve detection of adsorption. Over 75% of the measured K_d values in this study were negative. This observation requires explanation since it is not attributed simply to experimental error. Furthermore, the standard deviations of many of these negative K_d values did not include 0 mL/g, providing additional reason to believe that the values were indeed very slightly negative (Figures 3.15 and 3.16).

A mechanism to explain negative-K_d values from batch experiments is called anion exclusion or negative adsorption (Schofield 1947, Bower and Goertzen 1955, El-Swaify et al. 1967, Thomas and Swoboda 1970). It is commonly reported for the two anions, chloride and nitrate. Anion exclusion occurs when a negatively charged ion is repelled from a negative charged sediment surface. The result is a region very near the sediment, referred to as the double layer, that has much lower concentrations of anions than the solution not influenced by the sediment surface charge. In Figure 3.17A, no sediment is in the system and the anions are evenly dispersed throughout the solution volume. In Figure 3.17B, sediment has been added to the solution. This system can be thought of as having two different types of water: water between the sediment that is greatly affected by the double layer, interstitial water; and water not greatly influenced by the double layer, bulk solution. When anion exclusion occurs, the anion concentration in the interstitial water is reduced while that in the bulk water is increased. Thus, the anions become concentrated in the bulk solution.

Batch K_d values can be calculated from experimental data by Equation 8:

$$K_d = \frac{\frac{C_{\text{initial}} - C_{\text{final}}}{M_{\text{sediment}}}}{C_{\text{final}}} \tag{8}$$

where C_{initial} is the concentration of the radionuclide prior to contact with the sediment and C_{final} is the concentration of the radionuclide after contact with the sediment, and M_{sediment} is the mass of the sediment. The solution in Figure 3.17A represents $C_{initial}$. The bulk solution in Figure 3.17B represents C_{final}. It is the bulk solution that is sampled during batch K_d experiments. In an anion exclusion systems, C_{final} is more concentrated than $C_{initial}$, therefore a negative K_d value is calculated.

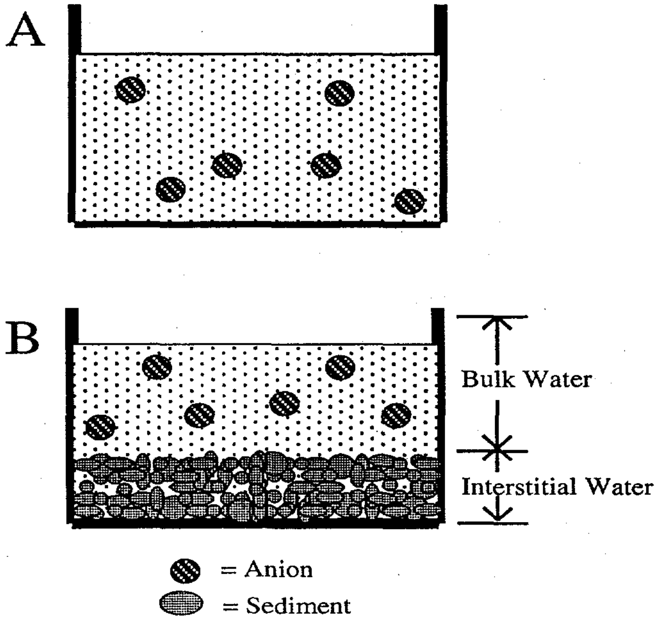

Figure 3.17. Schematic Representation of the Anion Exclusion Principle in Batch K_d Experiments. (A) System Containing a Solution with Anions. (B) System Containing a Sediment and a Solution with Anions.

A more accurate way to measure anion exclusion is through column studies. The only pertechnetate column studies conducted to date using Hanford sediments was reported by Gee and Campbell (1980). They reported that the breakthrough of pertechnetate was less than that of tritium. The breakthrough (the pore volume at which $C/C_0 = 0.5$) for pertechnetate was 0.91 and 0.87 and for tritium was 1.00 (Gee and Campbell 1980; Table 9). This result is consistent with the notion that anion exclusion of pertechnetate occurs in Hanford sediments.

