

YEARLY PROGRESS REPORT

Project Title: Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling

Covering Period: June 16, 2003 through June 15, 2004

Date report: June 14, 2004

Recipient: Johns Hopkins University

Award Number: EMSP 86748; Contract No. DE-FG07-02ER63498

Subcontractors: None

Other Partners: The project reported is being conducted at Johns Hopkins University in close collaboration with Dr. Chongxuan Liu of the Pacific Northwest National Laboratory. This project is also part of a larger collaborative effort being undertaken with other investigators at the Pacific Northwest National Laboratory (Dr. John M. Zachara, Dr. Chongxuan Liu, and Dr. Zheming Wang), the Los Alamos National Laboratory (Dr. Peter Lichtner), and Stanford University (Dr. Gordon E. Brown) to undertake research as described in a March, 2002 proposal to the FY-02 Environmental Management Science Program, entitled "Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling," under the direction of Dr. John M. Zachara, Principal Investigator. The project reported here has a narrower focus, and is specifically designed to better understand the coupled adsorption, diffusion, and transport of adsorbing U(VI) species in pristine subsurface materials from the Hanford site. The results from this project will ultimately be compared and integrated with those from other institutions to meet the objectives of the overall collaborative project.

Contact(s): PI: William P. Ball, JHU (bball@jhu.edu); **administrative contacts:** Christopher Thomas (cthomas@jhu.edu) and Timothy Allgire (tallgire@jhu.edu; Tel: 443-997-8967)

Project Objective(s):

The objectives of the overall collaborative EMSP effort (with which this project is associated) are to characterize sorption and desorption processes of U(VI) on pristine and contaminated Hanford sediments over a range of sediment facies and materials properties and to relate such characterization both to fundamental molecular-scale understanding and field-scale models of geochemistry and mass transfer. The research is intended to provide new insights on the mechanisms of U(VI) retardation at Hanford, and to allow the development of approaches by which laboratory-developed geochemical models can be upscaled for defensible field-scale predictions of uranium transport in the environment.

Within this broader context, objectives of the JHU-based project are to test hypotheses regarding the coupled roles of adsorption and impermeable-zone diffusion in controlling the fate and transport of U(VI) species under conditions of comparatively short-term exposure. In particular, this work will contribute toward the testing of the following hypotheses: (1) the primary adsorption process in the Hanford sediment over the pH range of 7 to 10 are surface complexation reactions of aqueous U(VI) hydroxycarbonate and carbonate complexes with amphoteric edge sites on detrital phyllosilicates in the silt/clay size fraction; (2) macroscopic adsorption intensity (at given aqueous conditions) will scale in proportion to silt/clay content (phyllosilicate surface area); and (3) equilibrium sorption and desorption will be observed to apply in short-term, laboratory-spiked pristine sediments; and (4) interparticle diffusion can be

fully understood in terms of a model that couples molecular diffusion of uranium species in the porewater with equilibrium sorption under the relevant aqueous conditions. Focus of the work is on developing and applying both models and experiments to test the applicability of "local equilibrium" assumptions in the modeling interpretation of interparticle diffusion, as relevant to processes of U(VI) diffusion in silt/clay layers. If time and resources permit, we also intend to explore our ability to use computer modeling to predict the manner in which diffusion-limited transport in impermeable silt regions can affect solute advection in adjacent coarser (sandy) materials.

Background:

Uranium (VI) is a ubiquitous contaminant at Hanford and other DOE sites, resulting from its central role in the nuclear fuel cycle. Underground migration of uranium (VI) at Hanford, WA, and other DOE sites is controlled by sorption and desorption processes with numerous different mineral solids possessing a range of material properties. Hanford vadose zone porewater and groundwater is generally in equilibrium with calcite that exists as a minor mineralogical component of all subsurface sediments. Within this context, the purpose of this study is to experimentally test the aforesaid hypotheses regarding the sorption and desorption of U(VI) and the interplay of such sorption with the interparticle transport of U(VI) species in water..

Status

I. Overview of approach

The studies are conducted at the laboratory bench scale, including both batch systems (well-mixed solid-water slurries) and specially constructed diffusion half-cells, in which a well-mixed water solution is placed adjacent to a fine-grained porous medium in which transport occurs only by diffusion. In the batch studies, we use an equilibration of uranium (VI) with sediment and water under well-mixed conditions in a closed laboratory vessel to study the distribution of U(VI) under a wide range of aqueous conditions, and we compare this distribution with expectations based on our understanding of solution and surface chemistry, including the development and testing of new hypotheses as needed. For these studies, we have conducted studies with both laboratory-grade calcite samples, with samples of "composite" Hanford sediment material (described subsequently), with specifically segregated size fractions of the Hanford sediments, and with chemically treated (modified) samples of selected Hanford samples. The Hanford sediments have been collected from the subsurface at the Hanford site by others (using deep coring techniques) and include both a Hanford Sand Composite (HSC) and a Hanford Fine Silt Composite (HFSC). The vast majority of our studies have been with the HFSC and with fractions thereof. The silt fraction of this material is also the porous medium of choice for our initial diffusion experiments, in which we will test our ability to understand and predict coupled processes of sorption, desorption, and transport..

II. Materials and Experimental Procedures:

Overviews of the materials and experimental procedures used in this research are described in subsections below. Details of the methods are documented in separate documents, referred to here as Protocols A through G. Parties interested in obtaining details of these protocols should contact the PI (William Ball).

