1 Desorption of plutonium from montmorillonite: An
2 experimental and modeling study

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ABSTRACT

Desorption of plutonium (Pu) will likely control the extent to which it is transported by mineral colloids. We evaluated the adsorption/desorption behavior of Pu on SWy-1 montmorillonite colloids at pH 4, pH 6, and pH 8 using batch adsorption and flow cell desorption experiments. After 21 days adsorption, the Pu(IV) affinity for montmorillonite displayed a pH dependency, with K_d values highest at pH 4 and lowest at pH 8. The pH 8 experiment was further allowed to equilibrate for 6 months and showed an increase in K_d , indicating that true sorption equilibrium was not achieved within the first 21 days. For the desorption experiments, aliquots of the sorption suspensions were placed in a flow cell, and Pu-free solutions were then pumped through the cell for a period of 12 days. Changes in influent solution flow rate were used to investigate the kinetics of Pu desorption and demonstrated that it was rate-limited over the experimental timescales. At the end of the 12-day flow cell experiments, the extent of desorption was again pH dependent, with pH 8 > pH 6 > pH 4. Further, at pH 8, less Pu was desorbed after an adsorption contact time of 6 months than after a contact time of 21 days, consistent with an aging of Pu on the clay surface. A conceptual model for Pu adsorption/desorption that incorporated known surface-mediated Pu redox reactions was used to fit the experimental data. The resulting rate constants indicated processes occurring on timescales of months and even years which may, in part, explain observations of clay colloid-facilitated Pu transport on decadal timescales. Importantly, however, our results also imply that migration of Pu adsorbed to montmorillonite colloids at long (50-100 year) timescales under oxic conditions may not be possible without considering additional phenomena, such as co-precipitation.

1. INTRODUCTION

Plutonium (Pu) mobility in the environment is a topic of key concern because of its radiological toxicity and extremely low EPA drinking water limit (equivalent to 10^{-12} mol L⁻¹ for ²³⁹Pu) (EPA, 1996). Given its presence in the environment, from the production and testing of nuclear weapons, nuclear accidents and authorized discharges of radionuclides, it is important to understand how Pu mobility is controlled in order to develop reliable predictive transport models (Montero and Sanchez, 2001; Morris et al., 2000; Nelson and Lovett, 1978; Smith et al., 2003). These transport models are necessary for risk assessments of both existing contaminated environments and future nuclear waste repositories.

Adsorption reactions are likely to play a key role in determining Pu transport in subsurface environments (Hixon et al., 2010; Lujaniene et al., 2012; Powell et al., 2011a; Powell et al., 2005; Romanchuk et al., 2011; Sabodina et al., 2006; Zavarin et al., 2012; Zavarin et al., 2005). On the one hand, evidence of strong sorption to bulk mineral phases suggests that Pu transport will be limited (Kaplan et al., 2004; Kaplan et al., 2007; Sanchez et al., 1985). On the other hand, strong adsorption to mobile, inorganic or organic colloids has led to Pu migration on the kilometer scale at some currently contaminated locations (e.g. Nevada National Security Site, USA, Rocky Flats and Mayak, Russia) (Kersting et al., 1999; Novikov et al., 2006; Santschi et al., 2002). Further, field-scale colloid transport experiments at the Grimsel Test Site, designed to simulate nuclear waste repository scenarios, demonstrate that Pu sorbed to bentonite colloids can migrate in fractured granite (Möri et al., 2003).

