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# Uranium(6+) Sorption on Montmorillonite: Experimental and Surface Complexation Modeling Study

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**Abstract.** Sorption interactions with montmorillonite and other clay minerals in soils, sediments, and rocks are potentially important mechanisms for attenuating the mobility of U(6+) and other radionuclides through the subsurface environment. Batch experiments were conducted (in equilibrium with atmospheric $P_{CO_2}$) to determine the effects of varying pH (2 to 9), solid-mass to solution-volume ratio (M/V = 0.028 to 3.2 g/L), and solution concentration ($2 \times 10^{-7}$ and $2 \times 10^{-6}$ M $^{233}$U) on U(6+) sorption on SAz-1 montmorillonite. The study focused on U(6+) surface complexation on hydroxylated edge sites as the sorption mechanism of interest because it is expected to be the predominant sorption mechanism at pHs typical of natural waters (pH ≈6 to ≈9). Thus, the experiments were conducted with a 0.1 M $NaNO_3$ matrix to suppress ion-exchange between U(6+) in solution and interlayer cations. The results show that U(6+) sorption on montmorillonite is a strong function of pH, reaching a maximum at near-neutral pH (≈6 to ≈6.5) and decreasing sharply towards more acidic or more alkaline conditions. A comparison of the pH-dependence of U(6+) sorption with that of U(6+) aqueous speciation indicates a close correspondence between U(6+) sorption and the predominance field of U(6+)-hydroxy complexes. At high pH, sorption is inhibited due to formation of aqueous U(6+)-carbonate complexes. At low pH, the low sorption values indicate that the 0.1 M $NaNO_3$ matrix was effective in suppressing ion-exchange between the uranyl ($UO_2^{2+}$) species and interlayer cations in montmorillonite. At pH and carbonate concentrations typical of natural waters, sorption of U(6+) on montmorillonite can vary by four orders of magnitude and can become negligible at high pH.

The experimental results were used to develop a thermodynamic model based on a surface complexation approach to permit predictions of U(6+) sorption at differing physicochemical conditions. A Diffuse-Layer model (DLM) assuming aluminol ($>AlOH^\circ$) and silanol ($>SiOH^\circ$) edge sites and two U(6+) surface complexation reactions per site effectively simulates the complex sorption behavior observed in the U(6+)—$H_2O$—$CO_2$-montmorillonite system at an ionic strength of 0.1 M and pH > 3.5. A comparison of model predictions with data from this study and from published literature shows good agreement and suggests that surface complexation models based on parameters derived from a limited set of data could be useful in extrapolating radionuclide sorption over a range of geochemical conditions. Such an approach could be used to support transport modeling by providing a better alternative to the use of constant $K_d$s in transport calculations.

**Key words:** sorption, uranium, uranyl, clays, montmorillonite, surface complexation, diffuse layer model

## 1. Introduction

The transport and fate of radionuclides in aqueous environments are of fundamental concern in nuclear waste management and in safety assessments of nuclear waste repositories. Sorption interactions with soils, sediments and rocks are potentially important mechanisms for attenuating the mobility of radionuclides through the subsurface environment. Because clay minerals are ubiquitous components of rocks, soils, and sediments, radionuclide sorption onto these minerals may play a key role in retarding radionuclide migration in many geologic environments. In addition, some disposal concepts for nuclear wastes propose the emplacement of a barrier of compacted bentonite, comprised mainly of montmorillonite, between the waste containers and the surrounding rocks in order to limit the potential movement of radionuclides from the repository (Grauer, 1994). Thus, a quantitative knowledge of radionuclide sorption onto clay minerals is important.

In this study, batch experiments were conducted to investigate U(6+) sorption onto montmorillonite. U was selected as the radioelement of interest because it is the predominant heavy metal in spent nuclear fuel, which is >95% $UO_2$, and because of its relevance in evaluating radionuclide migration from U mill tailings sites and from U ore deposits. In addition, its solubility is high in oxidizing and carbonate-rich surface and ground waters, such as those at the proposed high-level nuclear waste site at Yucca Mountain, Nevada, which increases its potential for dispersal to the environment. Furthermore, the aqueous chemistry of U(6+) is relatively well-known (e.g., Wanner and Forest, 1992), which is essential in interpreting results at various experimental conditions and in developing a thermodynamic model for the sorption reactions.

Several studies have been published on the sorption of U(6+) on montmorillonite (e.g., Borovec, 1981; Tsunashima *et al.*, 1981; Ames *et al.*, 1983; Sikalidis *et al.*, 1989; Zachara and McKinley, 1993; Akcay and Kurtulmus, 1995; McKinley *et al.*, 1995). Many of these were conducted over restricted ranges of pH. For example, initial pH used in the experiments reported by Tsunashima *et al.* (1981), Ames *et al.* (1983), and Sikalidis *et al.* (1989) was in the range 4 to 4.5, 7 to 9, and 3 to 4, respectively, whereas experiments by Borovec (1981) were conducted at an initial pH of 6.0. Because solution pH is a key parameter which controls the sorption of U and other actinides on mineral surfaces (e.g., Allard *et al.*, 1984; Hsi and Langmuir, 1985; Dozol and Hagemann, 1993; Pabalan and Turner, accepted for publication; Bertetti *et al.*, accepted for publication), it is important to have experimental data over a wide range of pH. Experiments by Zachara and McKinley (1993) and McKinley *et al.* (1995) covered a sufficiently broad range of pH (4 to 8.5) as well as ionic strength (0.001 to 0.1 M $NaClO_4$). However, their experiments were conducted in a $CO_2$(g)-free atmosphere and therefore do not provide data regarding the possible effect on sorption of carbonate ion, which forms strong aqueous complexes with U(6+) in many natural waters.

This study was designed to investigate the effects of varying pH, solid-mass to solution-volume ratio (M/V), and solution concentration on U(6+) sorption on montmorillonite. The experiments were conducted in equilibrium with atmospheric $P_{CO_2}$ to determine the effect of aqueous carbonate complexation on U(6+) sorption. Low U solution concentrations ($\leqslant 2.2 \times 10^{-6}$ M) were used to avoid the complicating effects of U-phase precipitation, which likely occurred in the experiments of Akcay and Kurtulmus (1995) who used U(6+) concentrations of $4.2 \times 10^{-3}$ M at pH up to 10.

Experimental data derived from this study were used in developing a thermodynamic model based on a surface complexation approach. The objective was to derive a model with a minimum number of parameters which can describe and predict U(6+) sorption behavior over wide ranges of geochemical conditions. The approach employed here was to use the results from one set of experiments (at a fixed initial U concentration but variable pH) to derive model parameters, and to evaluate the predictive capability of the model by comparing calculated values with data from the other sets of experiments and data from published literature.

Recent publications show that montmorillonites sorb U(6+) and other hydrolyzable metal ions through two distinct mechanisms – ion-exchange with interlayer cations and surface complex formation with hydroxylated edge sites (e.g., Zachara and McKinley, 1993; Zachara and Smith, 1994; Chisholm-Brause *et al.*, 1994; Morris *et al.*, 1994; McKinley *et al.*, 1995). Although a comprehensive description of U(6+) sorption on montmorillonite should include both ion-exchange and surface complexation reactions, interest in this study was focused on U(6+) surface complexation, which is the expected predominant sorption mechanism at pH values typical of natural waters (pH 6 to 9). Thus, the experiments were conducted using U solutions with a 0.1 M $NaNO_3$ matrix to suppress ion-exchange between U and interlayer cations. Although the derived model is applicable only under conditions where ion-exchange reactions are negligible, these types of reactions can be readily incorporated into the model if ion-exchange data are available.

## 2. Sorption Experiments

### 2.1. PREPARATION OF Na-MONTMORILLONITE

Samples of a Ca-montmorillonite (SAz-1) from Cheto, Arizona, were obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, Missouri). The <2 $\mu$m fraction used in the experiments was selectively obtained via centrifugation and was converted to the Na-form by contacting it with 2 M NaCl several times. The clay was rinsed free of $Cl^-$ and subsequently freeze-dried. The size of the clay particles was verified by scanning electron microscopy.

