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URANIUM PARTITIONING UNDER ACIDIC CONDITIONS IN A SANDY SOIL AQUIFER

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ABSTRACT

The partitioning of uranium in an aquifer down gradient of two large mixed waste sites was examined with respect to the solution and soil chemistry (e.g., pH, redox potential and contaminant concentration) and aqueous-phase chemical speciation. This involved generation of field-derived, batch sorption, and reactive mineral surface sorption data. Field-derived distribution coefficients for uranium at these waste sites were found to vary between 0.40 and 15,000. Based on thermodynamic speciation modeling and a comparison of field and laboratory data, gibbsite is a potential reactive mineral surface present in modified soils at the sites. Uranium partitioning data are presented from field samples and laboratory studies of background soil and the mineral surface gibbsite. Mechanistic and empirical sorption models fit to the field-derived uranium partitioning data show an improvement of over two orders of magnitude, as measured by the normalized sum of errors squared, when compared with the single K_d model used in previous risk work. Models fit to batch sorption data provided a better fit of sorbed uranium than do models fit to the field-derived data.

INTRODUCTION

For 33 years, low-activity liquid wastes from the chemical separation areas at the U. S. Department of Energy's Savannah River Site (SRS) were disposed of in unlined seepage basins. These basins were designed to allow the natural processes of evaporation and infiltration to dispose of the polluted effluent streams. These operations have resulted in groundwater in the vicinity of these basins with lowered pH values and elevated levels of metals, radionuclides and nitrate. Additionally, it is believed that acidic waste streams associated with basin operations have significantly altered the mineral surfaces on the soils downgradient of these basins through accelerated acid weathering. On November 7, 1988, discharge to the basins was terminated in accordance with requirements of the Resource Conservation and Recovery Act. Before a multi-layered cap was placed over the basins, the liquid was removed and each was filled with a gravel bed and topped with layers of calcium carbonate and blast furnace slag (1).

Attempts to select an appropriate remediation technology for groundwater at this site have been hampered by an inability to adequately predict the transport of pollutants through, and the amount of contaminants in, the subsurface environment. The models previously utilized for risk assessment employed a single literature reported or "best guess" distribution coefficient (K_d) and predict that certain contaminants should be sorbed by the soil and not substantially transported (2,3). Groundwater monitoring of the waste site, however, shows significant groundwater transport of some contaminants not predicted to be mobile (4,5).

K_d values (i.e. ratio of contaminant concentration sorbed to concentration in the aqueous phase) are generally valid only for the mineralogical and geochemical conditions under which they were determined. The inherent heterogeneity and geochemical variations of real aquifer systems, reduce the applicability of a single K_d value to natural systems (6,7,8). Additionally, equilibrium conditions may not be established if the groundwater velocity is fast relative to the sorption rate. These variables impact the partitioning of contaminants in natural systems; consequently, field systems are usually best represented as a function of these factors rather than a single constant K_d.

The objectives of this research were to: (1) develop a more representative model of uranium sorption at this SRS waste site which accounts for pH, ionic strength, and competitive ion sorption effects; (2) compare the uranium sorption data from field-derived porewater/soil sample sets to batch sorption studies with background soils and an aluminum hydroxide reactive mineral phase; and (3) evaluate the effects of using single K_d and non-linear isotherm approaches to predict remediation effectiveness for a simple system.

METHODS

Uranium partitioning was examined in sample sets collected at the waste site using an in-situ method and in the laboratory by performing batch sorption studies on an uncontaminated background soil and a gibbsite [$Al(OH)_3$] mineral surface.

Field-Derived Partitioning Data

Fifty-three sets of soil and porewater samples were collected under inert conditions from the saturated zone downgradient of the waste sites using an electric friction-cone penetrometer system (9). Both the soil and porewater samples in each set were collected from the same depth, at the same location. Sampling locations and depths were selected such that they spanned a range of groundwater pH (pH 3-7), and had previously shown groundwater contaminant concentrations above the analytical detection limits. The temperature, pH, redox potential, and conductivity of the porewater samples were measured immediately upon sampling.

Porewater samples were filtered through 0.45 μm filters and screened for ^3H using liquid scintillation counting. Cl^-, F^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} concentrations were determined using ion chromatography. Total organic and inorganic carbon concentrations were measured using an automated carbon analyzer. The filtered porewater samples were analyzed quantitatively using inductively coupled plasma (argon) mass spectrometry (ICP-MS) for 43 isotopes representing 28 elements. Additionally, a semi-quantitative ICP-MS scan was conducted for the isotopes of Hg and the actinides (mass less than 246 AMU).

Total digestion soil extracts were prepared in triplicate by digesting approximately 200 mg of air-dried soil in 1 ml of ultra-pure aqua regia and 10 ml of ultra-pure HF heated at 100°C for 3 hours in Parr acid digestion bombs. The extracts were then filtered through 0.45 μm Teflon filters, and diluted to 50 ml with deionized water. A seven step sequential extraction procedure modified from Miller (10) was performed on each soil sample to selectively remove uranium sorbed to particular soil surface coatings. This procedure was performed in triplicate using 0.75 g of air-dried soil in a 50-ml HDPE Oak Ridge centrifuge tube for each individual sample. Contaminants associated with the soil residue present after the final extraction step were HF acid digested as described above for the total digestions.

