Study of Sorption-Retarded U(VI) Diffusion in Hanford Silt/Clay Material

3 AUTHORS:

Jing Bai
Johns Hopkins University
6 PUBLICATIONS **94** CITATIONS

SEE PROFILE

Chongxuan Liu
Battelle Memorial Institute
147 PUBLICATIONS **3,926** CITATIONS

SEE PROFILE

William P Ball
Johns Hopkins University
132 PUBLICATIONS **4,440** CITATIONS

SEE PROFILE

Supporting Information for

Study of Sorption-Retarded U(VI) Diffusion in Hanford Silt/Clay Material

Jing Bai[*†], Chongxuan Liu[‡], and William P. Ball[†]

[†] Department of Geography and Environmental Engineering, Johns Hopkins University

3400 N. Charles Street, Baltimore, MD 21218, USA.

[‡] Environmental Dynamics and Simulations, Pacific Northwest National Laboratory

Richland, WA 99352

[*]Corresponding author. phone: (443)858-6618; fax: (410)516-8996. Email: *jbai@jhu.edu*.

Environmental Science & Technology

Number of pages (including this one): 16
Number of tables: 6
Number of figures: 2

1. Estimating Total and Labile Background Uranium in the HSC Materials

Total background uranium. The HSC (Hanford Silt Composite) material is a composite of sand- and silt-sized aggregates of finer grained materials that were collected from a background borehole (RCRA borehole # 299-W22-48, *1*) beneath the U.S. DOE Hanford site at selected depth intervals between 42 and 44 meters below ground surface (bgs). Nearby U(VI) plumes exist in these same sediment types. A composition analysis performed by Serne et al. (*1*) on the solids sampled from bounding layers (41.5 meters bgs and 44.5 meters bgs) found a background U(VI) of 0.68 μg/g and 3.55 μg/g, respectively, by using 8 mol/L heated HNO_3 extraction. However, X-Ray Fluorescence (XRF) studies in that work showed that these amounts accounted for only 9.1% and > 40.8%, respectively, of the total background U(VI), implying that total background U(VI) was roughly 7.6 μg/g and < 8.7 μg/g.

In this study, the silt/clay sized portion (< 53 μm) of the HSC (hereafter referred to as HSC S-C) was obtained by sieving. An independent experiment was performed to measure background U(VI) content in HSC S-C. Specifically, 0.5 g of HSC S-C sample (n=2) was added to 5 mL 15.75 mol/L (67% by mass) nitric acid solution and heated at 80° C for 10 minutes in a microwave digester (Microwave Accelerated Reaction System, Model MARS, CEM Corp., Matthews, NC). Extracted U(VI) in the acid solution was then diluted and measured by Kinetic Phosphorescence Analyzer (KPA-11, ChemChek Instr., Richland, WA). Results showed that the average background U(VI) extracted was 0.87 μg/g. However, if our results are similar to those of Serne et al., this amount may only represent a fraction of the total U(VI) in the solids because the acid could not fully dissolve U contained within rock fragments (*1,2*). Thus, the content of total background U(VI) could be 2.5 to 10 times as high as 0.87 μg/g (i.e., 2 to 9 μg/g), if we assume similar recoveries as in the two bounding layers described earlier in this report.

This total amount of background U(VI) is high considering the range of sorbed U(VI) concentration in our study. However, our background control studies for both the batch and column systems showed that only a small portion can be released to the solution phase under the reaction conditions. This conclusion is consistent with findings from other works using similar materials (*3*).

Labile Background U(VI). The past work of Serne et al. and our own preliminary results showed that most of the background uranium in HSC S-C exists as uranium minerals that

do not dissolve under our experimental conditions, such as uranophane ($Ca[UO_2(SiO_3OH)](H_2O)_5$) and Na-boltwoodite ($Na[UO_2(SiO_3OH)](H_2O)_{1.5}$), or in more stable mineral phases (such as Fe/Mn minerals) (*4*). However, a fraction of the uranium is more readily dissolved, presumably because it is adsorbed to the surface and/or present as more readily dissolved uranium salts that were perhaps precipitated from solution when the pore water was evaporated during the drying of the material. Such uranium can participate in the adsorption/desorption equilibrium and has been defined as "accessible", "exchangeable", or "labile" background U(VI) (*5,6*). One needs, therefore, to consider this amount of uranium in adsorption/desorption calculations.