Important results concerning the K_d values for technetium (in the chemical form of pertechnetate) include:

- A small degree of anion exclusion of pertechnetate may have occurred in these studies. If this is the case, then a slightly negative K_d value, on the order of about -0.1 mL/g may constitute the lower limit of possible K_d values for the PA. Column studies would have to be conducted to validate the occurrence of this phenomena.

- Pertechnetate-K_d values were very low and may have increased with increased contact time. For the PA, a very long contact time is expected. Based on these and other researchers' results, the best estimate for a K_d to be used for the PA is approximately 0 ± 0.1 mL/g.

- Negative batch K_d value is not necessarily the result of experimental error.

3.3 Iodine

3.3.1 Iodine-K_d Values: Effect of Contact Time

The extent to which iodine, in the form of iodide, I^-, adsorbed to three sediments as a function of contact time was studied. ^{125}I was spiked into Hanford groundwater. A sediment to solution ratio of 1:2 was placed on a slowly moving platform shaker. For all three sediments, the iodide-K_d increased as a function of time (Figure 3.18). The iodide K_d of the Trench 94 sediment increased from 0.19 to 9.82 mL/g, an increase of 5068%. The iodide K_d of the Trench AE-3 sediment increased from 2.09 to 4.72 mL/g, an increase of 126%. The iodide K_d of the TSB-1 sediment increased from 1.11 to 6.86 mL/g, an increase of 518%.

Similar increases in uranyl-K_d values with increased contact time were presented in Section 3.1.1. As discussed in that section, the cause for this increase is not known. It could be attributed to recrystallization of the surface over time resulting in the formation of additional iodide exchange sites. It may also be attributed to diffusion limitations; the idea being that the longer the iodide is in contact with the sediment the greater amount of time it has to diffuse into difficult to reach areas on/within the sediments. The increase in K_d values may be attributed to the generation of smaller particles during the shaking period. The shaking of the suspensions result in breaking apart particles or aggregates of particles, resulting in more surface adsorption sites for the iodide. Without doing additional studies, it is not possible to state which of these explanations are appropriate for this study. Finally, the increase in K_d value may be attributed to the generation of microorganisms over time that may increase the number of adsorption sites. The "breaking apart of particles" and the "diffusion limited" explanation seem the least possible. The sediment suspensions were purposely shaken very gently on a slow moving platform shaker. It is unlikely that the adsorption was diffusion limited for >1 yr, especially the Trench 94 sediment which was 99.55 % sand (Table 2.3). Such sandy soils have few small pores that would restrict the movement of molecules to the sediment surface. The "recrystallization" and "microbial growth" explanations can not be supported or refuted.

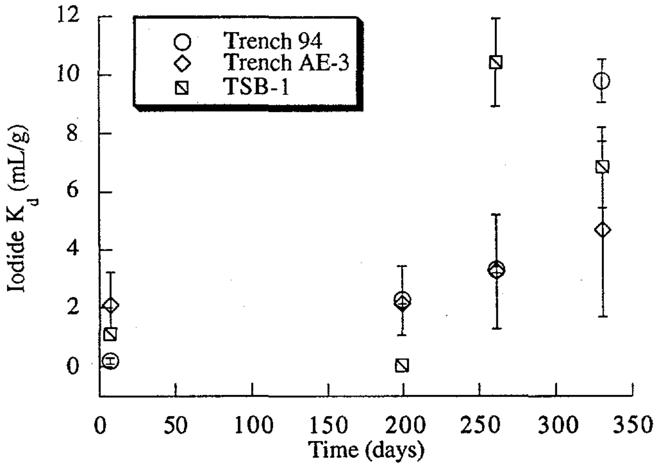

Figure 3.18. Iodide-K_d Values as a Function of Contact Time with Three Sediments (Sediment:Solution = 1:2; Background Solution = Hanford Groundwater; Initial ^{125}I activity = 100 µCi/L)