Like the porewater samples, isotopic concentrations of trace contaminants in the total digestion and sequential extracts were determined using ICP-MS. ^{235}U and ^{238}U concentrations in each extract were converted to soil concentrations. Concentrations of individual replicates were averaged using a weighted average method (11). In this work, it is assumed that any uranium remaining in the residual phase (after the seventh sequential extraction step) was associated with the soil matrix and not able to participate in equilibrium reactions with the uranium in the aqueous phase. The sorbed uranium concentration was assumed to be equal to the difference between the concentrations in the total digestion and residual digestion analyses. This definition of sorbed uranium probably represents the maximum amount of uranium that can participate in sorption reactions (i.e., exchangeable uranium). An alternative method to account for nonexchangeable uranium is to assume that the total concentration measured in unimpacted soil is equal to the nonexchangeable fraction. This approach was not applied because soil at the site was affected by an acidic plume and some natural uranium has presumably been leached. Uranium distribution coefficients for each sample were calculated by dividing the sorbed uranium concentration (in $\mu g\ kg^{-1}$) by the uranium concentration of the associated porewater sample (in $\mu g\ l^{-1}$).

In addition to contaminant concentration, other physical and chemical characteristics of each soil sample were also examined. The particle size distribution of each sample was determined in duplicate using the procedure presented by Gee (12). The cation exchange capacity (CEC) of each soil sample, also performed in duplicate, was measured using the barium-magnesium exchange technique described by Rhoades (13). Soil pH was determined using a procedure derived from ASTM procedure D4972-89 (14) and EPA method 9045 (15) in deionized water and 0.01 M $CaCl_2$. Net soil charge and the point of zero salt effect (pzse) were measured by an acid/base titration of the soil in 0.0, 0.002, 0.01, 0.1 and 1.0 M $CaCl_2$ backing electrolyte solutions (16).

Background Soil Batch Sorption Studies

Laboratory studies on the sorption of uranium to an uncontaminated soil collected from the same lithological unit upgradient of the waste site have been performed. In this study, 1.00 g of soil was allowed to react with 42 ml of 10^{-5} M $UO_2(NO_3)_2$ solution in a 50 ml HDPE Oak Ridge tube. Carbon dioxide was controlled in these experiments using a glove bag and CO_2 scrubbed air and reagents. Before adding the solution to each tube, the pH was adjusted to an initial value of between 3 and 10 using HNO_3 or NaOH. Two samples and one matrix blank at each initial pH were equilibrated overnight in a shaking water bath controlled at 25° C. Previous kinetics studies have shown that this amount of time was sufficient to achieve equilibrium. Samples were then centrifuged at 10,000 rpm (16,000 g) for 10 minutes, after which the supernate was decanted and filtered through a 0.45 μm cellulose nitrate membrane. After measuring the final pH, samples were acidified to 1% v/v with 70% ultra-pure HNO_3. The aqueous uranium concentration of each sample was measured via laser-induced fluoroscopy of the UO_2^{2+} ion. Sorbed uranium was calculated as the difference in concentration of the matrix blank solution and the final sample solution.

Gibbsite Batch Sorption Studies

Because thermodynamic models predict that the mineral gibbsite [$Al(OH)_3$] will precipitate from the groundwater at the waste site and, therefore, could be a reactive surface, a laboratory study to determine stability constants for uranyl ion sorption to gibbsite was performed. In this study, fresh gibbsite was prepared by precipitation from an $Al(NO_3)_3$ solution after pH adjustment with 50% w/w sodium hydroxide (17). The gibbsite was purified by dialysis to remove excess sodium nitrate salts and then lyophilized for storage as a dry powder. The gibbsite was characterized using x-ray diffraction and thermogravimetric analysis. The surface area of the mineral was determined to be 178 $m^2\ g^{-1}$ by a N_2 BET surface area measurement. Sorption experiments were similar to the above described in the background soil sorption experiments. A gibbsite to solution ratio of 1 g l^{-1} was used. Solutions had $NaClO_4$ backing electrolyte concentrations of 0.0, 0.05 or 0.1 M and were pH adjusted using either $HClO_4$ or NaOH. A 4 hour equilibrium time was used with total uranium concentrations of 10^{-4}, 10^{-5} and 10^{-6} M.

RESULTS

The field-collected porewater samples spanned a wide range of geochemical conditions. Sample pH varied from 3.1 to 7.1, while Eh values were between +41 and +442 mV. All samples typically had high nitrate and ^3H concentrations. Nitrate levels varied from 3.9 to 1600 mg l^{-1}. ^3H levels ranged from 180 to $1.12x10^6$ Bq l^{-1}. The major cations in the samples included Al^{3+}, Fe^{3+}, K^+, Mg^{2+}, and Na^+. Although not specifically analyzed for, other groundwater monitoring data from the waste site show that H_4SiO_4 is also present at elevated levels (4,5). The major ion chemistry is consistent with the dissolution of clay minerals (e.g. kaolinite) and existing surface mineral coatings (e.g., iron (oxy)hydroxides) resulting from the addition of large amounts of nitric acid to the system. Estimates of sample ionic strength based on major cation concentrations ranged from $1x10^{-4}$ to $4x10^{-2}$ M, with a mean value of $8x10^{-3}$ M. Conductivities varied widely and were inversely correlated with pH. At low pH values, where the effects of the contaminant plume were most obvious, sample conductivities ranged between 0.05 and 0.35 S m^{-1}.

