

**US Department of Energy, Office of Science
Office of Biological and Environmental Research (BER)
Environmental Remediation Science Division (ERSD, now CESD)
FY10 Second Quarter Performance Measure**

The second FY10 ERSD overall Performance Assessment Rating Tool (PART) measure for Pacific Northwest National Laboratory is to *‘Provide a report that describes the development of a field scale reactive transport simulator from laboratory scale studies that includes kinetic adsorption/desorption processes’*. This milestone is focused on research being performed at the Hanford Integrated Field Research Challenge (IFRC) site, located in the 300 Area of Hanford Site in southeastern Washington State. The 1600 m² Hanford IFRC site contains 36 groundwater monitoring wells placed within the footprint of the historic South Process Pond where uranium fuels-fabrication wastes were discharged. A 2 km² U(VI) groundwater plume exists at this location that exceeds regulatory limits. Uranium concentrations in the plume show complex seasonal changes that have not been predictable with any model applied. DOE is trying to identify a suitable and effective remedial strategy for the site.

The Hanford IFRC seeks to understand fundamental interactions between hydrologic, geochemical, and microbiologic processes that control uranium behavior in the plume with an emphasis on mass transfer. Mass transfer is a critical process controlling the longevity of the U plume, and involves the rate of U exchange between grain interiors and bathing fluids, and between less permeable and more permeable sediment facies. This understanding is developed through comprehensive field characterization, injection experiments with non-reactive tracers and different uranium concentrations, and monitoring experiments during periods of hydrologic transients and water table oscillations. An important aspect of the research is the development of model that can describe the field scale behavior of uranium, including geochemical reactions with vadose and saturated zone sediments, and advective and diffusive transport over multiple spatial scales. This model is needed to: i.) pre-model planned field experiments to optimize their design, ii.) simulate field experimental results to document system scale understanding, and iii.) integrate understandings and descriptive parameters for complex interactive processes over multiple scales.

In this, the second of four quarterly PART reports, we describe the development of a reactive transport simulator for uranium at the Hanford IFRC site that includes kinetic adsorption/desorption controlled by surface complexation and mass transfer. The model is initially based on laboratory experimentation, but it will evolve through application to, and calibration with, field experimental results. The model will be used in conjunction with a series of well-controlled laboratory and field experiments to evaluate hypothesis-driven research on uranium mass transfer and reactive transport processes at the site.

Introduction

Reactive transport models are an important tool to simulate how chemical agents move through subsurface systems (Steeffel et al., 2005). A sizeable literature base exists on

their development and application. These models generally integrate advective fluid flow with geochemical reactions including aqueous speciation, precipitation/dissolution, and/or surface complexation. They are an important tool because they integrate multiple processes whose individual or interactive behaviors may be non-linear, non-intuitive, and difficult to visualize. Both equilibrium and equilibrium/kinetic models exist that vary in sophistication. Other processes including diffusion, microbiologically driven reactions, colloid transport, or permeability changes may be included. The development of a reactive transport model for a given site generally involves the five following activities: i.) conceptual model development, ii.) process model development and parameterization, iii.) site characterization and development of geochemical and physical heterogeneity models; iv.) integration of heterogeneity models into a generic reactive transport code such as STOMP or PFLOTRAN, v.) field site application and calibration, and vi.) experiment or scenario simulation.

In this report we will emphasize the first two activities noted above, namely the development of a site conceptual model and parameterized process models for field scale application. The remaining aspects of reactive transport model development for the Hanford IFRC site will be discussed in reports for the final two interim measures. A report describing how physical and hydrologic properties have been characterized at the IFRC site for the purposes of developing a physical heterogeneity model was submitted as the first report in this series.

Conceptual Model Development

A conceptual model is a definition of key processes and boundaries within a given site that are believed to control water movement and chemical flux (Davis et al., 2004). A combination of field observations and laboratory experiments are used to define the conceptual model. The model, in turn, evolves in accuracy and detail as more is learned about the site, and properties of its contained materials defined through various types of characterization measurements. The conceptual model forms the basis or framework for numeric process and site simulation models that are parameterized through laboratory and field measurements.

A conceptual model of geochemical processes within the greater 300 A U-plume environment and the IFRC site has resulted from ERSP-supported laboratory study of sediments excavated from within the North and South Process Ponds (Figure 1). The collection and description of these materials is given by Zachara et al., (2005). This model has been difficult to establish because contaminant U concentrations in many of the sediments, with some notable exceptions, have been too low (< 50 mg/kg) to allow successful interrogation by X-ray absorption spectroscopy for definitive establishment of molecular speciation. However, a combination of wet chemical, spectroscopic (x-ray absorption and laser-induced fluorescence spectroscopy), and analytical electron microscopic analyses has provided important insights.

