INEEL/CON-02-00106
PREPRINT

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August 4, 2002 – August 8, 2002

Spectrum 2002

Estimating Uranium Partition Coefficients From Laboratory Adsorption Isotherms

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Abstract *—An estimated 330 metric tons of uranium have been buried in the radioactive waste Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL). An assessment of uranium transport parameters is being performed to decrease the uncertainty in risk and dose predictions derived from computer simulations of uranium fate and transport to the underlying Snake River Plain Aquifer. Uranium adsorption isotherms have been measured in the laboratory and fit with a Freundlich isotherm. The Freundlich n parameter was statistically identical for 14 sediment samples. The Freundlich* K_f *for seven samples, where material properties have been measured, is correlated to sediment surface area (*$r^2 = 0.79$*). Based on these empirical observations, a model has been derived for adsorption of uranium on INEEL sedimentary materials using surface complexation theory. The model was then used to predict the range of adsorption conditions to be expected at the SDA. Adsorption in the deep vadose zone is predicted to be stronger than in near-surface sediments because the total dissolved carbonate decreases with depth.*

I. INTRODUCTION

The Radioactive Waste Management Complex at the INEEL, established in 1952, is used for subsurface disposal and above ground storage of radioactive waste. Low-level waste is buried in shallow (depth < 22 ft) pits and trenches in the Subsurface Disposal Area (SDA). Prior to 1970, waste containing transuranic elements was also buried in these pits and trenches. Transuranic waste received since 1970 has been stored above ground in the Transuranic Storage Area (TSA). The stored wastes are in the process of being shipped to the Waste Isolation Pilot Plant in New Mexico for permanent disposal. The fate of the buried waste will be decided through the CERCLA remedial action process. Almost 330 metric tons of uranium are estimated to have been buried in the SDA since the early 1950's. Most of the uranium is in the form of depleted uranium with 99.3% of the total uranium mass in the form of U-238. Uranium represents a significant source term in the buried waste, and a long term potential threat to underlying ground water.

Predictions of uranium migration at the SDA have been made for compliance with DOE Orders[1,2] and to support CERCLA risk assessment.[3] In all of these simulation studies, transport of uranium was modeled using a linear, reversible partition coefficient (K_d) of 6 mL/g derived from laboratory measurement of K_d on a composite interbed sample.[4] Recognizing the need for improved defensibility of risk assessment models in support of the INEEL CERCLA remediation program, the INEEL Environmental Restoration Program has been funding studies at Clemson University to measure site-specific partition coefficients for SDA sediments.[5,6] Results from a recent set of adsorption isotherm experiments suggest that a more general model of adsorption can be derived from these data. We modeled the existing, small, data set as a basis to evaluate the applicability of more theoretical models of adsorption. Additional laboratory data are being collected to further validate this model. The results of this study will be couched in a form that the Environmental Restoration Program can use for immediate improvement in the defensibility of risk assessments at the SDA.

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II. SETTING

The SDA is located on the eastern Snake River Plain, a north-east trending structural basin about 200 miles long and 50 to 70 miles wide in southeastern Idaho. The plain is underlain by a layered sequence of Tertiary and Quaternary volcanic rocks and sedimentary deposits.[7] Volcanic rocks in this sequence consist of basaltic lava flows and cinder beds. During periods of volcanic quiescence, fluvial, lacustrine, and eolian sediments were deposited. Alternating periods of volcanic activity and sedimentary deposition have accumulated into a complex sequence of layers. The water table is at a depth of about 480 ft in the vicinity of the SDA.

There are several important sedimentary units beneath the SDA that are considered to be crucial barriers to downward migration of radionuclides from buried waste.[1,3] The ability of these interbeds to retard the migration of contaminants is the focus of characterization efforts. The fractured basalt units are not considered to provide significant retardation, and therefore are of secondary interest at this time.

The waste is buried in a layer of surficial sediment accumulated in a low area surrounded by basalt lava flows. The surficial sediment in the SDA is up to 22 ft thick and is deposited on top of the A basalt flow. The shallowest interbed is the A-B interbed (between basalt flows A and B), which is mainly found in the northern and western parts of the SDA. The depth to the top of the A-B interbed is between 18 and 55 ft below land surface. The B-C interbed ranges in depth from 87 to 131 ft and is commonly referred to as the "110-ft interbed." The thickness ranges from 0 to 40 ft and averages 13 ft. The C-D interbed ranges in depth from 218 to 253 ft and is commonly referred to as the "240-ft interbed." The C-D interbed ranges in thickness from 5 ft to 32 ft and average 17 ft in thickness.