Aqueous samples with minimal impact had typical conductivities of less than 0.03 S.m^{-1}. Aqueous inorganic carbon content was found to be < 1 mg l^{-1} in all samples.

As a result of basin operations, elevated levels of uranium have been observed in groundwater downgradient from the seepage basins. ^{238}U concentrations were above the detection limit in 43 of 54 porewater samples collected for this study. Concentrations of these samples varied from 0.082 µg l^{-1} to 3.2×10^3 µg l^{-1}. ^{235}U concentrations were measurable in 26 of 54 aqueous samples with values varying between 0.040 µg l^{-1} and 14 µg l^{-1}.

Equilibrium uranium speciation was calculated over the observed range of geochemical conditions using MINTEQA2 (18). The result was very similar to the theoretical speciation of a 10^{-6} M U/10^{-2} atm CO_2 system reported by Langmuir (19). Based on these calculations, the dominant uranium species in this study are UO_2^+, UO_2^{2+}, UO_2OH^+, and $UO_2CO_3^0$. At pH values less than 5.0, UO_2^{2+} is predicted to be the dominant aqueous species, between pH 5.0 and pH 5.7, UO_2OH^+ is dominant, while at pH values greater than 5.7, $UO_2CO_3^0$ is predicted to be the major aqueous uranium species present. The charge of the aqueous phase uranium species will have a large influence on binding to soil surfaces with the neutral and negatively charged species being generally more mobile. For example, groundwater with higher pH and inorganic carbon values is predicted to have a larger percentage of mobile uranium as the neutral $UO_2CO_3^0$ species is formed. For nearly all samples for which K_d values are reported in this work, groundwater chemistry is in the pH-Eh range for which UO_2^{2+} is the dominate form of uranium in the aqueous phase.

73% of the collected soils were determined to be sand or loamy sand; 25% sandy loam or sandy-clay loam, with the remainder being sandy clay. The mean CEC of the soils was 9.6±6.3 meq kg^{-1}. The total carbon content was determined for 27 of the soil samples and all were found to contain less than 0.05% w/w carbon. The net surface charge of all soils measured was found to be very low, less than 0.5 µeq g^{-1}, with a typical pzse of 3.8.

^{238}U concentrations were above the detection limit in all soil samples and ranged from 490 to 19,000 µg kg^{-1}. The average soil concentration of ^{238}U downgradient of the waste sites was 3500 ± 2800 µg kg^{-1} (1.2 ± 0.9 pCi g^{-1}). This compares with previously reported value of 1.05 ± 0.75 pCi g^{-1} for unimpacted shallow sediments at the SRS (28). ^{235}U was detected in 79 of 86 samples with a range of 4.23 to 115 µg kg^{-1}, with an average concentrations of 27±12 µg kg^{-1}.

Based on the difference between uranium concentration in the total soil and that of the residual phase remaining after the sequential extraction, an estimate of the uranium concentration potentially available for exchange with the groundwater was made. The concentration of sorbed ^{238}U in the 78 soil samples examined varied from 0 to 17,000 µg kg^{-1}, with an average value of 2700µg kg^{-1}. Expressed as a percentage of the total ^{238}U concentration, the soil phase exchangeable fraction ranged from 0 to 98% of the total soil concentration with a mean value of 70%. In the 50 soil samples in which ^{235}U concentrations were above detection limits in both the total digestion and residual phases, exchangeable ^{235}U represented between 0 and 98% (average of 46%) of the total concentration. This corresponds to a concentration range of 0 to 99 µg kg^{-1} with an average value of 14 µg kg^{-1}

The 38 ^{238}U and 16 ^{235}U samples for which the porewater, total soil, and residual soil concentrations were greater than the detection limit, had field-derived uranium distribution coefficients between 0.4 and 15,000 l kg^{-1}. Figure 1 shows that a marked increase in the fraction of uranium sorbed occurs above pH 4.0. Differences in the fraction of uranium sorbed at this waste site can be explained primarily by changes in aqueous pH, and, presumably, the associated change in soil surface charge. The partitioning behavior can not be explained in terms of the physical properties of the soils (i.e., particle size distribution, or CEC).

Laboratory data on uranyl sorption to kaolinite (20) and gibbsite are very similar to the field-derived data. Iron (oxy)hydroxides are mineral surface coatings that have also been shown to control the sorption of metal ions in many natural aquatic systems (21, 22). Iron surface coatings, however, were excluded from consideration in our model because the sorption edge of uranium in the field-derived partitioning curve occurs at hydrogen ion concentrations two orders of magnitude greater than previously reported laboratory data for uranium sorption to goethite (23). Recent data on the sorption of uranyl to ferrihydrite shows a sorption edge at a pH of about 4.5 (24). This is also consistent with the field-derived sorption data and will require further evaluation. Because sorption is not well correlated with the soil clay content or cation exchange capacity, a reactive mineral coating (e.g., gibbsite or ferrihydrite), rather than kaolinite, is thought to be the reactive phase present in the modified soils at the waste site.

