Np(V) and Pu(V) Ion Exchange and Surface-Mediated Reduction Mechanisms on Montmorillonite

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Ⓢ *Supporting Information*

ABSTRACT: Due to their ubiquity and chemical reactivity, aluminosilicate clays play an important role in actinide retardation and colloid-facilitated transport in the environment. In this work, Pu(V) and Np(V) sorption to Na-montmorillonite was examined as a function of ionic strength, pH, and time. Np(V) sorption equilibrium was reached within 2 h. Sorption was relatively weak and showed a pH and ionic strength dependence. An approximate $NpO_2^+ \rightarrow Na^+$ Vanselow ion exchange coefficient (Kv) was determined on the basis of Np(V) sorption in 0.01 and 1.0 M NaCl solutions at pH < 5 (Kv ~ 0.3). In contrast to Np(V), Pu(V) sorption equilibrium was not achieved on the time-scale of weeks. Pu(V) sorption was much stronger than Np(V), and sorption rates exhibited both a pH and ionic strength dependence. Differences in Np(V) and Pu(V) sorption behavior are indicative of surface-mediated transformation of Pu(V) to Pu(IV) which has been reported for a number of redox-active and redox-inactive minerals. A model of the pH and ionic strength dependence of Pu(V) sorption rates suggests that H^+ exchangeable cations facilitate Pu(V) reduction. While surface complexation may play a dominant role in Pu sorption and colloid-facilitated transport under alkaline conditions, results from this study suggest that Pu(V) ion exchange and surface-mediated reduction to Pu(IV) can immobilize Pu or enhance its colloid-facilitated transport in the environment at neutral to mildly acidic pHs.
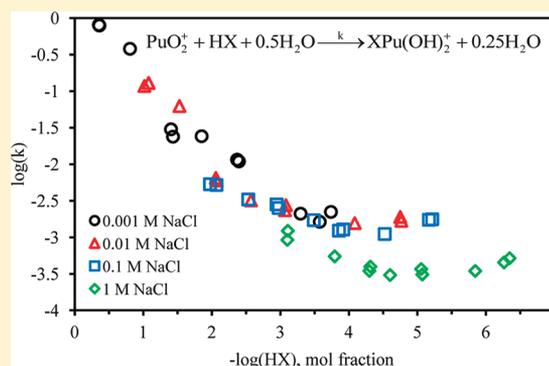
■ INTRODUCTION

The production and testing of nuclear weapons has created a legacy of Pu and Np contamination that exists today in a wide range of forms and locations. These include the Hanford Reservation where 4.37×10^{14} Bq (11,800 Ci) of ^{239}Pu and 2.04×10^{12} Bq (55 Ci) of ^{237}Np was disposed of as liquid waste in the near surface environment,[1,2] the Nevada Test Site where 8.88×10^{15} Bq (240,000 Ci) of $^{238–240}$Pu and 1.81×10^{12} Bq (49 Ci) of ^{237}Np was deposited in the subsurface as a result of underground nuclear testing,[3] Savannah River Site where 6.07×10^{11} Bq (16.4 Ci) of Pu was released into streams, seepage basins, or air and thousands of curies were buried as waste of various forms,[4] and elsewhere. Np(V) has also been identified as a dominant long-term dose contributor under certain nuclear waste repository scenarios.[5]

Aluminosilicate clays are ubiquitous in the environment, and improving our understanding of Np and Pu sorption to these minerals is essential to the accurate prediction of actinide transport rates. The proposed use of bentonite within engineered barrier systems for underground nuclear waste repositories provides additional importance to understanding Np and Pu interaction with smectite minerals.[6] Smectite minerals are known to sorb Np and Pu,[6–11] which will contribute to actinide immobilization. However, their sorption

to these same minerals may also result in colloid-facilitated transport (e.g., ref 12).

On the basis of Np redox potentials, the likely Np oxidation states under environmental conditions are Np(IV) and Np(V).[13] Np(IV) will form under anoxic conditions and in the presence of Fe(II).[6,14] Under mildly oxic conditions, Np(V) is likely to be the dominant oxidation state; Np(V) aqueous speciation is summarized in the online Supporting Information.