The mineralogy of the surficial sediments and sedimentary interbeds has been studied by the U. S. Geological Survey.[8,9] The sediment has a nominal mineralogy of 35% quartz, 30% feldspar, 4% calcite, 10% pyroxene, 2% dolomite, and 19% clays. Predominant clay minerals are illite, smectite, and kaolinite. The mineralogy of sediments at the SDA correlate with minerals from source areas in the adjoining mountains. Sediments in different interbeds are mineralogically very similar. This evidence indicates a fairly uniform depositional process over time, which has lead to a similar mineralogy in the sediments[9]. This similarity in source material and depositional processes over time may result in some uniformity in adsorption characteristics of sediments.

III. EXPERIMENTAL PROGRAM

A series of vadose zone boreholes was drilled in and around the SDA to install moisture monitoring equipment and to collect samples of sedimentary interbed material (Figure 1). Material properties determined from these samples will be used to parameterize computer models. Samples were collected from the B-C and C-D sedimentary

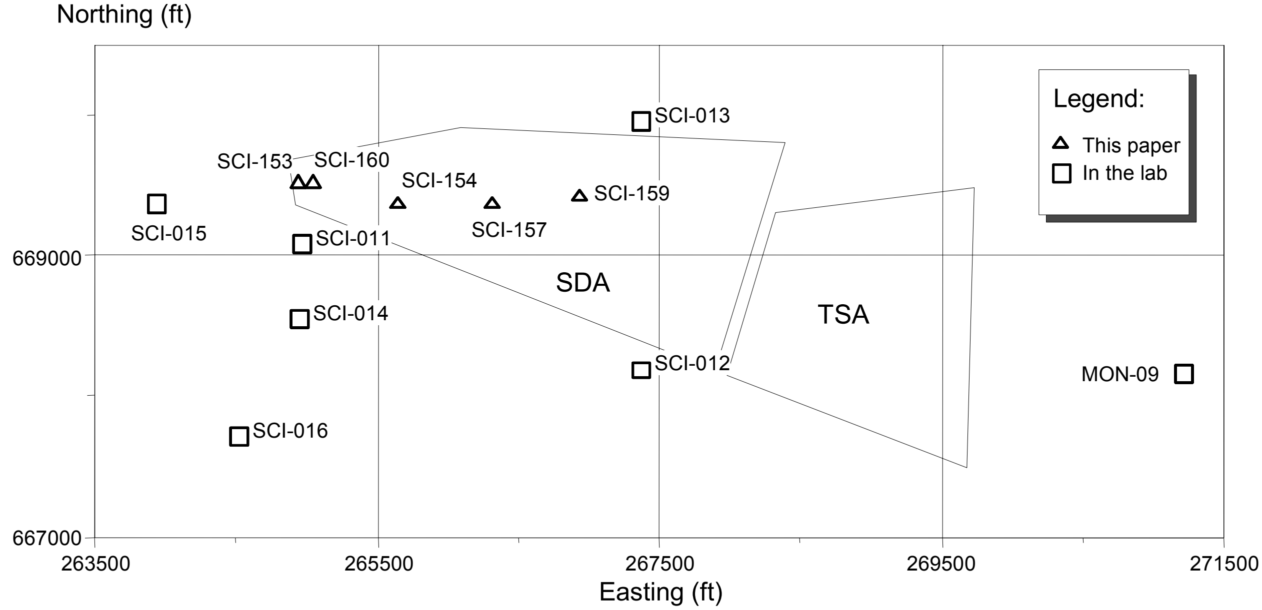

Fig. 1. Map of the Radioactive Waste Management Complex showing the wells where samples have been collected for measuring uranium adsorption isotherms. Samples from wells identified with triangles are discussed in this report. Samples from wells identified with squares are currently in the laboratory for analysis.

interbeds for hydrologic and geochemical characterization. The first round of samples sent for geochemical characterization were from the wells drilled inside the SDA. Seven samples (Table I) for which a complete set of geochemical properties and isotherm measurements have been completed, were a set of biased samples collected to cover the range of observed material properties from sand to clayey silt. The range of surface area and cation exchange capacity measured on these samples reflects the large range in textural characteristics.

III.A. Material Characterization

Material properties measured were bulk mineralogy, clay mineralogy, surface area, extractable oxides, cation exchange capacity, and exchangeable cations. Mineralogy was determined by x–ray diffraction. Surface area was determined by multipoint nitrogen absorption using Brunauer-Emmett-Teller (BET) surface area analysis. To quantify the amount of oxide coatings present on the soil, the soluble oxides were extracted from the sediment with sodium dithionite warmed to 80°C and the concentrations of iron, manganese, aluminum and silica determined in the supernatant by inductively coupled plasma emission spectrometry. Cation exchange capacity and exchangeable cations were determined independently. Cation exchange capacity was measured by sodium saturation followed by extraction with ammonium acetate. Exchangeable cations were determined by ammonium acetate extraction, with the difference that the sodium saturation step was bypassed. The collected extract was analyzed for calcium, magnesium, strontium, sodium, and potassium by inductively coupled plasma emission spectrometry.