MODELING

Seven types of models were fit to field-observed uranium partitioning data. Partitioning data from laboratory batch sorption experiments were fit to four models. (See Table I.) The goodness of fit of each model was evaluated by the normalized sum of error squared (NSES) for each set of model fitting parameters. For this purpose, NSES was defined as:

$$\mathrm{NSES} = \frac{\sum_{1}^{n}\left[\frac{(\text{Observed sorbed concentration - Predicted sorbed concentration})^2}{\text{Observed sorbed concentration}}\right]}{n}, \qquad \text{(Eq. 1)}$$

where n is the number of observations and concentrations are in M.

The sorption model most commonly applied in risk assessment is the single K_d model (Eq. 2a). In this isotherm, the concentration of contaminant sorbed (S) onto the soil surface is a linear function of the contaminant concentration in solution (C). Another isotherm commonly used to describe contaminant sorption is the Langmuir isotherm (Eq. 2b). The Langmuir isotherm is a linear model at low aqueous concentrations, but accounts for the finite number of sites that exist on a surface by limiting the sorbed concentration at higher aqueous concentrations. The Freundlich isotherm (Eq. 2c) may be used to model contaminant sorption at low aqueous concentrations. It has been shown that it may be considered as the log-normal distribution of the Langmuir terms (25) and is well suited for uses in heterogeneous media.

Models fit to the field-derived data showed an improvement of over two orders of magnitude, as measured by the NSES, when compared with the single K_d ($K_d = 40$) model used in previous risk assessments (Table 2). In fitting the Langmuir isotherm to field data, two methods were used to determine the number of available binding sites (parameter 'b' in Eq. 2b). In the first method, the maximum concentration of sites for each sample was determined based on the CEC of the sample. The second method assumed an equal concentration of sites for all samples, but allowed it to be an adjustable fitting parameter.

The fourth model examined in this work is an equilibrium model. Assuming the simplified case where a uranyl ion is bound exclusively to a negatively charged soil binding site ($\equiv XO^-$), the reaction may be described by the equation:

$$\equiv XO^- + UO_2^{2+} \leftrightarrow \equiv XOUO_2^+, \qquad \text{(Eq. 3)}$$

where $\equiv XOUO_2^+$ represents a soil sorbed uranyl ion. This equilibrium reaction has a stability constant (K) defined in terms of solid concentrations ([ ]) and aqueous activities ({}) as:

$$K = \frac{\left[\equiv XOUO_2^+\right]}{\left[\equiv XO^-\right]\left\{UO_2^{2+}\right\}}. \qquad \text{(Eq. 4)}$$

This equilibrium model was implemented using the nonlinear fitting program FITEQL 3.1 (26). It was assumed that the total concentration of available binding sites (i.e. sum of [≡XOH],[≡XO$^-$], {≡XOH$_2^+$] and [≡XOUO$_2^+$]) was equal to the CEC of each sample. All soil samples were assumed to have a bulk density of 1200 kg m^{-3}, a porosity of 0.3, and a surface area of 1000 m^2 kg^{-1}. Based on the combined soil titration data of 17 soil samples, the average protonation (log K$^+$) and deprotonation (log K$^-$) equilibrium constants of the soil samples were determined to be 2.00 and -5.44, respectively. Using these constants, functions relating the fraction of sites deprotonated (XO$^-$) and protonated (XOH$_2^+$) to -log[H+] were developed. Using these relationships, and the estimated total binding site concentration of each sample, K values for the reaction in Eq. 3 were determined for both field and laboratory uranium partitioning data.

The constant capacitance and diffuse layer electrostatic models were also fit in this work. Both of these models account for the electrostatic effects between the charged surface and ions in solution. The difference in the models is the way in which the surface potential (ψ, units of V) is determined. In the constant capacitance model (Eqs. 2e and 2f), the surface potential is directly related to the charge density of the surface (σ, units of C m^{-2}). This condition is applicable under conditions of constant ionic strength and low surface potential (18). The diffuse layer model (Eqs. 2e and 2g) accounts for electrostatic effects of all charged ions in solution by relating surface potential to ionic strength.

In implementing electrostatic models, the total charge on each surface was allowed to vary with aqueous pH. As in the simple equilibrium model, the concentration of protonated and deprotonated sites for each sample was assumed equal to the maximum concentration of sites, based on the CEC, multiplied by the -log[H$^+$] dependent site protonation and deprotonation functions developed in the simple equilibrium model. The total charge density was then calculated by the equation

$$\sigma = D\left(\left[\equiv XOH_2^{2+}\right]-\left[\equiv XO^-\right]\right) \qquad \text{(Eq. 5)}$$

where D is a conversion factor relating charge density in C m^{-2} to site concentration in molarity. Unlike the simple equilibrium model where uranium was assumed to only bind to the negatively charged sites, sorption was allowed on all sites in the electrostatic models.

In applying the constant capacitance model, Hayes (27) reports that fitting with a capacitance (C$_1$) outside of the range of 0.1 to 2.0 F m^{-2} is an indication the constant capacitance model is inappropriate. In modeling the batch uranium sorption data, a capacitance of 2.0 provided the best fit of the data. The constant capacitance model failed to provide an adequate fit of field-observed uranium partitioning data. The NSES continued to decrease as capacitance increased well beyond a capacitance of 2.0 F m^{-2}. This may be due to the varying ionic strength conditions present under natural conditions.