Np(V) sorption to smectite minerals has been previously investigated.[6,11] Above pH 5, Np(V) sorption is dominated by surface complexation and steadily increases with pH.[11] When carbonate is present, sorption will tend to decrease above pH 8 due to the stability of the aqueous $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{3-}$ complexes. Below pH 5, sorption has been attributed to ion exchange. Turner et al.[11] estimated a Np(V) K_d of 4–6 mL g^{-1} on Na-montmorillonite in 0.1 M NaNO$_3$. Earlier studies showed a wider range of K_ds at low pH but mostly within an order of magnitude of this value. Differences are attributable to variation in mineralogy (i.e., bentonite vs

montmorillonite, exchangeable counterion) and solution conditions (e.g., ionic strength). Kozai et al.[8,9] observed an increase in K_d with decreasing pH (pH 2–5 range). They suggested that sorption occurred on the smectite basal plane and increased with decreasing pH as a result of interlayer expansion and H^+ ion exchange. However, smectite dissolution, release of structural Fe(II), and reduction of the weakly sorbing Np(V) to the more strongly sorbing Np(IV) could also have led to higher K_ds at the lowest pHs.

Under environmental conditions, plutonium can exist in four oxidation states, possibly simultaneously.[15] The sensitivity of plutonium to oxidation state transformations is due to the relatively similar electrochemical potentials for each redox couple.[16] Pu(III) has been identified under anoxic conditions and in the presence of Fe(II) containing minerals.[17−19] Under mildly oxic conditions, the predominant oxidation states are Pu(IV) and Pu(V). These two oxidation states represent the Pu species with the highest (Pu(V)) and lowest (Pu(IV)) sub-surface mobilities.[20] Pu(V) and Pu(IV) aqueous speciation is summarized in the online Supporting Information.

The study of Pu sorption to smectite minerals is more limited than for Np. Vaniman et al.[21] investigated the partitioning of Pu(V) to tuffs from Yucca Mountain. While certain oxide minerals were found to exhibit strong Pu retention, a weaker but more ubiquitous association of Pu with smectite minerals was noted. Lujaniene et al.[10] performed Pu(IV) sorption experiments on smectite-rich sediments and measured K_ds ranging from 10 000 to 40 000 mL g^{-1} over pH 5 to 12. Hixon et al.[22] used both XANES and solvent extraction coupled with Mossbauer spectroscopy to determine that Pu(V) was reduced to Pu(IV) on Savannah River Site sediments and that the reductions rates correlated with Fe(II) concentrations associated with phyllosilicate clays.

Even under oxic conditions, any investigation of Pu(V) or Pu(IV) sorption or ion exchange is complicated by the simultaneous presence of both Pu(IV) and Pu(V) and the solubility limits imposed by Pu(IV) hydroxide colloid and/or mixed oxidation state precipitates.[23−26] Oxidation state analyses of Pu in the presence of redox active and redox-inactive minerals under oxic conditions provide strong indications of surface mediated reduction of Pu(V) to Pu(IV) with variable rates depending on the mineral composition and aqueous conditions (i.e., pH).[27−29] Under oxic conditions, a reductant has not been identified although various scenarios have been suggested,[28,30] as we discuss below.

Our investigation focuses on isolating the process of Np(V) and Pu(V) ion exchange on pure montmorillonite under oxic conditions and the associated reaction kinetics. A comparison of Np(V) to Pu(V) sorption provides an indirect means of identifying surface-mediated Pu(V) reduction rates. The data are fit to a model which accounts for H^+ ion exchange on montmorillonite and suggests that H^+ exchangeable cations facilitate the reduction of Pu(V) at neutral to mildly acidic pHs.

■ MATERIALS AND METHODS

Montmorillonite Preparation and Characterization. Details regarding the preparation of SWy-1 montmorillonite (Source Clays Repository of the Clay Minerals Society) for use in sorption experiments can be found in the online Supporting Information. Briefly, the montmorillonite was (1) pretreated in a 0.001 M HCl solution to dissolve any soluble salts, (2) reacted with a H_2O_2 solution to minimize the reducing capacity of any impurities, (3) treated in a 0.01 M NaCl solution to produce a homoionic clay suspension, (4) dialyzed in MQ H_2O (distilled−deionized water, 18.2 MΩ.cm resistivity) to remove excess salts, and (5) centrifuged at 1000 rpm for 5 min and 4500 rpm for 6 h to remove the >2 μm and <50 nm particles from the suspension. The suspension was then dried at 40 °C. A portion of the dried montmorillonite was resuspended in MQ H_2O to make a stock suspension with a montmorillonite concentration of 17.6 g L^{-1} (or 479 m^2 L^{-1}). The particles had a surface area of 27.2 m^2 g^{-1} (N_2(g)-BET Micromeritics Gemini), comparable to the reported value of 31.8 m^2 g^{-1} (Source Clays Repository). XRD patterns were obtained on a PAD-V X-ray diffractometer and compared favorably with the montmorillonite reference pattern from the International Centre for Diffraction Data. A second mineral phase was not observed, indicating that the prepared montmorillonite was relatively pure.