   To quantify the amount of background labile uranium, various techniques can be applied, as described below.

A. **Isotopic exchange method**. In this method, the distribution/ratio of uranium isotopes in the solid phase is measured and then experiments are conducted with an aqueous phase of different composition, to see if any desorptive exchange takes place. Examples are: 1) by the use of U-236/U-238 ratio, measured by gamma-spectroscope, with U-232 addition for quantification (*7*) and 7 days of reaction time; 2) by the use of U-233/U-238 ratio, measured by liquid scintillation counter (*6*), with reaction time of 10 months; and 3) by measuring U-233 activity directly, with reaction time of 1260 hours (52.5 days) (*3*).

B. **Extraction by Tamms acid oxalate (TAO).** Extraction by a solution containing 0.12 mol/L oxalic acid and 0.13 mol/L ammonium oxalate (*5*). This method is part of a five-step extraction method used to remove amorphous minerals of Fe, Al, Si and secondary U minerals (*5*). This solution will also attack a variety of more crystaline minerals, including iron-rich chlorite and biotite, magnetite, maghemite and some secondary manganese minerals (*5*).

C. **Extraction by a bicarbonate-carbonate solution (CARB)**. A CARB solution comprising $NaHCO_3$-Na_2CO_3-$NaNO_3$ system initially at pH = 9.45 and I = 0.022 M has been used by some researchers (*6,8*). In these cited works, which were conducted on sediments from Naturita, CO, the pH of the extraction fluid had dropped to ~8.2 after the two week extraction period.

   In considering and comparing these various methods, it is important to recognize that "liability" is clearly an operational parameter whose definition is dependent on the specific

materials and experimental conditions used. For example, isotopic exchange experiments using 300-Area Hanford sediments pre-equilibrated at pH 8.65 for 1260 hours have revealed that U-233 activity evolved continuously with time, even after 1200 hours (*3*). In the work of others (*6*), extraction with the CARB method gave similar results as 10-month isotopic exchange (using U-233/U-238 ratio), but needed much less reaction time. However, this finding may only apply to the particular solid material being studied. In addition, it is possible that the high pH of the CARB extraction could cause dissolution of some otherwise non-labile background U(VI) (*4*). Our preliminary studies showed that extracted background U(VI) was dependent on chemical conditions and pre-treatments of the solids, such as the solution pH, the extraction time and the pre-equilibrations of the solids. Because our primary interest is in the amount of the background labile U(VI) at pH 8.0 (±0.1), I = 0.02 M, we chose not to adopt the higher pH CARB extraction method.

In our studies, the HSC S-C samples were pre-equilibrated by U(VI)-free stock solutions four times (each lasting for 3 days) before the sediment was used for sorption study, such that a good portion of the background labile U(VI) was removed during the pre-equilibration. Our need, then, is to know the remaining background U(VI) that is still available to participate in the subsequent sorption/desorption equilibrium. In both the batch and column experiments, U(VI) washed off in the pre-equilibration solutions were measured. It can be reasonably assumed that the aqueous concentration of washed-off background U(VI) in the 4th pre-equilibration solution was at equilibrium with the concentration of the remaining background labile U(VI) in the solid phase. (See "Sorption/Desorption Kinetics Study" in later text.) The latter can be calculated using the sorption isotherm measured under the same conditions (pH 8.0±0.1). However, since the isotherm determination requires the amount of background labile U(VI) after the fourth washing to be known, an iterative calculation procedure was needed, as described below.