Pu adsorption behavior is linked to its oxidation state. Although Pu can exist in the (III), (IV), (V) and (VI) oxidation states under environmental conditions, Pu(IV) and Pu(V) are believed to predominate under oxic conditions at circumneutral pH (Choppin, 1991; Kaplan et

al., 2007; Nitsche and Edelstein, 1985; Orlandini et al., 1986). While both oxidation states may sorb to mineral surfaces, Pu(IV) tends to sorb more strongly than Pu(V) (Begg et al., 2013; Sanchez et al., 1985). It has also been demonstrated that the oxidation state of Pu can be altered on the surface of certain minerals (Felmy et al., 2011; Kirsch et al., 2011; Powell et al., 2004; Powell et al., 2005). For example, Pu(V) reduction to Pu(IV) has been observed, or inferred, to occur on Mn(II) and Fe(III) minerals as well as silica and montmorillonite (Begg et al., 2013; Hixon et al., 2013; Keeney-Kennicutt and Morse, 1985; Powell et al., 2011a; Powell et al., 2006; Powell et al., 2005; Sanchez et al., 1985; Zavarin et al., 2012). Depending on the minerals present, the rates of surface mediated reduction can vary by orders of magnitude (Begg et al., 2013). One consequence of surface mediated reduction is that given sufficient timescales, the extent of Pu(V) adsorption is very similar to that of Pu(IV), despite observations of initial differences in adsorption behavior for some minerals (Begg et al., 2013; Hixon et al., 2013; Sanchez et al., 1985; Zavarin et al., 2012; Zhao et al., 2016). This surface-mediated Pu(V) reduction is consistent with a previous definition of aging: “surface chemical process(es) that follow(s) the initial sorption reaction and cause(s) changes in contaminant surface speciation over time” (Tinnacher et al., 2011). One consequence of this redox aging is that adsorbed Pu(V), which is reduced to Pu(IV) on the surface, will likely be more resistant to desorption than the original Pu(V) (Smith et al., 2009; Wendling et al., 2009).

Desorption of Pu from mineral surfaces has not been as systematically studied as adsorption. Nonetheless, desorption will play a key role in determining the stability of Pu on both immobile and mobile mineral surfaces. Moreover, rates of desorption are particularly important as these will control the spatial and temporal extent of Pu migration, especially in colloid-facilitated transport scenarios (Cvetkovic et al., 2004; Saiers and Hornberger, 1996). Pu desorption is

typically investigated via batch experiments that have shown that the majority of adsorbed Pu remains associated with the mineral surface, consistent with the high sorption affinity of Pu(IV) for mineral surfaces. For example, Pu(IV) and Pu(V) batch desorption experiments with goethite and hematite have indicated that less than 1% of the solid associated Pu will be desorbed (Lu et al., 1998). Similarly, experiments with sediments from the Esk Estuary, near Sellafield, UK showed that only about 5% of surface-associated Pu(IV) could be desorbed (Hamilton-Taylor et al., 1987). However, greater extents of Pu desorption have been reported for montmorillonite and silica, where up to 20% of Pu was desorbed after a period of 293 days at pH 8.3 (Lu et al., 2003). While these results may be dependent in part on the experimental conditions, they do indicate that Pu desorption may be limited and mineral dependent. Further, they do not necessarily provide the quantitative measure of desorption rates needed for transport models.

As in the case of adsorption, desorption of Pu from minerals exhibits a pH dependency, with increasing desorption observed to occur with decreasing pH for both natural sediments and pure phase silica and alumina (Kaplan et al., 2006b; Kumar et al., 2012). Moreover, oxidation state also appears to be an important controlling factor for Pu desorption. Although both desorption of Pu(IV) and Pu(V) from sediments may occur, the oxidation of Pu(IV) to Pu(V) on the mineral surface appears to be an important mechanism in the desorption of Pu(IV) (McCubbin and Leonard, 1996; McCubbin et al., 2002). For example, experiments with sediments from Aiken, SC have shown that although adsorbed Pu was present as Pu(IV), desorbed Pu in solution was predominantly Pu(V) (Kaplan et al., 2006b). The mobilization of Pu(IV) associated with Irish Sea sediments following exposure to natural sunlight was found to be predominantly Pu(V) thought to be formed via photooxidation of Pu(IV) (McCubbin and Leonard, 1996). The importance of Pu oxidation in its remobilization from mineral surfaces is similar to the behavior

of other redox active radionuclides, such as Tc and U, where oxidation of reduced, solid-associated species results in their remobilization (Burke et al., 2006; McBeth et al., 2007; Moon et al., 2007; Newsome et al., 2014).

