NEPTUNIUM(V) 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 Np(V) and other radionuclides through the subsurface environment. Batch experiments 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. In the absence of CO_2, Np(V) sorption increases over the entire pH range examined (~ 3 to ~ 10), with measured sorption coefficients (K_D) of about 10 ml/g at pH < 6 to $K_D \sim 1000$ ml/g at a pH of 10.5. For experiments open to atmospheric CO_2 ($P_{CO_2}=10^{-3.5}$ atm), however, Np(V) sorption peaks at $K_D \sim 100$ ml/g 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.

The experimental results derived in this study were used to develop a thermodynamic model based on a surface complexation approach to permit predictions of Np(V) sorption at differing physicochemical conditions. A relatively simple two-site Diffuse-Layer Model (DLM)

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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.

1. INTRODUCTION

1.1 Background

A fundamental concern in evaluating the suitability of proposed sites for geologic disposal of high-level nuclear wastes (HLWs) 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 HLWs, especially at long time frames ($\sim$10,000 yr) (Wilson et al., 1994; TRW, 1995; Wescott et al., 1995), because of its long half-life (2.14×10^6 yr), suspected high radiotoxicity (Thompson, 1982), and reportedly low sorption characteristics (e.g., 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 work with.

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 (e.g., Grauer, 1994). For these reasons, a quantitative

knowledge of radionuclide sorption onto clay minerals is desirable.

A convenient representation of sorption data is the distribution coefficient, K_D, which can be defined as:

$$K_D \text{ (ml/g)} = \frac{\text{equilibrium mass of Np(V) sorbed on solid}}{\text{equilibrium mass of Np(V) in solution}} \times \left(\frac{V}{M}\right) \qquad (1)$$

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 (e.g., Wilson et al., 1994; Wescott et al., 1995). This approach is readily incorporated into existing transport codes and simplifies the numerical simulation of radionuclide transport. It is well-recognized, however, that sorption is dependent on the specific geochemical conditions of the system, especially pH and P_{CO_2} (e.g., Hsi and Langmuir, 1985; Sanchez et al., 1985; LaFlamme and Murray, 1987; Dzombak and Morel, 1990), instead of being constant for a given rock type. This type of chemistry-dependent sorption behavior is pronounced for readily hydrolyzable elements such as the actinides (e.g., Waite et al., 1994; Bertetti et al., 1997; Pabalan et al., 1997; Pabalan and Turner, 1997). Thus, to address radionuclide transport properly in performance assessment models it is important to account for the effects of system chemistry on sorption.

1.2 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. This 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., 1997; Pabalan and Turner, 1997). However, Np(V) K_Ds are generally lower than those for U(VI) and the Np(V) sorption edge (i.e., the point at which sorption increases sharply) is located at a pH higher than that for U(VI) (Bertetti et al., 1997).

For pH values of 5 and 8, Beall and Allard (1981) observed that Np(V) sorption on montmorillonite was greater than sorption on non-layered minerals such as quartz and fluorite. In the synthetic sodium-chloride-bicarbonate groundwater used by Beall and Allard (1981), Np(V) K_D decreased slightly in going from pH 5 to pH 8. Allard et al. (1984) conducted sorption experiments open to the atmosphere. For pH ranging from 6.3 to 8.75, Np(V) sorption remained relatively constant. At pH $>$ 9, however, measured Np(V) K_Ds increased sharply by more than an order of magnitude. Torstenfelt et al. (1988) used a natural sodium bicarbonate water collected from well J-13 at the Nevada Test Site (NTS) to investigate sorption on a bentonite at two pH values, 8.73 and 10.2. The Np(V) K_D at pH 10.2 is higher by more than a factor of two compared to the value at pH 8.73. Experiments by Sakamoto et al. (1990) covered a much wider pH range, from about 2 to 12, used a 0.01 M $NaClO_4$ background electrolyte, and were conducted in capped vials, which limited the amount of carbonate in the system. Their data

indicate that Np(V) sorption is relatively constant in the low to intermediate pH range, but increases continuously from pH ~9 to ~12 by almost an order of magnitude. Triay et al. (1993) reported low Np(V) K_Ds based on experiments using natural groundwaters with pH of 8.5 and 8.7 taken from NTS wells J-13 and UE-25p#1, respectively.

Ohe et al. (1993) investigated the effect of temperature on Np(V) sorption on a bentonite mixture of montmorillonite, quartz, chalcedony, and feldspar. The experiments were performed at 26, 40, and 70 °C in a N_2-atmosphere (no-CO_2), but measurable carbonate was observed in solution, possibly from dissolution of trace calcite and dolomite in the bentonite mixture. In contrast to other studies, the data of Ohe et al. (1993) indicated that Np(V) sorption increases continuously over the entire pH range studied. This pH-dependent sorption behavior was observed at the three temperatures studied, and the amount sorbed at a given pH was seen to increase with increasing temperature. Finally, Kozai (1994) performed Np(V) sorption experiments on Na-smectite over the pH range from ~2 to 7.5. In contrast to other data, Kozai's (1994) Np(V) K_D is highest at the lowest pH examined, decreases by about an order of magnitude with increasing pH up to pH~4.5, then remains constant up to a pH of 7.6.

2. SORPTION EXPERIMENTS

In this study, batch experiments were conducted to investigate Np(V) sorption onto Na-montmorillonite. Montmorillonite can sorb Np(V) through two distinct mechanisms, ion-exchange with interlayer cations and surface complex formation with hydroxylated edge sites. Although a comprehensive description of Np(V) sorption on montmorillonite should include both ion-

exchange and surface complexation, 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 $\sim$6 to $\sim$9). Thus, to suppress ion-exchange between Np and interlayer cations, sorption experiments were conducted using Np solutions with a 0.1 M $NaNO_3$ 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.

2.1. Preparation of Na-Montmorillonite

Montmorillonite (SAz-1, "Cheto") used in the Np sorption experiments was obtained from the Source Clays Mineral Repository (Columbia, Missouri). The montmorillonite is a Ca-smectite from Apache County, Arizona. Prior to its use in experiments, the montmorillonite was converted to Na-form and treated to isolate the fraction less than 2 μm in size. Na-montmorillonite was generated by treating 200-g batches of clay in approximately 1.5 L of 3 M NaCl. The clay-NaCl mixture was continuously stirred in a 2-L glass beaker. The NaCl solution was replaced every three days. After two weeks, the clay was allowed to settle and most of the NaCl solution was decanted. The remaining clay-NaCl slurry was transferred in about 40-g aliquots to dialysis membranes (SpectraPor-4) that were tied off at each end. The membranes were placed in a glass beaker that contained warm ($\sim$40 °C) deionized water. Water in the beaker

was replaced twice daily for one week and was heated using an electric hot plate. After one week the deionized H_2O was tested using 0.1 M $AgNO_3$ to check for the presence of Cl^-. A negative test for Cl^-, as determined by a lack of AgCl precipitate, was used as indication that the clay was rinsed free of excess NaCl. The clay was then removed from the dialysis membranes and suspended in a 2-L glass beaker filled with deionized H_2O. No flocculation was observed over a period of two days. Then 40-ml aliquots of the clay suspension were collected and centrifuged for 2 min at 1,500 rpm using a Fisher-Marathon 21K centrifuge and a six-position fixed-angle rotor (effective radius 10 cm). The resulting suspension, which contained clay particles less than 2 μm, was decanted and saved. Clay remaining in each tube was mixed with deionized H_2O, vortexed thoroughly, and centrifuged again to recover any of the 2-μm fraction that had been entrained by larger particles. All clay removed from suspension by centrifugation at 1,500 rpm was discarded. The remaining suspended material was decanted and combined with the supernatant from previous separations. The 2-μm fraction was then collected by centrifuging aliquots of the suspension at 10,000 rpm for 20 min. Any particles that remained suspended following the high-speed centrifugation step were decanted and discarded. The wet, compacted clay was then freeze-dried for storage prior to use in sorption experiments. Freeze-drying effectively removes excess water from the clay but prevents undue collapse of the clay structure, which can be induced by drying under heat. XRD analyses of the clay before and after Na-exchange, size fractionation, and freeze-drying showed a change in the interlayer spacing for montmorillonite consistent with ion exchange of Ca^{2+} for Na^+. The measured surface area (N_2–BET) of the freeze-dried Na-montmorillonite was 97 ± 2 m^2/g.

