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NEPTUNIUM(V) SORPTION ON MONTMORILLONITE: AN EXPERIMENTAL AND SURFACE COMPLEXATION MODELING STUDY

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Abstract—Batch sorption experiments at fixed initial Np(V) concentration ($\sim 1 \times 10^{-6}$ *M* ^{237}Np), M/V ratio (4 g L^{-1}), and ionic strength (0.1 molal $NaNO_3$) were conducted to determine the effects of varying pH and P_{CO_2} on Np(V) sorption on SAz-1 montmorillonite. The results show that Np(V) sorption on montmorillonite is strongly influenced by pH and P_{CO_2}. In the absence of CO_2, Np(V) sorption increases over the entire pH range examined ($\sim$3 to $\sim$10), with measured sorption coefficients (K_D) of about 10 mL g^{-1} at pH < 6 to $K_D \sim 1000$ mL g^{-1} at a pH of 10.5. However, for experiments open to atmospheric CO_2 ($P_{CO_2} = 10^{-3.5}$ atm), Np(V) sorption peaks at $K_D \sim 100$ mL g^{-1} at pH of 8 to 8.5 and decreases at higher or lower pH. A comparison of the pH-dependence of Np(V) sorption with that of Np(V) aqueous speciation indicates a close correlation between Np(V) sorption and the stability field of the Np(V)-hydroxy complex NpO_2OH^0 (aq). In the presence of CO_2 and aqueous carbonate, sorption is inhibited at pH > 8 due to formation of aqueous Np(V)-carbonate complexes. A relatively simple 2-site Diffuse-Layer Model (DLM) with a single Np(V) surface complexation reaction per site effectively simulates the complex sorption behavior observed in the Np(V)-H_2O-CO_2-montmorillonite system. The good agreement between measured and DLM-predicted sorption values 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 and could provide a better alternative to the current use of constant K_D values in performance assessment transport calculations.

Key Words—Diffuse-Layer Model, Montmorillonite, Neptunium, Sorption, Surface Complexation.

INTRODUCTION

Background

A fundamental concern in evaluating the suitability of proposed sites for geologic disposal of high-level nuclear waste (HLW) is the possibility of radionuclide migration to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is the sorption of radionuclides on minerals encountered along groundwater flow paths. Neptunium has been identified as a radioelement of concern with respect to disposal of HLW, especially at long time frames ($\sim$10,000 y) (Wilson et al. 1994; TRW 1995; Wescott et al. 1995) because of its long half-life (2.14×10^6 y), suspected high radiotoxicity (Thompson 1982) and reportedly low sorption characteristics (Triay et al. 1993). In addition, understanding the sorption behavior of neptunium, which is stable in oxidizing environments as Np(V), may provide insight into the sorption behavior of other pentavalent actinides such as Pu(V) and Pa(V) that are more redox sensitive and experimentally more difficult to study.

Because clay minerals are common components of rocks, soils and sediments, radionuclide sorption onto these minerals may play a key role in retarding radionuclide migration in many geochemical systems. In addition, some geologic disposal concepts for HLW propose the emplacement of a barrier of compacted bentonite, composed mainly of montmorillonite, between the waste containers and the surrounding rocks to limit the potential movement of radionuclides from the repository (Grauer 1994). For these reasons, a quantitative knowledge of radionuclide sorption onto clay minerals is desirable.

A convenient representation of sorption data is the sorption coefficient, K_D (in mL g^{-1}), which can be defined as:

$$K_D \text{ (mL g}^{-1}\text{)} = \frac{\text{equilibrium mass of Np(V) sorbed on solid}}{\text{equilibrium mass of Np(V) in solution}} \times \left(\frac{V}{M}\right) \quad [1]$$

where V is the volume of experimental solution in mL and M is the mass of solid in g. Representation of sorption data in terms of K_D has the effect of normalizing sorption results with respect to the solid-mass to solution-volume (M/V) ratio and provides a means of accounting for the change in solution concentration that occurs during the course of an experiment.

K_D is commonly used to represent retardation in transport models. In performance assessment studies, contaminant sorption is typically modeled assuming a constant K_D for a given radionuclide for each hydrostratigraphic unit (Wilson et al. 1994; Wescott et al. 1995). This approach is readily incorporated into ex-

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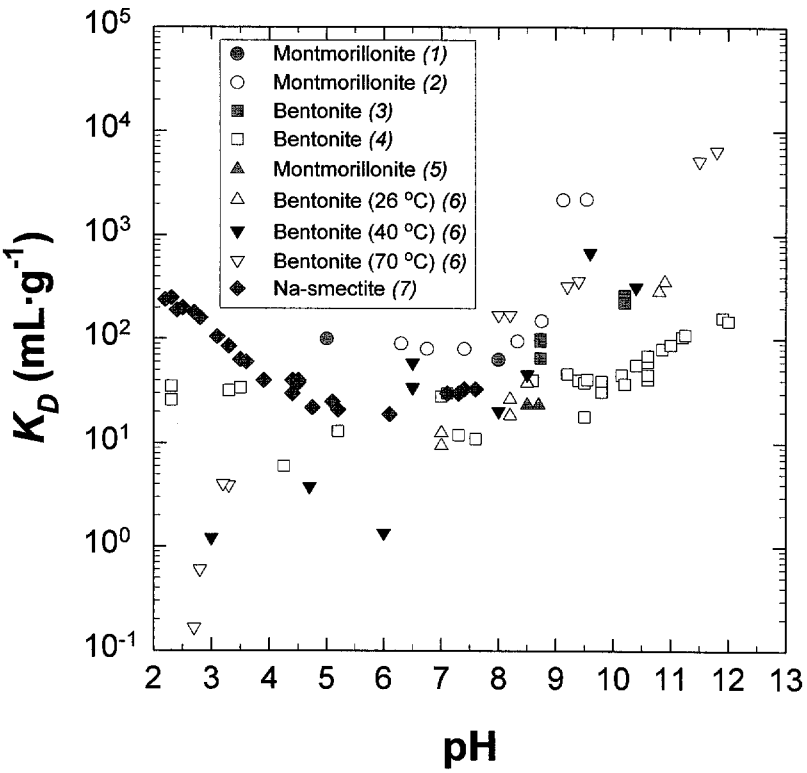


Figure 1. Comparison of Np(V) sorption data on montmorillonite and bentonite from various studies. Data sources include: *(1)* Beall and Allard (1981); *(2)* Allard et al. (1984); *(3)* Torstenfelt et al. (1988); *(4)* Sakamoto et al. (1990); *(5)* Triay et al. (1993); *(6)* Ohe et al. (1993); *(7)* Kozai (1994).

isting transport codes and simplifies the numerical simulation of radionuclide migration. It is well recognized, however, that sorption is dependent on the specific geochemical conditions of the system instead of being constant for a given rock type. Sorption behavior which is dependent on chemistry, especially pH and P_{CO_2}, is particularly pronounced for elements such as the actinides that readily hydrolyze or form aqueous carbonate complexes (Hsi and Langmuir 1985; Sanchez et al. 1985; LaFlamme and Murray 1987; Waite et al. 1994; Bertetti et al. 1998; Pabalan et al. 1998). Thus, to address radionuclide retardation properly in transport calculations, it is important to account for the effects of system chemistry on sorption.