III.B. Batch Isotherm Experiments

The fourteen sediment samples were air-dried, and sieved to remove material larger than 2 mm. The sieved sediment material was pretreated with simulated groundwater according to ASTM D 4319–93[10] in four contact intervals: three of 15 minutes and one of 24 hours. After the contact interval, the sediment was centrifuged at 1,000 g for 5 minutes and decanted. Sediment suspensions were prepared by adding a weighed amount of sediment to simulated groundwater to produce suspended solids concentrations between 50,000 and 100,000 mg/L. The pH of the test solutions was adjusted to 8.0 ± 0.2. Each isotherm was determined by duplicate equilibrations at each of five initial radionuclide concentrations. The final dissolved inorganic carbon concentration was measured for two of the test solutions and found to be 1.83 ± 0.02 and 2.25 ± 0.10 mmole/L. All calculations involving water chemistry of test solutions in this report use 2 mmole/L total dissolved carbonate and a pH of 8.0.

TABLE I

Sample depths and sample identification. Material properties of surface area and cation exchange capacity have been measured for seven of the sample materials. Freundlich adsorption constants (K_f) are given with the 95% confidence interval.

Well ID	Interval Top (ft bls)	Interval Bottom (ft bls)	Sample ID	Surface Area (m^2/g)	Cation Exchange (meq/100g)	log K_f (L/g)
SCI-153	103.0	103.6	7DS00101KD	75.24	43.9	-2.78±0.12
SCI-153	107.4	108.0	7DS00301KD	61.36	23.2	-2.94±0.12
SCI-153	109.0	109.4	I1S-INEEL-109			-3.13±0.12
SCI-154	103.0	103.5	7DS00701KD	19.29	14.8	-3.18±0.11
SCI-154	104.5	105.0	I2S-INEEL-105			-3.07±0.12
SCI-154	112.0	112.5	7DS00901KD	51.14	27.3	-3.03±0.12
SCI-157	229.2	229.7	I3D-INEEL-229			-3.25±0.11
SCI-157	231.0	231.5	7DS01701KD	36.58	23.2	-3.09±0.11
SCI-159	224.2	224.8	I4D-INEEL-224			-3.15±0.11
SCI-159	230.0	230.5	7DS02301KD	34.02	22.5	-3.10±0.12
SCI-159	230.5	233.5	I4D-INEEL-231			-3.20±0.11
SCI-159	233.5	234.0	I4D-INEEL-234			-3.34±0.12
SCI-160	234.0	234.5	I1D-INEEL-234			-2.98±0.12
SCI-160	238.1	238.6	7DS00501KD	46.39	19.4	-3.07±0.12

Stock uranium spike solution was prepared using U-233 at high activity in an acidic water. Test solutions were then prepared by adding a small volume of the spike solution the test solution/sediment suspension to achieve the desired final concentration in the test solution. The pH of the test solution was then adjusted to a value of 8.0 ± 0.2 using hydrochloric acid or sodium hydroxide. Batch adsorption experiments were carried out for time periods between 48 and 56 days based on results from a preliminary kinetic adsorption study.

IV. RESULTS

A Freundlich isotherm was fit to the fourteen data sets by a linear regression on the log transformation of the data. The log-transformed version of the Freundlich isotherm is given by:

$$\log[C_{ads}] = \log[K_f] + n \cdot \log[C_{sol}] \qquad (1)$$

K_f = empirical partition coefficient at equilibrium (L/g)

n = empirical coefficient

C_{ads} = concentration of parameter on the solid (mg/g, pCi/g, mole/g...)

C_{sol} = concentration of parameter in solution (mg/L, pCi/L, mole/L...)

Four statistical models were analyzed. These models tested the hypothesis that the isotherms shared common parameter values. The model with the greatest degrees of freedom and the lowest mean square error was a model that included a unique K_f for each sediment sample, but a common shared n parameter. Allowing n to vary between samples did not significantly improve the fit to the data (probability = 0.51). The fit of the isotherm model to some of the sediment samples is illustrated in Figure 2. The common slope (n) for uranium was found to be 0.79 ± .02 (95% confidence interval). The Freundlich adsorption constants (K_f) are listed in Table I.

The commonality in the n values calculated for the uranium adsorption isotherms on the 14 sediment samples from the SDA suggests that the suite of adsorption sites on the sediments is very similar. The n parameter compensates for a decrease in binding affinity to mineral surfaces as sites become filled. Because the mineralogy of the sediments is similar,[9] the suite of adsorption sites might also be expected to be similar.