2.2. Neptunium Solutions

^{237}Np standard solutions (1.24×10^{-3} M) were acquired in glass ampoules 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 $NpO_2OH(s)$, Np_2O_5, and Na-neptunyl-carbonates (Itagaki et al., 1992; Lemire et al., 1993; Nitsche et al., 1993, 1995; Neck et al., 1995) indicate 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 the 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).

2.3. Analytical Procedures

^{237}Np was analyzed by counting its alpha activity using a Packard 2505 TR/AB liquid scintillation analyzer (LSA). Liquid scintillation counting of alpha particles is convenient because little chemical preparation of samples is required prior to analysis, and the LSA counts alphas at, or very near to, 100% efficiency. Unfortunately, the immediate daughter of ^{237}Np is a short-lived beta emitter, ^{233}Pa, which rapidly ingrows in solutions containing ^{237}Np. Radionuclides like ^{233}Pa which emit beta particles at average energies high enough ($\sim$ 100 keV) to conflict with the alpha decay spectrum ($\sim$ 100–400 keV), can cause significant interference in quantifying the alpha activity present. The Packard 2505 LSA is capable of discriminating alpha and beta decay events in the same solution, but solutions of the pure alpha and beta emitters must be used to optimize the LSA pulse decay discriminator. A 1.24×10^{-3} M standard solution was used to generate the necessary samples. Based on 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. ^{233}Pa is eluted, while ^{237}Np is retained on the resin. A second 1-ml aliquot was mixed with 6 M HNO_3, loaded onto a separate silica gel column, and eluted with 6 M HNO_3 to isolate ^{237}Np preferentially based on a method modified from Hardy et al. (1958). The eluents were then evaporated, taken up in 0.02 M HNO_3, and sampled for use in the LSA. Once optimized, the same LSA setting is used for all subsequent analyses of solutions containing ^{237}Np and ^{233}Pa as the primary radionuclides. Statistics of counting associated with analysis of ^{237}Np-bearing solutions are based upon the alpha activity only. All solutions were counted for a period of time

such that the total number of alpha counts collected resulted in 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.

2.4. 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) and 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 (i) immediately capping the tubes after initial pH adjustment, or (ii) conducting the experiment in a controlled-atmosphere glove box using certified CO_2-free (less than 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 days to allow for equilibrium of both pH and the sorption reaction. Previous kinetics experiments (e.g., Yamamoto et al., 1990; Hart et al., 1994; Bertetti et al., 1997) suggest that Np(V) sorption reactions are ~98% complete within 48 hours, but the solutions used in this study typically required up to 10 days 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. Reversibility of the sorption reactions was evaluated from the NpM2(reverse) experiments. These experiments involved changing the pH of the solutions at the end of the NpM2(forward) experiments, reequilibrating for about 10 days, and resampling the experimental solutions.

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 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 days. 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.

3. 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) (e.g., Zachara and McKinley, 1993; McKinley et al., 1995; Turner et al., 1996; Pabalan et al., 1997; Pabalan and Turner, 1997). Np(V) sorption onto montmorillonite is greater than that observed for other non-layered/non-porous minerals such as quartz, hematite, alumina, and apatite (e.g.,

Allard et al., 1984; Nakayama and Sakamoto, 1991; Triay et al., 1993, Bertetti et al., 1997). The pH-dependence of Np(V) sorption onto montmorillonite, however, is very similar to those observed for other minerals. For solutions in equilibrium with atmospheric P_{CO_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 P_{CO_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 P_{CO_2} conditions were also observed (e.g., 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 M $NaNO_3$ matrix) are shown in Figures 3a, 3b, and 3c for a system which 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, 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 PCO_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 PCO_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. At low pH where NpO_2^+ is predominant, sorption is low indicating that Np(V) sorption through ion-exchange is largely suppressed under the relatively high ionic strength conditions. However, data from Kozai (1994) suggest that, in solutions of low ionic strength, ion-exchange between NpO_2^+ in solution and interlayer cations of montmorillonite occurs and results in higher sorption values. Even at the high ionic strength used here, some Np(V) sorption on montmorillonite observed in this study

are 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.

4. 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. 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.

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). Therefore, recent efforts have focused on developing a "standard" set of model parameters, either through parameter optimization studies and sensitivity analyses (e.g., 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 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 Np(V) 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

In applying SCMs to pH-dependent sorption, a surface is assumed to be comprised of amphoteric 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 contaminant complexation reactions. The equilibrium constants for these surface reactions is 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 those dissolved in the bulk solution and those specifically sorbed onto the solid.

The DLM uses a one layer representation of the mineral-water interface and has fewer fitting parameters than those included in multi-layer 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 multi-layer 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 (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 Np(V) and a surface sorption site can be written in the form:

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

where q is the protonation state of the sorption site (q=0, 1, or 2 for neutral, deprotonated, and protonated sites, respectively), and p and n are the reaction coefficients for NpO_2^+ and H_2O, respectively. NpO_2^+ and $[>XOH_q\text{-}(NpO_2)_p(OH)_n]^{p+q-n-1}$ 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 (e.g., K_+^{int}, K_-^{int} and $K^{int}_{[>XOHq-(NpO2)p(OH)n]}$) that are independent of surface charge. For sorption reactions of the type given in Eq. (2), $K^{int}_{[>XOHq-(NpO2)p(OH)n]}$ 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 constants (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 Eq. (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 Eq. (2) forward (increasing sorption), whereas formation of Np(V) aqueous carbonate-complexes reduces the activity of NpO_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 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. 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 direct comparison and performance evaluation of different models and will provide a consistent and useful modeling tool for use in performance assessment calculations of radionuclide transport.

Consistent with previous studies (Davis and Kent, 1990; Zachara and McKinley, 1993; McKinley et al., 1995; Turner et al., 1996), 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 M $NaNO_3$) which suppressed 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 comprised of silanol (>SiOH°) and aluminol (>AlOH°) 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-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 ($T_{>XOH}$) and, for the conceptual model developed here, the distribution of the total number of sites between >AlOH° and >SiOH°. 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. On this basis, an effective surface area of 9.7 m^2/g (10% of the measured N_2-BET specific surface area of 97 m^2/g) 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 $>AlOH^o$ to $>SiOH^o$ 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 $>SiOH^o$ and $>AlOH^o$ edge sites were derived based on potentiometric titration data for SiO_2 and α-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, 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), the numerical parameter optimization code FITEQL, Version 2.0 (Westall, 1982a,b) was used to determine binding constants for the Np(V)-montmorillonite sorption reaction(s) of the general form given in Eq. (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 two surface complexation reactions were determined to best describe the observed Np(V) sorption on montmorillonite:

$$>SiOH^\circ + NpO_2^+ = >SiOH\text{-}NpO_2^+ \tag{3a}$$

$$>AlOH^\circ + NpO_2^+ + H_2O = >AlO\text{-}NpO_2(OH)^- + 2H^+ \tag{3b}$$

The binding constants for these reactions are given in Table 2.