3.3.2 Iodine-K_d Values: Conclusions and Implications for the PA

These studies clearly show that iodide adsorbed to the sediment tested. Furthermore, the proportion of iodide adsorbed increased as a function of time. The values obtained in this study agree well with those previously reported on Hanford sediments (Kaplan and Serne 1995). Prior to this study, iodine-K_d values had been measured on four sediments: three sediments had K_d values of <1.4 mL/g and the fourth had an average K_d value of about 9.1 mL.g (Gee and Campbell 1980, Serne et al. 1993). The mean iodine-K_d value for the nine previous observations was 3.1 mL/g with a range of 0.7 to 15 mL/g (Kaplan and Serne 1995). The mean K_d value presented in Figure 3.18 is 3.85 ± 1.03 mL/g with a range of 0.07 to 9.8 mL/g.

Some of the more important results from this section include:

- In this study and all previous studies, some iodide adsorption has been measured. Thus, a K_d value greater than 0 mL/g is warranted for the PA.
- Iodide-K_d values increase with increased contact time with sediments. Extended sediment contact times is expected for the PA and therefore larger K_d values than those derived from conventional 30-d contact time experiments may be warranted for the PA.

3.4 Neptunium

3.4.1 Neptunium-K_d Values: Effect of Contact Time

The extent to which neptunium adsorbed to three sediments as a function of contact time was studied. ^{237}Np, in the form of NpO_2^{2+}, was spiked at a activity of 100 µCi/L into Hanford groundwater. A sediment:solution ratio of 1:2 was placed on a slowly moving platform shaker and samples were recovered at two contact times, 7 and 77 days. Neptunium-K_d values varied greatly between the three sediments (Figure 3.19). The increase in K_d values as a function of contact time also increased greatly between the three sediments. The Trench 94 sediment had a K_d value of 14.71 ± 1.16 at 7 days and 19.86 ± 0.45 at 77 days, a 35% increase during the 70 days. The Trench AE-3 sediment had a K_d value of 2.67 ± 0.22 at 7 days and 13.48 ± 0.49 at 77 days, a 405% increase during the 70 days. The TSB-1 sediment had a K_d value of 2.17 ± 0.35 at 7 days and 3.62 ± 3.70 at 77 days, a 34% increase during the 70 days.

3.4.2 Neptunium-K_d Values: Conclusions and Implications for the PA

As was the case with uranyl (Section 3.1.1) and iodide (Section 3.3.1), neptunium K_d values generally increased with time. Neptunium K_d values were clearly greater than 0 mL/g. The lowest K_d value was 2.17 ± 0.35 mL/g and the highest value was 19.86 ± 0.45 mL/g. Previously reported neptunium-K_d values in Hanford sediments were:

21.7 mL/g (Serne et al. 1993),
2.4 mL/g (Routson et al. 1976), and
15.4 and 20.2 mL/g (Sheppard et al. 1977).

The values reported in this study are within the range of values previously reported (Kaplan and Serne 1995). This data as well as those previously reported indicate that neptunium does adsorb to Hanford sediments and the extent to which it does is greater than a K_d value of 2 mL/g.

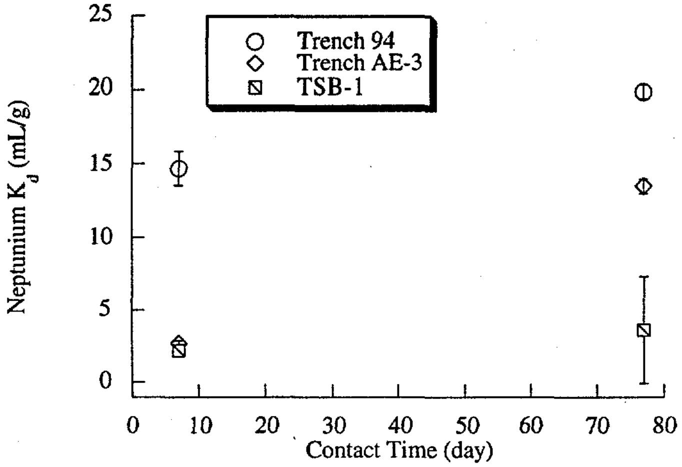

Figure 3.19. Neptunium-K_d Values as a Function of Contact Time with Three Sediments (Sediment:Solution = 1:2; Background Solution = Hanford Groundwater; Initial ^{237}Np (as NpO_2^{2+} activity = 100 μCi/L)