The resulting conceptual model concludes that contaminant U(VI) exists primarily in the precipitated state at shallow depths near the historic source term, and as adsorption or

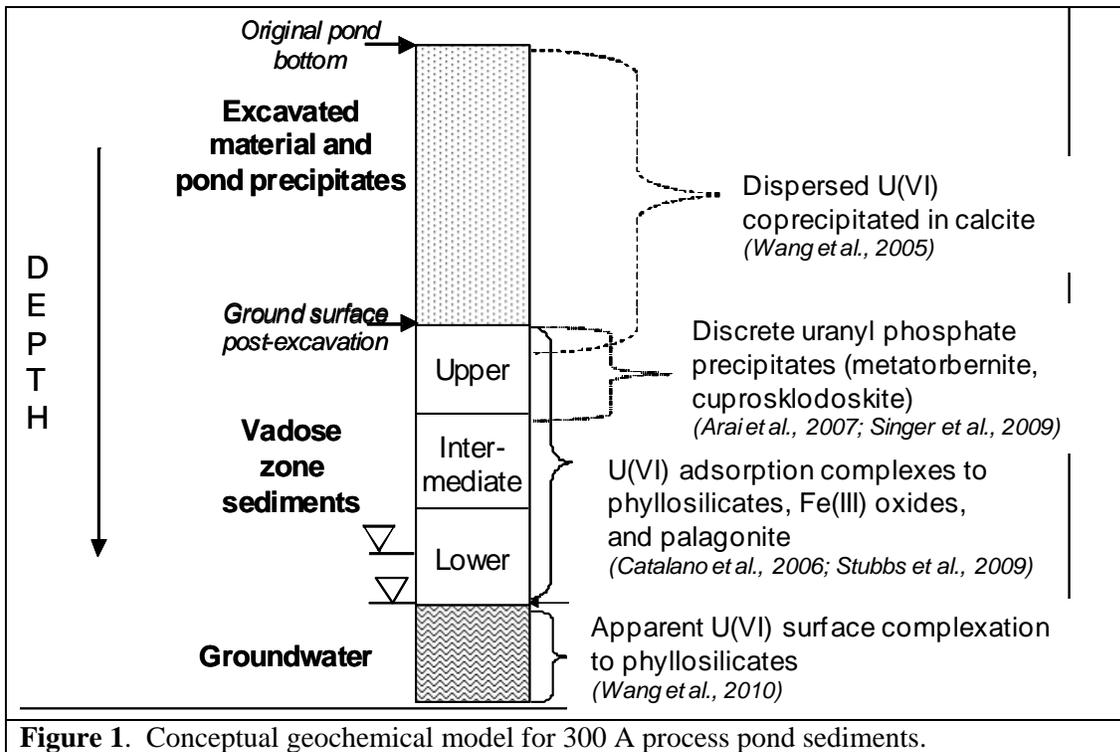


Figure 1. Conceptual geochemical model for 300 A process pond sediments.

surface complexes deeper in the vadose zone and the aquifer sediments. These different speciation states require different reaction series to describe their solid-liquid distribution. The upper 4m of contaminated pond and vadose zone sediments that contained >500 mg/kg of sorbed U(VI) have been excavated, removed, and replaced with backfill. Because vadose zone recharge is minimal at the semi-arid IFRC site, the primary reaction domains of interest are the lower vadose zone that experiences seasonal saturation from water table rise, and the aquifer sediments that host the groundwater U plume.

The research noted above and ongoing characterization measurements of IFRC site sediments indicate that U(VI) surface complexes distributed between multiple mineral phases represent the primary repository of sorbed, contaminant U(VI) within the hydrologically active domains of the site. Moreover, size fractionation studies with site sediments have revealed that sorbed contaminant U exists almost exclusively within the < 2mm size fraction of the sediment that represents, on average, from 15-25% of the field textured material. Consequently reactive transport model development has focused on the < 2mm fraction with surface complexation as the dominant reaction mechanism controlling U(VI) solid-liquid distribution, and migration. Both the forward (adsorption) and reverse (desorption) directions of the reaction are important.

Process Model Development and Parameterization

Approach

Here we describe the development of a reactive transport model for field scale application based on a bottom-up or reductionistic approach. The first step involved the parameterization of an equilibrium surface complexation model (SCM) based on

laboratory batch contaminant U(VI) desorption measurements on the < 2mm sediment size fraction over long time. In the second step, a stirred-flow reactor system was used to develop time series data on U(VI) desorption from the < 2 mm sediment, and a multi-rate mass transfer model (MTM) linked with the SCM (multi-rate SCM; MRSCM) was evaluated for its ability to describe the resulting kinetic data. The multi-rate model is described by three parameters, along with the extent of adsorption/desorption disequilibrium. Dynamic desorption/adsorption experiments with advective water flow (IFRC-SGW) were then performed with three intact, saturated zone cores where the < 2 mm fraction was present at in-situ mass concentrations of approximately 20%. The MRSCM, developed from the stirred-flow reactor studies, was then applied to, and recalibrated with U(VI) effluent data from the three intact cores with in-situ texture. Both single and multiple domain variants of the MRSCM were evaluated. The resulting parameters from the three cores were compared to one another to assess the apparent heterogeneity of “in-situ” reactivity. The MRSCM was then embedded in the 3-D STOMP reactive transport code (RTC), and a 1-D transport scenario relevant to the IFRC site was modeled to determine if computed behaviors conform to the test of intuition and reason. Details for each of these steps are given below.