4.3. Model Results

One test of the flexibility of the modeling approach is the 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 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 CO_2-free NpM1 experiments. As shown in Figure 5, the model accurately predicts both the sorption maximum ($K_D \approx 100$ ml/g) 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 $>SiOH_2\text{-}NpO_2(CO_3)^0$, or the competition for available sorption sites by carbonate species (e.g., $>AlOH_2\text{-}CO_3^-$). At present, there are no data to characterize quantitatively the sorption of carbonate species on montmorillonite. Instead, the 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 such 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 one to two orders of magnitude with further increases in pH. Reported sorption coefficients range from $K_D < 1$ to ~ 5000 ml/g in CO_2-free or low CO_2 experiments, although the bulk of the data fall between 10 to 100 ml/g. 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 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.

5. CONCLUSIONS

The experimental data derived in this study indicate that montmorillonite can contribute 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, the low sorption values indicate that ion-exchange interactions with the interlayer cations in montmorillonite are at least partly suppressed in the 0.1 M $NaNO_3$ 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 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_Ds currently used in transport calculations.

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CNWRA QA Manual. Data from other sources, however, are freely used. Referenced sources should be consulted for determining their level of QA. This work was funded by the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Regulatory Research, Division of Regulatory Applications, and by the NRC Office of Nuclear Material Safety and Safeguards, Division of Waste Management, under Contract No. NRC-02-03-005. This paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

References

Allard, B., Olofsson, U., and Torstenfelt B. 1984. Environmental actinide chemistry. *Inorg. Chim. Acta* **94**: 205–221.

Allison J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 user's manual.* EPA/600/3-91/021. Athens, GA: Environmental Protection Agency.

Beall, G.W., and B. Allard. 1981. Sorption of actinides from aqueous solutions under environmental conditions. *Adsorption from Aqueous Solutions*. P.H. Tewari, ed. pp. 193–212. Plenum Press, New York.

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. 1997. Studies of neptunium(V) sorption on quartz, clinoptilolite, montmorillonite, and α-alumina. *Metals in Geomedia: Sorption Processes and Model Applications*. E. Jenne, ed. Academic Press: New York, NY: (in press).

Bidoglio, G., G. Tanet, and A. Chatt. 1985. Studies on neptunium(V) carbonate complexes under geologic repository conditions. *Radiochimica Acta* 38: 21–26.

Bidoglio, G., P. Offermann, and A. Saltelli. 1987. Neptunium migration in oxidizing clayey sand. *Applied Geochemistry* 2: 275–284.

Danesi, P.R., R. Chiarizia, G. Scibona, and G.J. D'Alessandro. 1971. Stability constants of nitrate and chloride complexes of Np(IV), Np(V) and Np(VI) ions. *Inorg. Nucl. Chem.*?? 33: 3,503–3,510.

Davis J.A., and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67: 90–107.

Davis J.A., and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Reviews in Mineralogy: Volume 23. Mineral-Water Interface Geochemistry.* M.F. Hochella, Jr., and A.F. White, eds. Washington, DC. Mineralogical Society of America. pp. 177–260.

Dzombak D.A., and F.M.M. Morel. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York, NY: John Wiley and Sons.

Fuger, J. 1992. Thermodynamic properties of actinide species relevant to geochemical problems. *Radiochim. Acta* 59: 81–91.

Gauthier, R., V. Ilmstadter, and K.H. Lieser. 1983. Simultaneous determination of the various oxidation states of neptunium at low concentrations by spectrophotometry. *Radiochimica Acta* 33: 35–39.

Grauer, R. 1994. Bentonite as a backfill material in a high-level waste repository. *MRS Bulletin*.

19: 43–46.

Hardy, C.J., D. Scargill, and J.M. Fletcher. 1958. Studies on protactinium(V) in nitric acid solutions. *Journal of Inorganic and Nuclear Chemistry* 7: 257–275.

Hart, K.P., T.E. Payne, B.J. Robinson, and P. van Iseghem. 1994. Neptunium uptake on Boom clay - Time dependence and association of Np with fine particle. *Radiochimica Acta* 66/67: 19–22.

Hayes, K.F., G.G. Redden , W. Ela, and J.O. Leckie J.O. 1991. Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *Journal of Colloid and Interface Science.* 142: 448–469.

Hsi C-K.D., and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta.* 49: 1,931–1,941.

Itagaki, H., S. Nakayama, S. Tanaka, and M. Yamawaki, M. 1992. Effect of ionic strength on the solubility of neptunium(V) hydroxide. *Radiochim. Acta* 58/59: 61–66.

Kozai, N. 1994. Sorption characteristics of neptunium by smectite, in *Progress Report on Safety Research on Radioactive Waste Management for the Period April 1992 to March 1993. JAERI-M94-027.* Japan Atomic Energy Research Institute. Tokai, Japan: 39–41.

LaFlamme B.D., and J.W. Murray. 1987. Solid/Solution Interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochimica et Cosmochimica Acta.* 51: 243–250.

Lemire, R.J. 1984. *An assessment of the thermodynamic behavior of neptunium in water and model groundwaters from 25 to 150°C. AECL-7817.* Pinawa, Manitoba: Atomic Energy of Canada Limited.

Lemire, R.J., and F. Garisto. 1989. *The solubility of U, Np, Pu, Th, and Tc in a geologic disposal vault for used nuclear fuel. AECL-10009.* Pinawa, Manitoba: Atomic Energy of Canada Limited.

Lemire, R.J., G.D. Boyer, and A.B. Campbell. 1993. The solubilities of sodium and potassium dioxoneptunium(V) carbonate hydrates at 30, 50 and 75°C. *Radiochim. Acta* 61: 57–63.

Lieser, K.H., and U. Mühlenweg. 1988. Neptunium in the hydrosphere and in the geosphere 1. Chemistry of neptunium in the hydrosphere and sorption of neptunium from groundwaters on sediments under aerobic and anaerobic conditions. *Radiochimica Acta* 43: 27–35.

McKinley J.P, J.M. Zachara, S.C. Smith, and G.D. Turner. 1995. The influence of hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite. *Clays and Clay Minerals* 43: 586–598.

Nakayama, S., and Y. Sakamato. 1991. Sorption of neptunium on naturally-occurring iron-containing minerals. *Radiochim. Acta* 52/53: 153–157.

Neck, V., W. Runde, and J.I. Kim. 1995. Solid-liquid equilibria of neptunium(V) in carbonate solutions of different ionic strengths: Solubility of the solid phases. *Journal Alloys and Compounds* 225: 295–302.

Nitsche, H., R.C. Gatti, E.M. Standifer, S.C. Lee, A. Müller, T. Prussin, R.S. Deinhammer, H. Maurer, K. Becraft, S. Leung, and S. Carpenter. 1993. *Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater (J-13) from the Yucca Mountain Region Milestone Report 3010-WBS 1.2.3.4.1.3.1. LA-12562-MS.* Los Alamos, NM: Los Alamos National Laboratory.