The external surface area of the Na-exchanged montmorillonite was determined using a Coulter SA3100 surface area analyzer. The surface area sample was prepared by outgassing at 100°C for 24 h. The analyses, using a multipoint $N_2$-BET isotherm, gave a value of 97 ± 2 $m^2/g$. The reported standard deviation is based on replicate surface area measurements of the powder sample.

### 2.2. URANIUM SOLUTIONS

A $2.1 \times 10^{-6}$ M U stock solution was prepared by diluting a radiochemically-pure $^{233}U$ standard solution traceable to the U.S. Department of Energy New Brunswick Laboratory Certified Reference Material (CRM) 111-A. Stock solutions of $2.1 \times 10^{-7}$ M U were prepared from the $2.1 \times 10^{-6}$ M U solution. All dilutions were made with a 0.1 M $NaNO_3$ matrix. Samples from the stock solutions were taken immediately before the start of the experiments to permit calculation of the total mass of U ($U_{total}$) in each experimental solution.

### 2.3. ANALYTICAL PROCEDURES

Measurements of $^{233}U$ $\alpha$-decay activity were conducted using a Packard 1900TR or 2505TR/AB liquid scintillation analyzer (LSA). Prior to counting, duplicate 0.5 mL aliquots taken from experimental solutions were mixed with 0.5 mL of 0.02 M $HNO_3$ solution and 5 mL of Ultima-Gold (Packard) scintillation cocktail in 7-mL glass vials. The samples were acidified in order to minimize U sorption onto the glass LSA vials, which could affect counting results. The counting efficiency for the LSA procedure used is at or very near to 100% for $\alpha$-particles, and the contribution of other $\alpha$- or $\beta$-emitting U isotopes and decay daughters to the total activity of the sample is less than 0.1%.

Each sample was counted for a time period sufficient for the $2\sigma$ error of the sample activity in counts per minute (cpm) to be ±3%. Raw data in cpm, which in this case were equivalent to decays per minute, were converted into concentration units and, subsequently, into mass (g) or moles of U using the measured weight of the solution. Uncertainties in sorption data presented in later sections were propagated based on the $2\sigma$ counting errors.

Measurements of pH were made using a Ross combination pH electrode and an Orion 920A pH/ISE/mV/°C meter.

### 2.4. EXPERIMENTAL PROCEDURE

The sorption experiments were conducted by reacting weighed amounts of Na-montmorillonite with weighed quantities of $\approx 2 \times 10^{-7}$ or $\approx 2 \times 10^{-6}$ M U solutions (0.1 M $NaNO_3$ matrix) in Teflon-FEP (fluorinated ethylene propylene) centrifuge tubes. Four sets of experiments (M1, M2, M3 and M4), each set comprising 29 solutions at different pHs, were conducted. The initial conditions are summarized in Table I. To evaluate the effect of M/V on U(6+) sorption, experiments were conducted using 0.001, 0.01, or 0.1 g of solid in 30 to 40 mL of U solution, resulting in an M/V range of 0.028 to 3.2 g/L.

Table I. Summary of initial experimental conditions.

| Experiment | Initial U(6+) conc. (M) | Mass of solid (g) | Mass of solution (g) | Approx. M/V (g/L) |
|---|---|---|---|---|
| M1 | $2.45 \times 10^{-7}$ | 0.099 ± 0.002 | 32.8 ± 0.3 | 3.2 ± 0.1 |
| M2 | $2.06 \times 10^{-7}$ | 0.0104 ± 0.0002 | 38.9 ± 0.6 | 0.27 ± 0.01 |
| M3 | $2.10 \times 10^{-7}$ | 0.00105 ± 0.00004 | 37.9 ± 0.4 | 0.028 ± 0.001 |
| M4 | $2.16 \times 10^{-6}$ | 0.0104 ± 0.0005 | 37.5 ± 0.5 | 0.28 ± 0.01 |

Prior to addition of the solid phase, the initial pH of each U solution was adjusted to a value in the range 2.0 to 9.0 at approximately 0.25 pH intervals by addition of $HNO_3$ or $NaHCO_3$ solution. The amount of reagent needed to achieve the desired initial pH was estimated using the EQ3NR geochemical code (version 7) with database Data0.com.R12 (Wolery, 1992). The Teflon tubes, kept loosely capped to allow the solutions to maintain equilibrium with atmospheric $CO_2(g)$, were agitated using gyratory shakers. Due to somewhat slow mass transfer of $CO_2(g)$ during equilibration to atmospheric $P_{CO_2}$, some solutions required up to ten days to reach a constant pH.

After about ten days, the initial pH ($pH_i$) of each solution was measured and 0.5 mL samples were taken using Eppendorf micropipets to determine the initial U mass in each solution ($U_{soln,i}$). Data on $U_{soln,i}$ and $U_{total}$ provided information on the amount of U sorbed onto the teflon tubes (at $pH_i$) prior to addition of the mineral phase. Subsequently, weighed amounts of Na-montmorillonite were added to each solution and the mixtures allowed to equilibrate. After about ten days, 0.5 mL samples were taken to determine the final mass of U in each solution ($U_{soln,f}$). The equilibrium pH ($pH_f$) of the remaining solutions was also measured.

To determine reversibility of the sorption reactions, one set of reverse experiments was also conducted by adjusting the pH of some of the M1 solutions at the end of the forward experiments to lower or higher values by addition of $HNO_3$ or $NaHCO_3$. After an additional period of about 10 days, the equilibrium pH of the solutions was measured and aqueous samples were taken for U analysis.

Based on previous experiments (e.g., Pabalan *et al.*, 1994), it was anticipated that U(6+) sorption on the Teflon-FEP tubes would be significant, particularly in the pH range 4 to 8, and that there would be sorption competition between the mineral and container surfaces. The amount of U(6+) sorbed on the container was expected to be greater in experiments with low M/V. To quantify the amount of U sorbed on montmorillonite and on the competing substrate (container wall), a desorption step was added at the end of the forward experiments. This was started by separating the montmorillonite from several of the mixtures using an Eppendorf micropipet and transferring the solids (along with some entrained U solution) into 15-mL polypropylene (PP) bottles. Approximately 3 mL of 0.1 M $HNO_3$ solution were added to each PP bottle to desorb the U from the montmorillonite, whereas 0.5 mL

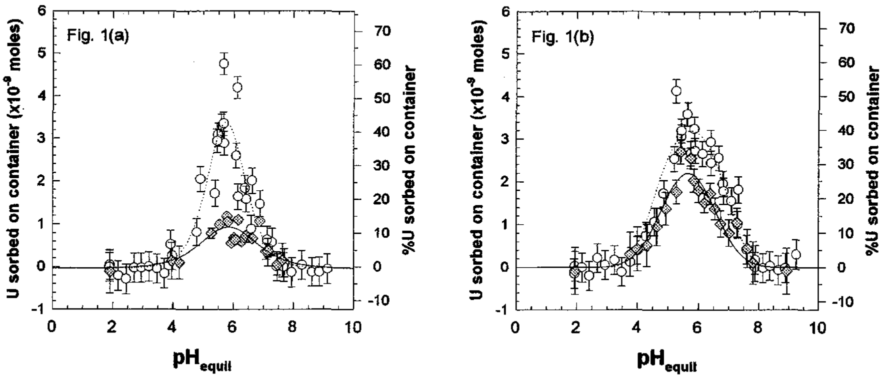

*Figure 1.* U(6+) sorption on teflon-FEP centrifuge tubes as a function of pH for experiments M2 and M3 [(a) and (b), respectively]. Container sorption before and after addition of montmorillonite is represented by circles and diamonds, respectively. Error bars represent propagated uncertainties based on $2\sigma$ errors in U analysis. Solid curves were fit to data on U(6+) sorbed on container in the presence of montmorillonite by nonlinear weighted regression and were used to interpolate container sorption for the specific pH of experimental solutions.

of 50% $HNO_3$ solution were added to the remaining solution in the centrifuge tubes to desorb the U from the container walls. After about 10 days, aqueous samples were taken to determine the mass of U desorbed from the montmorillonite, $U_{\mathrm{mont},d}$, and from the teflon container, $U_{\mathrm{cont},d}$. Measured values of $U_{\mathrm{mont},d}$ were corrected for the amount of U solution entrained with the solid during transfer.