Previous Studies

Relatively few studies have been conducted to investigate Np(V) sorption behavior on clay minerals such as montmorillonite as a function of system chemistry. A summary of some of the available data is presented in Figure 1. The data indicate that Np(V) sorption on montmorillonite is dependent on solution pH. Several studies indicate that Np(V) sorption on montmorillonite is typically greater than sorption on nonlayered minerals such as quartz and fluorite (Beall and Allard 1981; Bertetti et al. 1998). Reported Np(V)-clay K_D values range from ~0.2 mL g^{-1} at pH = 2.6 to ~6500 mL g^{-1} at pH = 11.8 (Ohe et al. 1993). Much of the variation between studies is likely due to differences in experimental conditions (M/V, T, P_{CO_2}) and materials used (bentonite mixtures vs. montmorillonite separates). Despite the wide range in reported K_D values, however, several consistent trends are observed. In general, with the exception of the studies by Ohe et al. (1993), sorption tends to decrease with increasing pH (Sakamoto et al. 1990; Kozai 1994) to pH = 5. Sorption remains relatively constant with further increases in pH. At pH = 8, however, sorption begins to increase with pH up to at least pH = 12. This type of pH-dependent sorption is similar to that observed for U(VI) (Zachara and McKinley 1993; McKinley et al. 1995; Turner et al. 1996; Pabalan et al. 1998; Pabalan and Turner 1997), but Np(V) K_Ds are generally lower than those for U(VI), and the Np(V) sorption edge (that is, the pH at which sorption increases sharply) is located at a pH higher than that for U(VI) (Bertetti et al. 1998).

SORPTION EXPERIMENTS

In this study, batch experiments were conducted to investigate Np(V) sorption onto Na-montmorillonite. Two distinct mechanisms, ion-exchange with interlay-

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er cations and surface complex formation with hydroxylated edge sites, are possible for uptake of Np(V) by montmorillonite. Although a comprehensive description of Np(V) sorption on montmorillonite may need to include both mechanisms, our interest in this study is focused on Np(V) surface complexation, which is the expected predominant sorption mechanism at pHs typical of natural waters (pH ~6 to ~9). Thus, to suppress ion-exchange between Np and interlayer cations, sorption experiments were conducted using Np solutions with a 0.1 molal $NaNO_3$ matrix. The study was designed to determine the effects on Np(V) sorption of varying pH and carbonate concentration. The experiments were conducted at low Np solution concentrations ($\leq 1 \times 10^{-6}$ *M*) to avoid the complicating effects of Np-phase precipitation. The results were then used to develop a geochemical sorption model based on a surface complexation approach to permit predictions of Np(V) sorption at differing physicochemical conditions.

Preparation of Na-Montmorillonite

Montmorillonite (SAz-1, "Cheto") was obtained from the Source Clays Mineral Repository (Columbia, Missouri). The SAz-1 is a Ca-smectite from Apache County, Arizona. For use in the experiments, the SAz-1 was converted to the Na-form by continuous stirring and reaction with 3 *M* NaCl over a period of 21 d. Every 3 d, the used NaCl solution was decanted off and replaced with fresh 3 *M* NaCl solution. After 21 d, the clay was rinsed free of excess NaCl by transferring the clay slurry into dialysis membranes (SpectraPor-4) and immersing it in deionized water. The water was replaced twice daily until no Cl^- could be detected with a $AgNO_3$ (0.1 *M*) test. The clay suspension was then centrifuged for 2 min at 1500 rpm using a Fisher-Marathon 21K centrifuge and a 6-position fixed-angle rotor (effective radius 10 cm) to separate the <2 μm clay particles for use in the experiments. The suspension was decanted, mixed with deionized water and centrifuged again at 1500 rpm to suspend any remaining <2 μm clay particles. All clay removed by centrifugation at 1500 rpm (>2 μm) was discarded. A final centrifugation for 20 min at 10,000 rpm was used to collect the <2 μm clay fraction. The wet, compacted clay was then freeze-dried for storage prior to use in sorption experiments. X-ray powder diffraction (XRD) analyses of the clay before and after Na-exchange, size fractionation and freeze-drying showed a change in the interlayer spacing consistent with ion exchange of Na for Ca. The surface area of the freeze-dried Na-montmorillonite was determined using a multipoint N_2-BET isotherm measured using a Coulter SA3100 surface area analyzer. The samples were prepared by outgassing at 100 °C for 24 h. The measured specific surface area was 97 ± 2 $m^2\ g^{-1}$.

Neptunium Solutions

^{237}Np standard solutions (1.24×10^{-3} *M*) were acquired in glass ampules from Isotope Products Laboratories (Burbank, California). The standard solutions were composed of neptunyl nitrate in 4 *M* HNO_3 matrix and were carrier-free. One standard solution was diluted with 0.1 molal $NaNO_3$ to make a stock solution of 1×10^{-6} *M* ^{237}Np for use in the sorption experiments. Comparisons of experimental conditions used in this study with solubility data for $Np_2OH(s)$, Np_2O_5, and Na-neptunyl-carbonates (Itagaki et al. 1992; Lemire et al. 1993; Nitsche et al. 1993, 1995; Neck et al. 1995) indicated that the experimental solutions remained undersaturated with respect to these phases under all experimental conditions.

A second 1.24×10^{-3} *M* Np standard solution was used to provide confirmation of the oxidation state of Np and the existence of NpO_2^+ in solution. Np has been shown to exist in the (V) oxidation state in $NaNO_3$ solutions (Nakayama and Sakamoto 1991). Under the pH and Eh conditions of the experiments reported here, the production and/or stability of Np(IV) or Np(VI) is not favored (Lieser and Mühlenweg 1988). Approximately 3 mL of the ^{237}Np standard solution were diluted using 0.1 molal $NaNO_3$ to make a 1×10^{-5} *M* ^{237}Np solution. Aliquots of this solution were analyzed in quartz cuvettes using a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer. Upon analysis, a peak of 0.004 absorbance units referenced to a blank of 0.1 molal $NaNO_3$ was observed at 981 nm. The peak height and location correspond well to the expected presence and quantity of NpO_2^+ species in solution (Gauthier et al. 1983) and confirmed the existence of Np(V).