Nitsche, H., K. Roberts, K. Becraft, T. Prussin, D. Keeney, S. Carpenter, and D. Hobart.

1995. *Solubility and Speciation Results from Over- and Undersaturation Experiments on Neptunium, Plutonium, and Americium in Water from Yucca Mountain Region Well UE-25p#1. LA-13017-MS*. Los Alamos, NM: Los Alamos National Laboratory.

Ohe, T., M. Tsukamoto, T. Fujita, R. Hesbol, and H-P. Hermansson. 1993. Temperature and pH dependence of Neptunium(V) sorption on bentonite. *1993 International Conference on Nuclear Waste Management and Environmental Remediation, Vol. 1*. Prague, Czhechoslovakia. 197–205.

Pabalan, R.T., and D.R. Turner. 1997. Uranium(6+) sorption on montmorillonite: Experimental and surface complexation modeling study. *Aquatic Geochemistry* (in submission).

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. 1997. Uranium(VI) sorption onto selected mineral surfaces: Key geochemical parameters. *Metals in Geomedia: Sorption Processes and Model Applications*. E. Jenne, ed. Academic Press: New York, NY: (in press).

Pickett, D.A., M.T. Murrell, and R.W. Williams. 1994. Determination of femtogram quantities of protactinium in geologic samples by thermal ionization mass spectrometry. *Analytical Chemistry* 66: 1,044–1,049.

Righetto, L., G. Bidoglio, G. Azimonti, and I.R. Bellobono. 1991. Competitive actinide interactions in colloidal humic acid-mineral oxide systems. *Env Sci. Tech.*?? 25: 1,913–1,919.

Sakamoto, Y., M. Konishi, K. Shirahashi, M. Senoo, and N. Moriyama. 1990. Adsorption behavior of neptunium for soil. *Radioactive Waste Management and the Nuclear Fuel Cycle* 15: 13–25.

Sanchez, A.L., J.W. Murray, and T.H. Sibley. 1985. The adsorption of plutonium IV and V on goethite. *Geochimica et Cosmochimica Acta* 49: 2,297–2,307.

Sverjensky, D.A., and N. Sahai. 1996. Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water. *Geochimica et Cosmochimica Acta* 60: 3,773–3,797.

Thompson, R.C. 1982. Neptunium - the neglected actinide: A review of the biological and environmental literature. *Radiation Research* 90: 1–32.

Torstenfelt, B., R.S. Rundberg, and A.J. Mitchell. 1988. Actinide sorption on granites and minerals as a function of pH and colloids/pseudocolloids. *Radiochimica Acta* 44/45: 111–117.

Triay, I.R., B.A. Robinson, R.M. Lopez, A.J. Mitchell, and C.M. Overly. 1993. Neptunium retardation with tuffs and groundwaters from Yucca Mountain. *Proceedings of the Fourth Annual International Conference on High-Level Radioactive Waste Management.* American Nuclear Society and American Society of Civil Engineers. La Grange Park, IL: 1,504–1,508.

TRW Environmental Safety Systems, Inc. 1995. *Total System Performance Assessment—1995: An Evaluation of the Potential Yucca Mountain Repository*. B00000000-01717-2200-00136, Rev. 01. Las Vegas, NV. TRW Environmental Safety Systems, Inc.

Turner D.R., and S.A. Sassman. 1996. Approaches to sorption modeling for high-level waste performance assessment. *Journal of Contaminant Hydrology* 21: 311–332.

Turner, G.D., J.M. Zachara, J.P. McKinley, and S.C. Smith. 1996. Surface-charge properties and UO_2^{2+} adsorption of a subsurface smectite. *Geochimica et Cosmochimica Acta* 60:

3,399–3,414.

Waite T.D., J.A. Davis, T.E. Payne, G.A. Waychunas, and N. Xu. 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica et Cosmochimica Acta* 58: 5,465–5,478.

Wanner H., Y. Albinsson, O. Karnl, E. Wieland, P. Wersin, and L. Charlet. 1994. The acid/base chemistry of montmorillonite. *Radiochimica Acta* 66/67: 733–738.

Wescott, R.G., M.P. Lee, T.J. McCartin, N.A. Eisenberg, and R.G. Baca, eds. 1995. *NRC Iterative Performance Assessment Phase 2: Development of Capabilities for Review of a Performance Assessment for a High-Level Waste Repository. NUREG-1464*. Washington, DC: Nuclear Regulatory Commission.

Westall J.C. 1982a. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 1.2*. Rpt. 82-01. Corvallis, OR. Department of Chemistry, Oregon State University.

Westall J.C. 1982b. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 2.0*. Rpt. 82-02. Corvallis, OR. Department of Chemistry, Oregon State University.

Westall J.C., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Advances in Colloid and Interface Science* 12: 265–294.

White G.N., and L.W. Zelazny. 1988. Analysis and implications of the edge structure of dioctahedral phyllosilicates. *Clays and Clay Minerals* 36: 141–146.

Wilson, M.L., J.H. Gauthier, R.W. Barnard, G.E. Barr, H.A. Dockery, E. Dunn, R.R. Eaton, D.C. Guerin, N. Lu, M.J. Martinez, R. Nilson,C.A. Rautman, T.H. Robey, B. Ross, E.E. Ryder, A.D. Lamont, I.R. Triay, A. Meijfer, and D.E. Morris. 1994. *Total-System Performance Assessment for Yucca Mountain—SNL Second Iteration (TSPA-1993) Volume 1 and 2.* SAND93-2675. Albuquerque, NM: Sandia National Laboratories.

Yamamoto, K., T. Yanagi, M. Senoo, and Y. Sakamoto. 1990. Sorption behavior of neptunium(V) ion on clay sorbent. *Journal of Nuclear Science and Technology* 27: 626–630.

Zachara J.M., and J.P. McKinley. 1993. Influence of hydrolysis on the sorption of metal cations by smectites: Importance of edge coordination reactions. *Aquatic Sciences* 55: 250–261.

Table 1. Experimental conditions.

Experiment	Atmosphere	Initial Np(V) conc. (M)	Mass of solid (g, $\pm$ 1σ)	Volume of solution (mL, $\pm$ 1σ)	Approx. M/V (g/L, $\pm$ 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 ($PCO_2=10^{-3.5}$ atm)	9.25×10^{-7}	0.0996 ± 0.0004	24.9 ± 0.1	4.01 ± 0.02
NpM2 (reverse)	open vial ($PCO_2=10^{-3.5}$ 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

Table 2. FITEQL model additions used to determine DLM binding constants for Np(V) sorption on montmorillonite.