In this study, we quantify rates of Pu desorption from montmorillonite colloids using a combination of batch and flow cell experimental techniques and numerical modeling. Experiments were performed at pH 4, 6, and 8 and included batch adsorption periods, a dynamic flow-cell period and, in selected cases, a static desorption period. Changes in flow rate during the flow cell experiment were made to examine the kinetics of desorption. The experimental results were fitted with a model evolved from one developed by Tinnacher *et al.* (2011). Our results provide broad estimates for the scale of possible colloid-facilitated transport times for Pu in currently contaminated environments whilst also emphasizing some of the key geochemical conditions to be considered in predictions for nuclear waste disposal scenarios.

2. MATERIALS AND METHODS

2.1 Plutonium stock preparation

A ^{238}Pu stock (99.77% ^{238}Pu , 0.16% ^{241}Pu , and 0.04% ^{239}Pu by activity) was purified using an anion exchange resin (BioRad AG 1 $\times$ 8, 100-200 mesh). Prior to loading on the resin, Pu was reacted with NaNO_2 to convert Pu to Pu(IV). The Pu was loaded onto the column in 8 M HNO_3 and the column was washed with three column volumes of 8 M HNO_3 . The Pu was stripped from the column using 0.1 M HCl which selects for the Pu(IV) oxidation state (Powell et al., 2011a). The Pu concentration in the purified stock solution was determined by liquid scintillation counting (LSC; Packard Tri-Carb TR2900 LSA) to be 5.1×10^{-8} M. The oxidation state of the Pu

stock was measured using a LaF_3 precipitation method and found to be 95% Pu(III)/(IV) and 5% Pu(V)/(VI) (Kobashi and Choppin, 1988).

2.2 Montmorillonite preparation

Unless stated otherwise, all solutions were prepared using ultrapure water (Milli-Q Gradient System, $>18 \text{ M}\Omega\cdot\text{cm}$) and ACS grade chemicals without further purification. Details regarding the preparation of SWy-1 montmorillonite (Source Clays Repository of the Clay Minerals Society) for use in sorption experiments have been reported previously (Begg et al., 2013; Zavarin et al., 2012). Briefly, the montmorillonite was treated with 0.001 M HCl and 0.03 M H_2O_2 to dissolve soluble salts and minimize the reducing capacity of any impurities. The treated montmorillonite was then homoionized in 0.01 M NaCl solution and dialyzed in MQ H_2O to remove excess salts. The homoionized montmorillonite was centrifuged at 180 g for 5 minutes to remove particles $>2 \text{ }\mu\text{m}$ from suspension. The suspension was then transferred to a new centrifuge tube and spun at 2500 g for 6 hours. The supernatant, containing particles $<50 \text{ nm}$ was discarded. The montmorillonite was then suspended in a 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution (pH 8) to make a suspension of $\sim 10 \text{ g L}^{-1}$. The buffer solution composition was a simplified low ionic strength sodium bicarbonate water similar to groundwater from the Nevada National Security Site (NNSS), NV. Stock suspensions of 1 g L^{-1} montmorillonite with pH values of 6 and 8 were prepared by dilution in the buffer solution and addition of dilute HCl as appropriate. At pH 8, 0.7 mM HCO_3^- is expected to be close to the equilibrium concentration considering a pCO_2 of 3.4. However, at pH 4 and 6 the HCO_3^- equilibrium concentration will be lower ($\sim 0.02 \text{ mM}$). These suspensions were left to equilibrate for 1 week under ambient atmospheric conditions and the pH measured and adjusted accordingly at regular intervals. The volume of HCl added during pH adjustment was less than 0.5% of the total suspension volume.