Analytical Procedures

^{237}Np was analyzed by alpha activity counting using a Packard 2505 TR/AB liquid scintillation analyzer (LSA). The immediate daughter of ^{237}Np is a short-lived beta emitter, ^{233}Pa, which rapidly ingrows in solutions containing ^{237}Np. ^{233}Pa emits beta particles with average energies high enough (~100 keV) to conflict with the alpha decay spectrum (~100 to 400 keV) and cause significant interference in quantifying the ^{237}Np alpha activity. Therefore, alpha and beta decay events were discriminated during counting by optimizing the LSA pulse decay discriminator with pure alpha and beta emitters. A 1.24×10^{-3} *M* Np standard solution was used to generate the necessary standards. ^{233}Pa was isolated by a method modified from Pickett et al. (1994). A 1-mL aliquot was evaporated to dryness, taken up in a 1 *M* HCl + 0.5 *M* HF matrix, loaded onto an AG1-X8 resin (Bio-Rad) anion exchange column and eluted with a mixture of 9 *M* HCl + 0.05 *M* HF. ^{237}Np was isolated based on a method modified from Hardy et al. (1958). A second 1-mL aliquot was

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Table 1. Experimental conditions.

Experiment	Atmosphere	Initial Np(V) conc. (M)	Mass of solid (g ± 1σ)	Volume of solution (mL ± 1σ)	Approx. M/V (g L^{-1} ± 1σ)
NpM1	capped vial (trace CO_2)	8.79×10^{-7}	0.0999 ± 0.0005	25.2 ± 0.1	3.97 ± 0.02
NpM2 (forward)	open vial ($P_{CO_2} = 10^{-3.5}$ atm)	9.25×10^{-7}	0.0996 ± 0.0004	24.9 ± 0.1	4.01 ± 0.02
NpM2 (reverse)	open vial ($P_{CO_2} = 10^{-3.5}$ atm)	9.25×10^{-7}	0.0996 ± 0.0004	23.5 ± 0.3	4.24 ± 0.07
NpM3	glove box (no CO_2)	9.46×10^{-7}	0.1001 ± 0.0006	23.8 ± 0.2	4.20 ± 0.05

mixed with 6 M HNO_3, loaded onto a separate silica gel column and eluted with 6 M HNO_3. The eluents were evaporated, taken up in 0.02 M HNO_3, and sampled for use in the LSA. Once optimized, the same LSA setting was used for all subsequent analyses of solutions containing ^{237}Np and ^{233}Pa as the primary radionuclides. Counting statistics associated with ^{237}Np-bearing solutions were based upon the alpha activity only. Samples were counted to achieve a maximum 2σ error of ±2% for 1×10^{-6} M ^{237}Np solutions.

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

Experimental Procedure

Four sets of Np(V) sorption experiments [NpM1, NpM2(forward), NpM2(reverse) and NpM3] were conducted with initial conditions summarized in Table 1. Equilibrium batch experiments were conducted at room temperature (20 ± 2 °C) over a pH range of about 4 to 11. Generally, the solids were immersed in 25 mL of Np(V) solution contained in 50-mL polycarbonate Oak Ridge-type centrifuge tubes. Solution pH was adjusted by adding appropriate amounts of HNO_3, $NaHCO_3$ or NaOH to the experimental solutions. The containers were left open for experiments in which solutions were allowed to equilibrate with atmospheric P_{CO_2}. Experiments at low P_{CO_2} were conducted by 1) immediately capping the tubes after initial pH adjustment, or 2) conducting the experiment in a controlled-atmosphere glove box using CO_2-free (<1 ppm CO_2) simulated air (21% O_2 and 79% N_2 by volume).

The experimental mixtures were agitated using gyratory shakers for at least 14 d to allow for equilibrium of both pH and the sorption reaction. Previous kinetics experiments (Yamamoto et al. 1990; Hart et al. 1994; Bertetti et al. 1998) suggest that Np(V) sorption reactions are ~98% complete within 48 h, but the solutions used in this study typically required up to 10 d for equilibration of pH when equilibrating with atmospheric P_{CO_2} due to relatively slow mass transfer of CO_2 between the gas and aqueous phases, similar to the times reported for pH equilibration in uranium solutions (Pabalan and Turner 1991).

To determine the amount of Np(V) sorbed on montmorillonite after reaching sorption equilibrium, Np(V) was desorbed from the solid surface with a HNO_3 solution. The procedure involved centrifuging the experimental mixtures for 20 min at 10,000 rpm to separate the clay from the aqueous phase, taking samples from the solution for Np analysis, decanting most of the aqueous phase into a polypropylene tube and adding ~8 mL of ~0.04 M HNO_3 to the polycarbonate tube, which contained the solid and some amount of solution, to desorb the Np. The solids were subsequently redispersed and a second set of samples for Np analysis was taken from the acidic solutions after about 10 d. Additional tests were also conducted to determine potential losses of Np(V) to container walls. These tests indicated that, under the experimental conditions of this study, sorption of Np(V) onto polycarbonate containers was negligible. Reversibility of the sorption reactions was evaluated from the NpM2(reverse) experiments. These experiments involved either increasing or decreasing the pH of the solutions at the end of the NpM2(forward) experiments by addition of HNO_3, $NaHCO_3$ or NaOH as appropriate, reequilibrating for about 10 d, and resampling the experimental solutions in the same manner described above.

EXPERIMENTAL RESULTS

Over the pH range considered, the magnitude of Np(V) sorption onto Na-montmorillonite (Figure 2) is typically less than the sorption onto montmorillonite observed for U(VI) (Zachara and McKinley 1993; McKinley et al. 1995; Turner et al. 1996; Pabalan et al. 1998; Pabalan and Turner 1997). Np(V) sorption onto montmorillonite is greater than that observed for other nonlayered/nonporous minerals such as quartz, hematite, alumina and apatite (Beall and Allard 1981; Allard et al. 1984; Nakayama and Sakamoto 1991; Triay et al. 1993; Bertetti et al. 1998). The pH-dependence of Np(V) sorption onto montmorillonite, however, is