Fits of the diffuse layer model to uranium partitioning data did not provide as good of a prediction of sorbed uranium concentration as the constant capacitance model. This may be because the diffuse layer model only has three adjustable parameters (K, K$^+$, K$^-$) , whereas the constant capacitance model had four adjustable parameters (K, K$^+$, K$^-$, C$_1$).

In addition to applying mechanistic models to the data, an empirical rise function was fit to the fraction sorbed versus aqueous pH of the field and soil batch study data using Eq. 2h. While this model results in the smallest NSES, it is purely empirical and, hence, can not be expected to fit the uranium sorption characteristics at other waste sites or under other experimental conditions.

Fitting parameters from sorption models were implemented in MINTEQA2 (18). Using typical field aqueous conditions, the fraction of uranium sorbed was predicted for varying pH and Eh conditions. Both the effects of uranyl ion adsorption and precipitation were accounted for in this modeling and reported as the fraction sorbed. Not surprisingly, the most empirical models (i.e. K$_d$, Langmuir, and Freundlich) were unable to account for the changes in the fraction of uranium sorbed with changing pH. The model that best represented field and laboratory partitioning data in these MINTEQA2 runs was the diffuse layer model. The thermodynamic modeling results using this model predicted that the fraction of uranium sorbed varied not only with pH, but also with Eh. Under slightly reducing conditions (Eh=-100), the sorption edge was at pH 2.9 and increases under more oxidizing conditions (+400 mV) to a pH of about 4.2. The constant capacitance model produced sorption edges at lower pH values, from 2.2 to 3.0, with no discernible trend with Eh.

To illustrate the potential impacts of the choice of sorption model and fitting parameters on the remediation of an actual waste site, a simple system was modeled using a single K_d model with values of 40 (a value used in previous risk assessment efforts) and 2.2 (the best-fit value from field data for the site) and the empirical rise function fit to field data. The simple system was assumed to have an initial pH of 3.0. The pH response of the system was calculated by assuming that pH 5.6 rainwater mixed with existing porewater and that one-half of the hydrogen ions were retained by the system due to soil buffering. All the aqueous-phase uranium was assumed to be removed from the system as a new porevolume of water was added to the system. From this, the fraction of remaining uranium in the system as a function of porevolume was calculated for the three models and is shown graphically in Figure 2. Modeling of a simple system suggests that a technology such as pump-and-treat would be more effective in removing uranium than previously predicted using literature K_d values . The use of the field data best fit K_d value of 2.2, however, will likely underestimate the time required for remediation because the aqueous fraction is expected to decrease as the pH of the system returns to more neutral conditions. Therefore, a model which accounts for the pH-dependence of uranium sorption is expected to provide a much better estimate of remedial effectiveness.

CONCLUSIONS AND IMPLICATIONS

The partitioning of a contaminant between the aqueous and solid phases in a natural system can not be described by a single linear isotherm in situations where the surface or aqueous-phase chemistry exhibit large variations. A simple method of obtaining the actual distribution of contaminants in a polluted aquifer is to analyze sets of porewater and soil samples obtained at the same location in the aquifer, at the same time. The actual distribution coefficients of an SRS waste site determined using this method vary several orders of magnitude.

In this study, uranium sorption can be explained largely in terms of aqueous sample pH. The sorption isotherm for uranium obtained laboratory data shows a significant increase in sorption above pH 4.0. The sorption isotherm for the field data has a sorption edge at a lower pH value than either the 10^{-6} M uranium on gibbsite or the 10^{-5} M uranium on background soils. This may be because the sorbed uranium phase, as defined by the sequential extraction, includes some nonexchangeable uranium. Further analysis of the sequential extracts is necessary to refine the uranium concentration in the sorbed phase.

This work demonstrates that the uranium in the low pH plume of the Water Table Aquifer at this waste site is more mobile then had been predicted in previous modeling efforts. The data also suggests that removal of aqueous-phase uranium will become less effective over time as the pH of the waste site aquifers returns to more neutral conditions. This is due to the gradual change in groundwater chemistry (i.e. increasing pH) due to the discontinuation of use and closure of the seepage basins. Since the inflection point of the uranium sorption isotherm in this study occurs at about pH 4.0, and a large fraction of the uranium at the site is currently associated with the low-pH portion of the plume, aqueous-phase uranium is expected to be more easily removed while the pH of the system is lower.