## 3. Experimental Results

Figures 1(a) and 1(b) show the amount of U(6+) sorbed on the teflon centrifuge tubes in experiments M2 and M3, respectively, as a function of pH before and after addition of montmorillonite. These data show that U(6+) sorption on the teflon-FEP tubes is significant [to at least 45% of the original amount of U(6+)] and is dependent on solution pH, reaching a maximum at pHs between 5.5 and 6.0. The data also show that container sorption decreases but remains significant upon addition of montmorillonite, at least for the M2 and M3 experiments which had low M/V ratios.

The amount of U(6+) sorbed on montmorillonite was calculated either by taking the difference between the initial and final U concentration in solution ($U_{\mathrm{soln},i}$ and $U_{\mathrm{soln},f}$, respectively) or from the measured amount of U desorbed from the montmorillonite ($U_{\mathrm{mont},d}$). In the former method, corrections were needed to account for U(6+) which remained sorbed on the teflon tubes. Because of the strong pH dependence of container sorption, it was necessary to interpolate the amount of U(6+) sorbed on the container for the specific equilibrium pH, $pH_f$, of the experimental solution. In order to do this, best fit equations were derived by nonlinear weighted regression of the data on container sorption in the presence of montmorillonite (i.e.,

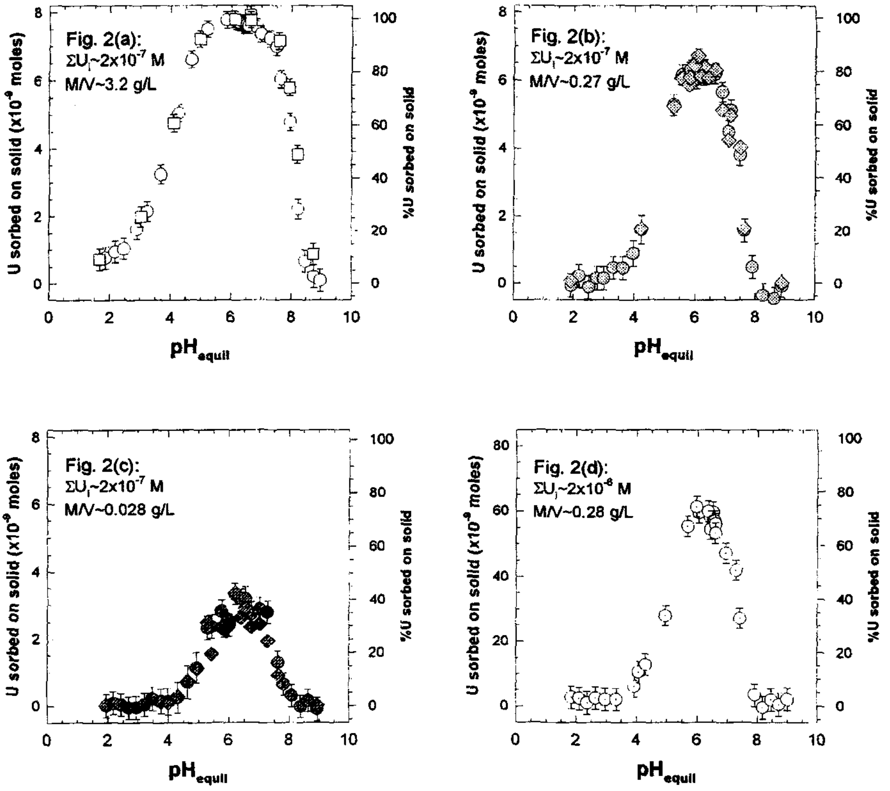

*Figure 2.* U(6+) sorption on montmorillonite as a function of pH: (a) experiment M1, (b) experiment M2, (c) experiment M3, and (d) experiment M4. Circles and squares in Figure 2(a) represent forward and reverse sorption data from experiment M1. Symbols in Figures 2(b) and 2(c) represent sorption values calculated either from differences in initial ($U_{soln,i}$) and final ($U_{soln,f}$) U(6+) solution concentration (circles) or from amount of U(6+) desorbed ($U_{mont,d}$) from montmorillonite (diamonds). Error bars indicate $2\sigma$ uncertainties associated with the sorption data. Note the different y-axis scale for Figure 2(d).

$U_{cont,d}$ versus $pH_f$; diamond symbols in Figure 1). These equations (represented by the solid curves in Figure 1) were used to calculate container sorption at the equilibrium pH of experimental solutions.

The data on U(6+) sorption on montmorillonite are shown in Figure 2 as a function of pH. These results demonstrate the strong pH dependence of U(6+) sorption. The amount of U sorbed on montmorillonite reached a maximum at near-neutral pH (≈6 to ≈6.5), and decreased sharply towards more acidic or more alkaline conditions. This pH dependence of U(6+) sorption has also been observed with other mineral sorbents, such as quartz and other silicate minerals (e.g., Allard *et al.*, 1980; Pabalan *et al.*, 1993; Zachara and McKinley, 1993; McKinley *et al.*, 1995; Pabalan *et al.*, accepted for publication; Bertetti *et al.*, in prep.) and

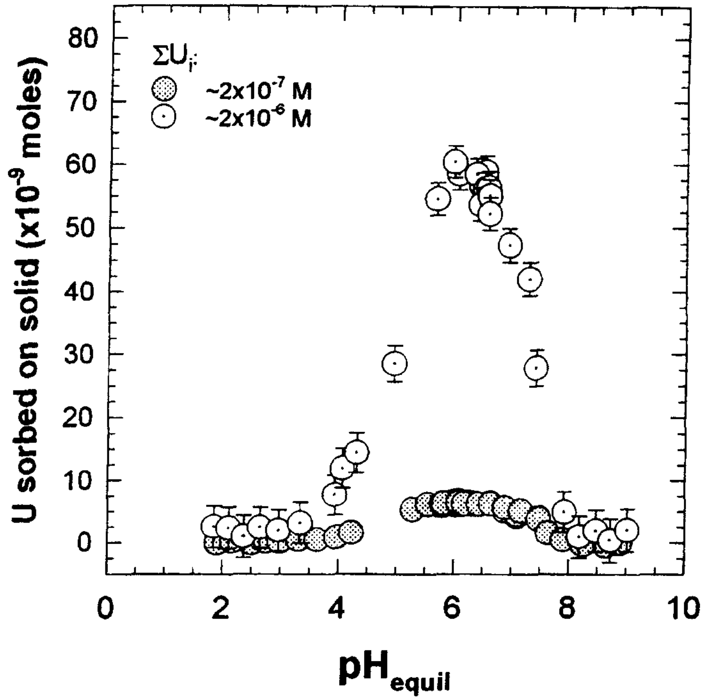

*Figure 3.* Sorption of U(6+) on montmorillonite at an M/V ratio of $\approx$0.27 g/L as a function of $\sum U_i$ and pH. Error bars indicate $2\sigma$ uncertainties associated with the sorption data.

aluminum- and iron-(hydr)oxides (e.g., Tripathi, 1984; Hsi and Langmuir, 1985; Prikryl *et al.*, 1994; Waite *et al.*, 1994).

The circles and squares in Figure 2(a) represent data from the forward and reverse directions, respectively, in experiment M1. The very good agreement between the forward and reverse data demonstrated that U(6+) sorption on montmorillonite is a reversible process and that sorption equilibrium was achieved during the time period used in the experiments. The circle and diamond symbols in Figures 2(b) and 2(c) represent, respectively, U(6+) sorption values calculated from differences in $U_{\mathrm{soln},i}$ and $U_{\mathrm{soln},f}$ (corrected for container sorption) and those calculated from $U_{\mathrm{mont},d}$. The good agreement in U sorption values calculated using the two methods provides confidence in the procedures used in correcting for container sorption and in separating the solid phase from the solution prior to the desorption step.