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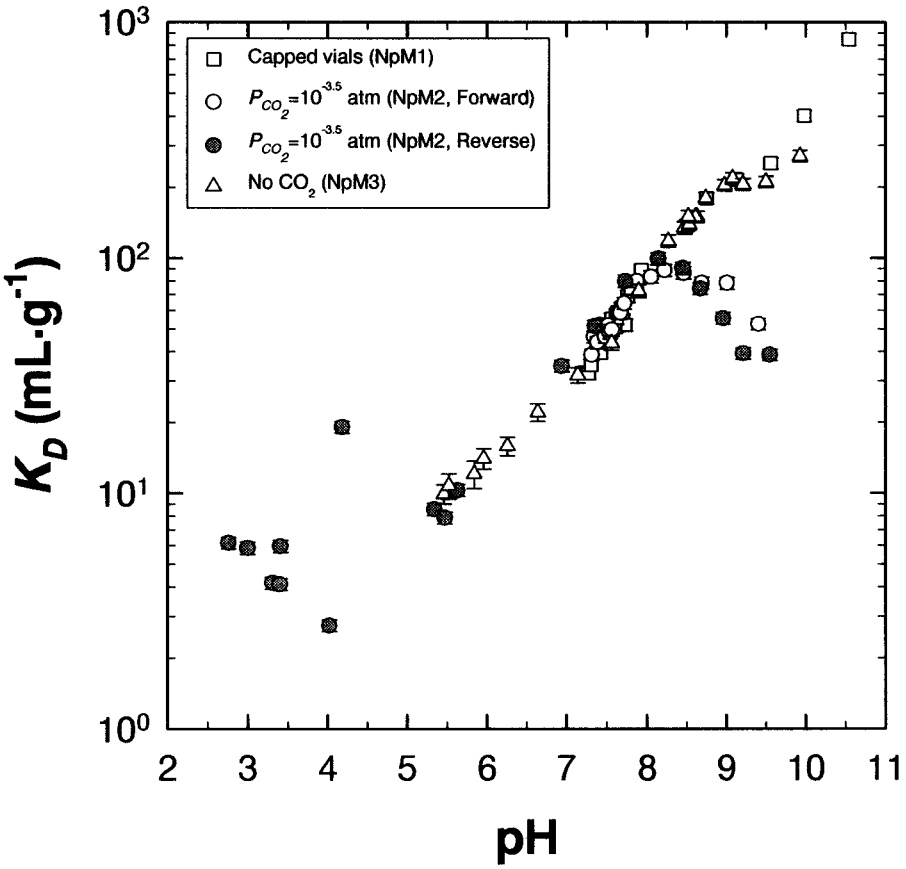


Figure 2. Np(V) sorption on montmorillonite plotted in terms of K_D (mL g^{-1}) versus pH for experiments with $Np_i \sim 9 \times 10^{-7}$ *M*. The uncertainty is typically less than the size of the symbol. Open triangles represent CO_2-free conditions (glove box, N_2-atmosphere). Open squares represent capped-vial experiments (25 mL of headspace). Open and closed circles represent forward and reverse sorption experiments, respectively, under conditions open to the atmosphere ($PCO_2 = 10^{-3.5}$ atm). Experimental conditions are listed in Table 1.

very similar to those observed for other minerals (Bertetti et al. 1998). For solutions in equilibrium with atmospheric PCO_2, the magnitude of sorption peaks near pH 8–8.5 and decreases towards more acidic or alkaline values. In contrast, solutions that remained under low PCO_2 (capped vials) or CO_2-free conditions show a continuous increase in sorption with increasing pH over the entire pH range studied. As shown in Figure 2, there is good agreement between data from forward and reverse experiments (open and closed circles, respectively) which indicate that sorption of Np(V) onto montmorillonite is reversible.

The results presented here compare favorably with other studies that have correlated a decrease in Np(V) sorption with an increase in Np-carbonate complexation in solution (Bidoglio et al. 1985, 1987). Also of note are published data on Np(V) sorption on other minerals such as biotite, hematite and feldspar. Though reported magnitudes of sorption on these minerals vary, the continuous increase in sorption with increasing pH when solutions are at low PCO_2 conditions was consistently observed (Allard et al. 1984; Nakayama and Sakamoto 1991; Righetto et al. 1991).

To aid in evaluating possible surface species, it is useful to compare Np(V) sorption behavior with Np(V) aqueous speciation. Speciation calculations were performed with the equilibrium geochemical code MINTEQA2 (Allison et al. 1991) using a database modified to include aqueous Np(V) species. Equilibrium constants for Np species used in the calculations are given in Table 2. The calculated relative stabilities of Np(V) species at 25 °C in a 9×10^{-7} *M* Np solution (0.1 molal $NaNO_3$ matrix) are shown in Figures 3a, 3b and 3c for a system that is CO_2-free, a system comprised of a capped 50-mL vial with 25 mL of headspace, and a system in equilibrium with atmospheric PCO_2 ($PCO_2 = 10^{-3.5}$ atm), respectively.

As shown in Figure 3, Np(V) aqueous speciation is dominated by NpO_2^+ at pH below 7 whether CO_2 is present or not. However, near pH ~7, Np hydrolysis becomes significant (~0.1 mole percent of Np in solution) and the amount of the Np(V) hydroxy species,

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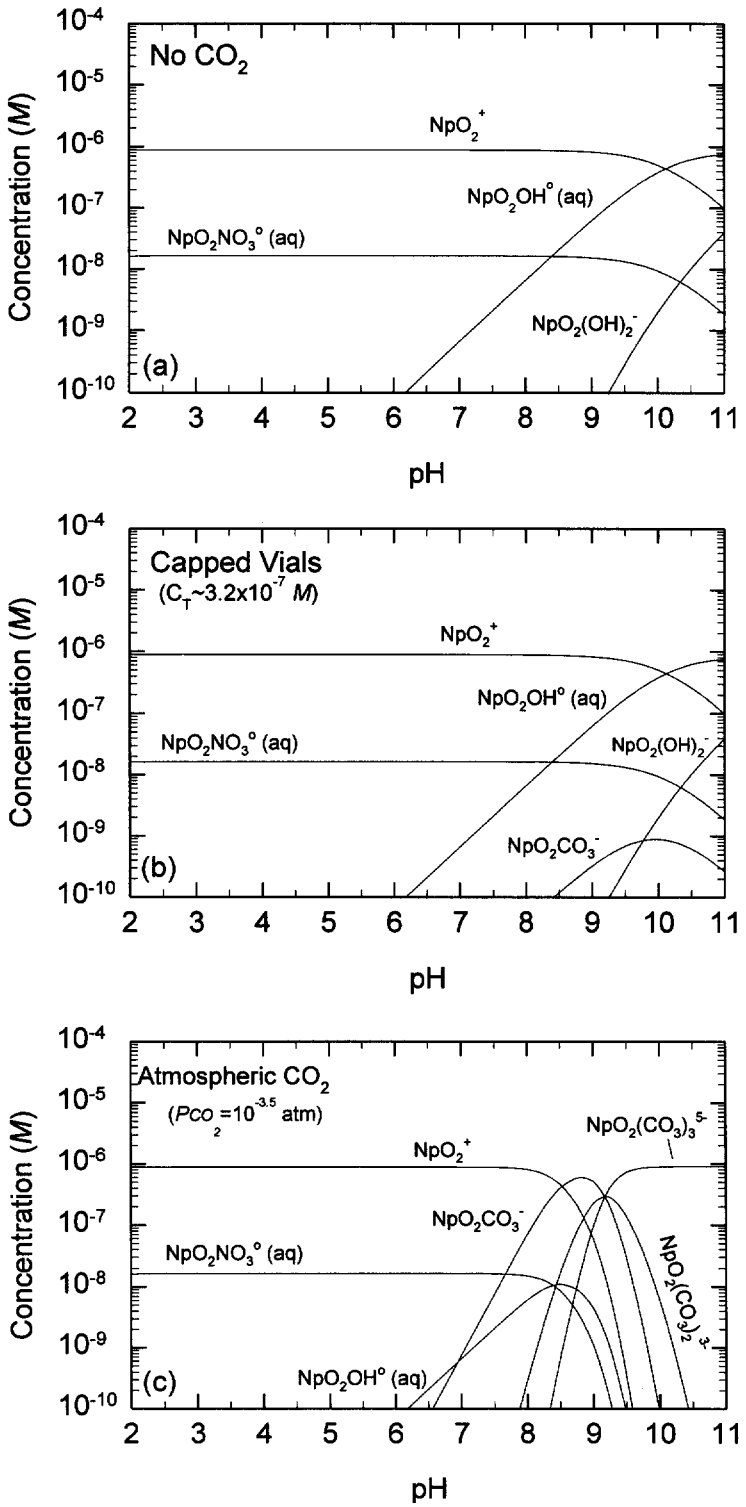