Neptunium Batch Sorption Experiments. Samples for batch sorption experiments were prepared in acid-washed 15 mL polypropylene centrifuge tubes by mixing 0.01 M HCl, 0.01 M NaOH, 2.0 or 1.0 M NaCl, MQ H_2O, and an aliquot of montmorillonite stock (~1 mL) to produce 10 mL of a 1.8 g L^{-1} suspension. The amount of NaCl was adjusted to achieve solution concentrations of 0.01 or 1.0 M. The amount of HCl or NaOH was adjusted to achieve the desired pH. Samples were prepared across the pH range of 3 to 7. Samples were not controlled for CO_2; CO_2 solubility over this pH range is low, and its effect on Np speciation is not significant (see online Supporting Information).

Initial suspensions were spiked with ~20 μL of 1.35×10^{-6} M Np(V) stock solution in 0.1 M HCl, and the pH immediately adjusted to the target pH using dilute NaOH. The resulting batch sorption experiments contained 2.7×10^{-9} M Np(V). The pH of each suspension was measured with an Orion Ross semimicroelectrode calibrated with standard pH buffers on an Orion 420A meter. After adjusting the pH to the target value, the samples were transferred to a Lab-line 3527 Orbital Environ-Shaker (Lab-line Instruments, Inc.) set to 150 rpm about the longitudinal axis.

At various time intervals, the pH of each suspension was measured. The aqueous Np concentration was determined by centrifuging a 1.8 mL subsample of the suspension at 10 000 rpm for 2 h. This centrifuge speed and time was calculated to remove particles greater than 30 nm from the supernatant. Np and major cations concentrations in solution were determined by ICP-MS. Blanks and controls were included in all batch sorption experiments. Sorption was measured as a function of time from 2 h to 60 days.

Plutonium Batch Sorption Experiments. A 1.2×10^{-6} M Pu(NO$_3$)$_4$ stock solution in 1 M HNO$_3$ containing 99.77% ^{238}Pu, 0.16% ^{241}Pu, and 0.04% ^{239}Pu by activity (Isotope Products, Valencia, CA) was used to prepare the Pu working solution. The stock solution was purified by anion exchange to remove the ^{241}Am from ^{241}Pu decay. Since Pu can exist in multiple oxidation states under ambient conditions, a relatively pure Pu(V) stock was prepared as described in the online Supporting Information. The Pu concentration and oxidation state distribution of the working solution was 1.17×10^{-8} M Pu and >95% Pu(V). The concentration and oxidation state distribution of the working (montmorillonite-free) solution did not change over the course of several weeks, indicating stability of Pu(V) in the absence of a sorbent at the trace concentrations used in these experiments.

Pu batch sorption experiments were performed according to the Np experiments described above. Batch Pu(V) sorption experiments were performed at NaCl concentrations of 0.001, 0.01, 0.1, and 1.0 M. Approximately 135 μL of Pu(V) working solution was added to each centrifuge tube to achieve a Pu(V) concentration of 1.5×10^{-10} M, eliminating the potential for Pu(IV)-colloid formation (log $K = -8.3 \pm 1$ at pH $\geq 6^{23}$). To measure Pu concentration in the aqueous phase, a 1.0 mL aliquot of the supernatant was centrifuged and the supernatant was mixed with 5 mL of Ecolume liquid scintillation cocktail for Pu determination via liquid scintillation counting (LSC). In selected cases, additional aliquots were removed from centrifuge tubes and passed through 3 kDa molecular weight cut-off (MWCO) filters (~<5 nm particle size) to verify that the centrifugation scheme was effectively removing the montmorillonite.

Oxidation state analysis of the Pu working solution and sorption experiment filtrate was performed using lanthanum fluoride coprecipitation and/or solvent extraction (see online Supporting Information). The Pu concentration in this work (<10^{-9} M Pu) was too low to employ more traditional spectroscopic techniques for Pu oxidation state characterization.[31,32] While the extraction schemes are inherently indirect, two independent extraction techniques were used to increase the confidence in our oxidation state analysis results.