2. Iterative Calculation of the Sorption Isotherm and Labile Background U(VI) from Batch Sorption Data

As discussed above, we assumed that the aqueous concentration of U(VI) in the 4th equilibration solution was at equilibrium with the concentration of the remaining background labile U(VI) in the solid phase, governed by the batch sorption isotherm but the background labile U(VI) must be included in the calculation of the sorption isotherm. To solve this problem, we first guessed a background labile value (S_L) to calculate the total sorbed U(VI) at sorption equilibrium (S_e), using Eqn. S1 below. Then the isotherm was obtained by regressing S_e with the aqueous U(VI) concentration at equilibrium, C_e.

$$S_e = \frac{C_0 V + S_L m - C_e V}{m} = S_L + S_{sorbed} \tag{S1}$$

S_e: total labile U(VI) in the solid phase at sorption equilibrium

S_L: background labile U(VI) concentration in the solid phase after the 4th pre-equilibration

S_{sorbed}: U(VI) sorbed to the solid phase from solution phase

C_0: initial U(VI) concentration in solution

C_e: U(VI) concentration in solution at sorption equilibrium

m: mass of solids in the batch system

V: volume of solution in the batch system

In our work, the Freundlich type of isotherm was found to describe the relationship between S_e and C_e, and isotherm parameters were obtained by non-linear least-square fitting (Optimization Toolbox, Matlab). Then, S_L was re-evaluated using the isotherm and used as the new guessed value for the next iteration. This iteration was repeated until the guessed value of background labile U(VI) and the isotherm-predicted value converged. The isotherm and the amount of background labile U(VI) concentration after convergence are shown in Table S1.

Results in Table S1 show that the amounts of total background U(VI) estimated for the 95 g/L batch system, the 185 g/L system, and the diffusion cell column are very close. This total amount of background labile U(VI) includes the remaining amount of background labile U(VI) remaining in solution after the 4th pre-equilibration and the amount of background labile U(VI) removed in rinsate from all four pre-equilibrations, as obtained by direct measurement of these solutions. The results indicate that the amount of total background labile U(VI) was on the order of 50 ng/g, and the background labile U(VI) after four pre-equilibrations of the HSC S-C solids

is on the order of 20ng/g. This estimate was consistent among both the batch and column systems, despite the methodological differences among the two systems.

Table S1. Results: Iterative calculation of the sorption isotherm and labile background U(VI) from batch sorption data. The 95 g/L batch sorption system was used for iterative calculation of sorption isotherm.

System	95g/L batch system	185g/L batch system	Diffusion cell
Leached U(VI) by four pre-equilibration washes (ng/g)	34.1±0.1 (n=3)	22.5±3.8 (n=3)	33.8
[U(VI)] in 4th wash solution (μg/L)	0.8± 0.07 (n=3)	0.7±0.16 (n=3)	0.6
Background labile U(VI) in solids, after 4th pre-equilibration wash, **guessed value** (ng/g)	23.6	--	--
Sorption isotherm by est'd background labile U(VI)	$S = 28.61C^{0.81}$	The same as with 95g/L batch	The same as with 95g/L batch
Background labile U(VI) in solids, after 4th pre-equilibration wash, **calculated value by isotherm** (ng/g)	23.6	21.7	17.5
Total background labile UI(VI) at pH 8.0 (ng/g)	57.7	44.2	51.3