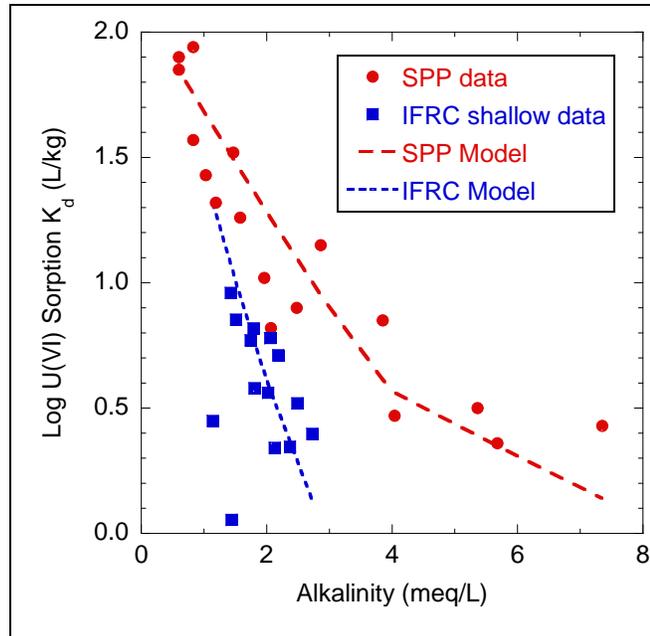


Figure 2. Experimentally determined and model-calculated U(VI) adsorption on IFRC composite sediments (IFRC data and Model, respectively). For comparison, experimentally determined and model-calculated U(VI) adsorption on vadose-zone sediments from previous excavations in the South Process Pond (SPP) are also shown (Bond et al., 2008). Model lines are spline fits through model-computed adsorption points, which exhibit a degree of scatter similar to the scatter in the experimental data. This scatter originates from minor differences in chemical conditions other than alkalinity.

Surface Complexation Model (SCM)

Batch desorption experiments were conducted with the < 2 mm fraction of U(VI)-contaminated sediments collected from the lower vadose zone and saturated zone at six locations within the IFRC experimental domain to provide a data base for SCM development and calibration. The composite sediments were created to be representative of the different hydrogeologic facies that exist at the site as shown by geologic, hydrologic, and geochemical/physical characterization. The principal aim of these experimental measurements was to calibrate a model that describes equilibrium adsorption of U(VI) on IFRC sediments over the full range of aqueous geochemical conditions which may exist given differences in groundwater and river composition. Desorption of adsorbed contaminant uranium required at least 1000 hours to reach an

approximate steady state condition, which is a long time. As expected, uranium adsorption generally decreases with increasing alkalinity (Figure 2).

Uranium adsorption data for all IFRC composite sediments were combined and fitted to various composite surface complexation models. The models assume the presence of a generic surface site (SOH) with unspecified mineralogic residence. The modeling approach followed that used previously for SPP vadose-zone samples (Bond et al., 2008). The highest quality fits were obtained using either reaction 1 or 2 in Table 1, with reaction 1 providing a significantly better fit as measured by the weighted sum of squares of the residuals divided by the degrees of freedom (WSOS/DF). Previous research on excavated vadose zone samples from the South Process Pond (SPP) showed that the best fit was obtained with a model that included both reactions in Table 1. Model fits for the current IFRC data set were not markedly improved by using any two-reaction model that included reaction 1, which is to say that reaction 1 accounted for the observed compositional variability in U(VI) adsorption. However, it is possible that data collected at the higher end of the range of alkalinities applicable to the Hanford 300 area will require a two-reaction fit. Indeed, a two-reaction fit was required for the intact core experiments discussed subsequently in this report.

Table 1. Results from the best-fit surface complexation model for the IFRC composite sediments.

Number	Reaction(s)	Log K	WSOS/DF
1	$\text{SOH} + \text{UO}_2^{2+} = \text{SO-UO}_2\text{OH} + 2\text{H}^+$	-4.56	4.8
2	$\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = \text{SO-UO}_2\text{HCO}_3 + 2\text{H}^+$	-0.87	13.9

The K_d values for the IFRC composite sediments were significantly lower than those obtained previously for vadose-zone sediments from the SPP (Figure 2). Fits to the U(VI) adsorption data for the SPP vadose-zone samples using only reaction 1 (Table 1) yielded a log K value of -4.43 (J. A. Davis, oral communication). This value is not significantly different than the corresponding value for the IFRC sediments which include materials from the saturated zone, indicating that the two sets of samples have a similar intrinsic U(VI) adsorption affinity. Specific surface areas for the SPP vadose-zone samples were 15 to 26 m^2/g . In contrast, specific surface areas for the IFRC composites were 9 to 12 m^2/g . Thus, higher K_d values for the SPP samples result from higher specific surface areas and, therefore, higher adsorption site concentrations.

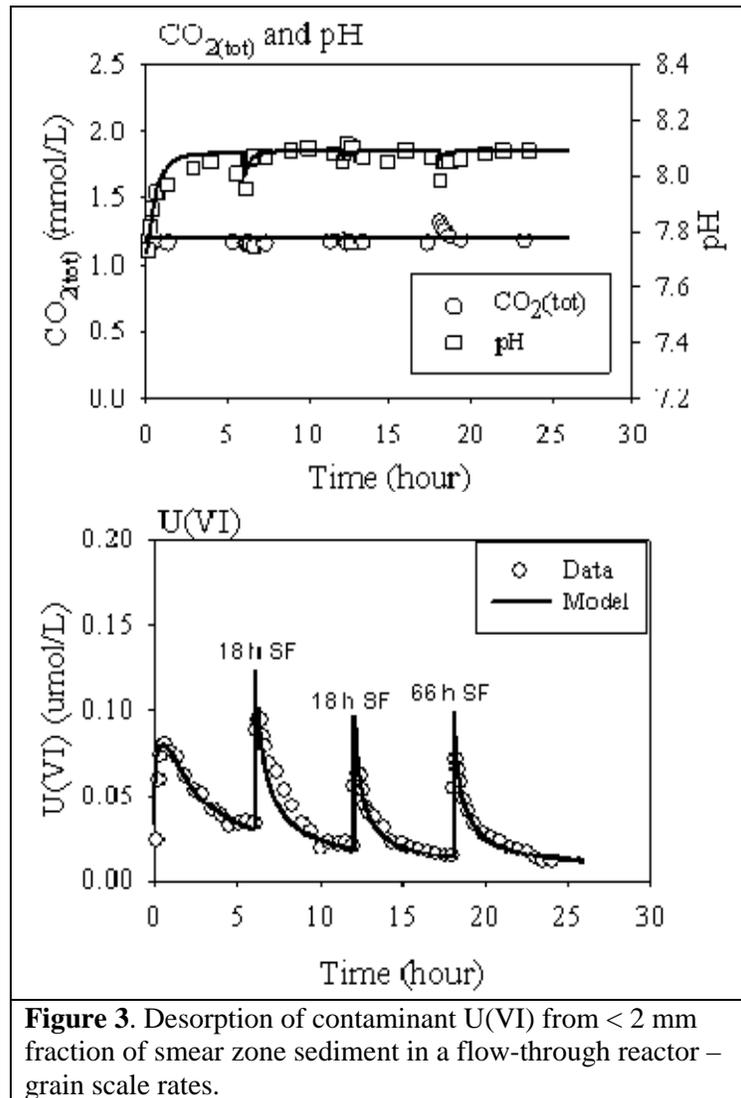
Additional experiments are underway to better constrain surface complexation model fits, and establish statistics (probability density function) for log K. These experiments will span a much larger range of alkalinity values and adsorbed and dissolved U concentrations than has been previously used. Results of these experiments will also allow SCM's to be obtained for each individual composite sample in order to quantify spatial variability in adsorption properties of sediments within the IFRC site. In the next step of model development, site-wide correlations will be developed between K_d , surface area, and grain size metrics to allow development of a heterogeneity model of surface complexation site concentration.