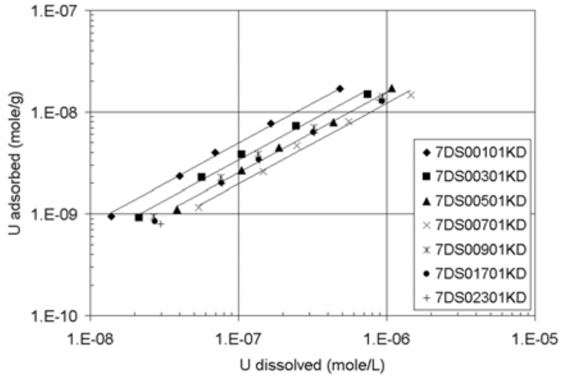

Fig. 2 Plot of seven uranium adsorption isotherms showing the fit of the Freundlich isotherm to the data using a common n parameter of 0.79 for all isotherms.

The Freundlich adsorption constants were significantly different among the sediment samples. The Freundlich K_f is an empirical parameter that is composed of three components, a binding constant, a term related to the number of adsorption sites, and solution composition. Because all experiments were conducted at essentially the same solution composition, it is not possible to extract any information on water chemistry. However, it may be possible to separate the surface sites from the binding energy terms.

We hypothesize that the binding energy parameter is a constant, and the number of surface sites will depend on an extensive material property. In a regression of K_f on a material property, the slope will be proportional to the binding constant times a conversion factor to convert the material property to the number of adsorption sites. As of now, we only have paired characterization and adsorption data for seven samples, so an exhaustive study of material property correlations was not warranted. The K_f parameters for these seven samples are correlated with surface area data (Figure 3). For surface area, the regression analysis gives a significant reduction in the residual sum of squares with an r^2 value of 0.79. The slope of the relation is 2.06E-5 ± 0.28E-5

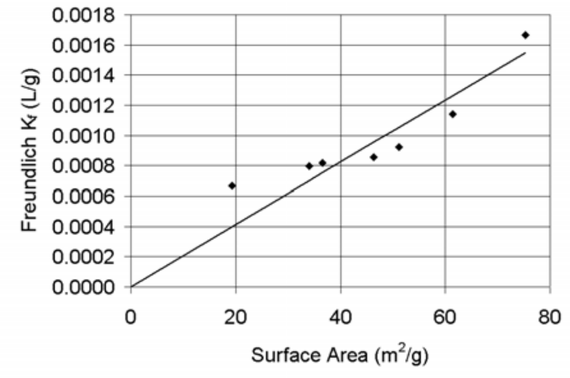

Fig. 3. Plot of Freundlich K_f as a function of BET surface area.

(95% confidence interval). The y-axis intercept is not significantly different than zero. This is consistent with the conceptual model, because when the material property goes to zero, there should be no adsorption sites available.

V. ADSORPTION ISOTHERMS

The commonality in the n parameter from the Freundlich isotherms, and the correlation between the K_f parameter and surface area suggests that a more process based model of adsorption can be derived from these data. Partitioning of dissolved constituents between an aqueous phase and solid minerals in soils and sediments is affected by three factors: a thermodynamic binding constant, the number of adsorption sites available, and the solution chemistry of the aqueous phase. Partitioning has commonly been described by an empirical partition coefficient that simply relates the total concentration of a dissolved species to the total concentration of the adsorbed species:

$$K_d = \frac{C_{ads}}{C_{sol}} \tag{2}$$

where:

K_d = empirical partition coefficient at equilibrium (mL/g, L/g, ...)

A site specific K_d partition coefficient can be measured under conditions appropriate to a specific location, and applied under those conditions to that location. The empirical K_d cannot be applied if conditions change nor can it be applied at a different location.[11] A mechanistic approach is needed that incorporates a theoretical understanding of the factors that affect partitioning. Such an approach for the SDA was proposed by Curtis and Hull.[12]

A class of adsorption models referred to as surface complexation models have evolved to describe adsorption of solutes to the surfaces of minerals. Taking a simple, non-electrostatic approach to adsorption,[13] adsorption can be described by a chemical mass action expression. The proton stoichiometry of the reaction can vary, but here is selected to be two following the lead of Kohler et al[14] and Gabriel et al[15].

$$\equiv SOH^0 + M^{+2} + H_2O \leftrightarrow \equiv SOMOH^0 + 2H^+ \tag{3}$$

where:

$\equiv SOH^0$ = surface adsorption site (moles/L)

M^{+2} = concentration of free metal ion in solution (moles/L)

An equilibrium constant expression can be written for the mass action expression given by Eq. 3:

$$\frac{\left[\equiv SOMOH^0\right]\left[H^+\right]^2}{\left[\equiv SOH^0\right]\left[M^{+2}\right]} = K_{ads} \tag{4}$$

where:

K_{ads} = effective thermodynamic equilibrium constant

The total number of adsorption sites on the solid associated with a liter of water (S_v moles/L) is the sum of the uncomplexed surface sites and the sum of the surface sites that have formed surface complexes:

$$S_v = \left[\equiv SOH^0\right] + \left[\equiv SOMOH^0\right] \tag{5}$$

Eq. 5 can be used to replace [$\equiv SOH^0$] in Eq. 4, which, after rearranging, gives an equation in the form of a Langmuir isotherm:

$$\left[\equiv SOMOH^0\right] = \frac{\frac{K_{ads}}{\left[H^+\right]^2} S_v \left[M^{+2}\right]}{\left(1 + \frac{K_{ads}}{\left[H^+\right]^2}\left[M^{+2}\right]\right)} \tag{6}$$

The concentration of metal in Eq. 6 is the free metal ion concentration in solution, and not the total metal concentration. Some of the metal may be bound up in aqueous complexes. The total metal ion concentration is given by the sum of the concentrations of the free metal ion and the metal ion complexes.

$$M_t = \left[M^{+2}\right] + \sum ML_m^{-mp+2} \tag{7}$$

Replacing the ligand concentration with the equilibrium constant expression, rearranging to solve for the free metal ion concentration, and substituting back into Eq. 6 gives:

$$\left[\equiv SOMOH^0\right] = \frac{\frac{K_{ads}}{\left[H^+\right]^2\left(1 + \sum K_L\left[L^{-p}\right]^m\right)} S_v M_t}{1 + \frac{K_{ads}}{\left[H^+\right]^2\left(1 + \sum K_L\left[L^{-p}\right]^m\right)} M_t} \tag{8}$$

Eq. 8 gives the concentration of an adsorbed metal in terms of a thermodynamic adsorption coefficient, solution chemistry (pH, metal ligand complexes in solution), and total number of surface sites. If we make the following substitutions in Eq. 8,

$$\alpha = \frac{K_{ads}}{\left[H^+\right]^2\left(1+\sum K_L\left[L^{-p}\right]^m\right)} \tag{9}$$

$$\beta = S_v\,\frac{\theta}{\rho} \tag{10}$$

we get the following equation:

$$C_{ads} = \left[\equiv SOMOH^0\right]\frac{\theta}{\rho} = \frac{\alpha\beta M_t}{1+\alpha M_t} \tag{11}$$

where:

ρ = bulk density (g of sediment / L of water)

θ = water content (L of water / L of sediment)

The analytical equation derived from surface complexation theory (Eq. 8) describes a Langmuir isotherm. The units are converted from a volume of fluid basis to a mass of solid basis by multiplying by the ratio of bulk density to water content. The adsorption coefficient of the derived Langmuir isotherm can be related to solution chemistry (pH, complexing ligands) and the thermodynamic binding constant between the metal and the surface sites on the sediment.

At very low metal concentrations, the product of the metal concentration and the equilibrium constant is small relative to 1. The denominator reduces to 1 and Eq. 11 can be simplified to:

$$C_{ads} = \alpha\,\beta M_t \tag{12}$$

The initial slope for the Langmuir adsorption site is $C_{ads} = \alpha\beta M_t$. A soil or sediment is comprised of many minerals, and consequently multiple adsorption sites. With multiple Langmuir adsorption sites, there are multiple isotherms, each with initial slopes $\alpha_1\beta_1$, $\alpha_2\beta_2$, ... $\alpha_i\beta_i$. Each subsequent slope is less that the previous slope. With a large set of Langmuir sites, the slopes begin to form a continuous set. This continuous set can empirically be described using a Freundlich isotherm.

$$C_{ads} = K_f C_{sol}^n = \left[\alpha\,\beta\, M_t^{n-1}\right]M_t \tag{13}$$

The exponent n is an empirical fitting parameter that describes the decrease in binding energy as more favorable adsorption sites are filled. Incorporating the definitions of α and β, we can incorporate the effects of water chemistry and material properties into the Freundlich isotherm equation. The number of surface sites will be the product of the surface area of the sediment, the number of sites per unit area, and a conversion factor to convert from sites to the unit of concentration measure (moles, pCi).

$$C_{ads} = \left[\left(\frac{K_{ads}S_a\,{}^{N_a}\!/\!_{A}}{\left[H^+\right]^2\left(1+\sum K_L\left[L^{-p}\right]^m\right)}\right)M_t^{n-1}\right]M_t \tag{14}$$

where:

S_a = specific surface area of sediment (m^2/g)

N_a = number of sites per unit area (sites/m^2)

A = conversion factor from sites to concentration units (sites/mole, sites/pCi, ...)

The Freundlich K_f value can be seen to be composed of material properties (a term for the binding strength, the number of adsorption sites, and the spectrum of binding energies) and water chemistry (the proton stoichiometry of the reaction and the formation of aqueous complexes). Eq. 14 accounts for some of the proton stoichiometry of the reaction, but does not take into account changes in surface charge as a function of pH. Over a limited range in pH values, however, the accounting may suffice.

VI. COMPONENTS OF THE FREUNDLICH ADSORPTION COEFFICIENT

Having derived Eq. 14 to describe uranium adsorption onto SDA sedimentary interbed material, the next step is to identify and quantify the components of the equation. There are three components to quantify, the effect of complexing in solution, the number of available surface sites, and the thermodynamic binding constant.

