Fate and Transport of Uranium (VI) in Weathered Saprolite

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1 **ABSTRACT**

2 Batch and column experiments were conducted to investigate sorption and transport of uranium
3 (U) in the presence of saprolite derived from interbedded shale, limestone, and sandstone
4 sequences. Sorption kinetics were measured at two initial concentrations (C_0 ; 1, 10 μM) and
5 three soil:solution ratios ($R_{s/w}$; 0.005, 0.25, 2 kg/L) at pH 4.5 (pH of the saprolite). The rate of U
6 loss from solution ($\mu\text{mole/L/h}$) increased with increasing $R_{s/w}$. Uranium sorption exhibited a fast
7 phase with 80% sorption in the first eight hours for all C_0 and $R_{s/w}$ values and a slow phase
8 during which the reaction slowly approached (pseudo)equilibrium over the next seven days. The
9 pH-dependency of U sorption was apparent in pH sorption edges. U(VI) sorption increased over
10 the pH range 4 to 6, then decreased sharply at $\text{pH} > 7.5$. U(VI) sorption edges were well
11 described by a surface complexation model using calibrated parameters and the reaction network
12 proposed by Waite et al. (1994). Sorption isotherms measured using the same $R_{s/w}$ and pH
13 values showed a solids concentration effect where U(VI) sorption capacity and affinity decreased
14 with increasing solids concentration. This effect may have been due to either particle
15 aggregation or competition between U(VI) and exchangeable cations for sorption sites. The
16 surface complexation model with calibrated parameters was able to predict the general sorption
17 behavior relatively well, but failed to reproduce solid concentration effects, implying the
18 importance of appropriate design if batch experiments are to be utilized for dynamic systems.
19 Transport of U(VI) through the packed column was significantly retarded. Transport simulations
20 were conducted using the reactive transport model HydroGeoChem (HGC) v5.0 that
21 incorporated the surface complexation reaction network used to model the batch data. Model
22 parameters reported by Waite et al. (1994) provided a better prediction of U transport than
23 optimized parameters derived from our sorption edges. The results presented in this study

- 1 highlight the challenges in defining appropriate conditions for batch-type experiments used to
- 2 extrapolate parameters for transport models, and also underline a gap in our ability to transfer
- 3 batch results to transport simulations.
- 4

1. INTRODUCTION

Uranium (U) is a major contaminant in soils at U.S. Department of Energy (DOE) weapons processing plants (RILEY et al., 1992). At the DOE plant in Oak Ridge, Tennessee, uranium isotopes were separated using an electromagnetic process and U-bearing wastes disposed on site. Soils at the waste disposal site in Oak Ridge are composed largely of weathered saprolite, similar to many other areas in the southeastern USA (LI et al., 1997; VEPRASKAS et al., 1991). Although groundwater flow and contaminant transport are not easily predicted due to the complex flow mechanism through saprolite (JARDINE et al., 1990; MAYES et al., 2003; Zhang et al., 2011), understanding contaminant transport is important to effectively remediate these disposal sites.

Uranium is most soluble and mobile in the hexavalent oxidation state (U(VI); (DUFF et al., 2002). Due to concern over the environmental and human health hazards associated with U(VI), sorption of U(VI) onto a range of soil solids has been comprehensively investigated. The U(VI) sorption studies using pure iron-containing minerals such as ferrihydrite (ALLARD et al., 1999; MORRISON et al., 1995; MOYES et al., 2000; WAITE et al., 1994), goethite (COMBES et al., 1992; KOHLER et al., 1992; TRIPATHI, 1984), hematite (BARGAR et al., 1999; HSI and LANGMUIR, 1985; TICKNOR, 1994; TRIPATHI, 1984), and phyllite (ARNOLD et al., 2001) showed that iron-containing minerals strongly adsorb U(VI). Sorption of U(VI) to clay minerals such as montmorillonite (MCKINLEY et al., 1995) and beidellite-dominated smectite (TURNER et al., 1996) were also studied. Other pure materials investigated for U(VI) sorption include sulfides (WERSIN et al., 1994), carbonates (MORSE et al., 1984), and various mixed materials (BARNETT et al., 2000; WAITE et al., 2000). Using three different heterogeneous soils with nearly identical iron oxide

1 contents, Barnett et al. (2000) concluded that the interaction of U(VI) with iron oxides controlled
2 U(VI) sorption onto the soils studied. The overall conclusion of these batch studies, using either
3 pure or heterogeneous materials, was that U(VI) is strongly adsorbed though the degree of
4 sorption is affected by chemical conditions.

5
6 Concerns have been raised about the extrapolation of batch results to dynamic systems. The
7 difficulty utilizing batch-derived parameters for transport model simulations likely results from
8 conditions in the column that are not adequately represented in the batch experiment (KOHLENER et
9 al., 1996). Transport model simulations with surface complexation parameters independently
10 estimated from batch experiments was not able to accurately predict U(VI) transport through
11 columns packed with quartz grains (KOHLENER et al., 1996). Uranium transport through sandstone
12 columns was poorly predicted by coupled chemical equilibrium transport models (Sims et al.,
13 1996). Barnett et al. (2000) also reported that simulations using batch experiment results did not
14 adequately predict U(VI) breakthrough curves (BTC's) from soil columns and suggested a rate-
15 limited reaction in the columns as a possible explanation. Gamerdinger et al. (GAMERDINGER et
16 al., 2001) reached a similar conclusion because the high velocity flow used in their transport
17 experiment resulted in less sorption than expected from the batch equilibrium test. Therefore,
18 the appropriate design of batch experiments is necessary to obtain results that are useful for
19 predicting U(VI) transport.