2.3 Adsorption equilibration

For flow cell experiments, the Pu stock was spiked into the 1 g L⁻¹ montmorillonite stock suspensions to give a final Pu concentration of 10⁻¹⁰ mol L⁻¹. Pu(IV) was chosen as the starting oxidation state as previous work has shown that Pu(IV) sorption to montmorillonite under ambient atmospheric conditions is faster than that of Pu(V). Moreover, it is also thought that Pu(IV) is the predominant stable oxidation state on the surface of the clay under these conditions (Begg et al., 2013). Previous mineral-free experiments performed under the same experimental conditions as those used here have shown that although there may be a decrease in the amount of Pu(III)/(IV) in solution (10-25%) following spiking, Pu solution oxidation state remains largely unchanged for periods up to 30 d (Begg et al., 2014). For the experiment at pH 8, tritium (³H) was added as a conservative tracer at a concentration of 1000 cpm mL⁻¹ to check for ideal mixing in the flow cell. The pH of each experiment was readjusted to the appropriate pH with dilute HCl or NaOH following spiking and monitored over a 3 week equilibration period during which suspensions were kept under ambient atmospheric conditions. To achieve a suspension at pH 4, a sub-sample of the Pu-spiked pH 8 suspension was adjusted accordingly with dilute HCl following the initial adsorption equilibration and equilibrated for a further 3 weeks before the start of the flow cell experiment. After the equilibration period, a small aliquot from each suspension was centrifuged (7,000 g for 1.5 h; 50 nm cut off) and the concentration of the Pu in the supernatant was measured via LSC. Oxidic conditions were used in all experiments in order to reflect both oxidic groundwaters at the NNSS and previous Pu montmorillonite sorption work (Begg et al., 2013; Hu et al., 2008). For the experiment at pH 8, a suspension sample was diluted for volumetric reasons to give a solid:solution ratio of 0.45 g/L and then equilibrated for a period

of 6 months to investigate the effect of aging. The focus on pH 8 was due to its relevance to conditions at the NNSS and aging was not investigated in experiments at pH 6 and pH 4.

2.4 Desorption experiments

A flow cell was used to measure the kinetics of Pu desorption from montmorillonite, similar to the approach of Tinnacher *et al.* (2011). The flow cell was made of Teflon, had a 20 mL hemispherical chamber and was fitted with a 100 nm pore size Millipore Teflon filter. Prior to use, the cells were washed in sodium dithionite, 10% HCl, and MQ water to remove trace impurities. A diagram of the flow cell is shown in Electronic Annex (EA) Figure EA1. Ultrafiltration (Nanosep 3K Omega; approximate metric size discrimination: 1 nm) of an effluent fraction from the pH 8 flow cell experiment did not significantly change the Pu concentration in solution, indicating that the filter retained both intrinsic Pu colloids and Pu pseudocolloids.

Following the adsorption equilibration period, a 20 mL aliquot of montmorillonite suspension was loaded into the flow cell with a stir bar added to ensure ideal mixing conditions. The stir bar speed was kept low to try to minimize any mineral grinding effects. To start the desorption experiment, atmosphere equilibrated, Pu-free 0.7 mM NaHCO₃, 5 mM NaCl buffer solution adjusted to pH 4, 6, or 8 was pumped through the cell at a rate of 0.4 mL min⁻¹ (average retention time of ~50 minutes). Effluent fractions were collected on a Spectra/Chrom CF-1 fraction collector and the volumes determined gravimetrically. Measurements of the effluent pH were periodically performed to ensure that the experiment remained at the desired pH. Collected fractions were acidified with 2% HNO₃ prior to Pu analysis. Pu concentration in the effluent fractions was measured by LSC. The detection limit for Pu analysis by LSC was determined to be 3.9×10^{-14} mol L⁻¹.