Mass Transfer Model (MTM)

Because of the long time-period observed for contaminant U desorption in batch experiments (e.g., >1000 h), stirred flow reactor studies were performed to quantify contaminant U desorption kinetics from the < 2 mm fraction. The experiments involved the placement of a small sediment mass (~1.5 g) in a 12 mL flow reactor containing synthetic site groundwater (SGW) where extra-particle transport processes are minimized by stirring. Sediment remains in the reactor, while SGW is allowed to pass through the reactor at a controlled steady rate, carrying away U(VI) that is released from the sediment by kinetically controlled desorption. The apparatus enables measurement of intra-grain mass transfer rates and desorption kinetics.

Uranium and other analytes were measured in the exiting SGW yielding time series data (Figure 3) for kinetic analysis. Generally, desorbed U(VI) concentrations decrease with time as SGW passes through the reactor, removes desorbed U, and reduces the total adsorbed U inventory. At certain time points (6, 12, and 19h), SGW flow through the reactor was stopped for either 18h or 66h to present different time-scales for the kinetic desorption process. During these “stop-flow” periods, U(VI) concentrations in the fluid-phase were observed to increase as a result of diffusion from grain interiors, while major ion concentrations in SGW (dissolved CO₂ and pH) remained relatively stable.

The data were modeled with a multi-rate U(VI) surface complexation model (MRSCM) linked with ion exchange (Table 2; Liu et al., 2009). Ion exchange controls aqueous Ca²⁺ and Na⁺ concentrations, which in turn, influence U(VI) speciation and the concentration of reactive species-“UO₂²⁺” (e.g., Tables 1 and 2). The kinetic desorption process is believed to result from diffusive mass transfer of U from adsorption sites in grain interiors residing in fractures and poorly connected pore space. In the model, the



mass transfer effect is described as a consequence of a log-normal distribution of adsorption sites with each exhibiting a different first order desorption rate. The driving force for mass transfer is desorption/adsorption disequilibrium ($Q_k - q_k$; Table 2, Liu et al., 2009).

The model provided excellent description of the experimental data (Figure 3) using the surface complexation reactions in Table 1, and by adjustment of the log-normal site distribution and magnitude of first order rates. Continuing research is repeating these measurements and modeling activities on a suite of representative materials from the IFRC site to develop a data base of mass transfer model parameters for statistical analysis and eventual use in reactive transport modeling activities.

Table 2. Multi-rate surface complexation model as applied to time-series data from the stirred-flow reactor study of < 2 mm sediments.

<p><u>Reactions:</u></p> <p>Surface complexation $>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+$ $>SOH + UO_2^{2+} + CO_3^{2-} = >SOUO_2HCO_3$</p> <p>Ion exchange $Ca^{2+} + 2NaX = CaX_2 + 2Na^+$ $Mg^{2+} + 2NaX = MgX_2 + 2Na^+$ $H^+ + NaX = HX + Na^+$</p>	<p><u>Multi-Rate SCM:</u></p> $\frac{\partial C_i}{\partial t} + \frac{(1-\theta)\rho_s}{\theta} \sum_{j=1}^{N_s} \left(a_{ij} \sum_{k=1}^{M_j} \frac{\partial q_j^k}{\partial t} \right) = L(C_i), \quad i = 1, 2, \dots, N$ $\frac{\partial q_j^k}{\partial t} = \alpha_j^k (Q_j^k - q_j^k), \quad j = 1, 2, \dots, N_s; k = 1, 2, \dots, M_j$ $L(C_i) = F(C_i^{in} - C_i)/V$ <p>Where C_i is the total aqueous concentration of chemical component i (mol/L); q_j^k is the concentration of adsorbed species j at adsorption site k (mol/kg); a_{ij} is the stoichiometric coefficient of chemical component i in adsorbed species j; θ is the porosity; ρ_s is the solid density (kg/L); N is the total number of chemical components in aqueous phase; N_s is the total number of adsorbed species; M_j is the total number of adsorption sites for adsorbed species j; α_j^k is the rate constant of adsorbed species j at site k (h^{-1}); and Q_j^k is the adsorbed concentration of species j at site k (mol/kg) in equilibrium with aqueous solution. $L(C_i)$ is the transport term where F is the flow rate (mL/hour), V is the aqueous volume of the flow cell reactor (mL), and C_i^{in} is the total concentration of chemical component i in the influent solution.</p>
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Parameterization of a Reactive Transport Model