Figure 3. Aqueous Np(V) speciation at 25 °C as a function of pH for a 9.0 × 10^{-7} *M* Np(V) solution (0.1 molal $NaNO_3$ matrix) for a) CO_2-free conditions, b) capped vials with 25 mL of headspace, and c) equilibrium with the atmosphere (P_{CO_2} = $10^{-3.5}$ atm). Speciation was calculated using the MINTEQA2 geochemical code (Allison et al. 1991) and the equilibrium constants given in Table 2.

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$NpO_2OH^0(aq)$ and $NpO_2(OH)_2^-$, increase with increasing pH. In the absence of CO_2, the relative stability of the Np(V) hydroxy species increases continuously with increasing pH and eventually dominates Np(V) aqueous speciation (Figure 3a). With the minor amount of carbonate present in the capped vial, $NpO_2CO_3^-$ forms, but there is no significant change in the stability fields of the Np(V) hydroxy species (Figure 3b).

Under atmospheric P_{CO_2} conditions (Figure 3c), the stability of the neutral hydroxy species reaches a maximum near pH 8.5 and decreases with further increases in pH. Although the neutral hydroxy complex does not become a predominant species in this solution, a comparison of Np(V) sorption data and aqueous speciation (Figures 2 and 3c, respectively) indicate that the pH dependence of the stability of the $NpO_2OH^0(aq)$ species is distinctly similar to the pH dependence of Np(V) sorption from solutions in equilibrium with atmospheric P_{CO_2}. The decrease in the amount of Np sorbed at pH > 8.5 can be related to the increasing importance of Np(V) carbonate-complexes with increasing pH.

Ion exchange sites in montmorillonite consist of permanent local negative surface charges created through isomorphic substitution of cations in the clay structure. Because the density of these sites is not affected by pH, ion-exchange is pH-independent (Bradbury and Baeyens 1994). At low pH where NpO_2^+ is the predominant aqueous species and other sorption processes such as surface complexation are less significant, ion exchange can dominate Np(V) sorption. Under relatively high ionic strength conditions, the background electrolyte cation such as Na^+ tends to occupy most of the available ion exchange sites and the sorption of NpO_2^+, present in trace concentrations, is suppressed. Under low ionic strength conditions, NpO_2^+ more effectively competes with Na^+ for fixed charge sites, and ion-exchange between NpO_2^+ in solution and interlayer cations of montmorillonite occurs at low pH. Such sorption behavior has been observed for U(VI)-Montmorillonite sorption (McKinley et al. 1995; Turner et al. 1996) and heavy metal sorption on Na-montmorillonite (Baeyens and Bradbury 1995). In this study, sorption is low at low pH, indicating that Np(V) sorption through ion-exchange is largely suppressed under relatively high ionic strength (I = 0.1 molal $NaNO_3$) conditions. However, even at the high ionic strength used here, some Np(V) sorption observed in this study is likely due to an ion-exchange mechanism. For example, data from experiment NpM2(reverse) below pH 5.5 (Figure 2) appear to level off at a K_D of about 4 to 6 mL g^{-1}.

DEVELOPING A SURFACE COMPLEXATION MODEL

Electrostatic surface complexation models (SCMs) have been used with success to simulate pH-dependent sorption (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. Because of the presence of an electrostatic double layer at the mineral surface, the activities of species at the mineral-water interface are different from those in the bulk solution. In SCMs, additional coulombic terms are included in the mass action expression for a surface reaction to account for these electrostatic effects.

Applications of SCMs have often relied on simultaneously adjusting different model-specific parameters to produce the best match to a given data set. Because SCMs typically have a potentially large number of adjustable parameters, this approach is likely to lead to nonunique fits that make comparison between studies difficult (Westall and Hohl 1980), and complicates their application in HLW performance assessment. Therefore, recent efforts have focused on developing a "standard" set of model parameters, either through parameter optimization studies and sensitivity analyses (Hayes et al. 1991) or through a thermodynamic approach using measured mineral surface properties (Sverjensky and Sahai 1996). This latter approach 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 a uniform approach to limit fitting parameters in applying the 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 the approach of Dzombak and Morel (1990) to Np(V) sorption, the current study has focused on the DLM and adopted many of the methods outlined in their study.

Model Description

In applying SCMs to pH-dependent sorption, a surface is assumed to be composed of amphoteric hydroxyl groups ($>XOH^0$, 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 contaminant complexation reactions. The equilibrium constants for these surface reactions are determined by fitting available potentiometric titration and sorption data. Mass balance and mass action relations, modified to include the electrostatic effects of a charged mineral surface, are used to determine the distribution of the elements between

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those dissolved in the bulk solution and those specifically sorbed onto the solid.

The DLM uses a 2-layer representation of the mineral-water interface and has fewer fitting parameters than those included in multilayer SCMs such as the Triple-Layer Model (TLM). The pH dependence of surface charge development is accounted for in the DLM, but in contrast to a multilayer model like the TLM, the DLM assumes that supporting electrolytes 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 effects of ionic strength on sorption, except through the charge-potential relationship (Davis and Kent 1990; Dzombak and Morel 1990). Details of the DLM and the simplified approach used in this study are described elsewhere (Davis and Kent 1990; Dzombak and Morel 1990; Turner and Sassman 1996) and only a brief overview is presented here.

A generalized pH-dependent sorption reaction between aqueous Np(V) and a variably charged surface sorption site can be written in the form:

$$>XOH^0 + pNpO_2^+ + nH_2O \leftrightharpoons [>XOH_q^-(NpO_2)_p(OH)_n]^{p+q-n-1} + (1+n-q)H^+ \quad [2]$$

where q is the protonation state of the sorption site (q = 0, 1 or 2 for deprotonated, neutral and protonated sites, respectively), and p and n are the reaction coefficients for NpO_2^+ and H_2O, respectively. NpO_2^+ and $[>XOH_q^-(NpO_2)_p(OH)_n]^{p+q-n-1}$ represent the aqueous Np(V) species and the Np(V) 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 (such as K_+^{int}, K_-^{int} and $K^{int}_{[>XOH_q^-(NpO_2)_p(OH)_n]}$) that are independent of surface charge. For sorption reactions of the type given in Equation [2], $K^{int}_{[>XOH_q^-(NpO_2)_p(OH)_n]}$ is commonly referred to as the binding constant.