VI.A. Formation of Uranium Complexes in Solution

To study the adsorption of uranium on sediments at the SDA, the formation of aqueous complexes in vadose zone water at the SDA must be calculated. During the mid-to-late 1980s, a network of suction lysimeters was installed in the SDA to monitor soil water chemistry.[16] Water samples collected from these lysimeters were used to define the expected soil water chemistry for pore water in the SDA. Buffering of pore water by calcite results in a limited range in pore water pH of 7 to 8.2. Important anions in the water are fluoride (median 0.04 mmole/L), chloride (median 3.8 mmole/L), sulfate (median 3.5 mmole/L), and bicarbonate (median 7.8 mmole/L).

Thermodynamic speciation calculations were performed to evaluate uranium complexes as a function of pH and concentration of the anions in solution. Uranium carbonate species dominate over the entire range of pH conditions encountered in vadose zone pore water at the SDA. Performing calculations where one anion in sequence is raised to the maximum concentration while the other three are held at the median concentration does not change this conclusion. Therefore, the aqueous model for uranium at the SDA need only consider a few aqueous complexes. The uranium species that are included in the model are $UO_2(OH)_2(aq)$, $UO_2CO_3^-$, $UO_2(CO_3)_2^{-2}$, and $UO_2(CO_3)_3^{-4}$. For the pH and total dissolved carbonate in the laboratory experiments, the calculated value of the ratio of free uranium to total uranium is 9.7E-8. A very small fraction of the total uranium is available as free uranium to take part in adsorption reactions.

VI.B. Surface Sites

To covert Eq. 14 into a Freundlich isotherm model, the number of adsorption sites must be estimated. A number of authors have adopted a value of 2.31 sites/nm^2 to use as the number of adsorption sites for minerals.[13,17,18] This value is adopted as the site density for SDA sediments.

VI.C. Estimate of Model Parameters from Experimental Data

The fit of the Freundlich isotherm to the laboratory data provides estimates of the product of α and β. From the definitions of alpha and beta, knowledge of the carbonate concentration and pH of the test solutions, and the measured surface area of the sample material, the value of K_{ads}, the thermodynamic adsorption coefficient, was calculated (Table II). There are a number of sources of uncertainty that contribute to the uncertainty in K_{ads} in addition to the uncertainty in estimating the Freundlich K_f value. Test solution composition provides uncertainty in the pH value (± 0.2 pH units) and total dissolved carbonate concentrations (± 0.2 mmole/L). There is also an uncertainty in the slope of the regression equation for the relation between K_f and the surface area. Based on all these sources of uncertainty, we estimate that the binding constant for uranium to SDA sediments is $\log K_{ads} = -8.21 \pm 1.75$.

TABLE II

Freundlich K_f constants determined by fitting the laboratory isotherms and the estimated K_{ads} value from Eq. 14.

Sample ID	K_f (L/g)	$\log K_{ads}$ (L/mole)
7DS00101KD	0.00167	-8.211
7DS00301KD	0.00114	-8.287
7DS00501KD	0.00086	-8.290
7DS00701KD	0.00067	-8.017
7DS00901KD	0.00093	-8.299
7DS01701KD	0.00082	-8.206
7DS02301KD	0.00080	-8.187
Average		-8.214

VI.D. Fit of the Model to the Experimental Data

Eq. 14 was then used to calculate the expected adsorption for the experiments and compared to the experimental results. Because, in this set of laboratory experiments, the water chemistry was held constant, all of the variation in the K_f parameter, and consequently the derived K_{ads} parameter, is attributed to variations in sample surface area. The comparison between the predicted and measured adsorption of uranium for three selected experiments is shown in Figure 4. The agreement is generally very good with the fit of the model to the data reflecting how well the sample fit the regression equation of K_f on surface area (Figure 3). Sample 7DS00701KD had the poorest fit to the surface area regression and has the poorest fit to the model (Figure 4).

Using Eq. 14 and the parameters estimated from the laboratory experiments, the effect of pH and total dissolved carbonate concentration on uranium adsorption can be evaluated. To illustrate the effect of water chemistry on partitioning, the adsorbed (C_{ads}) and total dissolved uranium (C_{sol}) concentrations were calculated over a range of pH and dissolved carbonate concentrations using Eq. 14. The ratio of adsorbed to dissolved uranium concentrations is also the definition of K_d (Eq. 2). An effective K_d value is used to illustrate the effects of pH and dissolved carbonate because this relates the calculated results to more traditionally recognized ways of measuring partitioning. The results of these calculations are shown in Figure 5. The effective K_d is low at low pH as hydrogen ion competes with uranium for adsorption sites. Adsorption increases as pH rises and peaks at a pH between 5 and 6. As pH increases above this range, carbonate complexing in solution inhibits adsorption of uranium onto the solid mineral surfaces. Higher concentrations of dissolved carbonate decrease adsorption by complexing uranium in the aqueous phase.