20
21 The objectives of this study are to investigate the rate and extent of U(VI) sorption onto saprolite
22 under various conditions and discuss the implications of these results with respect to predicting

U(VI) transport. We employed three different soil:solution ratios and two initial U(VI) concentrations to study the implications of various conditions on U(VI) sorption onto saprolite.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of saprolite

The sampling site was located on the ERSP Field Research Center (FRC) Background Site at Oak Ridge National Laboratory in East Tennessee (<http://www.esd.ornl.gov/nabirfrc/>) which is free of U contamination but is underlain by the same geologic formations as U waste disposal areas on site. Bulk samples of saprolite derived from interbedded shale, limestone, and sandstone sequences were collected from the C horizon approximately 1 m below the surface. Black manganese oxides were observed on fracture surfaces in the saprolite. Samples were transported to the laboratory and maintained at room temperature in sealed plastic bags. The samples were then crushed and sieved through a 2 mm screen prior to use in experiments. Chemical, physical, and mineralogical properties of the saprolite used in this study were determined and are provided in Table 1.

2.2. Experimental Methods and Procedures

2.2.1. Batch Sorption Experiments

All batch sorption experiments (edges, isotherms and kinetics) were conducted in 30 mL polycarbonate centrifuge tubes (Nalge Company) under ambient air at constant ionic strength (0.05 M adjusted with NaNO_3). Uranium solutions were prepared from depleted $\text{UO}_2(\text{NO}_3)_2$ salt. Kinetic experiments were performed at two initial concentrations (C_0 ; 1 and 10 μM) and three soil:solution ratios ($R_{s/w}$) of 0.005, 0.25, and 2 kg/L at pH 4.5 (pH of the saprolite). For $R_{s/w}$ of 0.005 and 0.25 kg/L, 0.1 g and 5 g of soil, respectively, were equilibrated with 20 mL of the U(VI)-bearing solution. For $R_{s/w}$ of 2 kg/L, 4ml of U(VI) solution were added to 8g of soil. The soil-solution samples were shaken from 1 min to 7 days on a reciprocating shaker table. The $R_{s/w}$ values were chosen based on (i) reported values used in other U sorption studies ($R_{s/w} = 0.005$; (BARNETT et al., 2002; BARNETT et al., 2000; WAITE et al., 1994), (ii) the value recommended by the ASTM standard sorption protocol ($R_{s/w} = 0.25$; ASTM D4646-03; (PORRO et al., 2000), and (iii) a value that approximates conditions in some laboratory transport experiments ($R_{s/w} = 2$; (BARNETT et al., 2000; PORRO et al., 2000).

Sorption edges were measured using two soil:solution ratios of 0.005 and 0.25 kg/L. The solution pH of U free samples was adjusted with 0.1 M NaOH or HNO_3 and then bubbled with moist air until a constant pH was reached. The samples were then spiked with U(VI) stock solution to achieve the target initial U(VI) concentration of 4.2 μM and equilibrated for 4 days prior to sampling. Preliminary kinetic tests indicated that this was sufficient time to achieve steady-state U concentrations. Sorption isotherms were obtained with three soil:solution ratios (0.005, 0.25, 2 kg/L) at pH 4.5. The initial solution U(VI) concentrations equilibrated with soils were 0.5, 0.9, 1.8, 3.3, 5.0, 6.0, 12, 20, 30, 50, 75, and 120 μM . Each soil-solution mixture was shaken for 4 days prior to sampling.

For all batch sorption experiments, the samples equilibrated on a reciprocating shaker table for the desired reaction time. Sacrificial samples were collected by rapid centrifugation ($1500 \times g$ for 4 minutes). The supernatant was subsequently filtered (0.2 μm polysulfone filter), acidified to $\text{pH} < 2$ with concentrated HNO_3 and stored at 4°C until analysis by kinetic phosphorescence analysis (KPA; Chemchek Instruments, city, WA). Uranium sorbed by the soil was calculated from the change in solution concentration. Two types of blank samples were run in parallel with the experimental replicates: 1) soil samples with no added U(VI) to quantify any naturally occurring U released by the soil (Table 1), and 2) samples with no soil to detect any U(VI) lost by contact with labware. All samples and controls were run in triplicate.

2.2.2. Transport Experiments

Crushed and sieved ($< 2 \text{ mm}$) saprolite was wet packed in a glass chromatography column (1 cm inner diameter) to a final bed length of 3 cm. The column was flushed with 0.05 M NaNO_3 ($\text{pH} 4.5$) at a specific discharge of 1.22 cm/h. Using the same flow rate, the influent solution was changed to 10 μM U(VI) plus 5 mM NaBr in 0.045 M NaNO_3 , $\text{pH} 4.5$, maintaining constant ionic strength throughout the experiment. After the desired breakthrough period, the inlet solution was switched back to a U(VI)-free, 0.05 M NaNO_3 solution. Effluent samples were collected with a fraction collector and effluent pH was measured. Samples for U analysis were acidified ($\text{pH} < 2$) with concentrated nitric acid and stored at 4°C until analysis by KPA. Bromide concentration in the effluent was measured by ion chromatography (IC).