Reactive transport experiments were performed with three intact cores from the upper, middle, and lower IFRC saturated zone (Figure 4). The individual core sections were selected to represent the three prominent facies types that our field hydrologic characterization measurements have shown to be present in the IFRC domain. The core sediments were field-textured and quite coarse, consisting of a matrix of river cobble with infilling sands and minor silt (e.g., < 2 mm material, Figure 5). Unexpectedly, all three columns/cores displayed comparable, if not identical behavior with respect to U(VI) release and retardation, and, for that reason, only one (ICE-1) will be discussed here. The absence of significant differences between the three cores was a good finding in that it implies that the reactive transport properties of the saturated zone are relatively homogeneous.



Figure 4. Experimental apparatus for intact core experiments including perfusion pumps, synthetic groundwater reservoir, 4” intact core with pressure transducers, and fraction collector for effluent sampling.

The experiments were run with three phases: A – desorption of in-situ contaminant U(VI), B – transport of non-reactive tracers (Br and PFBA) with continued contaminant U(VI) desorption, and C – adsorption and desorption of a 60 ppb U(VI) pulse. Qualitatively, the core experiments revealed rapid breakthrough through preferential flow-paths created during core collection, and strong retardation to fines (< 2mm size fraction) that were a minor physical component (~25 %) of the sediment. The tracer (Br and PFBA) and U effluent data were modeled with single (Qafoku et al., 2005) and dual-domain (Liu et al., 2008) advective transport models. The MRSCM was embedded in both domain models. A K_d adsorption model was also used in the dual-domain model for transparency. These models were previously developed for < 2mm and field-textured 300 A sediments from the North Process Pond. The more complex, dual domain transport model contains two porosity domains: mobile porosity associated with rapid advective flow (~75%), and diffusion-limited immobile porosity (~25%) associated with lithic fragment interiors and aggregated layer silicates. Adsorption sites in the immobile domain are slow to react (both through adsorption and desorption) as a result of mass transfer limitations to the mobile, advective domain.

The models provided a good description of the non-reactive tracer behavior (Figure 6). Only the dual domain results are shown in Figure 6, with model parameters summarized in Table 3, but both transport models could describe the non-reactive tracer data with equal accuracy. The estimated mass transfer coefficients (ω) for Br were larger than that for PFBA. This was consistent with a diffusion mechanism as the control of mass exchange between the mobile and immobile domains. Diffusive mass exchange was predicted to be faster for a species with a larger diffusion coefficient (Br) than for a species with a smaller diffusion coefficient (PFBA). The molecular diffusion coefficient ratio of Br versus PFBA is 2.67. The estimated ratio of the mass transfer coefficients of Br versus PFBA was 8.13, indicating that the mass transfer coefficient of a species was not simply scaled to its molecular diffusion coefficient.

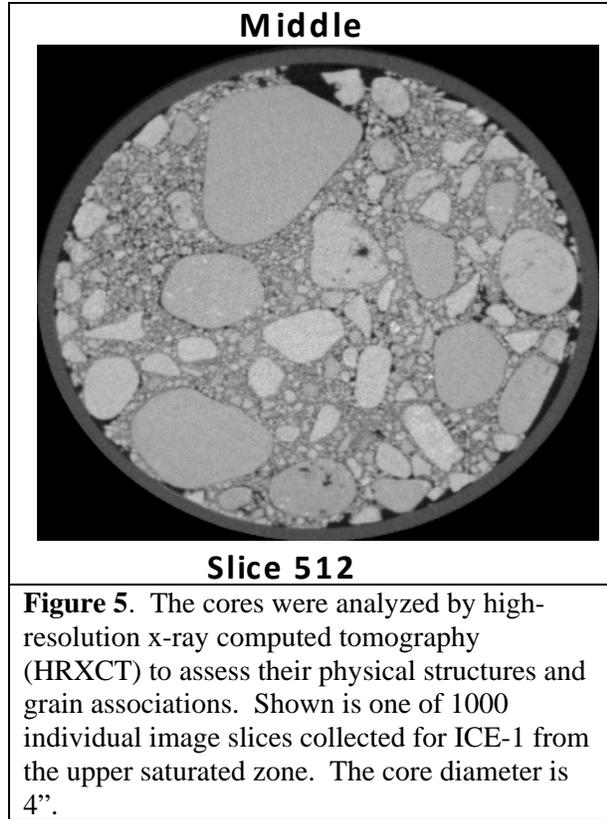


Figure 5. The cores were analyzed by high-resolution x-ray computed tomography (HRXCT) to assess their physical structures and grain associations. Shown is one of 1000 individual image slices collected for ICE-1 from the upper saturated zone. The core diameter is 4”.

Table 3. Parameters used in modeling tracers and U(VI) adsorption/desorption for ICE 1.