Solid concentration (M/V)	3.97 g/L
Site density	2.3 sites/nm^2
Surface area$_a$	9.7 m^2/g
Ionic strength	0.1 M $NaNO_3$
Σ^{237}Np(V)	8.79×10^{-7} M
Edge-Site Reactions:	**Log K**
$>AlOH^\circ + H^+ \rightleftharpoons >AlOH_2^+$	8.33$_b$
$>AlOH^\circ \rightleftharpoons >AlO^- + H^+$	-9.73$_b$
$>AlOH^\circ + NpO_2^+ + H_2O \Leftrightarrow >AlO\text{-}NpO_2(OH)^- + 2H^+$	-13.79$_c$
$>SiOH^\circ \rightleftharpoons >SiO^- + H^+$	-7.20$_b$
$>SiOH^\circ + NpO_2^+ \Leftrightarrow >SiOH\text{-}NpO_2^+$	4.05$_c$
Aqueous Speciation Reactions:	**Log K**
$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH^\circ + H^+$	-10.0$_d$
$NpO_2^+ + 2H_2O \Leftrightarrow NpO_2(OH)_2^- + 2H^+$	-22.4$_{d,e}$
$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$	4.6$_{e,f,g}$
$NpO_2^+ + 2CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$	7.0$_{e,f,g}$
$NpO_2^+ + 3CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$	8.5$_{f,g}$
$NpO_2^+ + NO_3^- \Leftrightarrow NpO_2NO_3^\circ$ (aq)	-0.5$_h$

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 α-Al_2O_3 from Turner and Sassman (1996).
c. This study. Binding constants determined using FITEQL, Version 2.0 (Westall, 1982a,b).
d. Lemire and Garisto (1989)
e. Fuger (1992)
f. Lemire (1984)
g. Lemire et al. (1993)
h. Danesi et al. (1971)

FIGURE CAPTIONS:

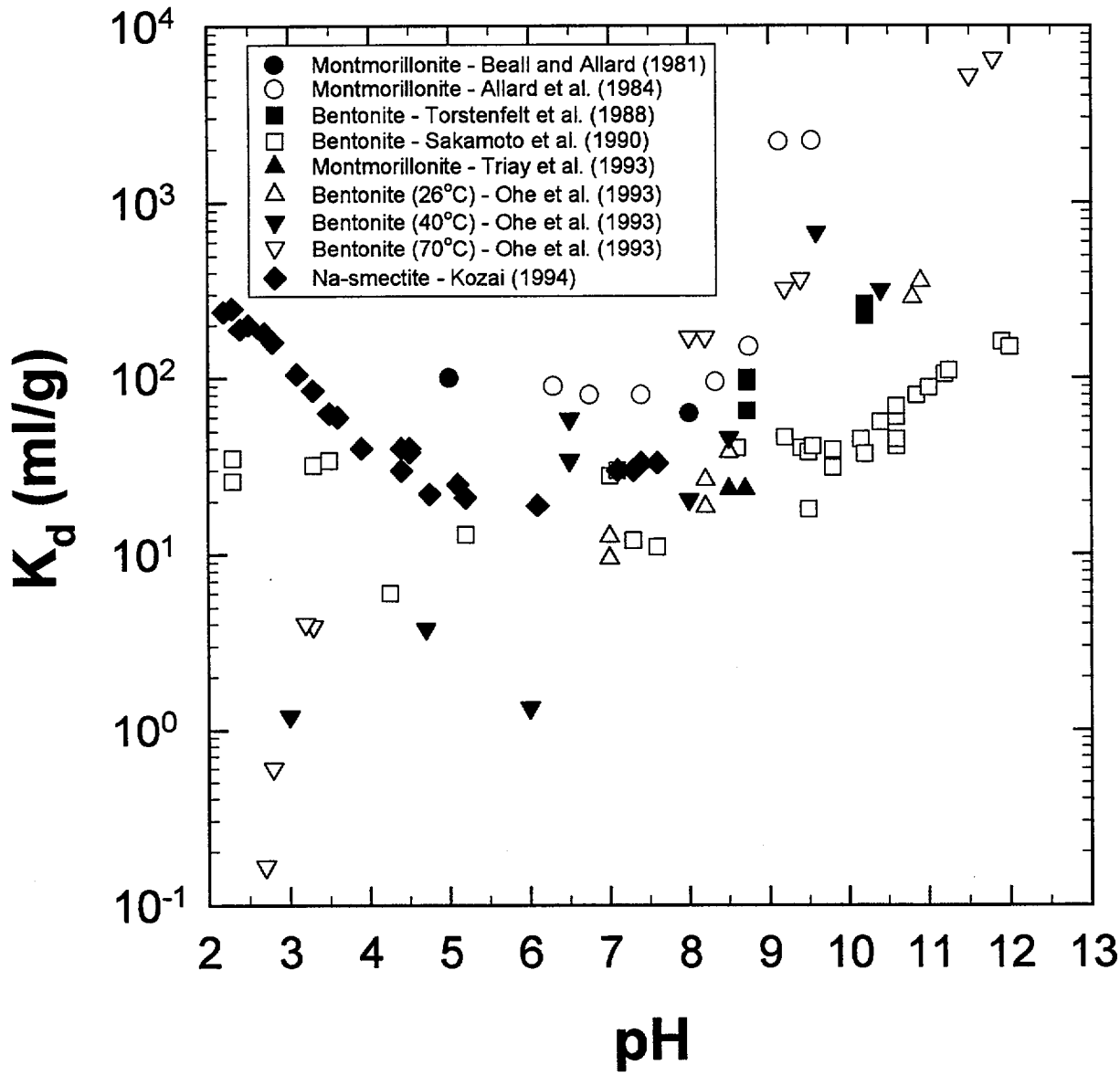
Figure 1. Comparison of Np(V) sorption data on montmorillonite and bentonite from various studies. References as noted.

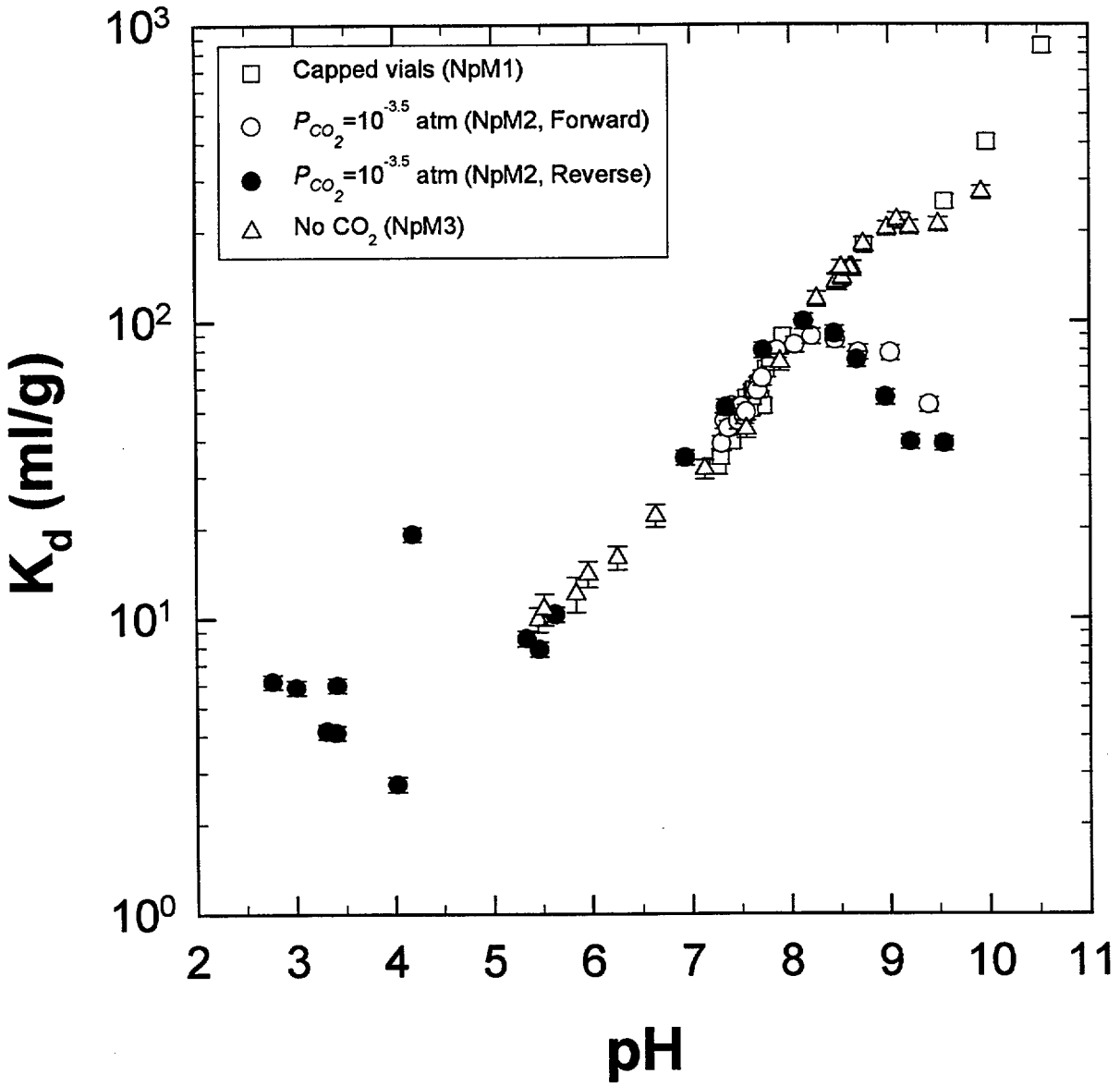
Figure 2. Np(V) sorption on montmorillonite plotted in terms of K_D (ml/g) versus pH for experiments with $\Sigma Np_i \sim 9\times10^{-7}$ M. The uncertainty is typically less than the size of the symbol. Open triangles represent CO_2-free conditions (glove box, N_2-atmosphere). Open squares represent capped-vial experiments (25 ml head space). Open and closed circles represent forward and reverse sorption experiments, respectively, under conditions open to the atmosphere ($P_{CO_2}=10^{-3.5}$ atm). Experimental conditions are listed in Table 1.