The results shown in Figures 2(a), 2(b), and 2(c) are for experiments at M/V ratios of 3.2, 0.27, and 0.028 g/L, respectively, and initial U(6+) concentration of $\approx 2 \times 10^{-7}$ M. These data show that U(6+) sorption on montmorillonite increases with increasing M/V ratio, although the change in sorption is not linear with the change in M/V. U(6+) sorption on montmorillonite is also dependent on the initial

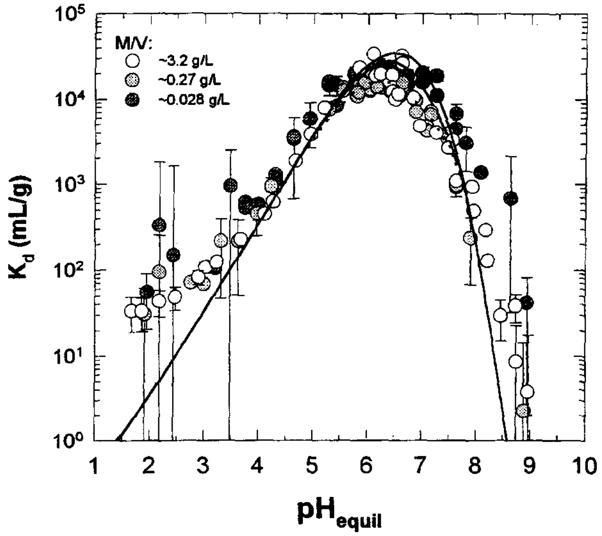

*Figure 4.* U(6+) sorption on montmorillonite plotted in terms of $K_d$ versus pH for experiments at a $\sum U_i \approx 2 \times 10^{-7}$ M. For clarity, error bars for some points were not included. The curves represents values calculated from the DLM with parameter values given in Table II using MINTEQA2 (Allison *et al.*, 1991) at M/V ratios of 3.2, 0.27, or 0.028 g/L (solid, dashed, and dotted lines, respectively).

concentration of U in solution. For example, a comparison of sorption data plotted in Figure 3 for experiments at an M/V of 0.27 g/L and $\sum U_i \approx 2 \times 10^{-7}$ or $\approx 2 \times 10^{-6}$ M indicates that the moles of U(6+) sorbed on montmorillonite increase with an increase in initial solution concentration of U.

An alternative method of representing sorption data in terms of a distribution coefficient, $K_d$, may be defined as

$$K_d\ (\mathrm{mL/g}) = \frac{\text{amount of U(6+) sorbed/gram of solid}}{\text{amount of U(6+) in solution/mL of solution}}. \tag{1}$$

Plotting data in terms of $K_d$ provides a means of normalizing sorption results with respect to sorbent concentration (or M/V ratio) and of taking into account the decrease in solution concentration of the radionuclide during the sorption process. Although it is convenient to represent sorption data in terms of moles of U(6+) sorbed or more typically as %U sorbed versus pH, results presented in these ways can be misleading with regard to effects on contaminant transport. For instance, although data plotted in Figures 2(a) to 2(c) appear to show that M/V has a large effect on U(6+) sorption behavior, the same data replotted in terms of $K_d$ (Figure 4) show that U(6+) sorption does not vary much with changes in M/V. Similarly, a comparison of Figures 3 and 5 indicates that plotting data in terms of moles of U(6+) sorbed overemphasizes the effect of U concentration on sorption.

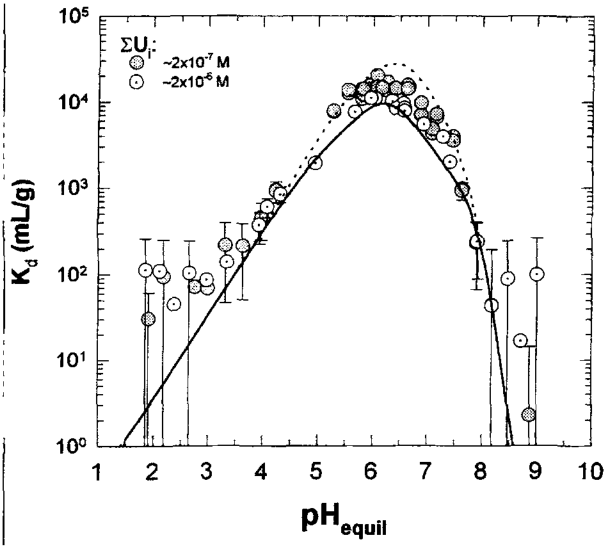

*Figure 5.* U(6+) sorption on montmorillonite plotted in terms of $K_d$ versus pH for experiments at an M/V ratio of ≈0.27 g/L. For clarity, error bars for some points were not included. The dashed and solid curves represent DLM-calculated values for solutions with $\sum U_i = 2.06 \times 10^{-7}$ and $2.16 \times 10^{-6}$ M, respectively, using parameters given in Table II.

To aid in evaluating possible surface complexes, it is useful to compare U(6+) sorption behavior with U(6+) aqueous speciation. Figure 6 shows the relative stabilities of the aqueous U(6+) species as a function of pH for a $2.1 \times 10^{-6}$ M U(6+) solution (0.1 M $NaNO_3$ matrix) in equilibrium with atmospheric $CO_2(g)$ ($P_{CO_2} = 10^{-3.5}$ atm). The U(6+) speciation was calculated using the MINTEQA2 geochemical code (Allison *et al.*, 1991) and uranium thermodynamic data taken from the Nuclear Energy Agency (NEA) database (Wanner and Forest; 1992), with an exception as noted below, and listed in Table II. The thick curve in Figure 6 represents the sum of the molarities of the U(6+) hydroxy-complexes. Comparison of Figures 4 and 5 with Figure 6 indicates a close correspondence between the pH dependence of U(6+) sorption on montmorillonite and the predominance field of the U(6+) hydroxy-complexes.

The decrease in the amount of U sorbed at alkaline pH is related to the increasing importance of carbonate-complexes with increasing pH. At low pHs, where the uranyl cation $UO_2^{2+}$ becomes predominant, U(6+) sorption through ion-exchange was suppressed under the relatively high ionic strength conditions of this study. However, for solutions at low ionic strength, ion-exchange between $UO_2^{2+}$ in solution and the interlayer cations of montmorillonite is expected to occur resulting in higher sorption values (e.g., Zachara and McKinley, 1993; McKinley *et al.*, 1995). Some of the data from this study may reflect the contribution of an ion-exchange mechanism. For example, data from experiment M1 below pH 2.5 [Figure 2(a)] appear to level off at about 8% U sorbed, instead of reaching 0%. In Figure 4, the

Table II. FITEQL model conditions used to determine DLM binding constants for U(6+) sorption on montmorillonite.