3. Schematic Illustrations of Diffusion Cell Construction and Operation
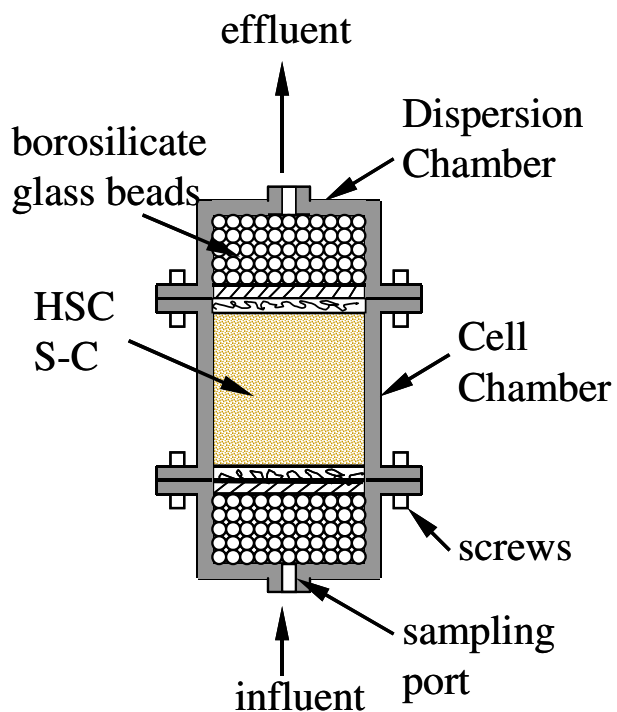

Figure S1. Schematic illustration of the diffusion cell as assembled for pre-equilibration of solids (as used for flushing and recirculation by four sequential U(VI)-free stock solutions – see main text for details.
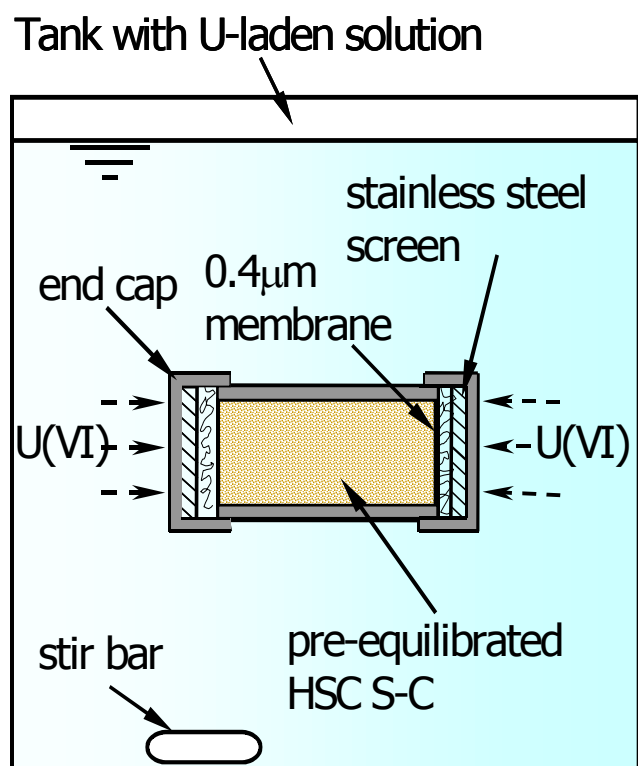
Figure S2. Schematic illustration of the "inward-flux" diffusion system.

4. Extent of Equilibrium in Sorption/Desorption Batch Kinetics Experiments

Table S2. Extent to equilibrium in sorption/desorption batch kinetic studies. f_{eq} was calculated as $f_{eq} = (C-C_0)/(C_{eq}-C_0)$, where C_0 is the initial [U(VI)] in solution and C_{eq} is taken as the concentration at the last sampling time (884 hours for sorption and 984 hours for desorption). From this table we can see that sorption equilibrium is achieved within ~260 hours and desorption equilibrium is achieved within ~500 hours. Therefore, 15 days of sorption and 21 days of desorption are considered adequate for equilibration in the batch sorption/desorption isotherm studies.

Kinetic Process	Time (hr)	Initial [U(VI)] = 0.25µM in sorption		Initial [U(VI)] = 0.92µM in sorption		Initial [U(VI)] = 2.39µM in sorption	
		[U(VI)] (µg/L)	f_{eq}	[U(VI)] (µg/L)	f_{eq}	[U(VI)] (µg/L)	f_{eq}
Sorption	0	58.7	0.00	218.3	0.00	570.6	0.00
	1	38.8	0.56	152.6	0.56	392.0	0.65
	3	37.6	0.59	144.5	0.63	384.6	0.68
	6	35.2	0.66	137.4	0.69	355.7	0.79
	9	31.2	0.77	128.1	0.77	342.9	0.83
	22	29.7	0.81	123.2	0.81	340.4	0.84
	29	29.1	0.83	120.7	0.83	335.4	0.86
	46	28.0	0.86	115.7	0.87	328.7	0.88
	70	26.9	0.89	119.3	0.84	326.6	0.89
	122	25.8	0.92	109.1	0.93	308.1	0.96
	188	24.3	0.97	102.0	0.99	299.0	0.99
	257	23.7	0.99	106.6	0.95	294.1	1.01
	405	22.7	1.01	101.4	0.99	276.5	1.07
	669	23.3	0.99	101.3	0.99	292.4	1.02
	884	23.2	1.00	100.5	1.00	297.0	1.00
Desorption	0	1.1	0.00	4.9	0.00	14.7	0.00
	1.5	6.7	0.52	28.4	0.58	74.4	0.59
	4	7.8	0.63	31.6	0.67	87.8	0.72
	10	8.4	0.68	33.9	0.72	86.2	0.70
	26	10.2	0.85	39.3	0.86	99.5	0.84
	97	10.2	0.82	39.1	0.82	102.9	0.84
	176	10.8	0.88	43.9	0.94	110.2	0.91
	279	10.9	0.89	43.5	0.93	113.0	0.94
	514	11.7	0.96	45.9	0.99	121.1	1.01
	984	12.1	1.00	46.4	1.00	119.7	1.00