Based on a numerical, nonlinear parameter optimization of available potentiometric titration data, Turner and Sassman (1996) determined the DLM acidity constant (K_+^{int} and K_-^{int}) necessary to define the protonation and deprotonation behavior of a number of different mineral surfaces. The values are model-specific, but the acid/base behavior of the surface is characterized and these values are fixed in the geochemical model. For the DLM, the remaining adjustable parameter to interpret Np(V) sorption data is the binding constant for Np(V) sorption reactions of the form given in Equation [2].

The observed dependence of Np(V) sorption on pH and P_{CO_2} is a consequence of mass action effects and equilibrium chemistry in the Np(V)-H_2O-CO_2-montmorillonite system. In a qualitative sense, an increase in the activity of NpO_2^+ drives the equilibrium reaction in Equation [2] forward (increasing sorption). In a CO_2 atmosphere, however, dissolved carbonate tends to form Np(V) aqueous carbonate-complexes, particularly at alkaline pH (Figure 3). Carbonate complexation of NpO_2^+ reduces the activity of the NpO_2^+ species, and drives the sorption reaction in Equation [2] in the opposite direction (decreasing sorption). This explanation of the Np(V) sorption dependence on pH and P_{CO_2} is, of course, simplistic due to the synergistic effects between solution chemistry, sorption site protonation state and speciation of the aqueous and surface complexes.

Modeling of Np(V) Sorption on Montmorillonite

An essential test of a simplified DLM approach is the development of a conceptual model that is capable of reproducing observed sorption behavior in the Np(V)-H_2O-CO_2-montmorillonite system. In this study, an approach has been adopted such that the simplest model that can describe the observed sorption behavior is preferred. The best test of this modeling approach would involve systematic variation of other key chemical parameters in addition to pH and P_{CO_2} examined here. Ideally, extension of this modeling approach to other radionuclide-mineral systems will lead to a set of parameters which are based on a common methodology and reference points. This in turn may allow for direct comparison and performance evaluation of different models, and may provide a consistent and useful modeling tool for use in performance assessment calculations of radionuclide transport.

Consistent with previous studies on U(VI) sorption (Davis and Kent 1990; Zachara and McKinley 1993; McKinley et al. 1995; Turner et al. 1996; Pabalan and Turner 1997), Np(V) sorption on montmorillonite was assumed to consist of ion-exchange at interlayer sites and pH-dependent sorption at crystallite edge sites. As discussed previously, experiments in this study were conducted at relatively high ionic strength (0.1 molal $NaNO_3$) which tended to suppress ion-exchange of NpO_2^+ with interlayer cations. Therefore, in modeling Np(V) sorption on montmorillonite, it was assumed here that the edge sites determined the sorption behavior and the contribution of ion-exchange was neglected.

Relative to simple oxides, aluminosilicates are considered to be more complex in that variably charged edge sites are likely to be composed of silanol ($>SiOH^0$) and aluminol ($>AlOH^0$) site types. Recent studies (Zachara and McKinley 1993; McKinley et al. 1995; Turner et al. 1996; Pabalan and Turner 1997) have successfully modeled the pH-dependent sorption behavior of aluminosilicates such as montmorillonite by using acidity constants determined for SiO_2 and Al-

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Table 2. Chemical equilibrium model used for DLM simulation of Np(V) sorption on montmorillonite.

Physical/Chemical Conditions used for Calibration (FITEQL):	
Solid concentration (M/V)	3.97 g L^{-1}
Site density	2.3 sites·nm^{-2}
Surface area†	9.7 m^2 g^{-1}
Ionic strength	0.1 molal $NaNO_3$
$\Sigma^{237}Np(V)$	8.79×10^{-7} *M*
Edge-Site Reactions:	Log *K* (Binding Constant)
$>AlOH^0 + H^+ \rightleftharpoons >AlOH_2^+$	8.33‡
$>AlOH^0 \rightleftharpoons >AlO^- + H^+$	−9.73‡
$>AlOH^0 + NpO_2^+ + H_2O \rightleftharpoons >AlO\text{-}NpO_2(OH)^- + 2H^+$	−13.79§
$>SiOH^0 \rightleftharpoons >SiO^- + H^+$	−7.20‡
$>SiOH^0 + NpO_2^+ \rightleftharpoons >SiOH\text{-}NpO_2^+$	4.05§
Aqueous Speciation Reactions:	Log *K*
$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH^0 + H^+$	−10.0¶
$NpO_2^+ + 2H_2O \rightleftharpoons NpO_2(OH)_2^- + 2H^+$	−22.4¶,#
$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^-$	4.6#,††,‡‡
$NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-}$	7.0#,††,‡‡
$NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$	8.5††,‡‡
$NpO_2^+ + NO_3^- \rightleftharpoons NpO_2NO_3^0$ (aq)	−0.5§§

† Effective edge site surface area assumed to be 10% of total N_2-BET surface area (97 m^2 g^{-1}). See text for detailed discussion.

‡ Acidity constants for am-SiO_2 and α-Al_2O_3 from Turner and Sassman (1996).

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

¶ Lemire and Garisto (1989).

Fuger (1992).

†† Lemire (1984).

‡‡ Lemire et al. (1993).

§§ Danesi et al. (1971).

oxyhydroxides to represent the acid-base behavior of the hydroxylated edge sites. This approach makes it possible to predict aluminosilicate sorption behavior based on the protonation and deprotonation chemistry of silanol and aluminol sites. The same approach has been adopted in the DLM conceptual model developed here.

In order to develop a DLM for the Np(V)-montmorillonite system, it was necessary to calculate the total number of edge sorption sites ($TOT_{>XOH}$) and, for the conceptual model developed here, the distribution of the total number of sites between $>AlOH^0$ and $>SiOH^0$. Based on potentiometric titration studies of montmorillonite, Wanner et al. (1994) estimated that crystallite edges comprised about 10% of the N_2-BET specific surface area. Pabalan et al. (1998) and Bertetti et al. (1998) used an effective surface area of 10% of the measured N_2-BET specific surface area as an empirical means of normalizing U(VI) and Np(V) sorption coefficients for porous and layered silicates relative to nonporous minerals. On this basis, an effective surface area of 9.7 m^2 g^{-1} (10% of the measured N_2-BET specific surface area of 97 m^2 g^{-1}) was 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 concentration of $>AlOH^0$ to $>SiOH^0$ sites (Table 2) was 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 $>SiOH^0$ and $>AlOH^0$ edge sites were derived based on potentiometric titration data for SiO_2 and α-Al_2O_3, as described in Turner and Sassman (1996). Possible complications from dissolution and readsorption of Al^{3+}, especially at lower pH (Turner et al. 1996), have been neglected in the simplified approach presented here.