As a check for nonequilibrium effects, either physical or chemical, during the desorption phase of the experiment a flow interrupt manipulation was conducted after ~810 pore volumes (~57 days; (BRUSSEAU et al., 1997). After 40 hrs of flow interruption (equivalent to ~24 pore volumes), the injection of U(VI)-free solution continued until the effluent U concentration reached zero. Mass balance for uranium and bromide was calculated by integrating the area under the measured breakthrough curves; 105 ± 5 % of the injected uranium was recovered in the column effluent.

2.3 Modeling

For clarity we reserve use of the terms “optimize” or “fit(ting)” to indicate that the value of one or more model parameters was adjusted to improve the model description of the data. The terms “simulation” or “prediction” indicate that the value of each model parameter was fixed to a specified value during the model run. Model simulations that were conducted using the reaction network and parameter values for U sorption reported by Waite et al. (1994) will be referred to as the Waite model for simplicity.

2.3.1 Batch Equilibrium Modeling

Uranium sorption (edges, isotherms, and kinetics) onto saprolite was modeled using a two-site surface complexation model (BARNETT et al., 2000; WAITE et al., 1994) that assumes a small number of high affinity (strong) sites and a larger number of lower affinity (weak) sites. The total number of sorbing sites is assumed to be proportional to the DCB extractable Fe content of the soil (0.875 mole sites/ mole Fe). Model simulations were conducted using the surface

complexation parameters reported by Waite et al. (1994). In addition, the model was fit to the data by optimizing the value of specified parameters as described below. Formation constants for U(VI) aqueous species were obtained from the NEA compilation (GRENTHE et al., 1992; GUILLAUMONT et al., 2003).

Model simulations of sorption edges and isotherms and fitting to the $R_{s/w}$ 0.005 sorption edge results were performed using FITEQL 4.0 (HERBELIN and WESTALL, 1999). Optimized parameter estimates were obtained using only the results from the $R_{s/w} = 0.005$ treatment by the following procedure. Using the data where $pH < 6$, the proportion of strong:weak sites was varied to locate the minimum value of the goodness-of-fit indicator, the sum of squares divided by the degrees of freedom (SOS/DF). In this pH range, under ambient air, carbonate aqueous and surface complexes have a minor impact on model-predicted U speciation. Using the optimal value of strong sites obtained from this procedure (1.02 ± 0.02 mmole strong sites/ mole Fe) the model was fit to the $pH < 6$ data by adjusting the value of the surface complexation constants for the reactions:

where UO_2^{2+} is a uranium species in the liquid phase, and $\equiv Fe_s(OH)_2$ and $\equiv Fe_w(OH)_2$ are strong and weak pH-dependent binding sites, respectively. Using the optimized values for the proportion of strong sites and the log K's (**K = reaction equilibrium constant**) determined for (1a)

and (1b), the model was fit to the data for pH > 6 by adjusting the value of the surface complexation constant for the reactions:

This final optimized parameter set was used to predict the U sorption edge for the $R_{s/w} = 0.25$ and U sorption isotherms for all three $R_{s/w}$ values. Our optimized parameter set was also used to predict U transport for the column experiment.

2.3.2 Batch Kinetic Modeling

The sorption kinetics data were modeled using a kinetic version of the surface complexation model that assumes sorption occurs simultaneously onto high and low affinity sites. The model included all aqueous and surface complexation reactions used in the equilibrium model. The U sorption reactions indicated by (1a) and (1b) were assumed to be the most kinetically limited. Model calculations were performed with the biogeochemical reaction model HydroGeoChem (HGC) v5.0 (YEH et al., 2004) that allows any combination of equilibrium and user-defined kinetic reactions. Forward and backward rate constants (k_f and k_b , respectively) for reactions (1a) and (1b) were estimated with the nonlinear parameter estimation program PEST (DOHERTY, 2002). All other model parameters (site density, equilibrium constants) were independently determined as described above and fixed during the rate coefficient inversion process. We attempted to fit the model to the kinetic data first by fixing the ratio of rate constants to be equal

to the independently determined equilibrium constants for the corresponding reactions and, second, by allowing the ratio $k_f:k_b$ to vary.

2.3.3 Transport Modeling

Uranium(VI) transport was predicted using the reaction based modeling approach incorporated in HydroGeoChem (HGC) v5.0. The model decouples fast and slow reactions, which enables robust numerical integration (YEH et al., 2004). Two simulations were performed, the first using the calibrated parameter values derived from our batch experiment, and the second using parameters reported by Waite et al. (1994).