5. Removal Efficiency for Sorbed Phase U(VI) Extraction by the Sequential Extraction Procedure

Table S3. Removal efficiency for sorbed-phase U(VI) extraction by the sequential extraction procedure.

Initial U conc. in sorption stage	Total sorbed U(VI) (ng/g) *	Total extraction of sorbed U(VI) (ng/g) **	% Recovery of sorbed U(VI)
~1×10^{-7}M	164.2 ± 1.4	152± 4.5	92.6 ± 3.1
~2.5×10^{-7}M	349.1 ± 2.7	354 ± 14.2	101.4 ± 4.1
~5×10^{-7}M	697 ± 20.9	665 ± 54.9	95.4 ± 8.8
~1×10^{-6}M	1352 ± 22.9	1253 ± 41.9	92.7 ± 3.7
~2.5×10^{-6}M	2641 ± 17.7	2580 ± 104.0	97.7 ± 4.1
~5×10^{-6}M	4889 ± 203	4927 ± 360.0	100.8 ± 8.4
~1×10^{-5}M	9170 ± 261	9082 ± 693.6	99.0 ± 8.2
~2.5×10^{-5}M	18989 ± 1006	18960 ± 1784.5	99.8 ± 10.8
0, control	16.8	16.8	--

*   Total sorbed U(VI) includes both the remaining (post pre-equilibration) portion of labile background U(VI) and the U(VI) sorbed from solution. See SI for details.
**   Total extraction of sorbed U(VI) excludes the non-labile portion of background U(VI). Of the total background U(VI) found in control samples (44.1±1.28 ng/g), 16.8 ng/g was estimated to be the labile (i.e. sorbed) at pH 8.0 (±0.1) based on aqueous measurements and isotherm results. The remainder (27.3 ng/g) was considered non-labile at pH 8.0 (±0.1) but was removed at pH 9.45 and 9.85, presumably owing to dissolution of U(VI)-bearing solids (*4*).

6. U(VI) Speciation

In this work, all of the batch and column experiments were carried out in electrolyte solution at pH 8.0 (±0.1) and I = 0.02M, under conditions that were saturated with respect to calcite solids (Fisher Scientific) and atmospheric CO_2 ($P_{CO2}= 10^{-3.5}$ atm). The system temperature was controlled at 22.5 °C. The concentrations of other major cations that may have come into solution from pre-equilibration washes and which could affect U(VI) speciation were measured or estimated, as listed in Table S3.

Table S4. Concentrations of major cations in the 95g/L batch sorption system.

Ions	Concentration (mmol/L)	Measurement method
K	<0.1	Measured as 0.1mM by ICP-OES at I = 0.05M, conc. at I = 0.02 M estimated to be less than 0.1mM
Mg	0.15	ICP-MS
Ca	3.86	Calculated by equilibrium speciation

As was found by Dong et al. (*9*), U(VI) can form ternary complex with Mg^{2+} and Ca^{2+}. The complexation constants are listed in Table S4. U(VI) speciation calculation for the conditions of our systems showed that >99% of the aqueous U(VI) should have been present as $Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$. Assuming $[Mg^{2+}]_{total} = 0.15mM$, the distribution of major species is calculated to be as follows: $Ca_2UO_2(CO_3)_3^0$ (68.3%), $CaUO_2(CO_3)_3^{2-}$ (30.8%), $UO_2(CO_3)_2^{2-}$ (0.5%), and $UO_2(CO_3)_3^{4-}$ (0.4%).