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REFERENCES

1. Westinghouse Savannah River Company, Closure Plan for the F-Area Hazardous Waste Management Facility.
2. Geotrans, Inc, "Groundwater Monitoring of Remedial Alternatives for the F- and H-Area Seepage Basins," 3017-002, Sterling, VA (1991).
3. Westinghouse Savannah River Company, "Remedial Action Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit. Vol II. Appendices A-I: Exposure Assessment Data." WRSC-RP-91-1017 (1992).
4. Westinghouse Savannah River Company, "F-Area Seepage Basins Groundwater Monitoring Report: Third quarter 1992," WRSC-TR-92-509 (1992).
5. Westinghouse Savannah River Company, "H-Area Seepage Basins Groundwater Monitoring Report: Third quarter 1992," WRSC-TR-92-510 (1992).
6. Y. INOUE, W. J. KAUFMAN, "Prediction of Movement of Radionuclides in Solution Through Porous Media," *Health Physics* 9:705-715 (1963).
7. M. T. VAN GENUCHTEN, J. M. DAVIDSON, P. J. WIERENGA. "An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media," *Soil Sci. Soc. Amer. J.* 38:29-35 (1974.).
8. E. J. READON, "K_d's - Can They Be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration?," *Groundwater* 19:279-286 (1981).
9. R. W. EDGE, K. CORDY, "The Hydropunch: An In Situ Sampling Tool for Collecting Ground Water From Unconsolidated Sediments," *Groundwater Monitoring Reviews* 9:177-183 (1989).
10 W. P. MILLER, D. C. MARTENS, L. W. ZELANZY, "Effect of the Sequence in Extraction of Trace Minerals from Soils," *Soil Sci. Soc. Am. J.* 50:598-601 (1986).
11. G. F. KNOLL, "Radiation Detection and Measurement," 2nd ed., New York: John Wiley (1989).
12. G. W. GEE, J. W. BAUDER, "Particle-Size Analysis," In: A. KLUTE, ed., Methods of Soil Analysis. Part 1. Madison, WI: Soil Science Society of America (1986).
13. J. D. RHOADES, "Cation Exchange Capacity," In: A. L. PAGE, R. H. MILLER, D. R. KEENEY, eds. Methods of Soil Analysis. Part 2. Madison, WI: Soil Science Society of America. (1982).
14. American Society for Testing and Materials, "Standard Test Method for pH of Soils," ASTM-D4972-89, (1989).
15. U. S. Environmental Protection Agency, "Soil pH," Method 9045 (1986).
16. G. UEHARA, G. GILLMAN, "The Mineralogy, Chemistry, and Physics of Tropical Soil with Variable Charge Clays". Westview Tropical Agriculture Series, No. 4, Boulder, CO: Westview Press (1981).
17. P. R. ANDERSON, M. M. BENJAMIN, "Surface and Bulk Characteristics of Binary Oxide Suspensions," *Envron. Sci. Techol.* 24:692-698 (1990).
18. J. D. ALLISON, D. S. BROWN AND K. J. GRADAC. MINTEQA2/PRODEFA2: A Geochemical Assessment Model for Environmental Systems: Version 3.0 Users Manual. U. S. Environmental Protection Agency, EPA/600/3-91/021 (1991).
19. D. LANGMUIR, "Uranium Solution-Mineral Equilibria at Low-Temperatures with Application to Sedimentary Ore Deposits," *Geochim. Cosmochim. Acta* 42:547-569 (1979).
20. T. D. WAITE, T. E. PAYNE, J. A. DAVIS, K. SEKINE, "Uranium Sorption; Alligator Rivers Analogue Proj., Final Report, 13," Australian Nuclear Science and Technology Organization (1994).
21. P. W. SCHINDLER, W. STUMM, In:W. STUMM, ed., Aquatic Surface Chemistry. New York: John Wiley & Sons. Chapter 4. (1987).
22. U. SCHWERTMANN, R. M. TAYLOR, In: J. B. DIXON, S. B. WEED, eds., Minerals in Soil Environments, 2nd ed. Madison, WI: Soil Science Society of America. Vol. 1, Chapter 8. (1989).

23. C. K. HSI, "Sorption of Uranium (VI) by Iron Oxides," Ph.D. Thesis, Golden, CO: Colorado School of Mines, Department of Chemistry and Geochemistry (1981).
24. T.D. WAITE, J.A. DAVIS, T.E. PAYNE, G.A. WAYCHUNAS, N. XU, "Uranium (VI) Adsorption to Ferrihydrite: Application of a Surface Complexation Model," *Geochim. Cosmochim. Acta* 58:5465-5478 (1994).
25. G. SPOSITO, "The Surface Chemistry of Soils," New York: Oxford University Press (1984).
26. A. HEBELIN, J. C. WESTALL, "FITEQL: A Computer Program for the Determination of Chemical Equilibrium Constants from Experimental Data, Version 3.1," Corvallis, OR: Oregon State University, Dept. of Chemistry (1994).
27. K. F. HAYES, G. REDDEN, W. ELA, J. O. LECKIE, "Surface Complexation Models: An Evaluation of Model Parameter Estimation Using FITEQL and Oxide Mineral Titration Data," J. Colloid Interface Sci. 142:448-469 (1991).
28. B. B. LOONEY, C. A. EDDY, M. RAMDEEN, J. PICKETT, V. ROGERS, M. T. SCOTT, P. A. SHIRLEY, "Geochemical and Physical Properties of Soils and Shallow Sediments at the Savannah River Site", WSRC-RP-90-1031 (1990).

Figure Captions

FIGURE 1. Fraction of Uranium Sorbed as a Function of pH from Field-Derived Data and Laboratory Experiments of U(VI) Sorption onto Gibbsite and a Background Soil.

FIGURE 2. Estimation of the Fraction of Uranium Remaining as a Function of Porevolume.