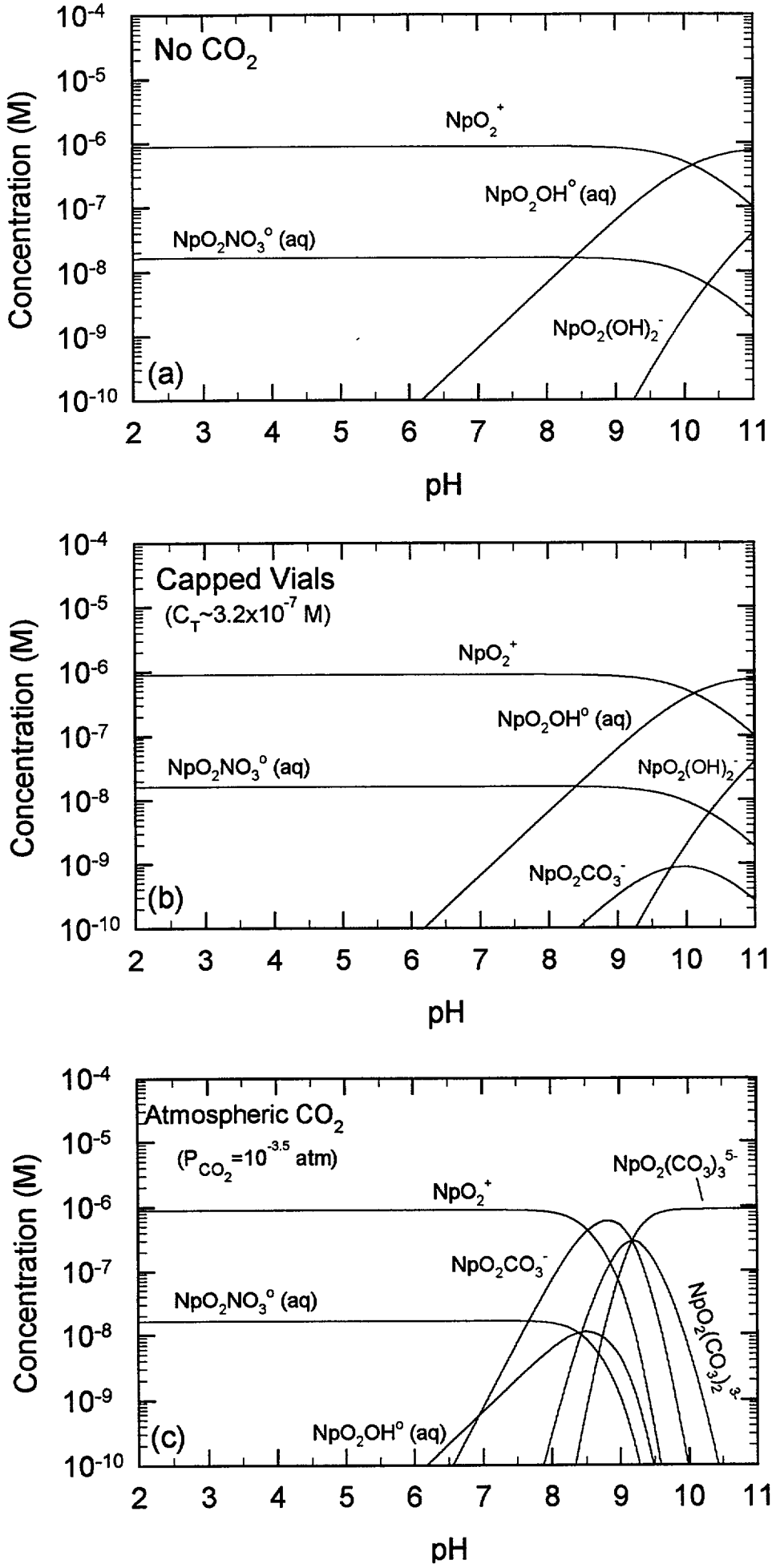
Figure 3. Aqueous Np(V) speciation at 25°C as a function of pH for a 9.0×10^{-7} M Np(V) solution (0.1 M $NaNO_3$ matrix) for (a) CO_2-free conditions, (b) capped vials with 25 ml of headspace, and (c) equilibrium with the atmosphere ($P_{CO_2}=10^{-3.5}$ atm). Speciation was calculated using the MINTEQA2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