A. Collection and processing of samples:

The primary Hanford materials studied were the Hanford Silt Composite (HSC) as well as carefully-split sub-fractions that included only the silt-and-clay size fraction or only the sand size fraction, and a silt-and-clay fraction from which carbonate minerals had been removed using

NaOAc-treatment (Zachara, Smith et al. 2002). The detailed procedures for processing these samples have been established and are referenced in protocol documents referred to here as Protocol A (“Collection, Preparation, and Processing of Sediments”) and Protocol B (“Extraction of Carbonates and Free Iron Oxides”). The percentage content of carbonate minerals in these samples was determined by the analytical method presented in Protocol C (“Determination of the Mass Content of Carbonate Minerals and Free Iron Oxides”). In addition, we use calcite as an additional sorbent to investigate its contribution to U(VI) sorption. The calcite is in the rhombic cleavage form and was obtained from Sargent-Welch Scientific. It was ground to a fine powder (<200 μm) using a ball mill.

B. Batch studies:

Various batch studies were designed to meet objectives (1) to (3). Batch sorption experiments were conducted with U(VI) concentrations ranging from 1.2×10^{-7} to 12×10^{-5} mol/L and pH ranging from 7.2 to 10.0 at 22.5 °C under a constant partial pressure of CO_2 ($P_{\text{CO}_2} = 10^{-3.5}$ atm), and at a constant ionic strength ($I = 0.05$ mol/L) with a 100 g/L of solid/solution ratio. The aqueous phase used both calcite-saturated and calcium-free solutions employing Na_2CO_3 - NaHCO_3 or HNO_3 solutions for pH control and NaNO_3 as support electrolyte. Protocol D (“Preparation of Calcite-Saturated Solutions and Calcium-Free Solutions”) presents the detailed procedure for preparation of calcite-saturated and calcium-free solutions. Protocol E (“Preparation of U(VI) Stock Solution and U(VI) Analysis”) presents the procedure of preparing the U(VI) stock solution and the method for U(VI) analysis. Protocol F (“Batch U(VI) Sorption and Desorption Experiments”) presents the experimental methods of studying U(VI) sorption kinetics, sorption-desorption reversibility, sorption isotherms, and pH-dependent sorption edges.

C. Diffusion studies:

We completed the design and method development of the diffusion cell experiment to meet objective (4), as described in Protocol G (“Experimental Design for Diffusion Experiments”)

D. Macropore studies:

The macropore experiments to meet objective (5) are not yet designed (see “Plans for Next Year”).

III. Results to Date:

A. Characterization of samples:

Our wet sieve analysis of HSC has revealed that roughly 31% of this material is in the sand size fraction (> 53 μm), 61% in the silt fraction (2-53 μm) and 6% in the clay fraction (<2 μm). The mass content of carbonate minerals was measured, with results as presented in Table 1. The calculation of soluble calcite based on data from Table 1 showed that the calcite in the original HSC and the silt/clay fraction was a sufficient source to saturate the batch solutions under our experimental conditions. This credited our approach of using calcite-saturated solutions in this study.

Table 1 The mass content of calcite in HSC and its sub-fractions, converted from total inorganic carbon content assuming inorganic carbon is contributed totally by calcite

Solid	original HSC	silt/clay fraction	sand fraction	carbonate-removed silt/clay fraction
converted calcite mass content	2.5%	3.0%	1.5%	0.0%

B. Batch Studies:

1. Preliminary study:

The experiment was designed to determine the ideal ratio of solid to solution for U(VI) sorption (to reach 20%-80% of sorption). U(VI) sorption was conducted in a range of solid concentrations of the silt/clay fraction in calcite-saturated solution under $P_{CO_2} = 10^{-3.5}$ atm, $pH=8.3\pm 0.1$, $I = 0.05$ mol/L (adjusted by $NaNO_3$), and 22.5 °C. The results are presented in Figures 1 and 2. Figure 1 shows that the U(VI) sorption increases from 15% to 90% when the solid/solution ratio varies from 10g/L to 500g/L. 100g/L ($m/V = 1g/10mL$) is selected as an ideal ratio of solid to solution for subsequent sorption experiments with about 60% sorption. Figure 2 shows that the distribution coefficient, K_d (ml/g), of U(VI) is independent of solid concentration with an average K_d value of 16 ± 1 ml/g for all solid concentrations in this study.

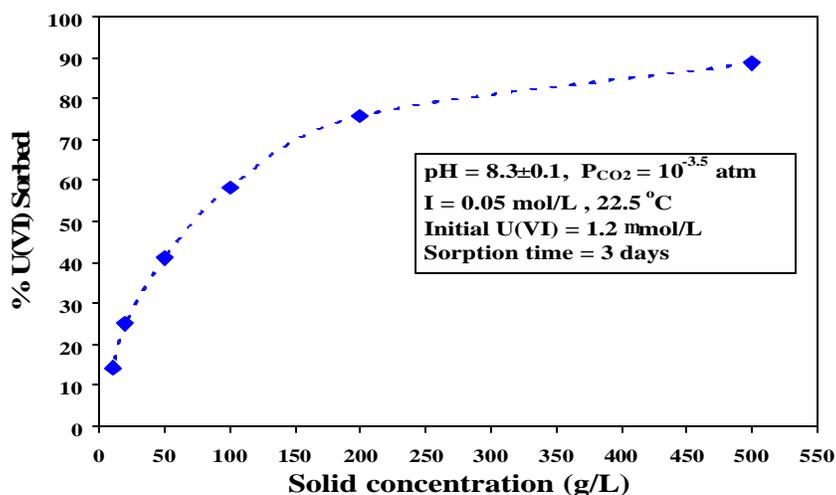


Figure 1 U(VI) sorption as a function of solid concentration of Hanford silt/clay fraction