3. RESULTS AND DISCUSSION

3.1. Batch Experiments

3.1.2. Sorption Edges

To investigate the effect of pH on U(VI) sorption, batch experiments were carried out at pH values in the range ~3.5 to 9.5 using two values of $R_{s/w}$ (0.005 and 0.25) and total U concentration of 4.2 μ M. At the lower $R_{s/w}$ U(VI) sorption increased sharply over a pH range of 4 to 6, then decreased at pH > 7.5 (Figure 1). Such sorption envelopes have been described for other solutes, and specifically U(VI), by other investigators (BARNETT et al., 2000; HINGSTON et al., 1967; TRIPATHI, 1984; WAITE et al., 1994; WAZNE et al., 2003). Decreased U(VI) sorption at alkaline pH results from the increased carbonate concentrations with increased pH resulting in

the formation of stable aqueous uranyl-carbonate complexes. For that reason, there is an increase in the estimated proportion of sorbed U attributed to surface uranyl-carbonate species with increasing pH (upper panel, Figure 1; equations 2a and 2b). Similar features are observed in the data collected at the higher $R_{s/w}$ with some notable exceptions (Figure 1). Virtually all the U(VI) sorbed over the experimental pH range. The edge positions where U sorption increased and then decreased were shifted to lower and higher pH, respectively, at the higher solids concentration. Waite et al. (1994) reported a similar result for U(VI) sorption onto ferrihydrite with increasing $R_{s/w}$. A decrease in aqueous U(VI) concentration with increased $R_{s/w}$ suggests that sorption reactions, rather than precipitation, controlled U(VI) concentration as the addition of more sorbent would not be expected to change the equilibrium solubility of an U solid phase.

The surface complexation model reaction network proposed by Waite et al. (1994) was fit to the experimental data for $R_{s/w} = 0.005$ by adjusting the ratio of strong sites: total sites and the stability constants for the reactions described by equations (1) and (2). The calibrated model described the observed data well (final SOS/DF = 0.13), capturing the general trends in the data as well as the extent of sorption over a broad pH range (Figure 1). In addition, the optimized parameter set provided a good prediction of U(VI) sorption behavior at the $R_{s/w} = 0.25$ (Figure 1). In contrast, the Waite model over-predicted U(VI) sorption for $R_{s/w} = 0.005$. At pH values < 6 U(VI) sorption in the model is predominantly due to the strong and weak surface species ($\equiv\text{FeO}_2$) UO_2 (Eq. 1). The higher amount of sorption predicted by the Waite model is primarily due to the larger fraction of strong:total sites used in that model as the formation constants for these complexes are similar for both models (Table 2). As the pH increases, U(VI) sorption in the model is increasingly due to the ($\equiv\text{FeO}_2$) $\text{UO}_2\text{CO}_3^{2-}$ complexes (Eq. 2). Larger formation

constants for these species in the Waite model account for over-predictions of U(VI) sorption at higher pH.

3.1.3. Sorption Isotherms

Sorption isotherms were established over a range of initial U(VI) concentrations and three $R_{s/w}$ values. All the U(VI) sorption isotherms were nonlinear and did not exhibit a trend toward an asymptote of maximum sorption, conforming well to the empirical Freundlich isotherm equation (Figure 2). Nonlinear sorption described by the Freundlich equation has been attributed to a decreasing affinity between sorbent and sorbate with an increasing extent of adsorption (SPOSITO, 1984). Nonlinear sorption isotherms are also described by surface complexation theory (STUMM and MORGAN, 1996) due to the finite number of sites available for solute sorption and the specification of sites of different affinity in some representations of surface complexation models.

Uranium sorption onto the saprolite was similar for $R_{s/w} = 0.005$ and 0.25 but decreased at the highest $R_{s/w} = 2$ (Figure 2a). These results are indicative of a solids-concentration effect in which solute sorption decreases with increasing sorbent concentration. Other investigators have reported experimental data (DITORO et al., 1986; HONEYMAN and SANTACHI, 1988; OSCARSON and HUME, 1998) and modeling studies (PHILLIPPI et al., 2007) that show a solids-concentration effect. McKinley and Jenne (MCKINLEY and JENNE, 1991) found no such effect using $R_{s/w}$ in the range 0.0000445 to 0.00445 (assuming the ferrihydrite they used had the formula $Fe_2O_3 \cdot H_2O$ (DZOMBAK and MOREL, 1990)) and suggested that when reported it was the result of experimental or data reduction errors. Nevertheless, when their recommended data reduction is

1 applied to our results, the solids-concentration effect remains evident. Additionally, when results
2 from the last sampling times of the kinetic experiments (independently derived data) are plotted
3 on the isotherms (Figure 2b, c, d), the same apparent dependence of U sorption on $R_{s/w}$ remains
4 suggesting that neither experimental nor data reduction errors underlie this observation.

5
6 The surface complexation model that was calibrated with the $R_{s/w}$ 0.005 sorption edge data
7 adequately predicted the general trends in the observed isotherms (Figure 2) but did not capture
8 the solids-concentration effect. The solids-concentration effect results from strong interactions
9 in multicomponent systems, e.g. between U(VI), carbonate, and sorption sites (PHILLIPPI et al.,
10 2007). At the pH of these experiments (4.4-4.7) carbonate is a minor component. The inability
11 of the model to reproduce this effect suggests that other, as yet unidentified, reactions are absent
12 from the reaction network constituting the surface complexation model. Only the $(\equiv\text{FeO}_2)\text{UO}_2$
13 (Eq 1) species are important surface complexes at the isotherm pH values (Figure 1). For the
14 lowest $R_{s/w}$ our calibrated model also generally captured the amount of sorption and showed the
15 biggest discrepancy with the Waite model (Figure 2a). The curvature for both models at
16 $\log(C_{eq})$ (where C_{eq} = final equilibrium aqueous-phase U concentration) = -7 to -6 reflects
17 saturation of strong (high affinity) binding sites and the transition to sorption onto weak sites, a
18 feature not reflected in the data. Our model, with fewer strong sites (Table 2), predicts earlier
19 strong site saturation and departure from the Waite model. The ratio of strong sites to total
20 uranium increased with increasing $R_{s/w}$, consequently the saturation feature becomes less
21 prominent as the model predicts sorption to occur predominantly on a single site $((\equiv\text{Fe}_s\text{O}_2)\text{UO}_2)$
22 and the two model predictions become more similar (Figure 2) as expected given the similarity
23 of their parameter values (Table 2). For comparison, results from the final sampling time of the

kinetic experiments (see below) are plotted on the isotherm plots and show good agreement with the isotherm data. We take this as indication that the 4 day equilibration period for the edge and isotherm experiments was sufficient.