Pore water velocity, v	10.36	cm/h	measured
Total porosity, θ	0.30		measured
Dispersion coefficient, D data	55.2	cm ² /h	PFBA and Br effluent
Mobile porosity, θ_m data	0.24		PFBA and Br effluent
Immobile porosity, θ_{im} data	0.06		PFBA and Br effluent
Mass transfer coefficient, ω	1.82×10^{-2}	h ⁻¹	PFBA effluent data
	1.48×10^{-1}	h ⁻¹	Br effluent data
Sediment bulk density, ρ_b	1.91	kg/L	independently estimated
<2 mm size mass fraction	22.3%		independently estimated
<2 mm size bulk density, ρ_b^f	0.43	kg/L	independently estimated
Labile U(VI) in < 2mm size fraction	210	ug/kg	independently estimated
Equilibrium constant for species >SO ₄ O ₂ OH (log K1)	-5.1		from U desorption data
Equilibrium constant for species >SO ₄ O ₂ HCO ₃ (log K2)	-0.9		from U desorption data
U distribution coefficient, K_d	9.4	mL/g	from SCM
Logarithm mean of rate constant, μ	-5.7	log(h ⁻¹)	from U desorption data
Deviation of log rate constant, σ	2.3	log(h ⁻¹)	from U desorption data

The dual domain MRSCM along with its K_d counterpart model well described the ICE-1 effluent U(VI) concentration in all phases (A, B, and C; Figure 7) with the same set of the parameters. The behavior of long-term contaminant U, and short-term spike U could thus be described with the same parameter set, indicating that they were both accessing the same set of surface sites and were subject to the same kinetic constraints. The < 2mm size fraction was assumed to be the only solid reactive fraction that was distributed between domains with mobile and immobile water. The model further assumed that uranium desorption in the immobile domain involved a two step mass transfer processes: from the < 2 mm solid to aqueous phase in the immobile domain, and from the immobile aqueous to mobile aqueous domains. The U(VI) desorption in the mobile domain only required one step, mass transfer from the < 2 mm solid to aqueous phase. Data from the other two intact cores were equally well described, but with slightly different parameter sets. The common, one domain model provided somewhat inferior simulations of U(VI) breakthrough for all three cores, but captured their essential trends.

Adsorption was formulated as the reverse of the surface complexation desorption processes, as described by the two surface complexation reactions in Table 3. Some refitting of log K (as compared to Table 1) was required because the surface area of the < 2 mm fraction of the core sediments was unknown at the time of modeling. The mass exchange rate of aqueous U(VI) between mobile and immobile phases was described using a multiple first-order rate expression (with μ and σ being key parameters, Table 3) with respect to the deviation of U(VI) adsorption from its equilibrium state $[(Q_j - q_j)$ Table 2; Liu et al., 2009]. The cores have now been deconstructed, and sieved to < 2mm and > 2mm. Physical and geochemical characterizations are underway on the sediments, and the results will enable more accurate estimation of the surface

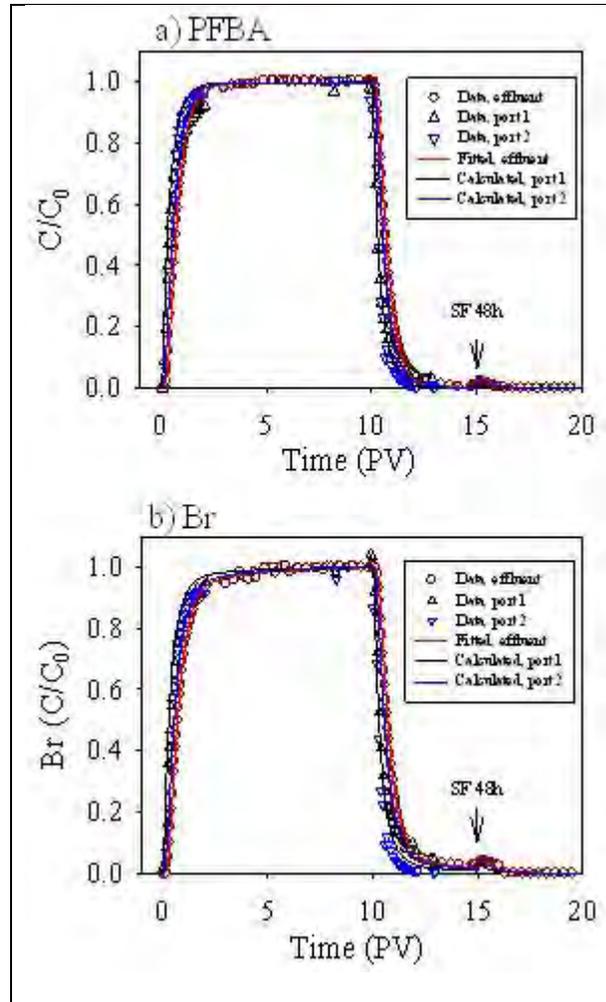


Figure 6. Measured and modeled breakthrough curves of PFBA (plot a) and Br (plot b) for Phase B of column ICE-1. SF denotes stop-flow event with SF duration noted in the plots. Sampling port 1 and 2 are 1/3 and 2/3 of the column length from the flow inlet end of the column. Measured and modeled breakthrough curves of PFBA (plot a) and Br (plot b) for Phase B of column ICE-1. SF denotes stop-flow event with SF duration noted in the plots. Sampling port 1 and 2 are 1/3 and 2/3 of the column length from the flow inlet end of the column, respectively.

complexation site concentration, log K, and intrinsic mass transfer rates of the <2 mm fraction.

IFRC Field Simulation

Although the dual domain MRSCM provided the best simulations of the intact core effluent data (Figure 7); the common, one domain model was embedded in STOMP for field scale application. This decision was made because it was felt that the physical parameters for the dual domain model (e.g., domain porosities and domain-specific mass transfer rates) might be too difficult or ambiguous to characterize in the field. Consequently, averaged, single domain reaction parameters for the three intact cores were used: $\mu = -8.6$ and $\sigma = 3.1$ (note that single and dual domain kinetic parameters are different), and $\log K1 = -5.2$ and $\log K2 = -1.0$.