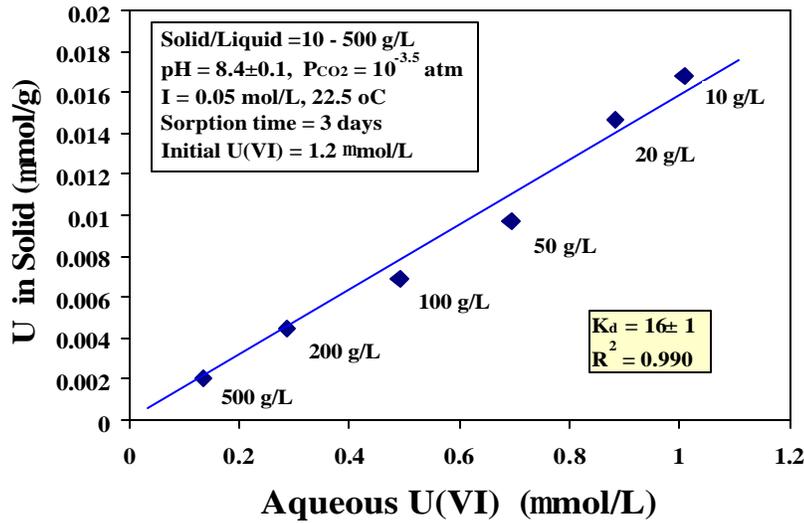


Figure 2 U(VI) distribution at different solid concentration of Hanford silt/clay fraction

2. Kinetic studies:

Experiments to determine the sorption kinetics of U(VI) onto Hanford silt/clay size fraction were conducted with an initial U(VI) concentration of 1.2 $\mu\text{mol/L}$, solid/solution ratio = 100g/L, pH = 8.3 \pm 0.1, I = 0.05 mol/L and in equilibrium with the CO₂ content of ambient air at 1 atmosphere. The sorption solution was pre-saturated with respect to calcium by bubbling with ambient air in the presence of calcite. (This solution was filtered prior to use – see Protocol F.) Figure 3 presents the U(VI) sorption as a function of contact time. It shows that U(VI) sorption equilibrium was established rapidly within 30 minutes. We used three days as the equilibration time for subsequent batch studies.

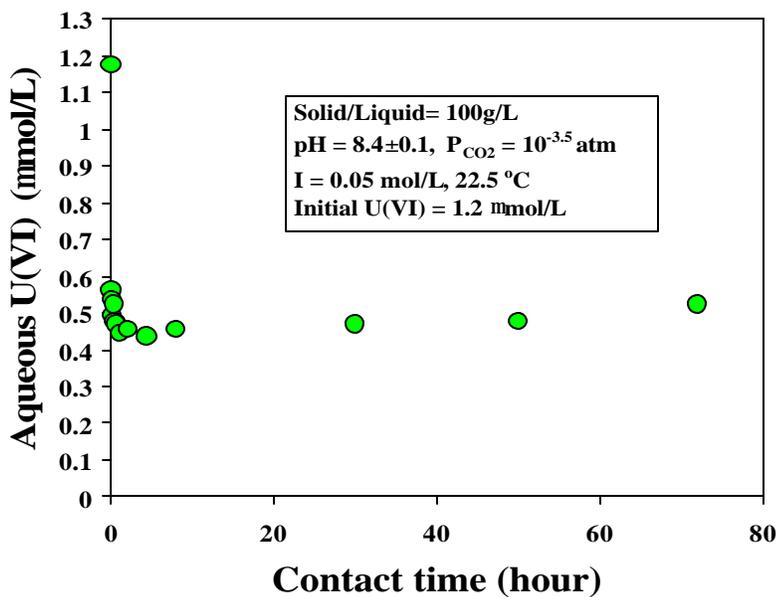


Figure 3 U(VI) sorption as a function of contact time on Hanford silt/clay fraction

3. Desorption studies:

Desorption of U(VI) was performed following sorption with a U(VI) concentration ranging from 1.2×10^{-7} to 1.2×10^{-5} mol/L in calcite-saturated solution (pH=8.2±0.1) under $P_{CO_2} = 10^{-3.5}$ atm, $I = 0.05$ mol/L (NaNO₃), and 22.5 °C. A slight sorption-desorption hysteresis was observed which suggested that U(VI) sorption was essentially reversible in Hanford silt/clay fraction (see Figure 4).

Additional desorption studies were performed for the original HSC and its sub-fractions as well as pure calcite on a mass basis of 100 g/L in calcite-saturated solution and the results are presented in Table 2. The desorption behavior of U(VI) on the original HSC sample was quite similar to that on the silt/clay fraction and on pure calcite mineral. The carbonate-removed silt/clay fraction was found to have a higher sorption affinity for U(VI) and the sand fraction is not a significant sorbent. U(VI) sorption-desorption behavior in calcite-saturated solution at pH = 8.4±0.1 was identical to that in calcium-free solution, which suggested that dissolved Ca²⁺ in calcite-saturated solution was too low to influence U(VI) aqueous speciation.