Overall, the ability of both models to predict the general trends in the sorption isotherms was acceptable. The results from the model predictions are encouraging given that the calibration data, obtained at discrete pH values and constant total U in the sorption edge experiments, represent a single point in an isotherm experiment conducted at constant pH and variable total U. Both models overpredicted U sorption as the $R_{s/w}$ increased and the magnitude of the error increased with $R_{s/w}$. Model failure of this kind would lead to the expectation that U is less mobile in the environment than the isotherm data would indicate.

3.1.1. Kinetic Experiments

In addition to preliminary scoping experiments conducted to guide the choice of reaction time for the equilibrium experiments, a more detailed set of kinetic experiments was performed using three $R_{s/w}$ and two C_0 values. Uranium loss from solution exhibited a faster phase with 80% loss from solution occurring in less than eight hours, and a slower phase during which the reaction approached steady state over the next seven days (Figure 3). The rate of U loss from solution ($\mu\text{mole/L/h}$) increased with increasing $R_{s/w}$ at both C_0 values to the extent that at the highest $R_{s/w}$ the reaction was >99% complete within 15 minutes.

Two-phase sorption kinetics has been previously reported for numerous solutes and specifically for U (BARNETT et al., 2000; HSI and LANGMUIR, 1985; WAITE et al., 1994). Investigators have attributed this behavior to a variety of mechanisms including distribution of site affinities, sorption onto outer versus internal surfaces (i.e., diffusion limitation), or fast initial sorption followed by slow structural rearrangement or recrystallization (BARROW et al., 1989; DAVIS et al., 1987; EVANS and JURINAK, 1976; FULLER and DAVIS, 1987; HARTER, 1991; SELIM and AMACHER, 1988). The nature of the data collected does not permit us to distinguish among these possible mechanisms. To maintain a consistent modeling approach, the surface complexation model used to model the equilibrium results was fit to the kinetic data by assuming the reactions represented by Eq (1) to be rate limiting. Modeling results from the equilibrium experiments indicated that the uranyl-carbonate surface complexes (Eq 2) were of minor importance and these were maintained as equilibrium reactions in the kinetic model. To be consistent with the results of the equilibrium modeling, we initially attempted to fit the model to the kinetic data by fitting the forward rate constants and estimating the backward rate constants by assuming the ratio of rate constants to be equal to the fitted equilibrium model formation constants. This approach generally resulted in poor model fits to the data (Figure 3; Table 3). Adjusting all four rate constants to fit the model to the data (i.e., allowing the rate constant ratio to vary) provided a significantly better fit for five out of the six cases (Table 3). However, the resulting rate constant ratios were not close to the equilibrium formation constants for either our model or Waite's model. The two parameter model was satisfactory for the conditions that most closely approximated the column transport experiment ($R_{s/w} = 2$; $C_0 = 10 \mu\text{M}$; Figure 3b; Table 3).

3.2. Transport Experiment

The ability of the surface complexation model to predict U(VI) transport was tested by packing a column with the same solid phase material that was used for the batch equilibrium and kinetic experiments. The packing materials were not compacted to mimic the porosity of the materials in the field to minimize occlusion of sorption sites and because prior experience with these clayey materials has shown that compaction results in a column of such low permeability as to make a transport experiment impractical. The final column contained 2.48 g of solids in a total volume of 2.45 cm³ with a porosity of 0.66 yielding an $R_{s/w}$ for the column of 1.5 and, at the measured volumetric flow rate (0.97 cm³/h), a fluid residence time of 1.7 hours. The influent U(VI) concentration was 10 µM. Results of the preceding kinetic and equilibrium sorption experiments led to the expectation that kinetic sorption reactions would not be important (Figure 3b) and that the equilibrium sorption model, calibrated only from the sorption edge at $R_{s/w} = 0.005$, would predict less U(VI) sorption (i.e., earlier breakthrough) than would be observed (Figure 2b, $\log(C_{eq}) = -5$). Each of these expectations was tested in the transport experiment.

Transport of the nonreactive bromide tracer was faster than that of U(VI) as expected, reaching complete breakthrough (relative concentration, $C/C_0 = 1$) within 1.4 pore volumes (PV) (Figure 4). A dispersion coefficient (D , L²/T) for the experiment was determined by fitting the standard convective-dispersive equation to the bromide data using CXTFIT (PARKER and VANGENUCHTEN, 1984) and assuming a retardation factor equal to one. The optimal value of D was 0.059 ± 0.006 cm²/h yielding a column Peclet (Pe) number of 102 ± 10 ($Pe = vL/D$; v = average linear porewater velocity (cm/h); L = column length (cm); D = dispersion coefficient (cm²/h)), which is indicative of advection-dominated mass transport.