RESULTS AND DISCUSSION

Np(V) Sorption as a Function of pH and Ionic Strength. Np(V) sorption in 0.01 and 1.0 M NaCl was weak and reached equilibrium within 2 h (Figure 1). Above pH 5, sorption increased with pH, particularly in the low ionic strength, 0.01 M NaCl samples. This is indicative of the onset of surface complexation at pH ~ 5 and consistent with previous observations of Np sorption to both montmorillonite and bentonite (see ref 11 and references therein). Between pH 3 and 5, no pH dependence was observed, suggesting that ion exchange is the predominant sorption mechanism over this pH range. Np sorption to smectite was previously reported to increase as pH decreases from 4 to 2.[8] This may have been caused by Np(V) reduction to Np(IV) as a result of smectite dissolution and release of structural Fe(II). The oxic conditions, less acidic pHs used in our experiments (pH > 3), and the treatment of montmorillonite with H_2O_2 may have minimized this effect here. Thus, while some montmorillonite dissolution likely occurred at low pH, it did not appear to affect the equilibrium sorption behavior of Np(V) or induce reduction to Np(IV). The apparent K_d between pH 3 and 5 was 24 ± 5 mL g^{-1} in 0.01 M NaCl and <6 mL g^{-1} in 1.0 M NaCl. These values are consistent with the previously reported K_d of 4 to 6 mL g^{-1} in 0.1 M NaNO$_3$.[11] On the basis of a Vanselow ion exchange model (equivalent to Gapon for homovalent ion exchange):

$$Kv = \frac{(NpO_2X)(Na^+)}{(NpO_2^+)(NaX)} \qquad (1)$$

an ion exchange constant of approximately 0.31 ± 0.06 was calculated using the 0.01 M NaCl data (0.765 meq g^{-1} cation exchange capacity and no activity correction). However, a more comprehensive set of data over a wide range of ionic strength and Np(V) concentration would be necessary to more accurately quantify this parameter.
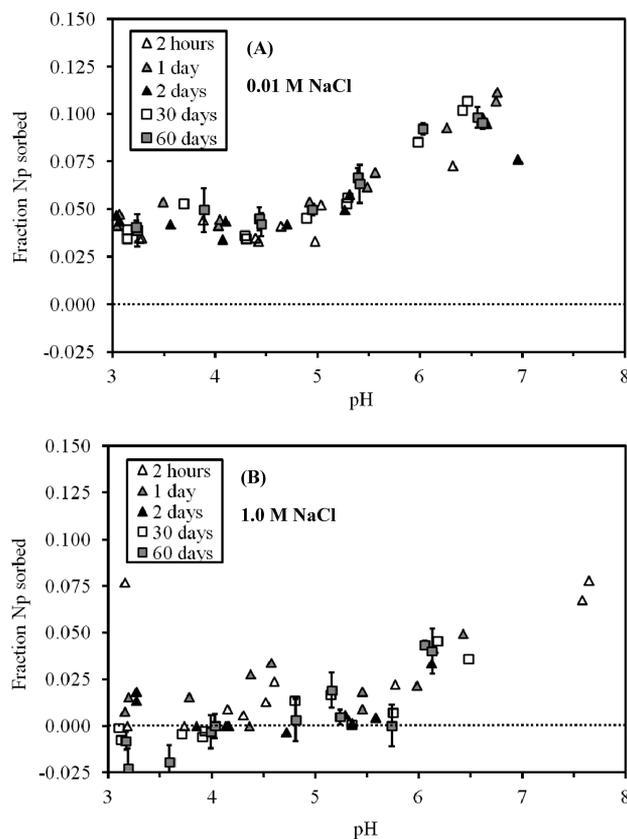
Figure 1. Np(V) sorption in (A) 0.01 and (B) 1.0 M NaCl. Error bars are one standard deviation in counting statistics for 60 day data. System Parameters: [montmorillonite] = 1.8 g L^{-1} (47.9 m^2 L^{-1}); [Np] = 2.7×10^{-9} M, initially added as Np(V).