| | |
|---|---|
| Solid concentration (M/V) | 0.28 g/L |
| Site density | 2.3 sites/nm$^2$ |
| Surface area[a] | 9.7 m$^2$/g |
| Total site concentration | $>$AlOH$^\circ$<br>$= 4.73 \times 10^{-5}$ mol sites/L<br>$>$SiOH$^\circ$<br>$= 5.69 \times 10^{-5}$ mol sites/L |
| Ionic strength | 0.1 M $NaNO_3$ |
| $\sum {}^{233}U(6+)$ | $2.16 \times 10^{-6}$ M |
| $P_{CO_2}$ | $10^{-3.5}$ atm |
| *Edge-Site Reactions:* | Log *K* |
| $>AlOH^\circ + H^+ \rightleftharpoons >AlOH_2^+$ | 8.33[b] |
| $>AlOH^\circ \rightleftharpoons >AlO^- + H^+$ | −9.73[b] |
| $>AlOH^\circ + UO_2^{2+} \Leftrightarrow >AlO\text{—}UO_2^+ + H^+$ | 2.70[c] |
| $>AlOH^\circ + 3UO_2^{2+} + 5H_2O \Leftrightarrow >AlO\text{—}(UO_2)_3(OH)_5^\circ + 6H^+$ | −14.95[c] |
| $>SiOH^\circ \rightleftharpoons >SiO^- + H^+$ | −7.20[b] |
| $>SiOH^\circ + UO_2^{2+} \Leftrightarrow >SiO\text{—}UO_2^+ + H^+$ | 2.60[c] |
| $>SiOH^\circ + 3UO_2^{2+} + 5H_2O \Leftrightarrow >SiO\text{—}(UO_2)_3(OH)_5^\circ + 6H^+$ | −15.29[c] |
| *Aqueous Speciation Reactions:* | Log *K* |
| $UO_2^{2+} + H_2O \Leftrightarrow UO_2OH^+ + H^+$ | −5.20 |
| $UO_2^{2+} + 2H_2O \Leftrightarrow UO_2(OH)_2^\circ\ (aq) + 2H^+$ | −13.0[d] |
| $UO_2^{2+} + 3H_2O \Leftrightarrow UO_2(OH)_3^- + 3H^+$ | −19.20 |
| $2UO_2^{2+} + 2H_2O \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+$ | −5.62 |
| $3UO_2^{2+} + 5H_2O \Leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$ | −15.55 |
| $UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3^\circ$ | 9.68 |
| $UO_2^{2+} + 2CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$ | 16.94 |
| $UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$ | 21.60 |
| $2UO_2^{2+} + CO_3^{2-} + 3H_2O \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3H^+$ | −0.86 |
| $UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$ | 0.30 |

[a] Effective edge site surface area assumed to be 10% of total $N_2$-BET surface area (97 m$^2$/g). See text for detailed discussion.

[b] Acidity constants for am-$SiO_2$ and $\alpha$-$Al_2O_3$ from Turner and Sassman (1996).

[c] This study. Binding constants determined using FITEQL, Version 2.0 (Westall, 1982a,b).

[d] All aqueous speciation Log K values from NEA Uranium Thermodynamic Database (Wanner and Forest, 1992), except for $UO_2(OH)_2^\circ$ (aq) which is taken from Fuger (1992). See text for detailed discussion.

M1 experiment $K_d$ values (open circles; M/V = 3.2 g/L) at pHs below 2.5 level off to about 30 mL/g, suggesting a changing sorption mechanism. Other data in Figure 4 (M/V = 0.27 and 0.028 g/L) below a pH of 2.5 show a similar trend, but there is larger uncertainty in those $K_d$ values.

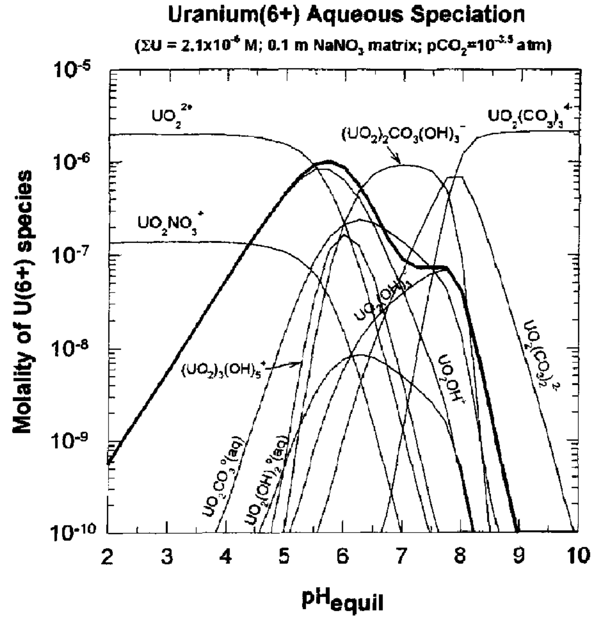

*Figure 6.* Aqueous U(6+) speciation at 25°C as a function of pH for a 2.1 × $10^{-6}$ M U(6+) solution (0.1 m $NaNO_3$ matrix) in equilibrium with $P_{CO_2} = 10^{-3.5}$ atm. Some minor species are not shown. Speciation was calculated using the MINTEQA2 geochemical code (Allison *et al.*, 1991) and the equilibrium constants listed in Table II. The heavy curve represents the sum of the moles of U(6+) hydroxy-complexes.

## 4. Surface Complexation Model

One of the goals of the sorption experiments is to provide data that will help in the development and calibration of geochemical models which are capable of simulating the influence of changing physicochemical conditions on radionuclide sorption behavior. A class of models that has been developed and used with success in modeling pH-dependent sorption is the electrostatic surface complexation model (SCM) (Davis and Leckie, 1978; Westall and Hohl, 1980; Davis and Kent, 1990; Hayes *et al.*, 1991). SCMs are based on the assumption of analogous behavior between aqueous complex formation in the bulk solution and formation of surface complexes with functional binding sites at the mineral-water interface. Surface reactions are written for sorbing species, and mass action and mass balance relations are used to determine sorption at the mineral surface as a function of system chemistry. Additional terms in the mass action expression for the surface reaction account for the effects of electrostatic interactions at the mineral surface on the system chemistry.

Traditional applications of SCMs have relied on simultaneously adjusting different model-specific parameters to produce the best match to a given data set. Because SCMs typically have a large number of potentially adjustable parameters [e.g., eight types for the Triple-Layer Model (TLM)], this approach is likely to result in a nonunique fit that makes comparison between models and between studies difficult (Westall and Hohl, 1980). Therefore, recent efforts have focused on developing a 'standard' set of model parameters (Dzombak and Morel, 1990; Hayes *et al.*, 1991; Bradbury and Baeyens, 1993; Turner and Sassman, 1996). This has the benefit of limiting the number of adjustable parameters and providing a set of uniform SCM parameters that share common reference values. Dzombak and Morel (1990) used such an approach in applying the Diffuse-Layer Model (DLM) to available data on the sorption of heavy metals such as $Zn^{2+}$, $Pb^{2+}$, and $SeO_4^{2-}$ on ferrihydrite. In an effort to extend this type of approach to U(6+) sorption, the current study has focused on the DLM and adopted many of the methods outlined in Dzombak and Morel (1990).

### 4.1. MODEL DESCRIPTION

The surface charge of many minerals, primarily oxides and oxyhydroxides, is known to vary as a function of pH (Davis and Kent, 1990). SCMs deal with this pH-dependence by assuming a surface comprised of hydroxyl groups ($>XOH^\circ$, where the $>X$ is used to represent functional surface groups for a metal X oxyhydroxide). Surface adsorption is described using a combination of equilibrium protonation ($>XOH_2^+$), deprotonation ($>XO^-$), and complexation reactions. Mass balance and mass action relations, modified to include the electrostatic effects of a charged mineral surface, can then be used to determine the distribution of the elements between those dissolved in the bulk solution and those specifically sorbed onto the solid.

Different SCM approaches use different conceptual models of the mineral-water interface. The DLM uses a one layer representation of the mineral-water interface and has fewer fitting parameters than multi-layer SCMs such as the TLM. The pH dependence of surface charge development is accounted for in the DLM, but in contrast to a multi-layer model like the TLM, the DLM assumes that supporting electrolyte ions such as $Na^+$ and $NO_3^-$ do not interact with the surface. For this reason, the DLM neglects the possible formation of outer-sphere complexes involving the background electrolytes and does not specifically address the effect of increasing electrolyte concentration on sorption except through aqueous activity coefficients and the charge-potential relationship (Dzombak and Morel, 1990). The details of the DLM and the simplified approach used in this study are described elsewhere (Dzombak and Morel, 1990; Davis and Kent, 1990; Turner and Sassman, 1996) and only a brief overview is presented here.