VII. APPLICATION TO THE INEEL SUBSURFACE DISPOSAL AREA

An effective K_d was calculated using Eq. 14, the K_{ads} determined from the laboratory isotherms and

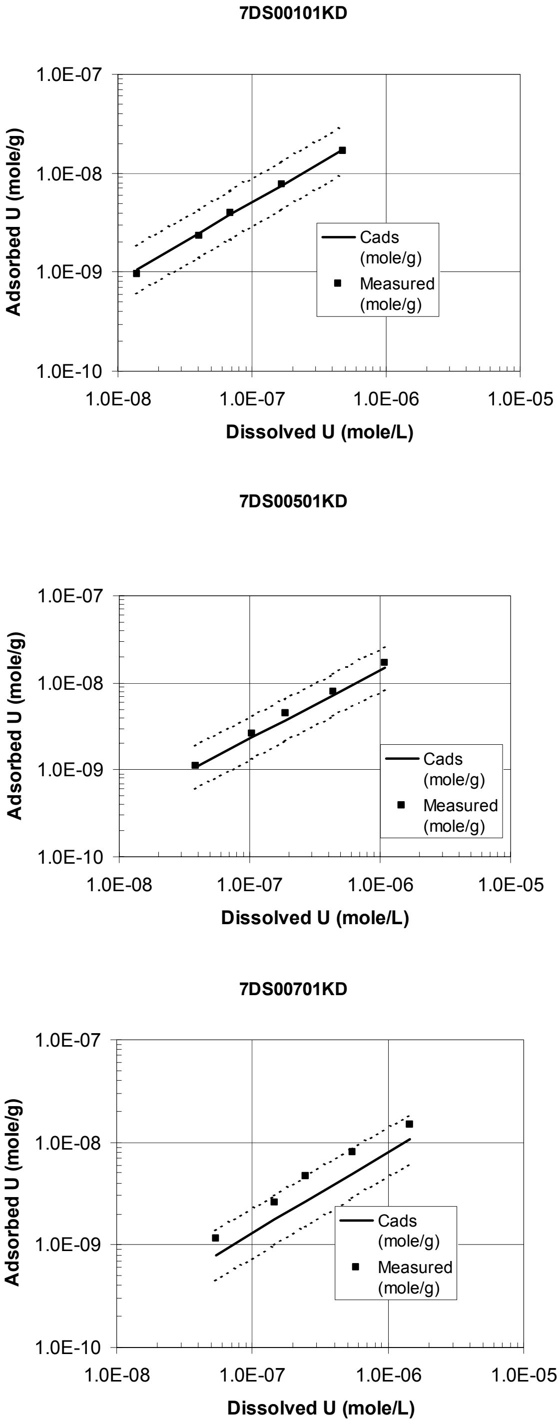

Fig. 4. Fit of analytical adsorption model (Eq. 14) to three of the uranium adsorption isotherms measured in the laboratory.

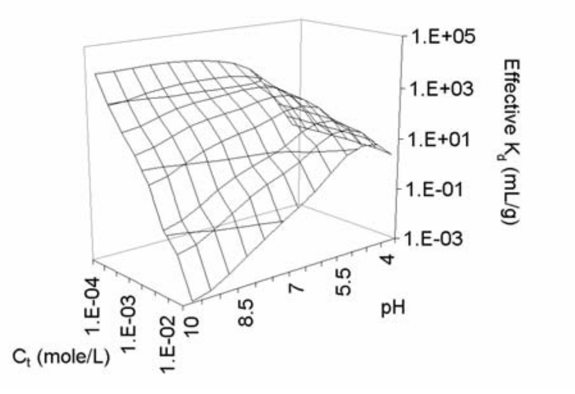

Fig. 5. Effect of water chemistry variables pH and total dissolved carbonate (C_t) on partitioning of uranium between solution and SDA sediments as measured by calculating an effective partitioning coefficient.

pH and dissolved carbonate measurements from water samples collected in the SDA. There is a wide range in dissolved carbonate in surficial sediments (depth less than 22 ft) at the SDA, with concentrations ranging from 1.4 to 29 mmole/L (diamonds in Figure 6). A few water samples have been gathered from deeper in the vadose zone at depths between 44 ft and 110 ft below ground surface (squares in Figure 6). For these deeper samples, the total dissolved carbonate concentrations cluster around 3.4 mmole/L. Most water in the surficial sediments is high in dissolved carbonate, and yields small (< 10 ml/g) calculated effective K_d values. Waters in surficial sediments with low carbonate concentrations can have effective K_d values as high as 100 ml/g. The deeper perched water contains an