4.0 Conclusions

The objectives of this study were to 1) measure iodine, neptunium, technetium, and uranium K_d values using laboratory conditions similar to those expected at the LLW PA disposal site, and 2) evaluate the effect of selected environmental parameters, such as pH, ionic strength, moisture concentration, and radionuclide concentration, on K_d values of selected radionuclides.

- Uranyl-K_d values increased with increased contact time with sediments. Extended sediment contact times are expected to occur at the proposed LLW disposal site and therefore larger K_d values are warranted for the PA than those determined from conventional batch experiments with 7 to 14 day contact times.

- Uranyl-K_d values remained constant between the uranyl solution concentrations of 3.3 and 100 µg/L. Since the K_d values remained constant, a more complicated sorption model, such as the Langmuir Model or uranyl-concentration-dependent K_d Model, is not warranted for the PA over this uranyl concentration range.

- Uranyl-K_d values doubled from 1.07 to 2.22 mL/g as the pH of the system increased from ambient levels, pH 8, to pH 10. Above a pH ~10, heterogeneous precipitation of uranium occurred resulting in apparent K_d values as high as 500 mL/g. Precipitation did not occur unless a sediment was present. Should high pH conditions exist in the study site, as might be the case in the near-field, elevated uranyl-K_d values may be warranted for that portion of the PA.

- Uranyl-K_d values varied as a function of moisture content. However, the trend was not consistent. In a coarse-grained sediment, the K_d values increased with increasing moisture saturation. In a more fine-grained sediment, the K_d values decreased with increasing moisture saturation. A unifying conceptual model was proposed to explain these differences based on the hydraulic conductivity within the fine pore spaces. Since most of the subsurface system being modeled by the PA contains coarse-grained sediments, a lower K_d value than that measured by conventional batch K_d methods may be warranted for the PA.

- Uranyl-K_d values did not decrease with increased ionic strength.

Important results concerning the K_d values for technetium (in the chemical form of pertechnetate) include:

- A small degree of anion exclusion of pertechnetate may have occurred in these studies. If this is the case, then a slightly negative K_d value, on the order of about -0.1 mL/g may constitute the lower limit of possible K_d values for the PA. Column studies would have to be conducted to validate the occurrence of this phenomenon.

- Pertechnetate-K_d values were very low and may have increased with increased contact time. For the PA, a very long contact time is expected. Based on these and other researchers' results, the best estimate for a K_d to be used for the PA is approximately 0 ± 0.1 mL/g.

Important results concerning the K_d values for iodine (in the chemical form of iodide) include:

- The average iodide-K_d value in this study was 3 mL/g. This average is identical to that previously reported for Hanford sediments. Based on these studies, an iodide-K_d value greater than 0 mL/g is warranted for the PA.

- Iodide-K_d values increase with increased contact time with sediments. Extended sediment contact times are expected for the PA and therefore larger K_d values than those derived from conventional 30-d contact time experiments may be warranted for the PA.

Important results concerning the K_d values of neptunium (in the form of NpO_2^{2+}) include:

- Neptunium K_d values generally increased with time.

- Neptunium K_d values were clearly greater than 0 mL/g indicating that the most conservative K_d estimate of 0 mL/g is not warranted for the PA. The lowest K_d value was 2.17 ± 0.35 mL/g and the highest value was 19.86 ± 0.45 mL/g.

These studies were conducted with sediments collected from the Hanford Site, primarily from the 200 W Area. These studies provided us with important insight as to the types of measurements that will be required once the site-specific sediments from bore holes become available. There will only be small amounts of the site-specific sediments available for sorption studies, thus their use will have to be carefully planned. These studies also improved our understanding of the sorption behavior of these radionuclides and provided us with important quantitative measures of the effects of several variables on sorption behavior.

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