A generalized pH-dependent sorption reaction between aqueous U(6+) and a surface sorption site can be written in the form:

$$>XOH^\circ + pUO_2^{2+} + nH_2O \leftrightarrows [>XOH_q - (UO_2)_p(OH)_n]^{2p+q-n+1} \\ +(1+n-q)H^+, \qquad (2)$$

where $q$ is the protonation state of the sorption site ($q$ = 0, 1, or 2), and $UO_2^{2+}$ and $[>XOH_q - (UO_2)_p(OH)_n]^{2p+q-n-1}$ represent the uranyl aqueous species and the U(6+) surface complex, respectively. In the SCM approach, a coulombic correction is incorporated into the mass action expressions for surface reactions to extract the intrinsic equilibrium constants (e.g.,, $K_+^{\mathrm{int}}$, $K_-^{\mathrm{int}}$ and $K_{>XOH_q-(UO_2)_p(OH)_n]}$) that are independent of surface charge. For sorption reactions of the type given in Equation (2), $K_{>XOH_q-(UO_2)_p(OH)_n]}$) is commonly referred to as the binding constant.

Turner and Sassman (1996) used the numerical, nonlinear parameter optimization code FITEQL, Version 2.0 (Westall, 1982a,b) to interpret potentiometric titration data and determine the DLM acidity constants ($K_+^{\mathrm{int}}$ and $K_-^{\mathrm{int}}$) necessary to define the protonation and deprotonation behavior of a number of different mineral surfaces. The values are model specific, but once defined, the acid/base behavior of the surface is characterized and these values become fixed in the geochemical model. For the DLM, the remaining adjustable parameter is the binding constant for U(6+) sorption reactions of the form given in Equation (2).

The observed dependence of U(6+) sorption on pH, M/V and U(6+) concentration is a consequence of mass action effects and equilibrium chemistry in the U(6+)—$H_2O$—$CO_2$-montmorillonite system. Qualitatively, one can say that an increase in M/V and U(6+) concentration increases the concentrations or activities of $>XOH^\circ$ and $UO_2^{2+}$, respectively, and drives the equilibrium reaction in Equation (2) forward (increasing sorption). Alternatively, formation of U(6+) aqueous carbonate-complexes which appear to be nonsorbing reduces the activity of $UO_2^{2+}$ and drives the reaction in the opposite direction (decreasing sorption). This explanation is, of course, simplistic due to the synergistic effects between solution chemistry, sorption site protonation state, and speciation of the aqueous and surface complexes.

### 4.2. MODELING OF U(6+) SORPTION OF MONTMORILLONITE

An essential test of the adequacy of the DLM is the development of a conceptual model capable of reproducing the observed sorption behavior in the U(6+)—$H_2O$—$CO_2$-montmorillonite system. This is an especially challenging test given that the DLM was developed principally to model sorption on oxides and oxyhydroxides, such as $\alpha$-$Al_2O_3$ and goethite, instead of more complex aluminosilicates, such as montmorillonite. In this study, an approach has been adopted such that the simplest model that can describe the observed sorption behavior is preferred. Ideally, extension of this approach to other systems will lead to a set of parameters which are based on a common methodology and reference points. This in turn will allow for the direct comparison and performance evaluation of different models and provide a consistent modeling tool for use in performance assessment calculations of radionuclide transport.

Prior studies established that sorption on a clay such as montmorillonite consists of ion-exchange at interlayer sites and pH-dependent sorption at crystallite edge sites (Zachara and McKinley, 1993; Chisholm-Brause *et al.*, 1994; Morris *et al.*, 1994; Zachara and Smith, 1994; Wanner *et al.*, 1994; Degueldre *et al.*, 1994, McKinley *et al.*, 1995). As discussed previously, experiments in this study were conducted at relatively high ionic strength (0.1 M $NaNO_3$) which suppressed ion-exchange of $UO_2^{2+}$ with interlayer cations. Therefore, in modeling U(6+) sorption on montmorillonite, it was assumed that edge sites dominate the sorption behavior and ion-exchange was not explicitly incorporated in model construction.

In contrast to oxides, the surfaces of aluminosilicate minerals are likely to be more complex in terms of site types. Recent studies have successfully modeled the pH-dependent sorption behavior of layered aluminosilicates such as montmorillonite and kaolinite by assuming crystallite edges are comprised of silanol ($>SiOH^\circ$) and aluminol ($>AlOH^\circ$) sites which compete for available adsorbate but otherwise do not interact with each other (Rai *et al.*, 1988; Zachara and Smith, 1994; Marmier *et al.*, 1995; McKinley *et al.*, 1995; Turner, 1995). This makes it possible to predict aluminosilicate sorption behavior using protonation and deprotonation chemistry of silanol and aluminol sites. This approach has been adopted in this study.

To develop a DLM for the U(6+)-montmorillonite system, it was necessary to calculate the total number of edge sorption sites ($T_{>XOH}$) and the distribution of these sites between the $>AlOH^\circ$ and $>SiOH^\circ$ site types. Wanner *et al.* (1994) estimated that crystallite edges accounted for about 10% of the $N_2$-BET specific surface area measured for their Na-montmorillonite specimen. Assuming the same relative value of 10% observed by Wanner *et al.* (1994), an effective crystallite edge surface area of 9.7 $m^2/g$ (10% of the measured $N_2$-BET specific surface area of 97 $m^2/g$) was calculated for the Na-montmorillonite used in this study. The effective surface area, together with a “standard” site density of 2.3 sites/$nm^2$ recommended for all minerals by Davis and Kent (1990) based on the ferrihydrite work of Dzombak and Morel (1990), was then used to calculate the total number of available edge sites. In the absence of more quantitative information, the concentrations of $>AlOH^\circ$ and $>SiOH^\circ$ sites (Table II) were calculated assuming an Al/Si ratio at the crystallite edges of 0.83 as proposed for montmorillonite by White and Zelazny (1988). The acidity constants used for the protonation and deprotonation of the $>SiOH^\circ$ and $>AlOH^\circ$ edge sites were derived from potentiometric titration data for $SiO_2$ and $\alpha$-$Al_2O_3$ as described in Turner and Sassman (1996).

In addition to data describing the mineral properties and the acid/base behavior of the surface (Table II), FITEQL requires the input of an equilibrium aqueous speciation model. For this reason the resultant binding constants are dependent on the quality and extent of the thermodynamic data available for the system of interest. For U(6+) the equilibrium constants for aqueous species are listed in Table II. These values were taken from the NEA thermodynamic database (Wanner and Forest, 1992) with the exception of the value for the neutral hydroxy complex, $UO_2(OH)_2^\circ(aq)$. Due to experimental uncertainties, Wanner and Forest (1992) could only recommend an upper limit to the stability constant of $UO_2(OH)_2^\circ(aq)$. The value used with FITEQL and listed in Table II was taken from Fuger (1992). This value is 2.7 log units lower than the upper limit recommended by Wanner and Forest (1992), but as pointed out by Fuger (1992) a lower value is consistent with the work of Choppin and Mathur (1991).

Using the mineral properties described previously (listed in Table II) and the U(6+) sorption data for the higher surface loading conditions of experiment M4 ($\sum \mathrm{U}_i = 2.16 \times 10^{-6}$ M; M/V = 0.28 g/L), FITEQL was used to determine binding constants for the U(6+)-montmorillonite sorption reaction(s) of the general form given in Equation (2). Using mass balance and mass action constraints imposed by the chemical equilibrium model, FITEQL adjusts the binding constant for the postulated sorption reaction(s) until the difference between calculated results and experimental data is minimized.

There is typically a lack of independent analytical data supporting the formation of a particular surface complex. In the absence of these data, the exact form of the surface reaction is usually selected based on analogous speciation reactions in the aqueous phase and qualitative or quantitative goodness-of-fit criteria. Model-predicted U(6+) aqueous speciation at $\sum \mathrm{U}_i = 2.16 \times 10^{-6}$ M ($I$ = 0.1 M $\mathrm{NaNO_3}$) suggests that important aqueous species in the pH range 4 to 7 include $\mathrm{UO_2^{2+}}$, $\mathrm{UO_2OH^+}$, and $\mathrm{(UO_2)_3(OH)_5^+}$. Using the TLM, Zachara and Smith (1994) and McKinley *et al.* (1995) proposed the formation of $\mathrm{>XO\text{-}UO_2^+}$ and $\mathrm{>XO\text{-}(UO_2)_3(OH)_5^\circ}$ surface complexes at the pH dependent edge sites. The goodness-of-fit results from our FITEQL regression to the M4 experimental dataset support this surface speciation for the DLM.