Table S5. Major species and complexation constants for U(VI)

Species	logK	Source
$Ca_2UO_2(CO_3)_3^0$	29.75 ± 0.07 at I =0	Dong and Brooks (*9*)
$CaUO_2(CO_3)_3^{2-}$	27.18 ± 0.06 at I=0	"
$Mg_2UO_2(CO_3)_3^0$	28.36 ± 0.20 at I=0	"
$MgUO_2(CO_3)_3^{2-}$	26.11 ± 0.04 at I=0	"
$UO_2(CO_3)_3^{4-}$	21.6	CRITICAL (*10*)
$UO_2(CO_3)_2^{2-}$	16.94	"
$UO_2(CO_3)^0$	9.67	"
$UO_2(OH)_3(CO_3)_3^{2-}$	-0.86	"
$UO_2(OH)^-$	-5.2	"

7. Estimation of D_0 for U(VI) Species

The free solution diffusion coefficient of U(VI) species may be estimated by various methods. In our work, the calculated dominant U(VI) species was $Ca_2(UO_2)(CO_3)_3^0$ (68.3%, see "U(VI) speciation"). We estimated D_0 values for this species using two methods. First, we used the Stoke-Einstein Equation (*11*) for the estimation:

$$D_{aq} = \frac{K_B T}{6\pi r_m \eta} \quad [cm^2/s] \tag{S1}$$

where T is the temperature [Kelvin], η is the water viscosity [centipose], K_B is the Boltzmann constant (1.38×10^{-32} J/K), and r_m is the radius of the diffusing species. Spectroscopic studies of $Ca_2(UO_2)(CO_3)_3^0$ have estimated the U-Ca bond distance to be 4.1Å, and the U-C-O_{dist} bond distance to be 4.2 Å(*12*). The radius of Ca^{2+} has been reported to be 1.14 Å for coordination number of 6 (tetrahedron) and 1.26Å for coordination number of 8 (*13*). With the exact coordination number of Ca^{2+} in the above complex species unknown, we used 1.14Å as the radius. Adding this to the U-Ca path distance, we estimate the radius of unhydrated $Ca_2(UO_2)(CO_3)_3^0$ to be 5.24Å. This gives $D_0 = 4.7\times10^{-6}$ cm^2/s using the Stokes-Einstein Equation, for the unhydrated $Ca_2(UO_2)(CO_3)_3^0$.

The second method used an equation suggested by Worch in Grathwohl(*14*), when the formula weight of the diffusing species, m_s, is more readily accessible than the ion radius or volume:

$$D_{aq} = \frac{3.595\times10^{-7} T}{\eta m_s^{0.53}} \quad [cm^2/s] \tag{S2}$$

By this equation, we obtain a D_0 value of 4.3×10^{-6} cm^2/s for unhydrated $Ca_2(UO_2)(CO_3)_3^0$ and of 4.5×10^{-6} cm^2/s for unhydrated $CaUO_2(CO_3)_3^{2-}$.

It is noteworthy that in the aqueous solutions, the dominant U(VI) species will be hydrated and the values of r_s and m_s in Eqs (S1) and (S2) have to be modified. Unfortunately, due to lack of knowledge of the hydration conditions of these U(VI) species, D_0 values of the hydrated species cannot be estimated. In addition, the estimation equation S1 is strictly valid only for large spherical molecules, and equation S2 is a crude empirical correlation that gives no consideration to specific solute-solvent interactions, such as dipole-dipole interactions or

hydrogen bonding. For all of these reasons, the estimated values should be considered only for their potential as "order-of-magnitude" checks on the measured results.

8. Experimental Data for the Diffusion Cell

Table S6. Experimental data for the diffusion cell.