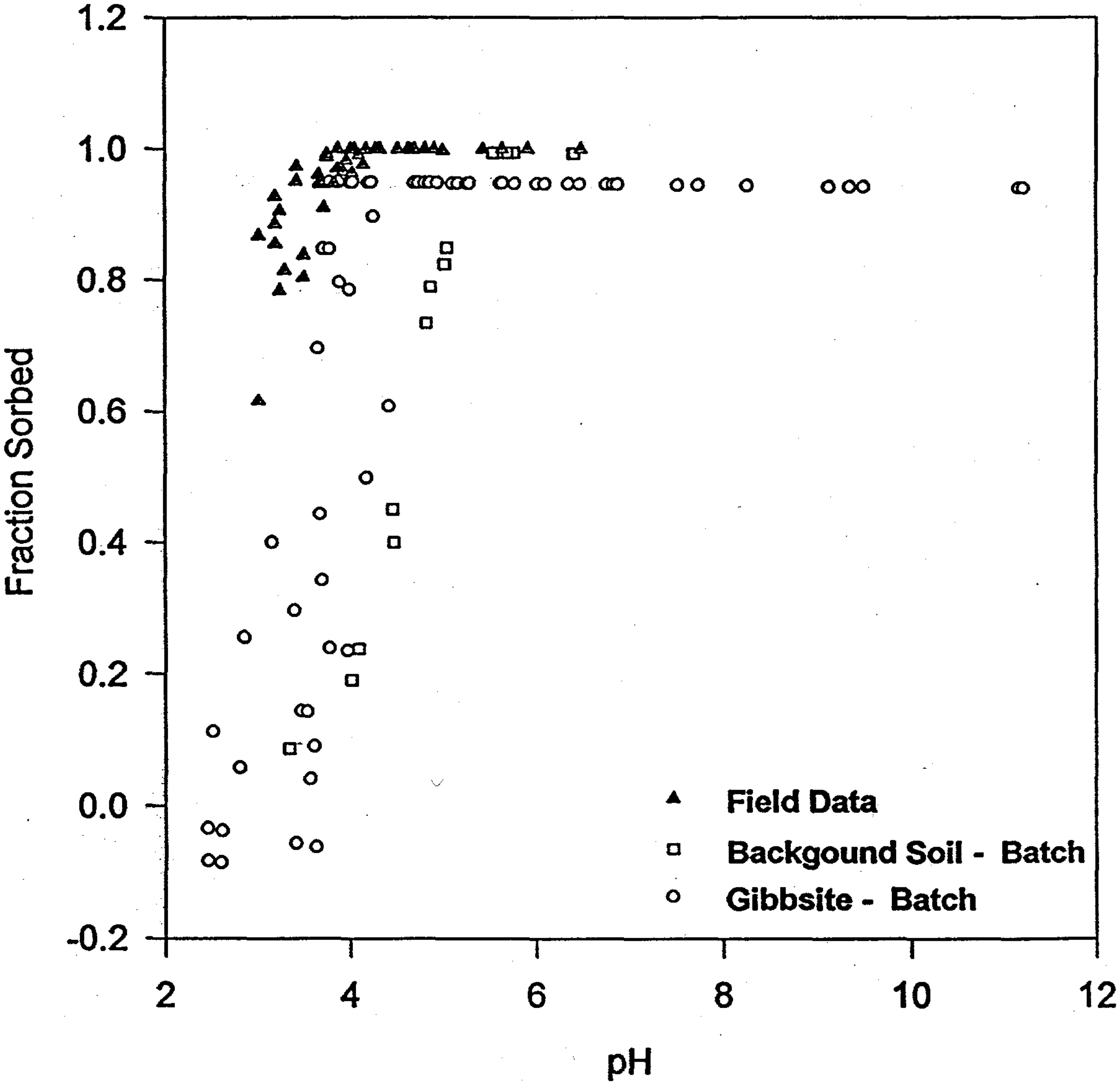
TABLE I. "Best Fit" Model Parameters and Normalized Sum of Errors Squared for Observed ^{238}U Contaminant Partitioning in Field Samples and Batch Sorption on a Background Soil.

	Model Fitting Parameters			
Model	**Parameter 1**	**Parameter 2**	**Parameter 3**	**NSES**
Distribution (field)	$K_d = 2.2$ $K_d = 40$			1.0×10^{-5} 1.3×10^{-3}
Langmuir (field)	$\text{Log } K_l = 8.41$ $\text{Log } K_l = 2.11$	$b = 1.1 \times 10^{-5}$ $b = [XOH]_{total}$		6.6×10^{-6} 1.1×10^{-5}
Freundlich (field)	$\text{Log } K_f = -4.23$	$b = 0.13$		6.8×10^{-6}
Equilibrium				
- field-observed	$\text{Log } K = 4.18$			8.8×10^{-6}
- batch experiment	$\text{Log } K = 6.95$			4.8×10^{-6}
Constant Capacitance				
- field-observed	$\text{Log } K_{ccm} = 2.51^*$	$C_1 = 2.0^*$		1.2×10^{-5}
- batch experiment	$\text{Log } K_{ccm} = 2.78$	$C_1 = 2.0$		2.4×10^{-6}
Diffuse Layer				
- field-observed	$\text{Log } K_{dlm} = -0.097$			1.2×10^{-5}
- batch experiment	$\text{Log } K_{dlm} = -2.12$			3.8×10^{-6}
Exponential Rise Fit				
- field-observed	$a = 373.3$	$b = 2.44$	$c = 372.3$	1.7×10^{-6}
- batch experiment	$a = 17.1$	$b = 0.844$	$c = -16.2$	5.6×10^{-7}

*NSES is not minimumized under these conditions.