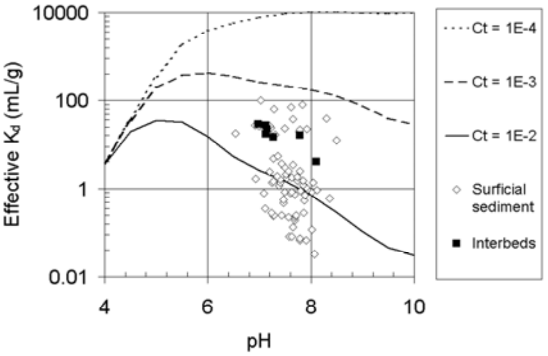

Fig. 6. Calculated effective partition coefficient (K_d) as a function of pH over the range of expected total dissolved carbonate concentrations (C_t, moles/L) at the Subsurface Disposal Area.

intermediate level of dissolved carbonate and the calculated effective K_d values for the deeper vadose zone water generally fall around 20 ml/g.

From Eq. 14, C_{ads} will change as a linear function of surface area. Water chemistry parameters such as pH and dissolved carbonate have exponential components to the functions. Changing the surface area by a factor of 5, changes the effective partitioning by a factor of five (Figure 7). Changing the dissolved carbonate concentration by a factor of 5, however, changes the effective partitioning by a factor of 30 (Figure 7). Plotting the calculated effective partitioning for water samples collected from the SDA versus dissolved carbonate shows almost 4 orders of magnitude variation in partitioning (Figure 8). The scatter at a given dissolved carbonate value reflects variations in pH. While pH can have a significant effect on adsorption, in a vadose zone environment with calcite present, the pH is buffered over narrow enough a range so that pH becomes a secondary effect.

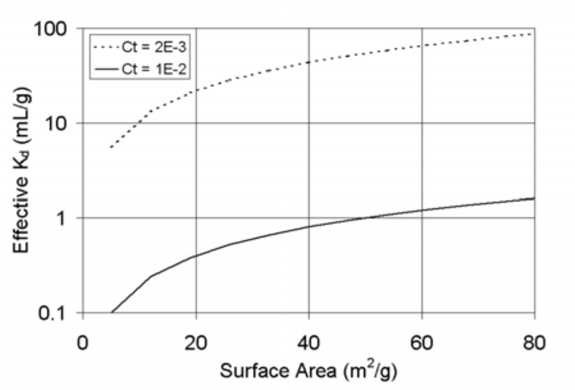

Fig. 7. Relative effect of total dissolved carbonate and sediment surface area on the partitioning of uranium between solution and mineral surfaces. Dissolved carbonate is far more important than surface area in affecting partitioning.

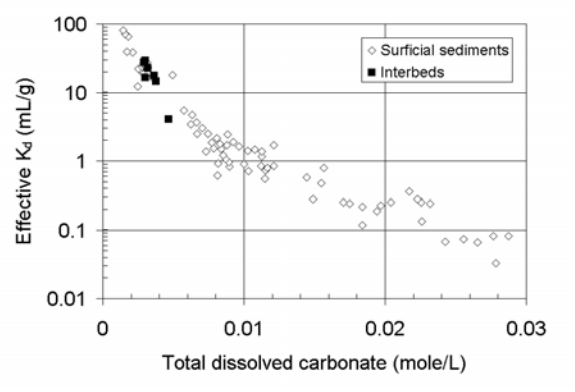

Fig. 8. Calculated partitioning coefficients for vadose zone pore waters at the SDA as a function of total dissolved carbonate concentration.

VIII. CONCLUSIONS

From empirical observations on the adsorption of uranium to interbed samples collected at the SDA, a model was derived to describe the adsorption of uranium. The model mixes theoretical concepts of surface complexation theory with the empirical Freundlich isotherm. The resulting model is considered empirical because the parameters are based on site specific measurements. The model is derived from seven samples, and requires validation with a broader set of data. Additional samples are at various stages in the analysis process, and the final data set will consist of 36 samples.

The theoretical model identifies that the Freundlich isotherm K_f parameter includes a number of effects including an intrinsic binding constant, number of surface sites, and solution chemistry. Using surface complexation theory, these effects were parameterized. Parameters were determined from literature values and measurement of material properties. The remaining unknown parameter was the intrinsic binding constant. Assuming this value to be a constant for all SDA sediments, the K_{ads} value was estimated from the laboratory isotherm experiments by allowing only the surface area of the material to vary. With this assumption, the model was able to fit the lab experiments fairly well.

The adsorption model was then applied to conditions expected to be found at the SDA. The effect of pH, water chemistry, and sediment surface area were all considered. The most important factor by far for controlling variation in adsorption for the sediments under the SDA is the dissolved carbonate content of the water.

IX. ACKNOWLEDGEMENTS

Funding for this research was provided by the U.S. Department of Energy under contract DE-AC07-99ID13727.

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