In addition to data describing the mineral properties and the acid/base behavior of the surface, 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 Np(V), the equilibrium constants used in the chemical equilibrium model are listed in Table 2.

Using the mineral properties and aqueous thermodynamic data given in Table 2 and the Np(V) sorption data from experiment NpM1 ($\Sigma Np_i = 8.79 \times 10^{-7}$ *M*; *M/V* = 3.97 g L^{-1}), the numerical parameter optimization code FITEQL, Version 2.0 (Westall 1982a, 1982b) was used to determine binding constants for the Np(V)-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 such data, the exact form of the surface reaction is usually selected by the modeler based on analogous speciation reactions in the aqueous phase and qualitative or quantitative goodness-of-fit criteria. The calculated Np(V) aqueous speciation (Figure 3) suggests that the most important aqueous species in the pH range 5 to 9 include NpO_2^+ and NpO_2OH^0 (aq). Based on the goodness-of-fit-results from the FITEQL regression of the NpM1 dataset, the following 2 surface complexation reactions were determined to best describe the observed Np(V) sorption on montmorillonite:

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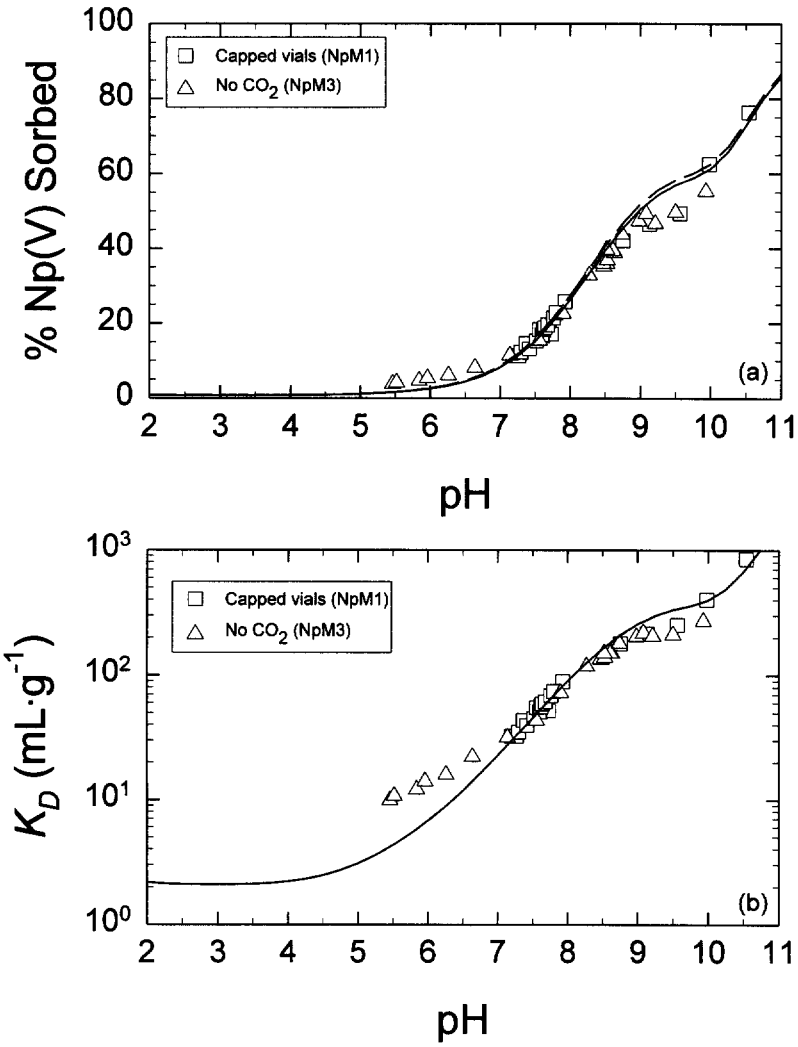


Figure 4. Np(V) sorption on montmorillonite plotted in terms of a) percent sorbed versus pH, and b) K_D (mL g^{-1}) versus pH for experiments NpM1 (no CO_2) and NpM3 (capped vials, low CO_2). The dashed and solid curves represent DLM-calculated values for solutions analogous to NpM1 and NpM3, respectively, using experimental conditions given in Table 1 and DLM parameters listed in Table 2.

$$>SiOH^0 + NpO_2^+ \rightleftharpoons >SiOH\text{-}NpO_2^+ \quad [3]$$

$$>AlOH^0 + NpO_2^+ + H_2O \rightleftharpoons >AlO\text{-}NpO_2(OH)^- + 2H^+ \quad [4]$$

The binding constants (Log K) for these reactions are given in Table 2.

Model Results

As discussed above, a test of the flexibility of a sorption modeling approach is its ability to reproduce observed changes in sorption behavior induced by changes in geochemical conditions. The model developed here reproduces the NpM1 sorption data very well as a function of pH in terms of both percent sorbed and K_D (Figure 4). There is a slight underprediction, however, of sorption for pH < 6.5. The underprediction at low pH may be due to the contribution to the measured sorption of an ion-exchange mechanism that is not accounted for in the model. In a CO_2-free system, the DLM correctly calculates that sorption will continue to increase over the pH range 5 to 11. For conditions relevant to the capped vials, the DLM calculates slightly lower sorption compared to the CO_2-free system due to the presence of some amount of carbonate, but the calculated values still match the experimental data very well. It is interesting to note that the model also accurately predicts the inflection points observed in the sorption data at pH 9 and 10 for CO_2-free and capped-vial experiments.

As discussed previously, Np(V) K_Ds for systems in equilibrium with atmospheric CO_2 exhibit a maximum