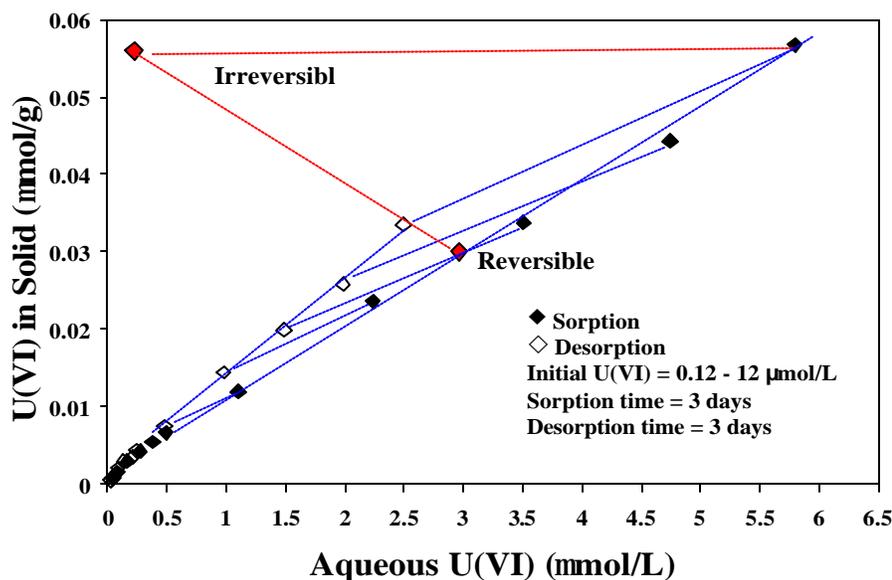


Figure 4 U(VI) sorption and sorption isotherms on Hanford silt/clay fraction

Table 2 Comparison of U(VI) sorption and desorption coefficients on the original HSC, its sub-fractions and calcite with sorption and desorption time of 3 days each. Initial U(VI) concentration = 1.2×10^{-6} mol/L, I = 0.05 mol/L (NaNO₃), pH = 8.4±0.1, P_{CO2} = 10^{-3.5} atm, T = 22.5 °C

Solid	Solution	Sorption K _d	Desorption K _d
Original HSC	Calcite-saturated	17±1	22±1
Silt/Clay	Calcite-saturated	18±1	23±1
Carbonate-removed Silt/clay	Calcite-saturated	35±4	58±1
Carbonate-removed Silt/clay	Calcium-free	36±4	57±1
Sand	Calcite-saturated	6±1	14.5±0.5
Calcite	Calcite-saturated	18±2	22±1

4. Relative roles of silt/clay and sand for U(VI) sorption:

In order to investigate the relative roles of silt/clay size fraction and sand size fraction for U(VI) sorption in Hanford subsurface sediment, U(VI) sorption experiments were conducted as a function of pH and the results are shown in Figure 5. It indicates that silt/clay fraction is the dominant sorbent at pH < 9 and sand fraction become a significant sorbent at pH > 9.0. The component additivity approach can be applied to approximately estimate the U(VI) sorption on original HSC sample from those on silt/clay and sand fractions ($K_d(\text{HSC}) = f_{\text{silt/clay}} K_d(\text{silt/clay}) + f_{\text{sand}} K_d(\text{sand})$), $f_{\text{silt/clay}}$ and f_{sand} are percentage fractions of silt/clay and sand in the original HSC, respectively). A particularly interesting observation was that the sorption of U(VI) on the original HSC, and the silt/clay and sand fractions of HSC exhibited a maximum sorption at pH = 8.4±0.1.

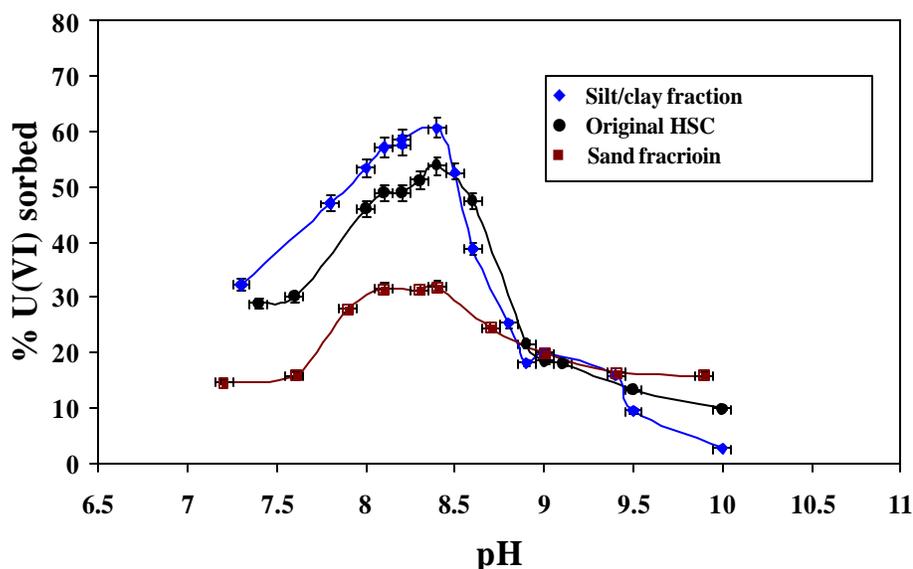


Figure 5 Relative roles of silt/clay and sand fractions for U(VI) sorption with an initial U(VI) concentration of 1.2×10^{-6} mol/L under solid/solution = 100 g/L, I = 0.05 mol/L (NaNO₃), pH=8.4±0.1, P_{CO2}=10^{-3.5} atm and 22.5 °C, and 3 days sorption

5. Role of carbonate minerals for U(VI) sorption:

Figure 6 presents the U(VI) sorption isotherms on original HSC and its sub-fractions as well as on pure calcite with the initial U(VI) concentration ranging from 1.2×10^{-7} to 1.2×10^{-5} mol/L in calcite-saturated solution under $P_{\text{CO}_2} = 10^{-3.5}$ atm, $\text{pH} = 8.2 \pm 0.1$, solid/solution = 100 g/L, $I = 0.05$ mol/L (NaNO_3), and 22.5°C . The carbonate removed silt/clay fraction was found to have a higher sorption affinity for U(VI) than untreated silt/clay fraction. This result indicates that calcite or other removed phases may cover or block access to higher affinity sorption sites for U(VI). U(VI) sorption on silt/clay fraction was identical to that on calcite minerals, which suggests that solid calcite is also an important sorbent. The sorption isotherm on the original HSC was lower than those on other solid samples, probably due to the large particle size with a low specific surface area.