TABLE II. Models Used in Study. ([A] is the Aqueous Concentration; [S] is the Sorbed Concentration)

Distribution	$[S] = K_d[A]$	(Eq. 2a)
Langmuir	$[S] = b\left(\frac{K_l[A]}{1+K_l[A]}\right)$	(Eq. 2b)
Freundlich	$[S] = K_f[A]^b$	(Eq. 2c)
Equilibrium	$[S] = \frac{[XO^-][A]}{K}$	(Eq. 2d)
Electrostatic Models	$[S] = [XOH]_{Total} K[A]\, e^{-\frac{\psi F}{RT}}$	(Eq. 2e)
-Constant Capacitance	$\psi = \frac{\sigma}{C_1}$	(Eq. 2f)
- Diffuse Layer	$\psi = 0.051 \sinh^{-1}\left(\frac{\sigma}{0.1174\sqrt{\text{Ionic strength}}}\right)$	(Eq. 2g)
Exponential Rise Fit	$\frac{[S]}{[S]+[A]} = a\, e^{-b\,pH} + c$	(Eq. 2h)



1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Fraction Sorbed
2
4
6
8
10
12
pH
▲ Field Data
□ Backgound Soil - Batch
○ Gibbsite - Batch

Figure 1

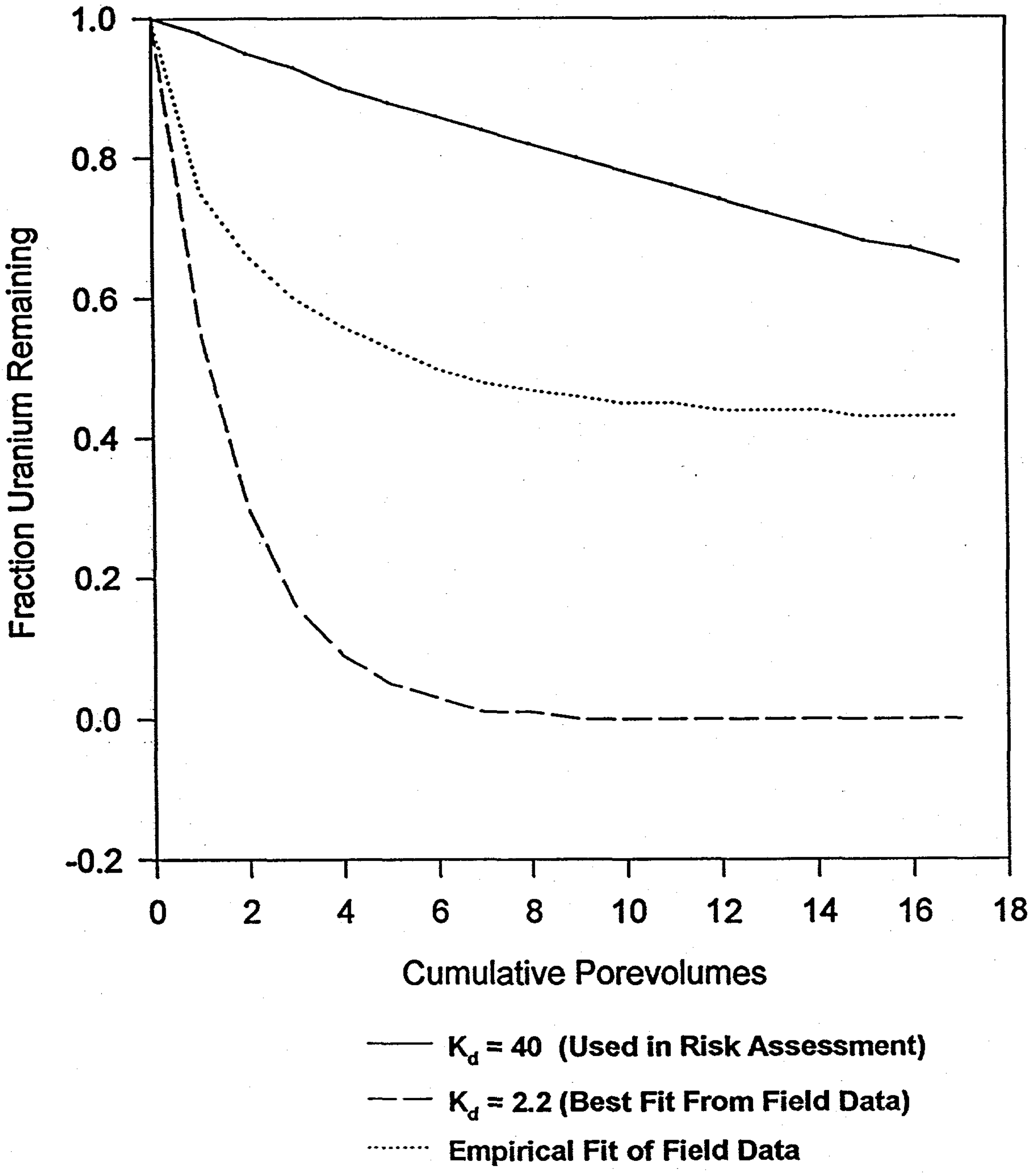

1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Fraction Uranium Remaining
0
2
4
6
8
10
12
14
16
18
Cumulative Porevolumes
K_d = 40 (Used in Risk Assessment)
K_d = 2.2 (Best Fit From Field Data)
Empirical Fit of Field Data

Figure 2