Layer number	Avg.thickness (mm)	Distance from right end (mm)	S* (ng/g)	S_{eq} (est'd by C, ng/g)	C (μg/L)	C_{eq} (est'd by S, μg/L)	% to equilibrium (C_{eq}/C)
R1	2.58	1.29	4661.6	4845.7	531.0	542.33	102.13%
R2	3.33	4.24	2231.7	2744.7	263.0	218.19	82.96%
R3	3.03	7.41	907.1	1740.7	149.8	71.70	47.86%
R4	2.80	10.33	389.9	428.5	26.5	25.25	95.33%
R5	2.75	13.10	154.2	167.1	8.3	8.02	97.02%
R6	3.15	16.05	42.5	141.8	6.8	1.63	24.18%
R7	2.98	19.11	32.5	44.4	1.6	1.17	72.68%
L7	2.95	22.08	137.8	141.8	6.8	6.98	103.34%
L6	2.20	24.65	219.3	156.0	7.6	12.40	163.20%
L5	2.15	26.83	58.3	140.9	6.7	2.41	36.00%
L4	3.20	29.50	693.8	735.2	51.6	51.48	99.72%
L3	3.07	32.63	1465.2	1668.2	142.1	129.70	91.26%
L2	2.65	35.49	2616.7	2951.4	287.7	265.63	92.32%
L1	3.13	38.38	4545.6	4796.1	524.3	525.70	100.26%

* S is the total sorbed U(VI), which was calculated as the total extracted U(VI) (by the four sequential extraction steps) excluding the extracted "non-labile" background U(VI) of 26.8ng/g, which was obtained from control experiments for the diffusion cell. S includes both the sorbed labile background U(VI) and the newly sorbed U(VI) from the pore solution. Details are discussed in the main text.

9. Goodness of Fit in Modeling of Batch Rate Data and Diffusion Cell Results

The relative goodness of fit of model simulations was determined by comparing the sum of squared percentage error (SSPE) between the model-calculated concentrations and the experimental data. Division of this sum by the number of data points is thus an "average" squared error. The square root of (SSPE/number of data points).is referred to as the root-mean squared error (RMSE) and provides a measure of absolute value of the percentage error between model calculations and observed data.

For the batch sorption or desorption systems, all experimental data including data from three concentrations were used in the calculation of SSPE. Note that the data used are the averaged data for the duplicate samples for each of the three concentrations. A total of 45 data

points were used for batch sorption and a total of 30 data points were used for batch desorption. Using this approach, the calculated RSME value for the batch sorption kinetic results was 4.7% and that for batch desorption kinetics was 3.2%.

For estimating RMSE from spatial results within the diffusion cell system, we used only those data points from locations where the measured U(VI) concentration in the pore water was above the effective measurement detection limit of 10 μg/L. (see main text).

For the LEA-based model within the diffusion cell, the RMSE was determined using model-calculated values for both C and C_{eq}, using the definitions for these parameters as discussed in the main text. Specifically, we calculated the model-based concentrations for pore water [U(VI)] (hereafter referred to as C_{model}) at the locations where pore [U(VI)], C, was measured and where C was above 10 μg/L. At such locations, C_{eq} was also calculated as the aqueous concentration that would be in equilibrium with measured solid phase [U(VI)], S, by the Freundlich isotherm of the batch sorption study. Then we calculated the RMSE in two ways: (1) by comparing C_{model} and C, and (2) by comparing C_{model} and C_{eq}. The number of compared data points is thus double the number of sampled locations. A total of 8 sampled locations were available for both C and C_{eq}. These data points were located in the range of 1-11mm away from both the constant concentration boundaries.

For the kinetics-based modeling within the diffusion cell, RMSE was calculated using separate model-generated estimates for both porewater and sorbed-phase concentrations of U[VI] (C_{model} and S_{model}) and we compared these to observed values of C and S at the locations where C was above 10 μg/L. RMSE was then calculated as previously described, and again the number of compared data points was equal to sixteen, or double the number of sampled locations

Using the above-described approach, the RMSE of the LEA-based model was calculated to be 22.6% and that of the kinetics-based model was 16.9%. We also separately estimated the average modeling error for U(VI) using only locations further away from the constant concentration boundaries (4-11mm). For this case, a total of 6 data points for C and 6 points for C_{eq} (for the LEA-based model) or for S (for the kinetics-based model) were included. Using only these 6 locations, the RMSE for the LEA-based model was 25.4% and for the kinetics-based model was 20.8%. The slightly greater error for the LEA in this second case could arguably be interpreted as an indication of greater non-equilibrium at locations further away from the cell boundaries – i.e., where exposure time to U(VI) was shorter; however, the differences between

the overall RMSE and that for the interior subset were small. Moreover, the differences between the two types of model predictions (5.7% and 4.6%, respectively) are small and well within the cumulative error of the extraction process. Thus, these detailed results also support our conclusion that the LEA is a valid approach for modeling these data.