The four surface complexation reactions used in our DLM conceptual model can be written as:

$$\mathrm{>SiOH^\circ + UO_2^{2+} = >SiO{-}UO_2^+ + H^+} \quad (3a)$$

$$\mathrm{>SiOH^\circ + 3UO_2^{2+} + 5H_2O = >SiO{-}(UO_2)_3(OH)_5^\circ + 6H^+} \quad (3b)$$

$$\mathrm{>AlOH^\circ + UO_2^{2+} = >AlO{-}UO_2^+ + H^+} \quad (3c)$$

$$\mathrm{>AlOH^\circ + 3UO_2^{2+} + 5H_2O = >AlO{-}(UO_2)_3(OH)_5^\circ + 6H^+} \quad (3d)$$

The binding constants for these reactions are given in Table II.

### 4.3. MODEL RESULTS

One test of the flexibility of the model is the ability to reproduce observed changes in sorption behavior induced by changes in geochemical conditions. The model developed here reproduces the M4 sorption data very well as a function of pH [Figure 7(a)]. The binding constants derived from the M4 data were used to predict the effect of changing M/V ratio (and the resultant change in total site concentration) on U(6+) sorption on montmorillonite. A comparison of DLM results with measured values is shown in Figure 7(b) for the experiments with M/V ratios of 0.028, 0.27, and 3.2 g/L. As shown in the figure, the sorption envelopes predicted for an M/V of 3.2 and 0.27 g/L agree well with experimental data, although there is a slight underprediction of sorption at an M/V of 3.2 g/L for pHs $< 3.5$. The underprediction at low pH is probably due to the contribution of ion-exchange mechanism to the measured sorption not accounted for in the model. The predicted sorption behavior at M/V=0.028 g/L is acceptable, although there is some underprediction of sorption at pHs $> 6$.

Comparisons between model and experimental results in terms of $K_d$ versus pH are shown in Figures 4 and 5. It is clear from these figures that the model adequately represents the pH dependence of U(6+) sorption on montmorillonite, except at very low pHs ($<3.5$) where ion-exchange may occur. It is interesting to note that for the pH range typical of natural waters ($\approx 6$ to $\approx 9$), U(6+) sorption on montmorillonite changes by four orders of magnitude and reaches negligible values at the high pH end. Figure 4 shows that for the range of M/V used in this study, both modeling and experimental results indicate that changes in M/V have relatively little effect on the partitioning of U(6+) between the aqueous and solid phases. The experimental data and model results plotted in Figure 5 indicate that an increase in $\sum U_i$ results in lower $K_d$s particularly in the intermediate pH range. The effect is greater at higher $\sum U_i$ due to the nonlinearity of the sorption isotherm (Pabalan *et al.*, accepted for publication). Calculated variations in surface speciation with changing uranium concentration are similar to those predicted for aqueous speciation. The DLM results indicate that the multinuclear surface complex $>XO{-}(UO_2)_3(OH)_5^\circ$ is only significant at the higher uranium concentrations of the M4 experiment. At lower $\sum U_i$, $>XO{-}(UO_2)_3(OH)_5^\circ$ diminishes and $>XO{-}UO_2^+$ increases in importance analogous to the relative decrease of $(UO_2)_3(OH)_5^+$ and relative increase of $UO_2^{2+}$ in the aqueous phase.

Under conditions in equilibrium with atmospheric $CO_2$, U(6+)-montmorillonite sorption at alkaline conditions exhibits a trend of decreasing sorption with increasing pH similar to that observed for U(6+) sorption on other minerals such as Fe-oxyhydroxides (e.g., Tripathi, 1984; Hsi and Langmuir, 1985; Waite *et al.*, 1994). This trend has been attributed to both competition for sorption sites by carbonate species, such as $CO_3^{2-}$ and $HCO_3^-$ (LaFlamme and Murray, 1987; van Geen *et al.*, 1994) and competition for U(6+) by the formation of U(6+)- (hydroxy)-carbonate aqueous complexes (e.g., Payne *et al.*, 1992). The conceptual model developed here does not explicitly invoke the formation of either uranium- carbonate surface species such as $>SiOH_2{-}UO_2(CO_3)_2^-$ or the competition for available sorption sites by carbonate species (e.g., $>AlOH_2{-}CO_3^-$). At relatively low carbonate concentrations, this is a reasonable assumption. At high carbonate concentrations studies of carbonate sorption on Fe-oxyhydroxides (van Geen *et al.*, 1994) suggest that coverage of surface sites by carbonate ions may become significant and could lead to reduced sorption of radionuclides. At present, there is insufficient data to characterize quantitatively the sorption of carbonate on montmorillonite. Instead,

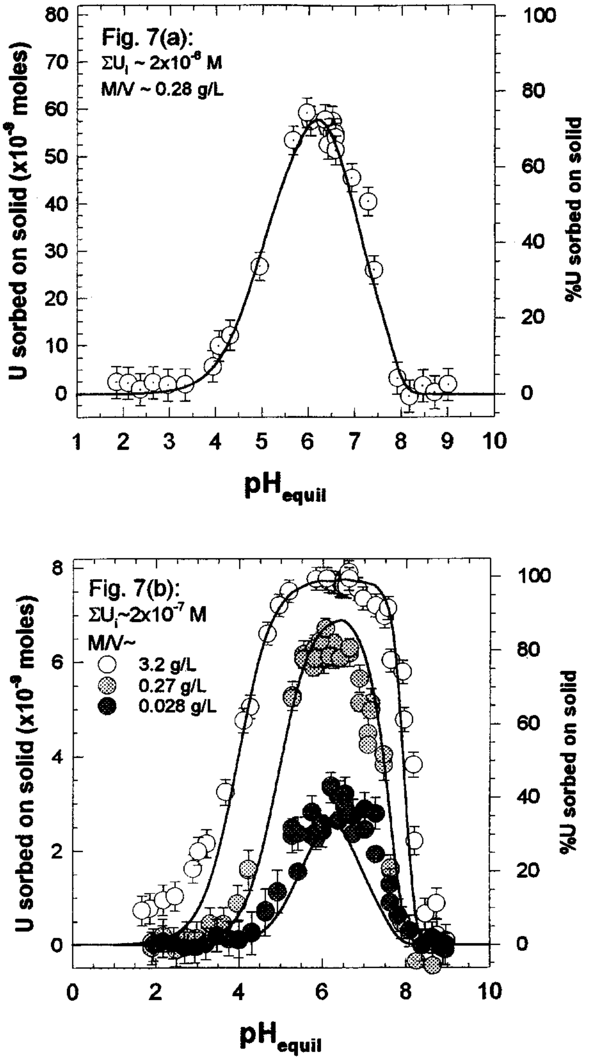

*Figure 7.* Comparison of Diffuse-Layer Model results with sorption data for: (a) experiment M4, and (b) experiments M1, M2, and M3. Binding constants given in Table II were derived using FITEQL and sorption data from experiment M4. The same binding constants were used to predict U(6+) for the conditions of experiments M1, M2, and M3.

the trend of decreasing sorption at higher pH is attributed to the increased carbonate concentration and the more effective complexation in the bulk solution by the carbonate ligand of available U(6+) relative to that by the surface sites.