Pu(V) Sorption as a Function of Montmorillonite Concentration. Initial sorption experiments were performed as a function of montmorillonite concentration to test surface mediated Pu(V) reduction behavior (Figure 2). Experiments
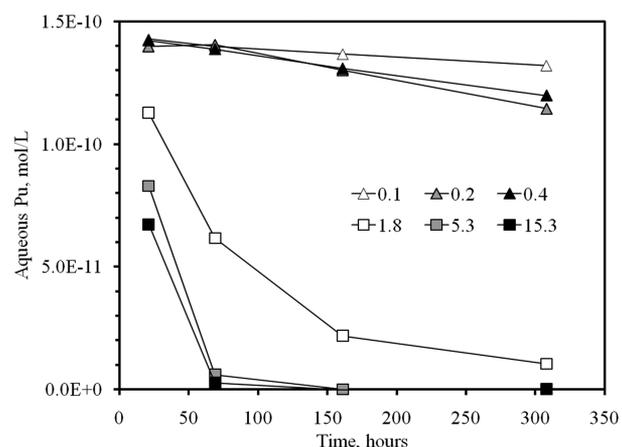
Figure 2. Pu(V) sorption as a function of time and montmorillonite concentration (0.1 to 15.3 g L^{-1}). System parameters: pH ~ 4; [NaCl] = 0.01 M; [Pu] = 1.5×10^{-10} M, initially added as Pu(V).

were conducted at pH ~ 4, montmorillonite concentrations of 0.1 to 15.3 g L^{-1}, and 0.01 M NaCl. Pu(V) sorption was much stronger than Np(V) but occurred on the order of days to weeks, presumably owing to its slow reduction to Pu(IV) on
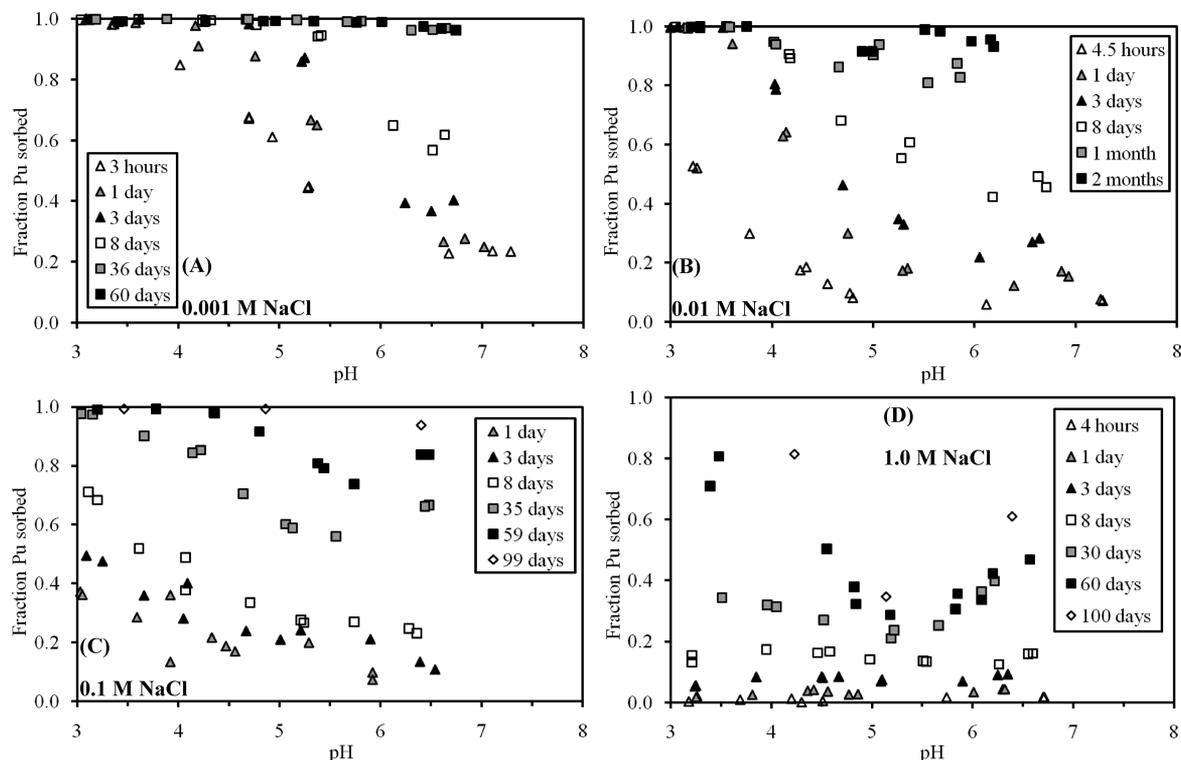
Figure 3. Sorption of Pu(V) to SWy-1 Na-montmorillonite in (A) 0.001, (B) 0.01, (C) 0.1, and (D) 1.0 M NaCl. Error bars associated with counting statistics (not shown) are smaller than the size of the data symbols. System Parameters: [montmorillonite] = 1.8 g L^{-1} (47.9 m^2 L^{-1}); [Pu] = 1.5×10^{-10} M, initially added as Pu(V).