1
2 In contrast to bromide, uranium transport through the column was significantly retarded, first
3 appearing in the column effluent at 105 PV with complete breakthrough ($C/C_0 = 1$) achieved
4 after ~161 PV (Figure 4). Uranium injection continued for an additional 454 pore volumes at
5 which time the influent was switched to bromide- and U(VI)-free 0.05 M NaNO₃. Bromide
6 washout was essentially a mirror image of the breakthrough curve (BTC) and was not detected in
7 the effluent after 1.5 PV of the washout phase; 99 ± 1 % of bromide was recovered in the column
8 effluent.

9
10 Uranium washout from the column took much longer than bromide and exhibited pronounced
11 tailing. Whereas U breakthrough was achieved over a span of 56 PV, U washout required nearly
12 880 PV (Figure 4). The mechanism responsible for U retention on the solids was reversible as
13 105 ± 5 % of the injected U was recovered in the effluent. Solute breakthrough curves with
14 sharp fronts and tailing during washout can result from nonlinear equilibrium sorption isotherms.
15 Time-dependent phenomena (chemical or physical nonequilibrium) can also produce tailing.
16 Several characteristics of the data suggest that rate-limited processes were not responsible for the
17 observed U tailing. Physical nonequilibrium (e.g., diffusion into aggregates) should impact the
18 nonreactive bromide tracer as well as U, yet the observed Br BTC did not exhibit early
19 breakthrough or tailing on either the ascending or descending limbs. Numerical simulations of
20 rate-limited sorption show that, for linear sorption isotherms, the same tailing profile is apparent
21 during breakthrough and washout, i.e., as the relative concentration approaches 1 and 0,
22 respectively (BRUSSEAU et al., 1997; SELIM et al., 1990). When the underlying isotherm is
23 nonlinear similar, but not identical, tailing is evident in the breakthrough and washout (SELIM et

al., 1990). The uranium breakthrough curve (ascending limb) exhibited tailing; a relative concentration of 0.5 was reached over a span of 21 pore volumes, the rise from $C/C_0 = 0.5$ to 1 required ~35 pore volumes. However, the breakthrough tailing was minor by comparison and not similar to that observed for the washout portion. Finally, results of the batch sorption kinetic experiments suggested that the sorption reaction would largely be complete within the 1.7 hour fluid residence time and kinetics should not affect U breakthrough (Figure 3b). Although our sorption results cannot be used to infer a characteristic time frame for desorption, other investigators have reported the rapid (< 1 hour) desorption of U(VI) from goethite even after 6.5 months aging (GIAMMAR and HERING, 2001).

As a direct test for time-dependent processes affecting the U breakthrough curve we conducted a flow interrupt manipulation during the washout portion of the transport experiment. When the relative U concentration in the effluent reached ~0.25 the pump was stopped for 40 hours (equivalent to 23.5 pore volumes). If nonequilibrium processes were controlling the release of U, we anticipated that when flow resumed U concentration in the effluent would be higher than before the interrupt. Immediately following the flow interrupt we measured a small but statistically insignificant decrease in U concentration (Figure 4, inset). The short duration and small magnitude of the perturbation suggest that nonequilibrium processes do not exert a significant influence on U transport for this experiment.

Uranium transport simulations were performed by incorporating the surface complexation reaction network into the multicomponent reactive transport code HydroGeoChem (HGC) v. 5.0 (YEH et al., 2004). For the simulations, the column was discretized with 20 nodes and 4 equal

size elements ($0.886 \text{ cm} \times 0.886 \text{ cm} \times 0.779 \text{ cm}$ each). The dispersion coefficient was determined from the bromide breakthrough curve as described above. The simulation was performed for a total duration of 2500 hours ($\sim 1490 \text{ PV}$) with a constant time-step size of 0.1 hour. Further details on the model, its capabilities, and implementation can be found in Zhang et al. (ZHANG et al., 2007). All reactions were assumed to be equilibrium reactions (i.e., no kinetic limitations). The flow interrupt was not included as part of the transport simulations. Two transport simulations were performed, one using the model parameter values optimized to the $R_{s/w}$ 0.005 sorption edge results and the second using the parameter values reported by Waite et al. (1994).

Our optimized parameter set predicted uranium breakthrough that occurred at $\sim 26 \text{ PV}$, nearly 80 pore volumes earlier than observed; simulated U(VI) washout was also more rapid than observed. This result was expected given that the same model underpredicted U(VI) sorption in the equilibrium isotherms (Figure 2b). Transport simulations using Waite's parameters provided a much better prediction of the U(VI) BTC which was unexpected as this model overpredicted U(VI) sorption isotherms for all conditions. As for the isotherms, the difference in the two models is related to the difference in the estimated number of strong sites. The underlying reason why Waite's parameter set was able to predict U(VI) transport remains unclear.