Compared to those from the batch kinetics, the RMSE values from the diffusion cell system were higher. The major contribution to RMSE for the cell system, however, derives from a few data points located at 4.2mm, 7.4 mm and 10.3 mm from the left cell boundary. (See Figure 3 of the main text.) The overall fitting to the experimental data by visual inspection is reasonably good. Moreover, the diffusion cell experimental data could have higher uncertainties due to the more complex measurement procedures. The smaller number of data points available in the diffusion cell system, as limited by the diffusion cell design, also contributes to the larger error.

References for the Supporting Information

(1) Serne, R.; Bjornstad, B. N.; Schaef, H. T.; Williams, B. A.; Lanigan, D. C.; Horton, D. G.; Clayton, R. E.; LeGore, V. L.; O'Hara, M. J.; Brown, C. F.; Parker, K. E.; Kutnyakov, J. N.; Serne, J. N.; Mitroshkov, A. V.; Last, G. V.; Smith, S. C.; Lindenmeier, C. W.; Zachara, J. M.; Burke, D. S. *Characterization of vadose zone sediment: uncontaminated RCRA borehole core samples and composite samples.*; PNNL-13757-1; Pacific Northwest National Laboratory, Richland, WA, 2002.

(2) Curtis, G. P.; Fox, P.; Kohler, M.; Davis, J. A. Comparison of in situ uranium K_D values with a laboratory determined surface complexation model. *App. Geochem.* **2004**, *19*, 1643-1653.

(3) Bond, D. L.; Davis, J. A.; Zachara, J. M. Uranium(VI) release from contaminated vadose zone sediments: Estimation of potential contributions from dissolution and desorption. In *Adsorption of Metals by Geomedia II: Variables, Mechanisms, and Model Applications*; Barnett, M. O., Kent, D. B., Eds.; Elsevier: Amsterdam., 2008; pp 375-416.

(4) Liu, C.; Zachara, J. M.; Qafoku, O.; McKinley, J. P.; Heald, S. M.; Wang, Z. Dissolution of uranyl microprecipitates from subsurface sediments at Hanford Site, USA. *Geochim. Cosmochim. Acta* **2004**, *68*, 4519-4537.

(5) Davis, J. A.; Payne, T. E.; Waite, T. D. Simulating the pH and pCO_2 dependence of uranium(VI) adsorption by a weathered schist with surface complexation models. *Geochemistry of Soil Radionuclides, SSSA Special Publication* **2002**, *59*, 61-86.

(6) Kohler, M.; Curtis, G. P.; Meece, D. E.; Davis, J. A. Methods for estimating adsorbed uranium(VI) and distribution coefficients of contaminated sediments. *Environ. Sci. Technol.* **2004**, *38*, 240-247.

(7) Payne, T. E.; Waite, T. D. Surface complexation modeling of uranium sorption data obtained by isotope exchange techniques. *Radiochim Acta* **1991**, *52*, 478-493.

(8) Davis, J. A.; Meece, D. E.; Kohler, M.; Curtis, G. P. Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments. *Geochim. Cosmochim. Acta* **2004**, *68*, 3621-3641.

(9) Dong, W. M.; Brooks, S. C. Determination of the formation constants of Ternary Complexes of Uranyl and Carbonate with Alkaline Earth Metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) Using Anion Exchange Method. *Environ. Sci. Technol.* **2006**, *40*, 4689-4695.

(10) Martell, A. E.; Smith, R. M.; Motekaitis, R. J.; 7.0 ed.; Gaithersburg, MA, 2003.

(11) Cussler, E. L. *Diffusion Mass Transfer in Fluid Systems*; 2nd ed.; Cambridge University Press: New York, 1997.

(12) Kelly, S. D.; Kemner, K. M.; Brooks, S. C. X-ray absorpiton sepctroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations. *Geochim. Cosmochim. Acta* **2007**, *71*, 821-834.

(13) WebElements [http://www.webelements.com/]; accessed May 15, 2009.

(14) Grathwohl, P. *Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics*; Kluwer Academic Publishers, 1998.