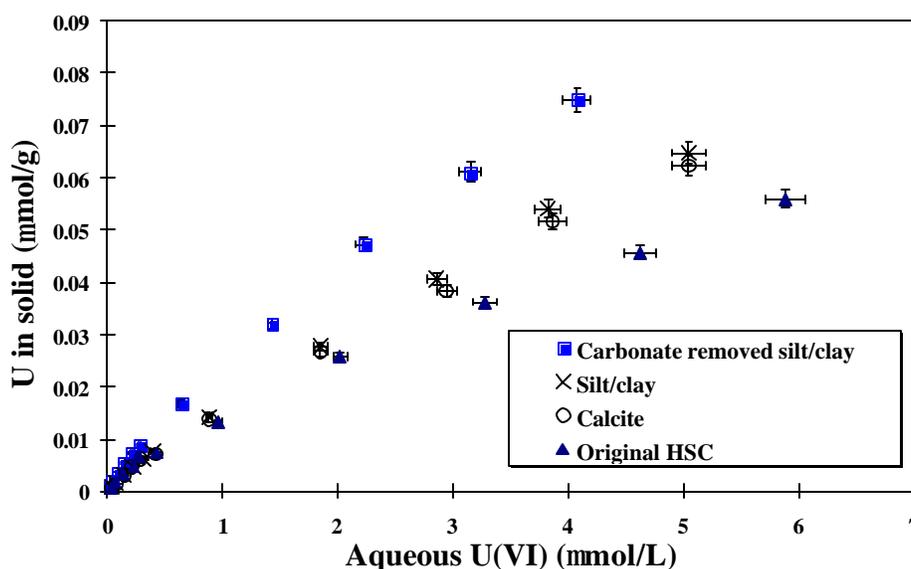


Figure 6 U(VI) sorption isotherms on the original HSC and its sub-fractions as well as pure calcite after three days of sorption

6. Role of dissolved calcium for U(VI) sorption:

Figure 7 presents U(VI) sorption on carbonate-removed silt/clay fraction in calcite-saturated and calcium-free solutions with an initial U(VI) concentration of 1.2×10^{-6} mol/L under $P_{\text{CO}_2} = 10^{-3.5}$ atm, solid/solution = 100 g/L, $I = 0.05$ mol/L, $T = 22.5^\circ\text{C}$. A particularly interesting observation was that, for the calcite-saturated aqueous condition, the sorption of U(VI) on silt/clay fraction of HSC exhibited a maximum sorption at $\text{pH} = 8.4 \pm 0.1$, with decreased sorption at both lower and higher pH. Results obtained in the range of pH 7.0 to 8.0 in calcite-saturated solutions are in stark contrast with results from in the same pH range (pH 7.0 to 8.0) in this study and prior studies in calcite-free systems (Waite et al., 1994; Barnett et al., 2002), which found strong U(VI) sorption in this pH range. Our independent calculations of aqueous U(VI) speciation under calcite-saturated solutions showed that the aqueous complex of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (Kalmykov and Choppin, 2000) should dominate at pH below 8.4 and should be responsible for the lesser sorption (Figures 8 and 9). $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complex has been confirmed by Laser Induced Fluorescence Spectrometry in our calcite-saturated sorption solutions at $\text{pH} = 7.5$ by measurement at Pacific Northwest National Laboratory. Given that the maximum sorption occurred at $\text{pH} = 8.4 \pm 0.1$ in calcite-saturated solutions, one conceivable explanation for the results at low pH is that the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species did not strongly associate with amphoteric edge sites on detrital phyllosilicates to form surface complexes in the silt/clay size fraction,

whereas in calcium-free solutions the U(VI) hydroxycarbonate and carbonate complexes strongly reacted with amphoteric edge sites on detrital phyllosilicates to form inner-sphere surface complexes and showed a strong sorption.

Figure 7 also presents results of the U(VI) sorption on untreated silt/clay fraction both in calcite-saturated and calcium-free solutions. The similar sorption edge was observed in both solutions. The initial calcium-free solutions are likely saturated with respect to calcite in untreated silt/clay fraction at sorption equilibrium. Our calculation with respect to calcite solubility indicates that the calcite content of the untreated silt/clay fraction (see Table 1) is a sufficient source to saturate the initially calcium-free solutions under given experimental conditions.

In any case, the results from Figures 5, 7 and 8 clearly show that U(VI) sorption in calcite-saturated systems is lower at pH < 8.4 than what has been observed in this study (see Figure 7) and in previous studies in calcite-free systems. Overall, the results clearly show that U(VI) transport in calcite-saturated systems will be a strong function of pH, with the sorption at pH < 8.4 being much less extensive than what would be predicted if calcium were not considered.

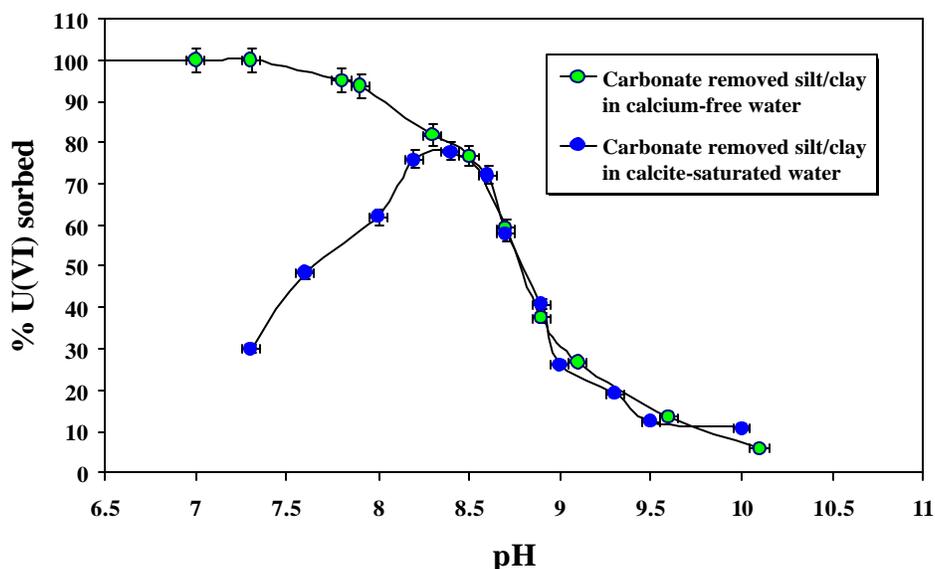


Figure 7 U(VI) sorption on carbonate removed silt/clay fraction in initial calcite-saturated and initial calcium-free solutions with an initial U(VI) concentration of 1.2×10^{-6} under $P_{CO_2} = 10^{-3.5}$ atm, solid/solution = 100 g/L, I = 0.05 mol/L ($NaNO_3$), and 22.5 °C.