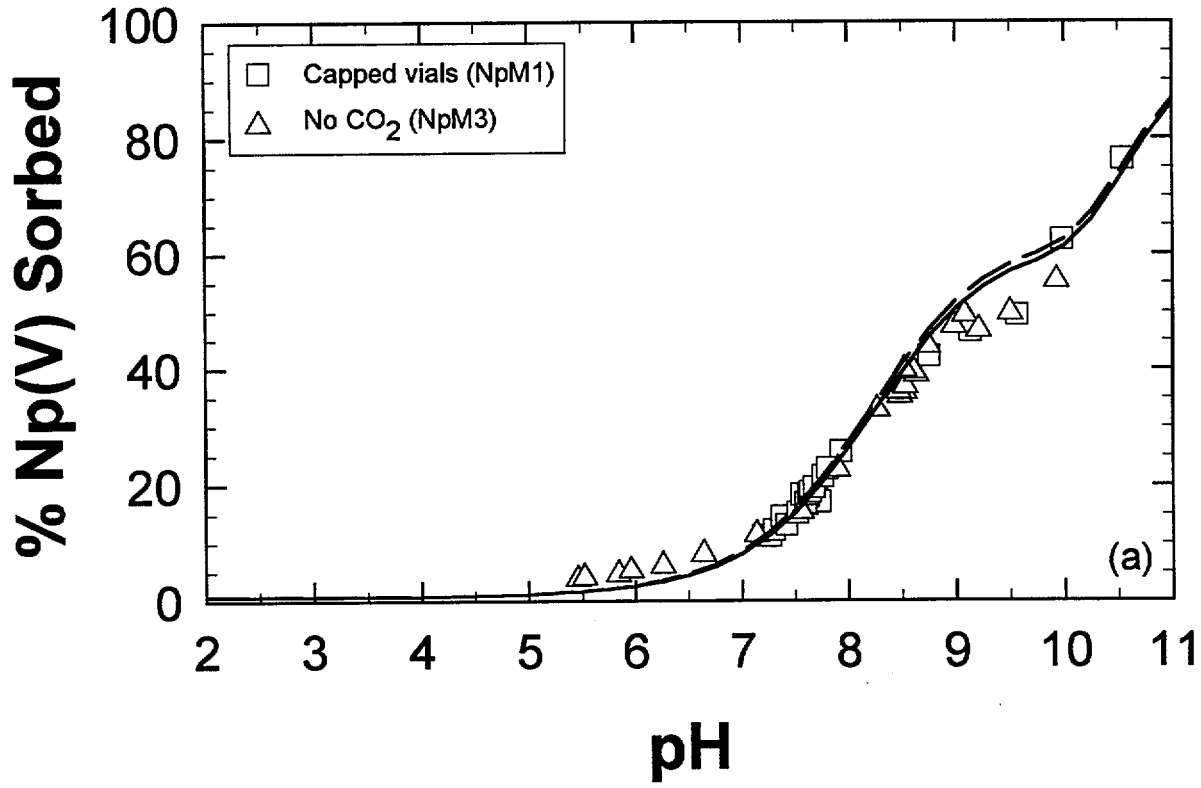
Figure 4. Np(V) sorption on montmorillonite plotted in terms of (a) percent sorbed versus pH, and (b) K_D (ml/g) versus pH for experiments NpM1 (no CO_2) and NpM3 (capped vials, low CO_2). The dashed and solid curves represent DLM-calculated values for solutions analogous to NpM1 and NpM3, respectively,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

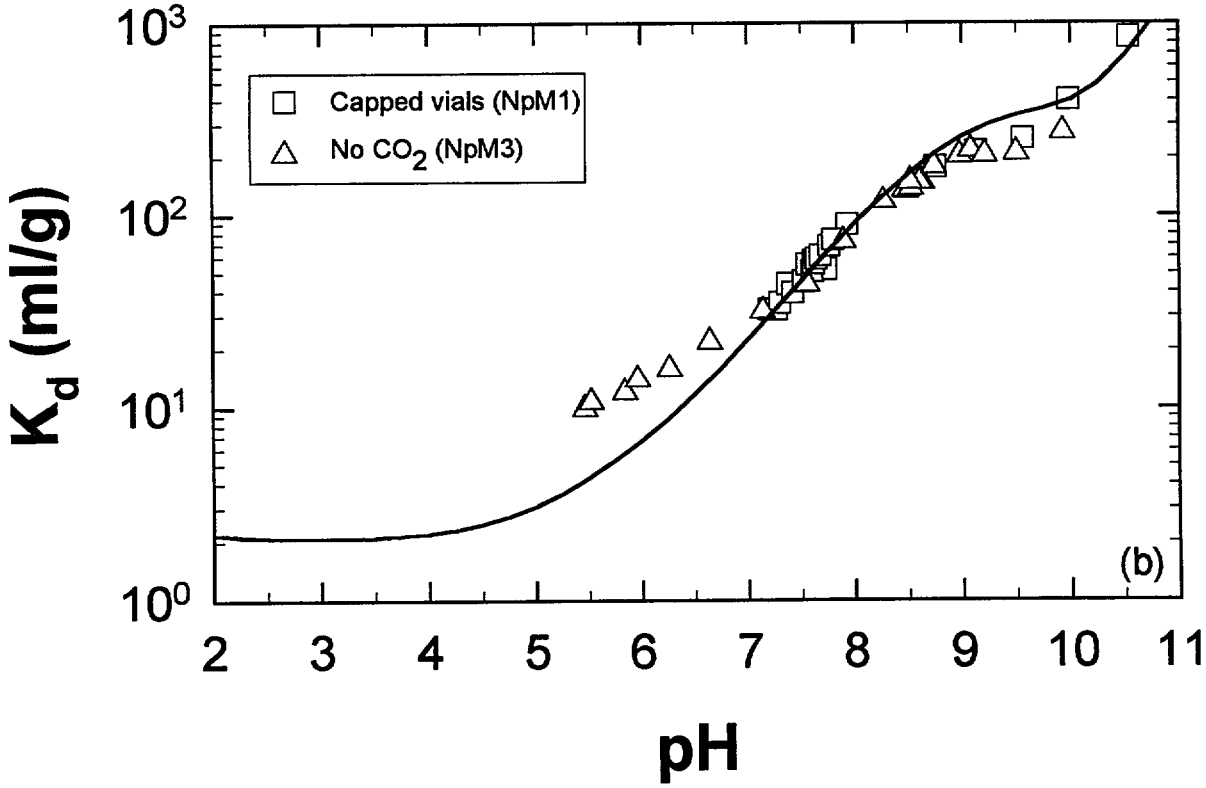
Figure 5. Np(V) sorption on montmorillonite plotted in terms of (a) percent sorbed versus pH, and (b) K_D (ml/g) versus pH for experiments NpM2(forward) and NpM2(reverse) in equilibrium with the atmosphere ($Pco_2 = 10^{-3.5}$ atm). The dotted curve represents DLM-calculated K_Ds for solutions in equilibrium with atmospheric Pco_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 shown for reference.