The field simulations assumed that the IFRC site exhibited uniform porosity (19%), mass fraction of < 2mm sediment (22%), and initial U(VI) concentration (adsorbed U in equilibrium with 35 ug/L groundwater U). A simple three-layer hydraulic conductivity model was used for the saturated zone (intermediate-shallow, low-intermediate, and high-deep) as described in our first report.

Hydrologic boundary conditions for the simulation (heads around the IFRC periphery) were taken from those recorded during the first two weeks of November 2009. These conditions and properties will sequentially be made more realistic in future modeling scenarios that will be described in the next two reports. Model calculations evaluated two scenarios for a time period when in-situ dissolved U concentrations were 35 ug/L: i.) injection of 70,000 gallon of 5 ug/L U groundwater to evaluate in-situ U desorption, and ii.) injection of 70,000 gallon of 100 ug/L U groundwater to evaluate in-situ U adsorption.

The objective for the field simulations was to assess whether the computed breakthrough behavior was consistent with tracer movement known from past field experiments, and the degree

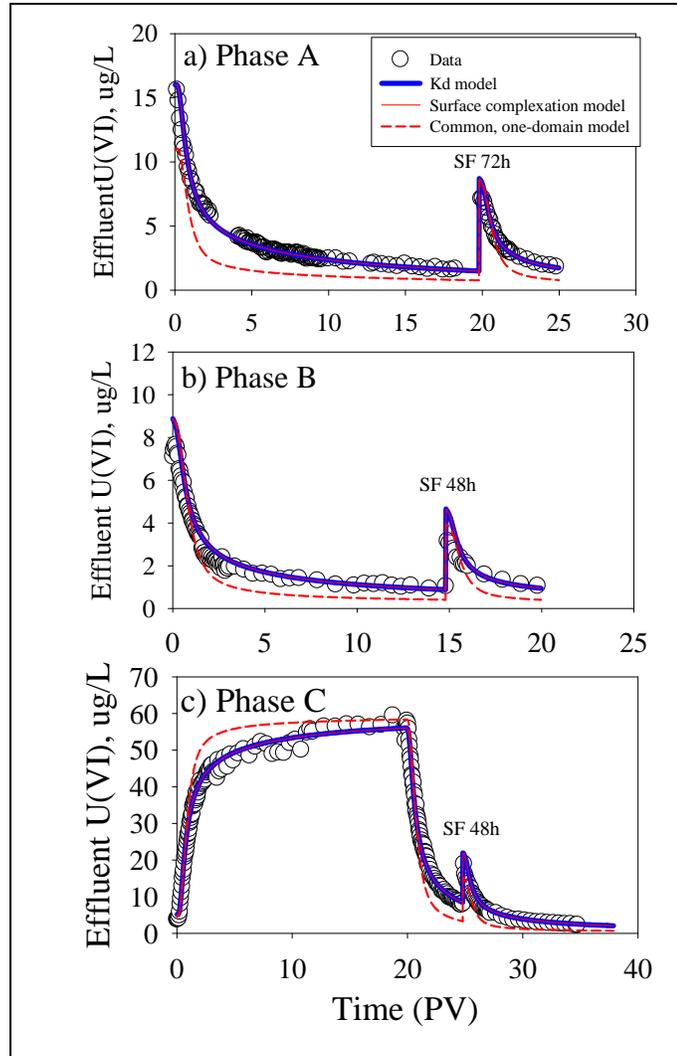


Figure 7. Measured and modeled breakthrough curves of U(VI) in desorption phase A (plot a), tracer breakthrough with desorption phase B (plot b), and adsorption/desorption phase C (plot c) in column ICE-1. Data in phase A was used to fit the U(VI) mass transfer parameters in the sediment. The mass transfer model with the fitted parameters was then used to predict the effluent U(VI) in phases B and C.

of retardation measured in the intact core experiments. Simulation results for the desorption and adsorption injection experiments are shown in Figure 8 for fully screened well 2-14 that is located 20 m from the injection well. Note that the IFRC experimental domain is 60 m in length. Both simulations display tracer (Br) breakthrough at approximately 5000 minutes with either a minimum or maximum in U(VI) concentration occurring at approximately the same time (Figure 8 a and c). The average linear “plume” velocity for both U and Br was approximately 5.8 m/day. The U(VI) peaks are significantly broadened from dispersion and variable transport velocities in the different hydraulic conductivity zones. There is also minimal retardation. These effects were anticipated from the intact core experiments. The right hand (b and d) plots for Figure 8 display the aqueous U concentration and the adsorbed U concentration on four surface sites varying in adsorption or desorption rate, where $R_6 > R_5 > R_4 > R_3$. The rates and concentrations of these surface sites were fitted from the intact core experiments. The experimental time-scale as determined by the groundwater flow velocity is sufficiently rapid that only the fastest rate sites, R6 and R5, desorb or adsorb over the time period of plume passage. These “fast” sites represent only 20% of the total site concentration. Thus the small extent of U retardation evident in the figures may be explained by the low concentration of fines in the system (22%), and a short experimental time-scale that only allows the participation of a small subset of surface complexation sites with the injected plume.