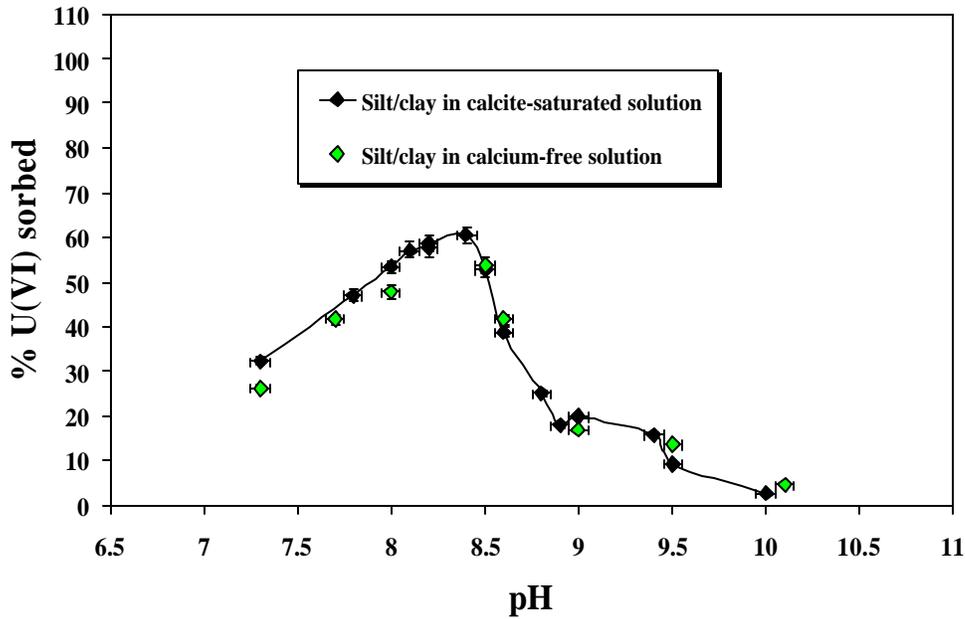


Figure 8 U(VI) sorption on untreated silt/clay fraction in initial calcite-saturated and initial calcium free solutions with an initial U(VI) concentration of 1.2×10^{-6} under $P_{\text{CO}_2} = 10^{-3.5}$ atm, solid/solution = 100 g/L, $I = 0.05$ mol/L (NaNO_3), and 22.5°C .

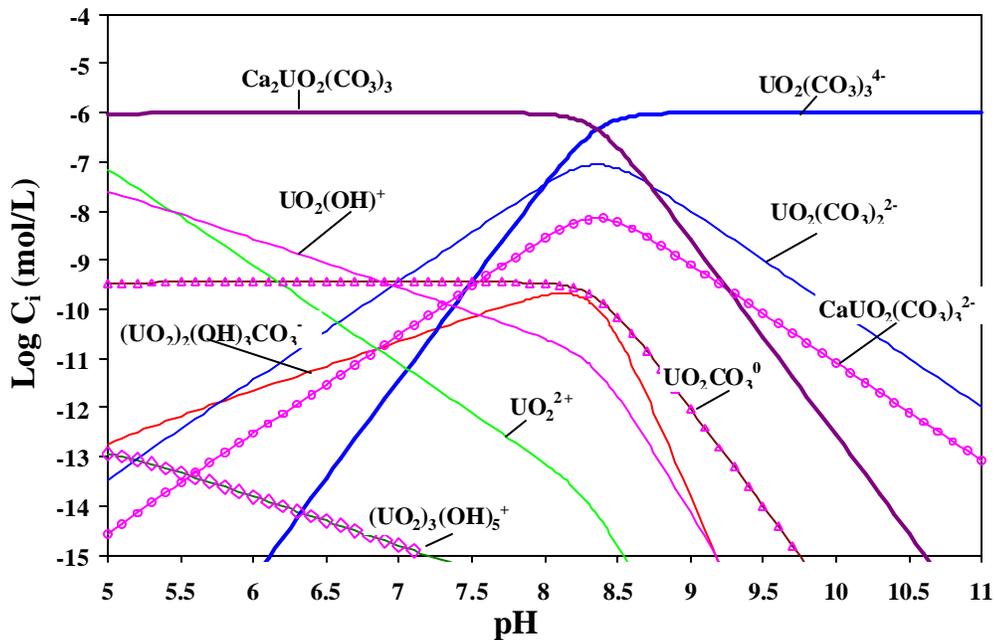


Figure 9 U(VI) speciation in calcite-saturated solution with an U(VI) concentration of 1.0×10^{-6} mol/L under $I = 0.05$ mol/L, $P_{\text{CO}_2} = 10^{-3.5}$ atm and 22.5°C . The complex constants of all U(VI) species from Grenthe et al, 1992.