the mineral surface. The apparent sorption rate was calculated on the basis of a rate equation of the following form:

$$\frac{dC}{dt} = -kCS \tag{2}$$

where C is the concentration of the (free) aqueous PuO$_2^+$ reactant (M), S is the concentration of the solid phase (g L^{-1}), and k is a rate constant (L g^{-1} hr^{-1}). When far from equilibrium, a plot of $\ln(C)/S$ as a function of t will produce a linear slope, k. On the basis of fits to the far from equilibrium data (restricted to data in which aqueous Pu concentrations are 1 order of magnitude above the predicted equilibrium concentration), the Pu(V) apparent sorption rate constant was determined to be $10^{-2.4 \pm 0.2}$ L g^{-1} hr^{-1}. The reaction appears to be first order with respect to the solid phase concentration. This rate can be compared to rate constants for Pu(V) sorption and surface mediated reduction on hematite, goethite, and magnetite[28,33] to determine the effectiveness of this process on montmorillonite relative to other minerals. To achieve a meaningful comparison, data from refs 28 and 33 were extrapolated to pH 4 by fitting a curve to the apparent sorption rate constants vs pH and all data were surface area normalized to produce a rate constant at pH 4 with units of L m^{-2} hr^{-1} (details in online Supporting Information). The resulting rate constants for hematite, goethite, and magnetite are $10^{-3.9}$, $10^{-3.3}$, and $10^{-3.3}$ L m^{-2} hr^{-1}, respectively, and are comparable to that of montmorillonite ($10^{-3.8 \pm 0.2}$ L m^{-2} hr^{-1}). In the case of hematite and magnetite, these rates were the result of surface mediated Pu(V) reduction to Pu(IV). The rate-limited sorption observed on montmorillonite at pH 4 is most likely a result of a similar surface mediated reduction process. However, in the case of montmorillonite, ionic strength and pH affect the rate of Pu(V) sorption in a manner

that is distinct from hematite, goethite, and magnetite, as we describe below.

Pu(V) Sorption as a Function of pH and Ionic Strength. Pu(V) sorption in 0.001 to 1.0 M NaCl and between pH 3 and 8 is slow and a function of both ionic strength and pH (Figure 3). The slow sorption kinetics (compared to Np(V)) are likely due to the surface mediated reduction of Pu(V) to Pu(IV), as has been previously shown with a number of minerals and sediments.[18,22,27−29,33−36] Most notably, Pu(V) reduction to Pu(IV) was observed on surfaces expected to be either oxidizing or redox-inactive such as pyrolusite (β-MnO$_2$),[27] birnessite (δ-MnO$_2$),[34] hematite (α-Fe$_2$O$_3$),[28] and goethite (α-FeOOH),[28,36] as well as gibbsite (α-Al(OH)$_3$), silica (SiO$_2$), and montmorillonite.[29] In some studies, reduction of Pu(V) was verified using direct (XANES)[27] and indirect (solvent extraction) methods.[28,34,36]

Neither here nor in previous studies of Pu(V) sorption to oxidizing or redox-inactive minerals has a reductant been positively identified. Several mechanisms for Pu(V) reduction have been proposed, including (1) the presence of a trace reductant (e.g., Fe(II)), (2) Pu(V) disproportionation, (3) electron shuttling (semiconducting) properties of certain oxide phases, and (4) self-reduction by α particle induced radiolysis products such as peroxide and hydrated electron formation.[27,28,30,37] Romanchuk et al.[30] recently ruled out self-reduction and disproportionation mechanisms at trace Pu concentrations; their determination is likely to hold true in these montmorillonite experiments. Unlike certain iron oxide minerals (e.g., hematite[28]), electron shuttling in montmorillonite will not occur. The effect of trace quantities of reductants (e.g., Fe(II) released as a result of montmorillonite dissolution) cannot be ruled out. However, as we discuss below, the pH and ionic strength dependent rates observed in our data

are not consistent with this being the rate-determining mechanism. On the basis of the known thermodynamic favorability of Pu(IV) hydroxide species, another plausible hypothesis is that the reduction of Pu(V) is based upon a Nernstian behavior where the free energy of the Pu(IV) surface species is sufficiently energetically favorable that reduction of Pu(V) to Pu(IV) can be facilitated by water.