4. SUMMARY AND CONCLUSIONS

Batch and column experiments were conducted to investigate U(VI) sorption onto and transport through saprolite derived from interbedded shale, limestone, sandstone sequences. A surface

1 complexation model was calibrated to our data and subsequently used to predict sorption
2 equilibria, kinetics, and transport. Although prediction of batch experiments using our calibrated
3 model generally performed as well as or better than model predictions using Waite's parameter
4 set it was inferior predicting U(VI) transport. The reaction network constituting the surface
5 complexation model could not reproduce a solids-concentration effect evident in the data. This
6 may be due to the fact that most batch-type laboratory experiments employ low solid:solution
7 ratios where the effect is not seen. Consequently the models developed to describe these results
8 do not include the requisite reactions.

9
10 The transport of U(VI) through the packed column was significantly retarded, reaching $C/C_0=1$
11 at approximately 300 PV. During the washout phase of the experiment U exhibited prolonged
12 tailing, which is typical for solutes with a nonlinear sorption isotherm. Although the model
13 using optimized parameters was arguably better than Waite's model in describing the sorption
14 edge and comparable in describing the isotherms, Waite's sorption model provided a much better
15 prediction of U transport. This discrepancy in the transport predictions is related to differences
16 in the estimated concentration of strongly sorbing sites a parameter that, to date, is an adjustable
17 parameter in model fitting rather than a directly measured quantity.

18
19 Ideally, batch sorption experiments can be used to make predictions about solute transport.
20 Recent papers suggest that surface complexation modeling is now mature enough to enable the
21 blind prediction of solute sorption behavior (RICHTER et al., 2005a; RICHTER et al., 2005b). The
22 results presented in this study for U(VI) highlight the challenges that remain in defining correct
23 conditions for batch-type experiments (e.g., solid to solution ratio), the development of the

1 reaction networks used to describe those experiments and used to parameterize transport models,
2 and also underline a gap in our ability to transfer batch results to transport simulations.

3
4
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- 21
22

Table 1. Physical, chemical, and mineralogical properties of saprolite.

pH ^a	4.27 ± 0.02
Cation Exchange Capacity ^b	11.3 ± 0.3 cmol ₊ /kg
Exchangeable Cations (cmol ₊ /kg)	
Ca	2.07 ± 0.05
Mg	1.43 ± 0.03
K	0.116 ± 0.003
Al	3.4 ± 0.1
Mn	0.0113 ± 0.0002
Fe	0.0043 ± 0.0003
Exchangeable Acidity ^c	7.7 ± 0.3 cmol ₊ /kg
Extractable Fe	
CBD ^d	340 ± 10 mmole/kg
(NH ₄) ₂ oxalate ^e	11.8 ± 0.2 mmole/kg
Extractable Mn ^f	3.3 ± 0.1 mmole/kg
U content ^g	12.4 ± 0.2 μmole/kg
Mineralogy ^h	
Major (95%)	Qz ₃₈ , Ill ₃₀ , K-fd ₂₇
Minor (<5%)	HIV>> Ver, Gt, Lp > Fr, Kn

^a Soil pH determined on 5g of soil and 10 mL 10 mM CaCl₂ slurry.

^b Exchangeable cations were determined using 0.1M BaCl₂ as an index ion (HENDERSHOT and DUQUETTE, 1986). CEC = Exchangeable acidity + exchangeable cations - exchangeable Al.

^c Exchangeable acidity was measured by BaCl₂ – triethanolamine (TEA) method (PEECH, 1965).

^d Citrate-bicarbonate-dithionate (CBD) extractable (total) Fe was conducted in an 80°C water bath (LOEPPERT and INSKEEP, 1996).

^e Ammonium oxalate extractable (amorphous) Fe was measured after shaking 4hr in the dark (LOEPPERT and INSKEEP, 1996).

^f NH₂OH·HCl extractable (total) Mn (GAMBRELL, 1996).

^g Total naturally occurring U in the saprolite. Determined by instrumental neutron activation analysis, ActLabs, Tucson, AZ.

^h Abbreviation: Qz- quartz, Ill- illite, K-fd- potassium feldspar (microcline+ Orthoclase), HIV- hydroxy interlayered vermiculite, Ver- vermiculite, Gt- goethite, Lp- lepidocrocite, Fr- ferrihydrite, Kn- kaolinite.

Table 2: Surface complexation model parameters determined from this study from the sorption edge data with $R_{s/w} = 0.005$ and those reported by Waite et al. (1994).

	This study	Waite model
mole strong sites per mole Fe*	0.00102	0.0018
Surface Complex	log(formation constant)	
$(\equiv\text{Fe}_s\text{O}_2)\text{UO}_2$	-2.17	-2.57
$(\equiv\text{Fe}_w\text{O}_2)\text{UO}_2$	-7.06	-6.28
$(\equiv\text{Fe}_s\text{O}_2)\text{UO}_2\text{CO}_3^{2-}$	2.67	3.67
$(\equiv\text{Fe}_w\text{O}_2)\text{UO}_2\text{CO}_3^{2-}$	-1.43	-0.42

*both models assume 0.875 mole total sites per mole Fe

Table 3. Estimated rate coefficients for the two site kinetic model.