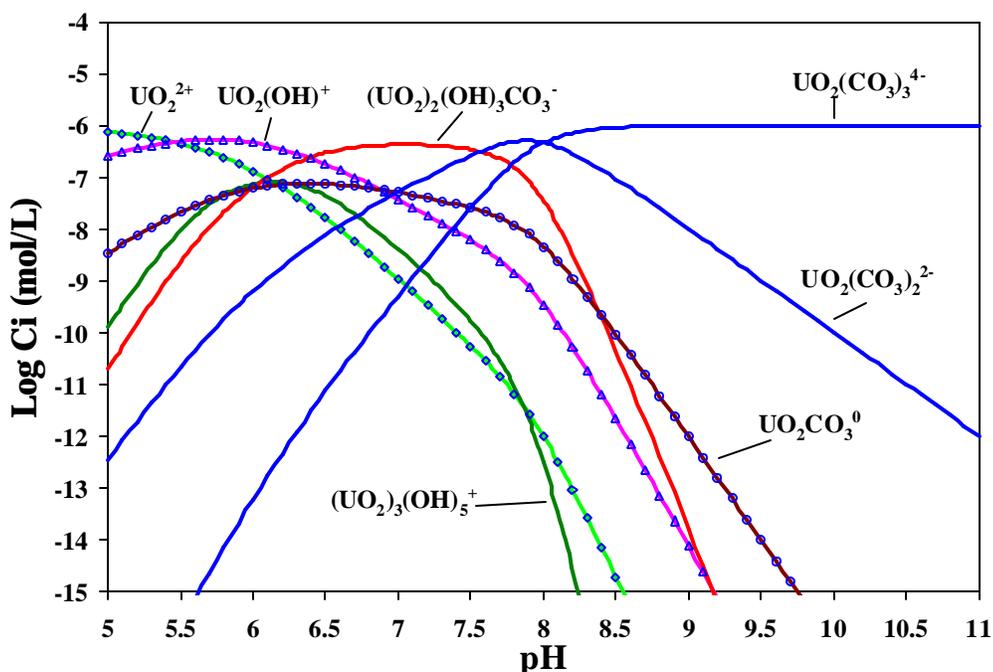


Figure 10 U(VI) speciation in calcium-free solution with an U(VI) concentration of 1.0×10^{-6} mol/L under $I = 0.05$ mol/L, $P_{\text{CO}_2} = 10^{-3.5}$ atm and 22.5°C . The complex constants of all U(VI) species from Grenthe et al (1992) and Kalmykov and Choppin (2000).

C. Diffusion cell studies:

The design of two alternative diffusion half-cell systems has been completed. Preliminary experiments during system design were conducted using 1-millimeter-diameter glass beads and microbeads (whose diameter was estimated to be $< 0.2\text{mm}$) as trial materials and using two types of deep-colored chemicals as diffusion tracers. The two diffusion cell setups were then compared in regard to their ability to achieve good mixing and uniform concentration of an adjacent bulk-solution phase while still avoiding convective water flow within the diffusion cell (i.e., the adjacent porous medium). In one setup, the diffusion half-cells were short plexiglass columns that were packed with porous media, pre-saturated with diffusant-free aqueous solution, and then immersed into a large reservoir containing a constant concentration of the diffusant -- i.e., the dye that was intended to simulate eventual presence of U(VI) dissolved species (Cormenzana et al., 2003). In the other setup, the diffusion half-cell comprised a glass chromatography column that was packed with porous medium and pre-saturated by means of advective flow of diffusant-free water through the column. After pre-saturation, one end of the column is sealed off and a bulk-solution reservoir created at the end chamber between the inlet fittings and the top filter at the other end of the column. Diffusant solution at constant concentration was then circulated through this bulk-solution reservoir (end chamber) by means of continuous recirculatory pumping from a large reservoir. The first type of setup has been selected to be experimented on in our future studies.

Initial experiments will be conducted at higher pH values in order to have lower sorption and more readily measured diffusion. Based on our a priori modeling of sorption-retarded diffusion, we estimate the required diffusion period to be roughly 90-200 days for the given diffusion cell lengths and the intended conditions ($\text{pH} = 8.5$ to 10) and. This estimate is also

based on U(VI) detection limits and sizes of porous media “slices” that will be taken at the conclusion of the experiment.

For preliminary diffusion studies, we intend to maintain constant aqueous chemistry throughout the porous medium for the full duration of the study. Therefore, in addition to the design and testing of the diffusion cell setups, we have also developed methods of pre-saturating and “washing” (pre-equilibrating) the porous medium in order to ensure that pore water chemistry will remain in accordance with that of the reservoir water during the diffusion period. The soil in the diffusion cell will be washed four times using calcite-saturated water ($I=0.05$ mol/L, open to air, $P_{\text{CO}_2}=10^{-3.5}$ atm) at the intended pH, consistent with the washing procedure that was previously used in the batch sorption studies. Methods of air expulsion from the soil, of soil sectioning and of extraction of U(VI) in different portions of the soil system have also been developed (Protocol G), and operation of the diffusion cell columns has been started.

III. Conclusions (based on three objectives):

A. The role of aqueous speciation and surface complexation

The results of the batch studies are generally consistent with currently available models of U(VI) aqueous speciation and the hypothesis that sorption is dominated by surface complexation. Generally, we expect that the solids-specific sorption isotherms developed in this portion of the work will provide accurate means of estimating solid-water distribution for HFSC and its components over a wide range of water quality conditions (pH, alkalinity, total carbon content, and ionic strength). These will provide a solid foundation for subsequent development of coupled transport models.

One somewhat unexpected and important finding is that sorption to solid carbonate species could be important to consider in its own right, and that these solids may also play a role in affecting sorption to other types of surfaces. In the latter regard, some of the evidence for increased sorption after carbonate removal suggested that calcite may have blocked access to higher-affinity surface sites for U(VI).