The rates of surface-mediated reduction of Pu(V) to Pu(IV) are affected by pH. Powell et al.[28,33] found a −0.39, −0.21, and −0.34 order dependence on the H^+ concentration for the rate of Pu(V) reduction on hematite, goethite, and magnetite, respectively (i.e., the rate of reduction increases with pH). The data presented here show the inverse behavior, favoring faster sorption and Pu(V) reduction with decreasing pH (Figure 3). This difference is proposed to be driven by the underlying mechanisms controlling Pu reduction rates. Ion exchange processes control Pu(V) sorption and subsequent reduction on montmorillonite at low pH while surface complexation controls Pu(V) sorption and subsequent reduction on iron oxides[28] and other minerals at high pH.

At neutral to low pH values, Pu(V) has been shown to be the dominant aqueous phase species under oxic conditions. Pu(V) was the stable aqueous oxidation state in slightly acidic to neutral solutions including ocean and lake water and in Pu(IV) solubility experiments.[23,38−40] Pu(V) has also been found to be the predominant aqueous phase oxidation state in mineral suspensions.[27,28,34−36,41] This predominance of Pu(V) in the aqueous phase was tested in our current work as well. For a subset of samples, the oxidation state of the supernatant was measured using LaF_3 coprecipitation. The results invariably showed that Pu(V) is the predominant aqueous phase oxidation state.

Using eq 2, the rate of Pu(V) sorption to montmorillonite was calculated for each sorption sample (Figure 4). The rate
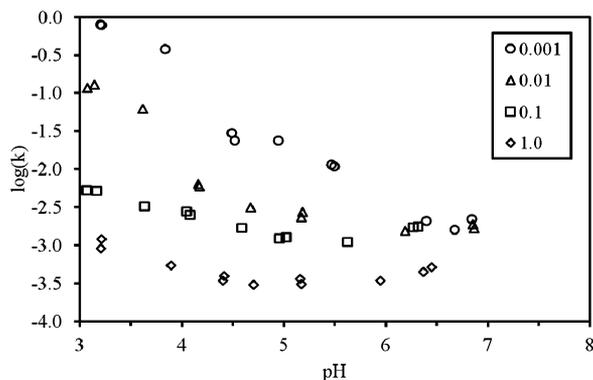
Figure 4. Pu(V) apparent sorption rate as a function of pH in 0.001, 0.01, 0.1, and 1.0 M NaCl. Rate constants based on first order reaction with respect to the PuO_2^+ free ion concentration.

was calculated as a function of the free PuO_2^+ species activity in solution. This was nearly equivalent to the total Pu in solution except in 1.0 M NaCl where complexation with Cl^- was predicted to be significant. The lack of an available complexation constant for PuO_2Cl^0 necessitated the use of the NpO_2Cl^0 stability constant as an analog ($\log(K) = -0.4$ from ref 42). However, this approximation is probably only accurate to within ±1 (i.e., $\log(K_{PuO2Cl(aq)}) = -1.4$ to 0.6). Irrespective of this adjustment to the free ion activity, the prominent ionic strength and pH dependence of Pu(V) sorption rates remains.

In the pH range where ion exchange is the dominant sorption mechanism (<5), the rate of Pu sorption was inversely related to the NaCl concentration (Figure 4). On the basis of the pH and ionic strength dependence of the sorption rates, we hypothesize that H^+ located on montmorillonite ion exchange sites facilitates the surface-mediated reduction of Pu(V) to Pu(IV). The ion exchange constant that quantifies the mol fraction of H^+ on montmorillonite as a function of pH and ionic strength is known.[43,44] Fletcher and Sposito[44] reported the following reaction:

$$H^+ + NaX \leftrightarrow HX + Na^+ \tag{3}$$

with $K = 1.26$. When plotted as a function of HX, the Pu(V) sorption rate constants no longer exhibit an ionic strength dependence (Figure 5). The Pu(V) sorption rate constants,
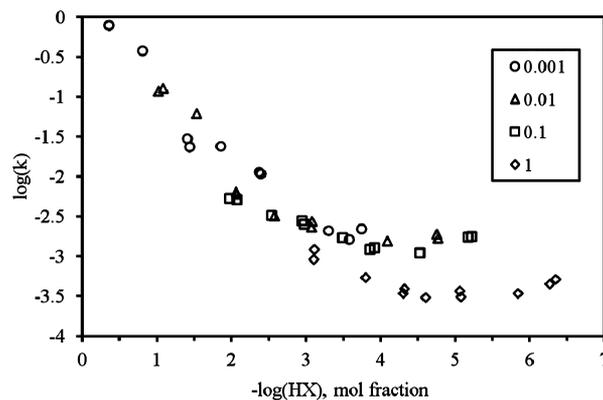
Figure 5. Dependence of apparent sorption rate constant on mol fraction of exchangeable H^+ for Pu(V) sorption experiments performed at 0.001, 0.01, 0.1, and 1.0 M NaCl.

instead, indicate a HX-dependent (slope ∼ 1) and a HX-independent (slope = 0) component ($k \sim 10^{-3}$). The calculated rates for the 1.0 M NaCl data diverge somewhat from other data. However, they are very sensitive to the choice of PuO_2Cl^0 complexation constant, which is highly uncertain. The HX-dependent rate calculations suggests that the surface-mediated reduction of Pu(V) at montmorillonite ion exchange sites may be described by the following reaction:

$$PuO_2^+ + HX + 0.5H_2O \rightarrow XPu(OH)_2^+ + 0.25O_2 \tag{4}$$
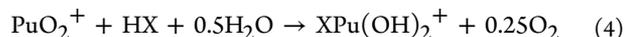
in which PuO_2^+ reduction to a surface-associated Pu(IV) species is mediated by exchangeable H^+ cations. While we assume that H_2O is the electron donor in eq 4, trace reductants (e.g., Fe(II)) in montmorillonite are also plausible electron donors. However, surface-mediated reduction rates appear to be controlled by exchangeable H^+.

It is known that H^+ exchanged forms of montmorillonite are not stable and lead to its eventual destruction (i.e., dissolution).[45] However, the rates of montmorillonite dissolution are slow at low temperatures; homoionic H^+ montmorillonite may persist for a period of months at 0 °C.[45] In our case, the relatively low temperature (25 °C) and only partial substitution of H^+ into ion exchange sites (<0.1 mol fraction for all but three samples (Figure 5)) minimize any effects of montmorillonite dissolution. Nevertheless, some montmorillonite undoubtedly dissolved during these batch sorption experiments. With respect to the possible reduction of Pu(V) as a result of montmorillonite dissolution and release of structural Fe(II), there are several lines of evidence that suggest this is not the rate-controlling mechanism.

First, an increase in Np(V) sorption over time which would be indicative of Fe(II) release and Np(V) reduction was not observed. Second, montmorillonite dissolution at low pH has been found to increase with ionic strength[46] which is opposite to the trend in surface-mediated Pu(V) sorption and reduction rates. Third, subppm levels of Fe, as well as ppb to ppm levels of Si and Al, were detected in batch experiments. However, none showed an ionic strength or pH dependence consistent with the observed patterns of PuO_2^+ sorption rate dependencies. While we cannot completely exclude the effects of montmorillonite dissolution and/or Fe(II) release on Pu(V) surface mediated reduction, the data presented here favor the conclusion that H^+ located on montmorillonite ion exchange sites facilitates Pu(V) reduction. Similar surface-mediated reduction of Np(V) was not observed in the oxic solution conditions and time scales (30–60 day) of these experiments though its ion exchange was quantified. While surface complexation may play a dominant role in Pu sorption and colloid-facilitated transport under alkaline conditions, results from this study suggest that Pu(V) ion exchange and surface-mediated reduction to Pu(IV) can immobilize Pu or enhance its colloid-facilitated transport in the environment at neutral to mildly acidic pHs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Speciation diagram of Np(V), Pu(IV), and Pu(V) and discussion of Pu(IV) intrinsic colloid formation. Description of montmorillonite and Pu(V) stock preparation and oxidation state analysis. Derivation of mass-normalized sorption rate constants based on refs 28 and 33. This information is available free of charge via the Internet at http://pubs.acs.org/.

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