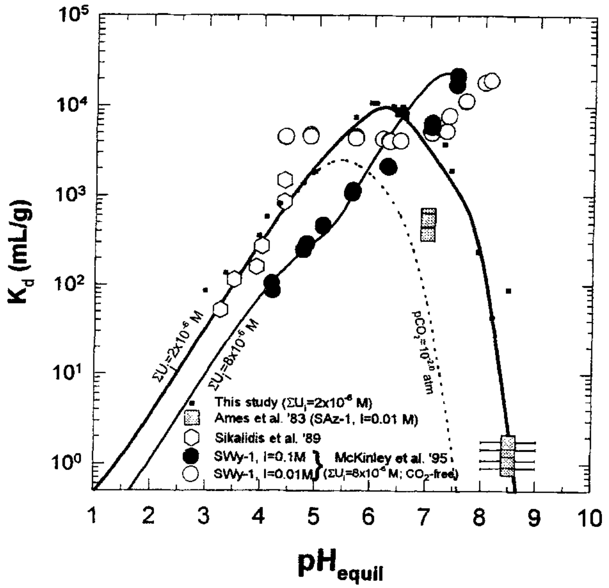

*Figure 8.* Comparison of U(6+) sorption data on montmorillonite from various studies. The heavy line represents DLM-calculated $K_d$s for M4 experimental conditions ($\sum U_i = 2.16 \times 10^{-6}$ M, ionic strength = 0.1 m, $P_{CO_2} = 10^{-3.5}$ atm, edge site surface area = 9.7 $m^2/g$ (total specific surface area = 97 $m^2/g$), and M/V = 0.28 g/L. The dashed line represents DLM-predicted $K_d$s for conditions similar to those of experiment M4, but at a higher $P_{CO_2}$ ($10^{-2.0}$ atm). DLM-predicted $K_d$s for conditions similar to those of McKinley *et al.*'s (1995) experiments [$\sum U_i = 8.4 \times 10^{-6}$ M, ionic strength = 0.1 M, no $CO_2(g)$, total specific surface area = 31 $m^2/g$, and M/V = 0.59 g/L] are represented by the light line.

## 5. Comparison With Other Data

A number of experimental studies have been published on U(6+) sorption on montmorillonite (e.g., Borovec, 1981; Tsunashima *et al.*, 1981; Ames *et al.*, 1983; Sikalidis *et al.*, 1989; Zachara and McKinley, 1993; McKinley *et al.*, 1995). These experiments were conducted using different solution chemistry (pH, ionic strength, U concentration, carbonate concentration), montmorillonite specimen, M/V, and/or sorbent preparation methods, all of which could affect U(6+) sorption. Thus, comparison of sorption data from different studies can be complicated. For experimental data sets at U solution concentrations which are relatively close, a convenient method for comparing different data sets is in terms of $K_d$. As discussed previously, representing sorption data in terms of $K_d$ normalizes the results with respect to sorbent concentration (or M/V) and accounts for the effect of changing U solution concentration. Plotted in Figure 8 are sorption data from various studies in terms of $K_d$ versus pH. The heavy curve in the figure represents values calculated from the DLM model discussed previously for a $\sum U_i$ of $2.1 \times 10^{-6}$ M, $P_{CO_2}$ of $10^{-3.5}$ atm, and assuming an effective edge surface area of 9.7 $m^2/g$.

McKinley *et al.* (1995) conducted U(6+) sorption experiments on a reference smectite (SWy-1 montmorillonite, Na-exchanged) at an initial U solution concentration of $8.4 \times 10^{-6}$ M, at three ionic strengths (0.001, 0.01 and 0.1 M $NaClO_4$), under $CO_2$-free conditions, and at pH 4 to 8.5. $K_d$ values calculated from their data at an ionic strength of 0.1 M $NaClO_4$ are represented by hatched circles in Figure 8. Their $K_d$s below pH 6.5 show the same trend with pH as the results from this study, although their results are lower most likely due to the lower surface area (hence, a lower total number of sorption sites) of their sorbent material. The reported external ($N_2$-BET) surface area for SWy-1 montmorillonite is 31 $m^2/g$, compared with 97 $m^2/g$ for the SAz-1 clay used in this study. Using the DLM model developed in this study and assuming that the proportion of edge sites is the same for Swy-1 and SAz-1 montmorillonite (10% of total $N_2$-BET surface area), $K_d$s were predicted for the experimental conditions used by McKinley *et al.* (1995). The model predictions, which are represented by the light line in Figure 8, agree well with the measured $K_d$s.

Results from McKinley *et al.*'s (1995) experiments conducted at a lower ionic strength of 0.01 M $NaClO_4$ are also plotted in Figure 8 to illustrate ionic strength effects. Below a pH of 7, their $K_d$s in 0.01 M $NaClO_4$ solutions are higher than their $K_d$s at 0.1 M $NaClO_4$ solutions due to an ion-exchange sorption mechanism. Data from Sikalidis *et al.* (1989) are also plotted in Figure 8 for comparison. The experiments by Sikalidis *et al.* (1989), which were conducted using a different montmorillonite material (Upton, Wyoming bentonite) and higher $\sum U_i$ ($8.4 \times 10^{-4}$ to $8.4 \times 10^{-3}$ M), resulted in $K_d$s much higher than would be predicted by our DLM model. The higher values are most likely due to the predominance of ion-exchange as the sorption mechanism in those experiments.

Above a pH of 6.5, $K_d$s from McKinley *et al.* (1995) continue to increase with increasing pH, in contrast to results from this study. This difference is due to the lack of aqueous carbonate in their system which would have complexed with U(6+) and inhibited its sorption on the clay. Additional data plotted in Figure 8 emphasize the importance of carbonate-complexation in controlling U(6+) sorption on clay minerals. For example, Ames *et al.* (1983) measured $K_d$s less than 2 for U(6+) sorption on SAz-1 montmorillonite in 0.01 $NaHCO_3$ solutions ($\sum U_i$ of $10^{-4}$ to $10^{-7}$ M), in good agreement with results from this study. The dashed curve represents DLM predicted $K_d$s at higher $CO_2$ partial pressures ($10^{-2.0}$ atm) which show that U(6+) sorption will be substantially lower at $P_{CO_2}$s typical of groundwater systems.

Ames *et al.*'s (1983) results in 0.01 M NaCl solutions (pHs reported as ≈7) are also plotted in Figure 8, but those $K_d$s are much lower than would be predicted by our DLM model, even though they used a similar sorbent material (SAz-1 montmorillonite, Na-exchanged) and their range of $\sum U_i$ ($\approx 10^{-7}$ to $\approx 10^{-4}$ M) overlaps with ours. The external surface area of their montmorillonite specimen was not reported, but any difference with that of the clay used in this study will probably not account for all of the difference between their $K_d$s and those predicted by our model.

## 6. Conclusions

Experimental data derived in this study indicate that montmorillonite can be a strong sorber of U(6+) and could contribute to the retardation of U(6+) migration in many geochemical environments where clay is commonly an important component. However, U(6+) sorption is strongly sensitive to pH and to the formation of aqueous U(6+)-carbonate complexes. Thus, in natural waters of typical pH ($\approx$6 to $\approx$9) and carbonate concentration (values in equilibrium with atmospheric $P_{CO_2}$ or higher), sorption of U(6+) onto montmorillonite can vary by four orders of magnitude and can become negligible at the high pH end.

Comparison of the pH-dependence of U(6+) sorption with that of U(6+) aqueous speciation indicates a close correspondence between U(6+) sorption and the predominance field of the U(6+)-hydroxy complexes. This correspondence suggests that at high pH sorption of U(6+)-carbonate species is unimportant. At low pH where the uranyl ($UO_2^{2+}$) aqueous species is predominant, the low sorption values indicate that ion-exchange interactions between the uranyl species and the interlayer cations in montmorillonite were suppressed in the 0.1 M $NaNO_3$ matrix used in this study.

A useful method of representing U(6+) sorption data is in terms of $K_d$ (e.g., as a function of pH) because it normalizes the effect of changes in M/V and accounts for the effect of changes in U(6+) solution concentration. Thus, it allows comparisons to be made of experimental data derived using different experimental conditions. Results from this study were compared with data from the published literature and showed good agreement with those data.

A DLM model with four U(6+) surface complexation reactions effectively simulates the complex sorption behavior observed in the U(6+)—$H_2O$—$CO_2$-montmorillonite system. The good agreement between measured and DLM-predicted sorption values suggests that conceptual models based on an SCM approach, such as the one developed here, could be useful in extrapolating radionuclide sorption over a range of geochemical conditions based on model parameters derived from a limited set of data and could provide a better alternative to the constant $K_d$s used in transport calculations.

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