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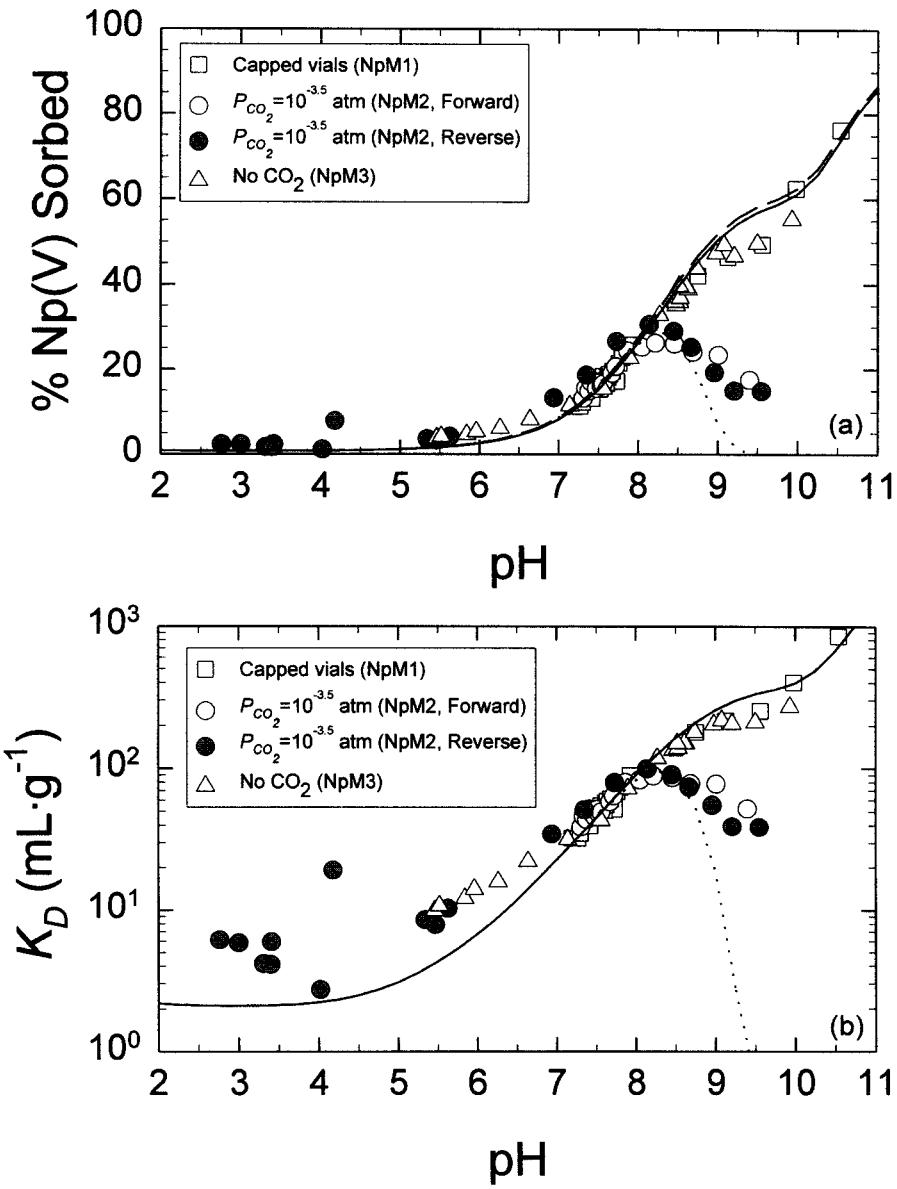


Figure 5. Np(V) sorption on montmorillonite plotted in terms of a) percent sorbed versus pH, and b) K_D (mL g^{-1}) versus pH for experiments NpM2(forward) and NpM2(reverse) in equilibrium with the atmosphere (P_{CO_2} = $10^{-3.5}$ atm). The dotted curve represents DLM-calculated K_Ds for solutions in equilibrium with atmospheric P_{CO_2}. The calculations were done using experimental conditions given in Table 1 and DLM parameters listed in Table 2. Data and DLM predictions from Figure 4 are shown for reference.

when plotted as a function of pH. Neptunium(V) sorption on montmorillonite from solutions in equilibrium with atmospheric CO_2 were predicted using the DLM parameters derived previously from the low CO_2 NpM1 experiments. As shown in Figure 5, the model accurately predicts both the sorption maximum ($K_D \approx$ 100 mL g^{-1}) and the decrease in sorption at pH > 8.5. However, the model overpredicted the decrease in sorption with increasing pH and anticipated an essentially zero sorption by pH ~9.5 which was not observed in the experiments.

The conceptual model developed here does not explicitly invoke the formation of either Np-carbonate surface species, such as >$SiOH_2$-$NpO_2(CO_3)^0$, or the competition for available sorption sites by carbonate species (such as >$AlOH_2$-CO_3^-). At present, there are no data to characterize quantitatively the sorption of carbonate species on montmorillonite. Instead, the

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trend of decreasing sorption at higher pH was attributed to the increased carbonate concentration and the more effective complexation of available Np(V) by the aqueous carbonate ligand relative to that by the surface sites. In particular, the anionic complexes $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ strongly dominate Np(V) aqueous speciation at pH > 8.5 (Figure 3c). Given the high ionic charge of these species, the activity coefficients of $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ calculated by MINTEQA2 using the Davies equation are sufficiently small that the concentrations of these species could be overestimated and lead to the sharp decrease in predicted sorption for pH > 8.5.

In general, results from previous research (Beall and Allard 1981; Allard et al. 1984; Torstenfelt et al. 1988; Sakamoto et al. 1990; Ohe et al. 1993; Triay et al. 1993; Kozai 1994) and from the current study suggest that Np(V) sorption on montmorillonite (and bentonite) is relatively constant at pH less than about 6 to 7, and increases by 1 to 2 orders of magnitude with further increases in pH. Reported sorption coefficients range from $K_D < 1$ to ~6500 mL g^{-1} in CO_2-free or low CO_2 experiments, although the bulk of the data fall between 10 to 100 mL g^{-1}. These various experiments were conducted using different solution chemistries (pH, ionic strength, Np concentration, carbonate concentration), different montmorillonite/clay specimens and container materials, different *M/V* and/or different sorbent preparation methods, all of which could affect Np(V) sorption behavior. For these reasons, comparison of sorption data from different studies can be complicated.

The DLM simulations for Np(V) sorption on montmorillonite, nevertheless, show general trends similar to observed Np(V) sorption on various minerals. The constant K_D at low pH is effectively predicted by the DLM, as well as the 1 to 2 order of magnitude increase in K_D at higher pH. The model also predicts the effects of increased P_{CO_2}, although it overpredicts the decrease in sorption with increasing pH.

CONCLUSIONS

The experimental data derived in this study indicate that montmorillonite can contribute significantly to the retardation of Np(V) migration in many geochemical environments where clay is commonly an important component. However, Np(V) sorption is sensitive to pH and to the formation of aqueous Np(V)-carbonate complexes. A comparison of the pH-dependence of Np(V) sorption with that of Np(V) aqueous speciation indicates a close correlation between Np(V) sorption and the stability field of the Np(V)-hydroxy complexes. Sorption of Np(V) decreases under conditions in which Np(V)-carbonate complexes are important. At low pH where the NpO_2^+ aqueous species is predominant and Np(V) surface complexation is less important, the low sorption values indicate that NpO_2^+ ion-exchange interactions with the interlayer cations in montmorillonite are at least partly suppressed in the 0.1 molal $NaNO_3$ matrix used in this study.

A relatively simple DLM model with two Np(V) surface complexation reactions effectively simulates the complex sorption behavior observed in the Np(V)-H_2O-CO_2-montmorillonite system. The good agreement between measured and DLM-predicted sorption values suggests that conceptual models based on a simplified 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. These models could provide a better alternative to the constant K_Ds currently used in transport calculations.

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