Forward rate constants (k_f , k_{f2}) fitted and the backward rate constants (k_b , k_{b2}) estimated based on the stipulation that the ratio k_f/k_b is fixed and equal to the fitted equilibrium model formation constants (Table 2).								
$R_{s/w}$	C_0 (μM)	k_f ($\text{h}^{-1}\text{M}^{-1}$)	k_b ($\text{h}^{-1}\text{M}^{-2}$)	k_{f2} ($\text{h}^{-1}\text{M}^{-1}$)	k_{b2} ($\text{h}^{-1}\text{M}^{-2}$)	RMSE ^a	$\log(k_f/k_b)$	$\log(k_{f2}/k_{b2})$
0.005	1	1.11E+04	1.65E+06	2.56E+06	2.87E+13	0.2929	-2.17	-7.06
0.25	1	1.13E+03	1.68E+05	2.47E+05	2.77E+12	0.1182	“	“
2	1	5.26E+05	7.78E+07	3.56E+01	4.00E+08	0.0008	“	“
0.005	10	6.29E+03	9.30E+05	1.93E+04	2.17E+11	1.5707	“	“
0.25	10	1.30E+05	1.92E+07	6.94E+02	7.79E+09	0.3281	“	“
2	10	5.93E+05	8.77E+07	1.00E-38	1.12E-31	0.0202	“	“

Forward and reverse rate constants adjusted to fit the model to the data (ratio k_f/k_b allowed to vary).

$R_{s/w}$	C_0 (μM)	k_f ($\text{h}^{-1}\text{M}^{-1}$)	k_b ($\text{h}^{-1}\text{M}^{-2}$)	k_{f2} ($\text{h}^{-1}\text{M}^{-1}$)	k_{b2} ($\text{h}^{-1}\text{M}^{-2}$)	RMSE ^a	$\log(k_f/k_b)$	$\log(k_{f2}/k_{b2})$
0.005	1	1.02E+06	5.94E+07	5.62E-01	1.50E+10	0.0504*	-1.77	-10.43
0.25	1	6.15E+05	3.66E+07	7.31E+03	8.10E+13	0.0157*	-1.77	-10.04
2	1	2.11E+05	1.69E+07	4.13E+02	1.53E+08	0.0004*	-1.90	-5.57
0.005	10	1.06E+05	1.00E-38	9.69E+03	9.85E+09	0.7523*	43.03	-6.01
0.25	10	2.79E+05	4.37E+07	1.00E-38	7.61E+09	0.2530*	-2.19	-47.88
2	10	6.25E+05	1.27E+08	1.00E-38	1.00E-31	0.0201	-2.31	-7.00

^a RMSE = root mean squared error = $\sqrt{\frac{\sum_{i=1}^n (y_{i,pred} - y_{i,obs})^2}{(n - p)}}$; $y_{i,pred}$ and $y_{i,obs}$ = model predicted and observed data points, respectively; n = number of observations; p = number of adjustable parameters in the model. * 4-parameter model provided significantly better fit than the 2-parameter model ($P < 0.01$).

FIGURE CAPTIONS

Figure 1. Observed, fitted and predicted U(VI) sorption as a function of pH. Two solid:solution ratios, $R_{s/w}$, of 0.005 and 0.25 were used. Error bars representing ± 1 standard error are smaller than the symbols. The solid line represents the surface complexation model fit to the $R_{s/w}$ 0.005 data; the dashed line shows the prediction for $R_{s/w}$ 0.005 from Waite's model (1994); the dash-dot line shows the predicted U(VI) sorption edge for $R_{s/w}$ 0.25 using the optimized parameter set. The initial U(VI) concentration is $4.2\mu\text{M}$. The upper panel indicates the estimated distribution of sorbed U on surface sites for the $R_{s/w}$ 0.005 case (see equations 1a through 2b).

Figure 2. Observed and predicted U(VI) sorption isotherms. (a) data for all $R_{s/w}$ conditions tested. Panels (b), (c), and (d) data and model predicted U(VI) sorption isotherms. The experimental pH is indicated in each panel. Error bars representing ± 1 standard error are smaller than the symbols. The horizontal line in each panel indicates the concentration of strong sites (mole/kg) according to our optimized parameter set. The vertical dashed line in each panel indicates U(VI) aqueous concentration in equilibrium with the solid phase schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$). Uranyl-carbonate surface complexes are predicted to make a minor contribution to U sorption (panel (c)).

Figure 3. Experimental and modeling results of sorption kinetic experiments with the initial U(VI) concentration of (a) $1\mu\text{M}$ and (b) $10\mu\text{M}$; error bars represent ± 1 standard error. The dashed lines represent the model fit when stipulating that the k_f/k_b ratio is equal to the fitted equilibrium model formation constant. The solid lines represent the model fit when the ratio k_f/k_b is allowed to vary. The vertical line in panel (b) indicates the fluid residence time for the

1 transport experiment. Uranium concentration in equilibrium with schoepite at the experimental
2 pH is $\sim 220 \mu\text{M}$.

3

4 **Figure 4.** Observed and predicted breakthrough curves for the packed saprolite column. The
5 upper panel shows the bromide breakthrough curve and model fit obtained by adjusting the value
6 of the dispersion coefficient. Vertical dashed lines in the lower panel indicate when the washout
7 phase of the experiment began and when the flow interrupt manipulation was performed. Inset:
8 detailed presentation of the data in the few pore volumes surrounding the slow interrupt.

1 | **Figure 1.**

1 **Figure 2.**

Data		Model	
		k_t/k_b fixed	k_t/k_b variable
●	$R_{s/w} = 0.005$	—	—
▽	$R_{s/w} = 0.25$	—	—
■	$R_{s/w} = 2$	—	—

1 **Figure 3.**

1 **Figure 4.**