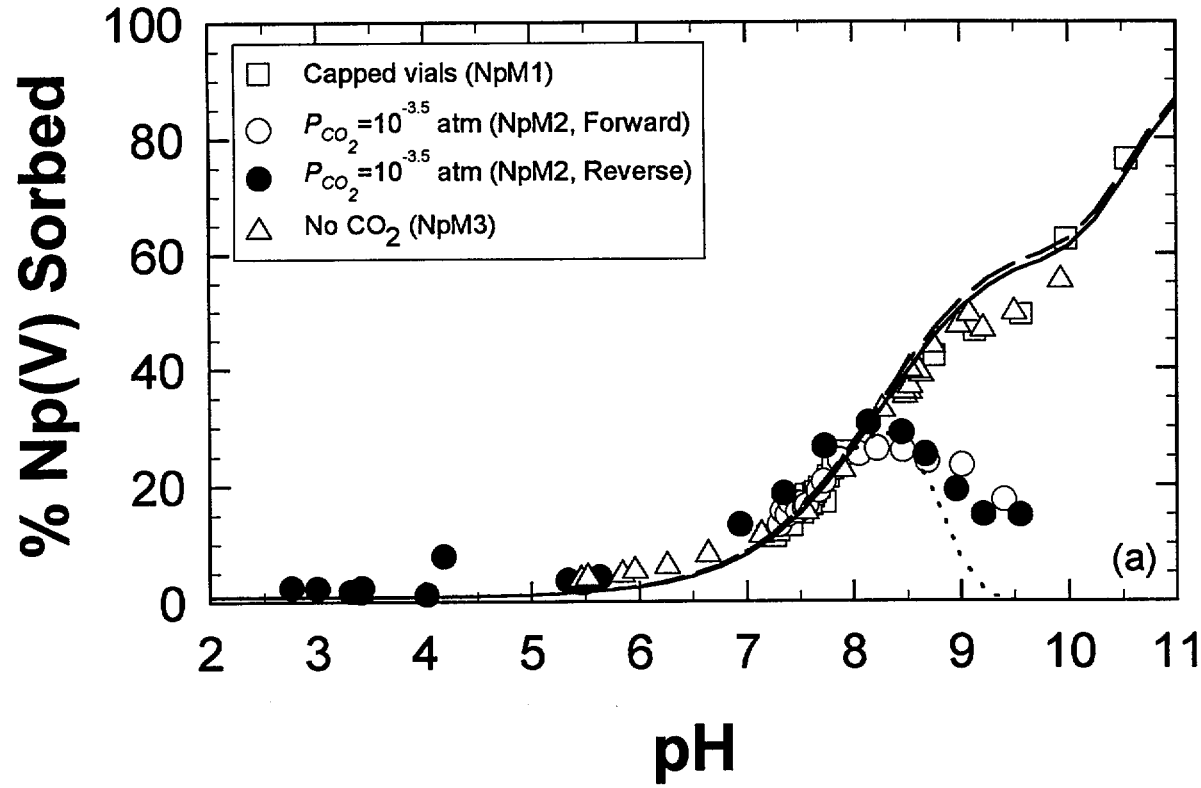

Montmorillonite - Beall and Allard (1981)
Montmorillonite - Allard et al. (1984)
Bentonite - Torstenfelt et al. (1988)
Bentonite - Sakamoto et al. (1990)
Montmorillonite - Triay et al. (1993)
Bentonite (26°C) - Ohe et al. (1993)
Bentonite (40°C) - Ohe et al. (1993)
Bentonite (70°C) - Ohe et al. (1993)
Na-smectite - Kozai (1994)
K_d (ml/g)
10^4
10^3
10^2
10^1
10^0
10^{-1}
2 3 4 5 6 7 8 9 10 11 12 13
pH

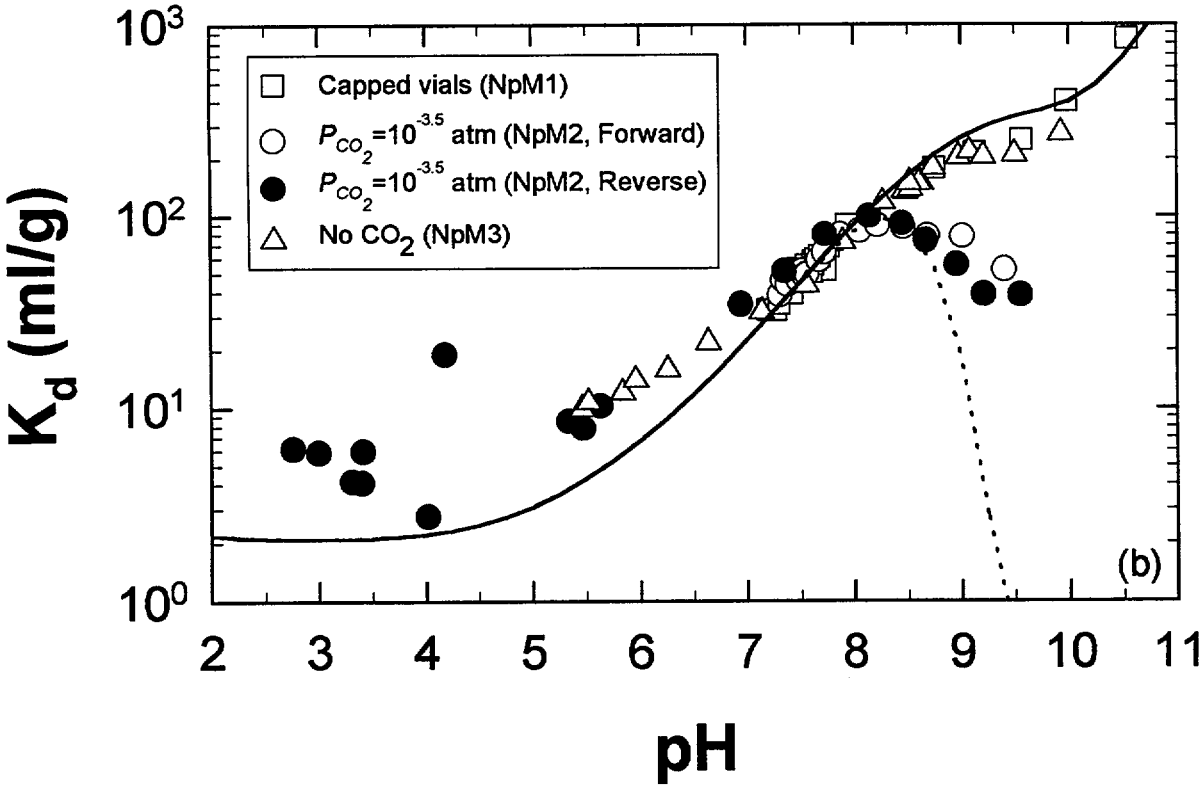

Capped vials (NpM1)
$P_{CO_2}=10^{-3.5}$ atm (NpM2, Forward)
$P_{CO_2}=10^{-3.5}$ atm (NpM2, Reverse)
No CO_2 (NpM3)
K_d (ml/g)
10^3
10^2
10^1
10^0
2
3
4
5
6
7
8
9
10
11
pH


No CO_2
NpO_2^+
NpO_2OH^o (aq)
$NpO_2NO_3^o$ (aq)
$NpO_2(OH)_2^-$
(a)
Concentration (M)
pH
Capped Vials
(C_T~3.2x10^{-7} M)
NpO_2^+
NpO_2OH^o (aq)
$NpO_2NO_3^o$ (aq)
$NpO_2(OH)_2^-$
$NpO_2CO_3^-$
(b)
Concentration (M)
pH
Atmospheric CO_2
(P_{CO_2}=10$^{-3.5}$ atm)
$NpO_2(CO_3)_3^{5-}$
NpO_2^+
$NpO_2CO_3^-$
$NpO_2NO_3^o$ (aq)
$NpO_2(CO_3)_2^{3-}$
NpO_2OH^o (aq)
(c)
Concentration (M)
pH


100
80
60
40
20
0
% Np(V) Sorbed
Capped vials (NpM1)
No CO_2 (NpM3)
(a)
2
3
4
5
6
7
8
9
10
11
pH


10^3
10^2
10^1
10^0
K_d (ml/g)
Capped vials (NpM1)
No CO_2 (NpM3)
(b)
2
3
4
5
6
7
8
9
10
11
pH


% Np(V) Sorbed
100
80
60
40
20
0
2
3
4
5
6
7
8
9
10
11
pH
Capped vials (NpM1)
P_{CO_2}=10$^{-3.5}$ atm (NpM2, Forward)
P_{CO_2}=10$^{-3.5}$ atm (NpM2, Reverse)
No CO_2 (NpM3)
(a)


K_d (ml/g)
10^3
10^2
10^1
10^0
2
3
4
5
6
7
8
9
10
11
pH
Capped vials (NpM1)
P_{CO_2}=10$^{-3.5}$ atm (NpM2, Forward)
P_{CO_2}=10$^{-3.5}$ atm (NpM2, Reverse)
No CO_2 (NpM3)
(b)