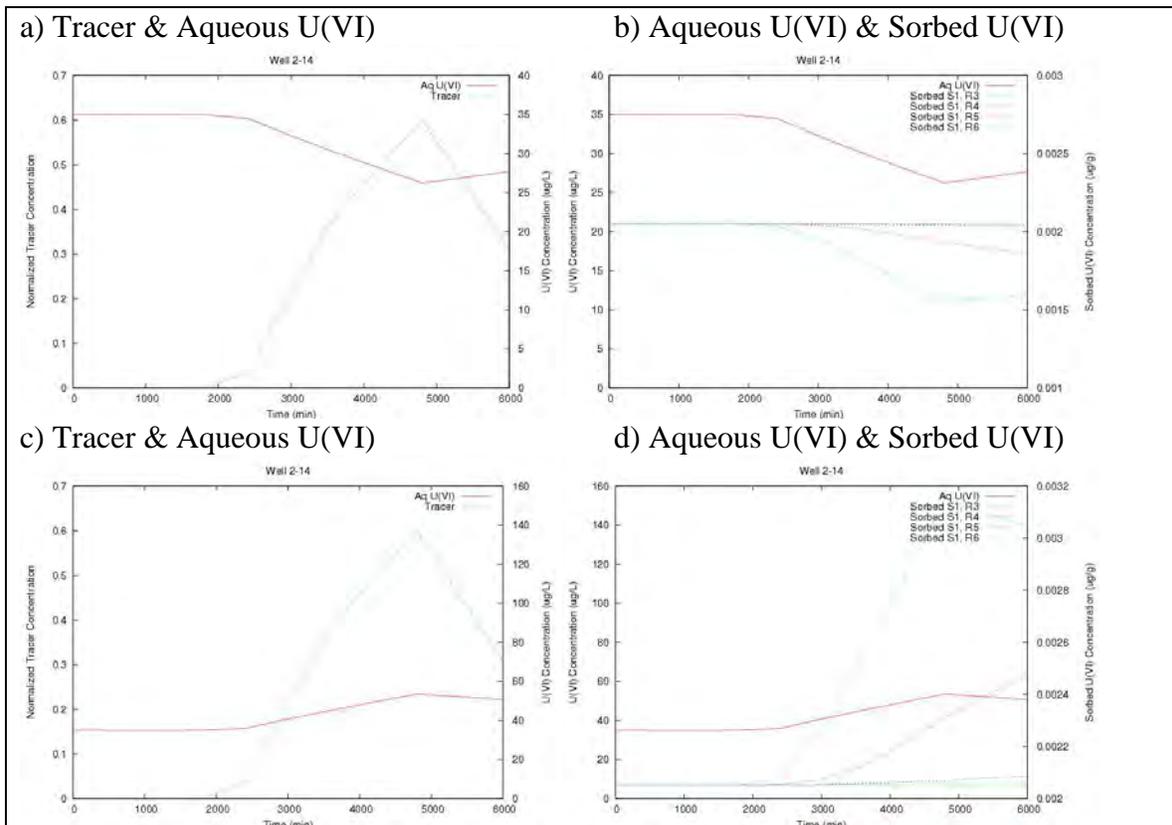


Figure 8. Simulated breakthrough behavior at well 2-14. (a) non-reactive tracer (Br⁻) and U(VI) following injection of a 5 µg/L pulse of U(VI) into well 2-9 of the IFRC site; (b) aqueous U(VI) and adsorbed U(VI) on four sites that exhibit different desorption rates where $R_6 > R_5 > R_4 > R_3$; (c) non-reactive tracer (Br⁻) and U(VI) following injection of a 100 µg/L pulse of U(VI) into well 2-9; and (d) aqueous U(VI) and adsorbed U(VI) on four sites that exhibit different adsorption rates where $R_6 > R_5 > R_4 > R_3$.

Concluding Remarks

The activities shown herein demonstrate that a self-consistent kinetic model of U(VI) interaction with IFRC site sediments (MRSCM) can be developed that spans multiple time scales, grain size distributions, and degrees of sediment structuring. One model with identical reaction parameters can describe the kinetic release of contaminant U(VI) and the adsorption-desorption behavior of spiked U(VI) under conditions of 1-D SGW flow in intact sediment cores from the three primary facies types in the IFRC saturated zone. This finding was unexpected and attests to the relatively low degree of heterogeneity in reaction parameters of the saturated zone.

The MRSCM that was developed from batch and stirred-flow reactor studies of < 2mm sediment, and parameterized from laboratory studies of intact cores suggests that retardation will be low in the field, and adsorption will be kinetically controlled at the in-situ groundwater velocity (~5 m/day). The calculations suggest that only 20% of surface sites are active at these flow velocities, and consequently the active or effective site concentration is quite low. Thus, future U-injection experiments must be carefully designed in terms of injection volumes and duration to assure that appropriate time scales are being accessed for a successful experiment.

In the next report in this series, we will utilize the MRSCM version of STOMP along with the 3-D hydraulic conductivity field of the IFRC site to pre-model a series of U(VI) injection experiments at the IFRC. The pre-modeling goals are to identify injection volumes, rates, durations, and sequences that will enable field experimental evaluation of in-situ desorption/adsorption kinetics. Desorption will be evaluated by injecting site groundwaters with lower dissolved U than is present within the site, while adsorption will utilize groundwaters with higher concentration as shown in figure 8. Successful experimentation demands very specific in-situ time scales and concentration gradients given potential field scale reaction rates and known groundwater advective velocities. In the final report we will describe how geochemical heterogeneities can be incorporated in the model. This complex model with geostatistical distributions of hydrologic and geochemical properties will be used to simulate and interpret IFRC field experiments.

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