In addition, our results provide valuable new experimental evidence for the role played by di-calcium tri-carbonato species in calcite-saturated solution. In particular, these species are shown to have an especially important affect on sorption in the pH between 7.2 and 8.4 under conditions in equilibrium with HSC solids. Our observations show that, for the calcite-saturated aqueous condition, the sorption of U(VI) on the original HSC and its sub-fractions exhibited a maximum sorption at $\text{pH} = 8.4 \pm 0.1$, with decreased sorption at both lower and higher pH values. The results in the range of pH 7.2 to 8.4 are in stark contrast with results in the calcium-free systems in the same pH range. Speciation modeling (based on thermodynamic data from other investigators) indicates that the aqueous species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ dominates at pH below 8.4, suggesting that this species is responsible for the lesser sorption in this pH range. Our proposed explanation is that the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species do not as strongly associate with the amphoteric edge sites on detrital phyllosilicates to form surface complexes. This is in contrast to the situation in calcium-free solutions, where U(VI) showed strong sorption at pH below 8.4. We propose that the hydroxycarbonate and carbonate species (which dominate under these calcium-free conditions) reacted with amphoteric edge sites on detrital phyllosilicates to form inner-sphere surface complexes. Finally, our results with unmodified HSC and *initially* calcite-free solution demonstrate that the calcite present in HSC can dissolve to form a concentration of aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ that is sufficient to inhibit U(VI) sorption.

Overall, our results provide important empirical results necessary for subsequent work involving Hanford subsurface sediments and also represent important new evidence for the role

of carbonate solids and dissolved calcium in ground water that is at equilibrium with calcite minerals.

B. The relative roles of silt/clay and sand fractions in regard to macroscopic sorption intensity.

As expected, overall sorption is shown to be an additive effect from the silt/clay and the sand fractions. Although the silt/clay fraction of HSC was confirmed to be the dominant sorbent at $\text{pH} < 9$, the sand fraction was found to also provide a significant contribution to sorption at $\text{pH} > 9.0$.

C. Sorption and desorption rate in laboratory-spiked (initially pristine) sediments

Sorption equilibrium of U(VI) on the silt/clay fraction of HSC was found to be established rapidly (in 30 minutes). The sorption and desorption of U(VI) observed was shown to be essentially reversible for HSC and its sub-fractions, and the K_d of U(VI) sorption was found to be independent of the solid/solution ratio. These results all tend to support the hypothesis that equilibrium sorption will be applicable under many transport scenarios involving the diffusion or slow advection of uranium past initially pristine sediments.

Plans for Next Year:

Planned activities for the next year are to use the HFSC sample (and selected fractions thereof) in both batch studies of U(VI) sorption and in diffusion studies of coupled sorption and transport. Our initial focus will be on the silt/clay fraction of the HSC material, for which an investigation of the coupled effects of surface complexation and diffusion will be carried out in the coming months using our developed diffusion half-cell system. The preliminary results from these studies will further our understanding of the magnitude of sorption, test our understanding of concentration effects on extent of sorption (i.e., test our preliminary findings of approximately linear isotherms), and help us evaluate whether accurate predictions can be made when the “local equilibrium” assumption is used to couple pure diffusive mass transport with sorption. We expect that initial experimental observations may indicate the need for improvements in the design of our experimental methods and diffusion cell system. If so, the preliminary experiments (coupled with continued literature review) will be used to guide the experimental modifications and continued experimentation.

In order to support numerical modeling of the results in the aforementioned studies, we will also be (1) conducting batch U(VI) sorption experiments in a high pH range to obtain pH isotherms, and (2) developing, in collaboration with Dr. C. Liu of PNNL, numerical models of diffusion and transport that include appropriate formulations for accounting the effects of U(VI) speciation and surface complexation. We currently envision the diffusion-cell experiments to involve studies with the silt/clay fraction and the original HSC sample to inspect the effect of pH at fixed p_{CO_2} and ionic strength, and the effects of ionic strength and p_{CO_2} at fixed pH. Several pH values have been chosen according to the sorption isotherms and sorption edge curves we have already obtained from batch studies.

On the basis of the diffusion cell results, the batch sorption experiments, and the initial modeling of these results, subsequent work will then be designed for possible further investigation with both types of materials (HSC and HFSC). Such efforts may include the study of combined sorption and mass transfer effects on advective transport in columns, including study of transport through the more coarser material (HFSC) and transport through either this material or a more idealized medium (e.g. glass or plastic bead medium) under conditions that are influenced by diffusion to and from a surrounding medium of the HSC. These latter studies are referred to as “macropore” studies, and have been previously applied in our laboratory for

the study of coupled sorption and diffusion of organic contaminants (Young and Ball, 1998; Young and Ball, 2000).

References Cited:

- Barnett, M.O. Jardine, P.M., Brooks, S.C., 2002. U(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. *Environ. Sci. Technol.*, 36: 937-942.
- Cormenzana, J.L., Gutierrez, M.G., Missana, T. and Junghanns, A., 2003. Simultaneous estimation of effective and apparent diffusion coefficients in compacted bentonite. *J. Contam. Hydrol.*, 61: 63-72.
- Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A., Xu, N., 1994. Uranium(VI) adsorption to ferrihydrite—application of a surface complexation model. *Geochim. Cosmochim. Acta*, 58: 5465-5478.
- Grenthe, I., J. Fuger, et al., 1992. Chemical Thermodynamics of Uranium, North-Holland Elsevier Science.
- Kalmykov, S. N. and Choppin, G. R., 2000. Mixed $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$ complex formation at different ionic strengths. *Radiochim. Acta*, 88: 603-606.
- Young, D.F. and Ball, W.P., 1998. Estimating diffusion coefficients in low-permeability porous media using a macropore column. *Environ. Sci. Technol.*, 32: 2578-2584.
- Young, D.F. and Ball, W.P., 2000. Column experimental design requirements for estimating model parameters from temporal moments under nonequilibrium conditions. *Adv. Water Resour.*, 23: 449-460.
- Zachara, J.M., Smith, S.C., Liu, C., McKinley, J.P., Serne, R.J., Gassman, P.L., 2002. Sorption of Cs+ to micaceous subsurface sediments from the Hanford site, USA. *Geochim. Cosmochim. Acta*, 66: 193-211.