In order to evaluate the kinetic nature of desorption, the flow rate was reduced to 0.2 mL min⁻¹ (100 minute retention) after approximately 10 chamber volumes (cv) had been passed through the cell. After a further 10 cv, the flow rate was reduced to 0.04 mL min⁻¹ (500 minute retention) and again after a further 10 cv to 0.02 mL min⁻¹ (1000 minute retention). The total elapsed time for each flow cell experiment was 12 days (approximately 40 cv). In the following discussion, experiments are referred to by their pH and the adsorption equilibration period: pH 8 3-week; pH 8 6-month; pH 6 3-week; pH 4 3-week. Following the cessation of the pH 8 3-week, pH 8 6-month and pH 6 3-week flow cell experiments, the montmorillonite suspensions were removed from the flow cell and transferred to 50 mL polyethylene centrifuge tubes and placed on an orbital shaker at 125 rpm in the dark for 6 months at room temperature. We refer to this period as static desorption to contrast with flow cell desorption. At the end of the static desorption period, the suspension was centrifuged at 25000 g for 2 hours and Pu concentration in the supernatant was measured as stated previously.

2.5 Modeling

A simple, flexible model was developed to describe the adsorption/desorption results. The model was based on the approach of Tinnacher *et al.* (2011), who modeled Np(V) adsorption and desorption kinetics in similar flow cell experiments. One important aspect of the Tinnacher *et al.* (2011) Np(V) model was the assumption that reduction of Np(V) to Np(IV) was unlikely under the oxic conditions used in their experiment. However, in the case of Pu, additional model complexity was needed to address the known surface-mediated and rate-limited reduction of Pu(V) to Pu(IV) on montmorillonite as well as the initial presence of Pu(V)/(VI) in our stock (Begg *et al.*, 2013; Zavarin *et al.*, 2012). Further, previous studies indicate that the oxidation of Pu(IV) to Pu(V) on mineral surfaces will play an important role in Pu(IV) desorption and so we

also include this reaction in our model (Begg et al., 2014; Kaplan et al., 2006a; McCubbin and Leonard, 1996; McCubbin et al., 2002). We discount the presence of significant amounts of Pu(VI) in the aqueous phase based on previous speciation modeling for a Pu/NaHCO₃ solution in equilibrium with the atmosphere (Kersting, 2013). The expanded conceptual model used to simulate Pu adsorption and desorption is shown in Figure 1. In this conceptual model, both Pu(V) and Pu(IV) are present in the aqueous phase (Pu(V)_{aq} and Pu(IV)_{aq}, respectively). The aqueous species are both allowed to adsorb to the solid phase to produce adsorbed species (Pu(V)_{s1} and Pu(IV)_{s2}, respectively). Reactions between these two sorbed species represent surface mediated redox aging. A second Pu(IV) sorbed species (Pu(IV)_{s3}) is included in the model to account for aging processes other than redox aging. This additional Pu(IV) aging process was included because (1) it was identified as a necessary modeling concept in earlier Np(V) desorption experiments and (2) it was found to be a necessary modeling concept for fitting the Pu desorption data presented here. This additional aging process is discussed later in the text.

The details of this approach are discussed fully in Tinnacher *et al.* (2011) and are mentioned here only briefly. Relatively simple first order reactions were arranged *in-silico* based on a finite difference approach (Euler method). In the present case, the code was written using Microsoft® Visual Basic 2010 Express Version 10 software and linked to the PEST (Parameter ESTimation) program (Doherty, 2004). PEST is a model-independent parameter optimizer that uses least square minimization based on the Gauss–Marquardt–Levenberg method. For model optimization, data points were uniformly weighted (in PEST: Weight = 1/C_i, where C_i is the aqueous Pu concentration data used in the minimization of the objective function). Optimization

based on the individual analytical errors in aqueous Pu data (in PEST: Weight = 1/absolute error) were tested and yielded similar parameter estimates.

In the Pu model (as in the Np(V) model), each reaction is described by an equation that can represent linear and non-linear equilibrium sorption, first order and empirical sorption/desorption kinetics, as well as hysteresis effects for Pu(V) and Pu(IV). The equilibrium equations are based on an expanded Freundlich sorption equation:

$$S^{n_{-1}} = K \times C^{n_1} \quad (1)$$

in which a reaction constant (K) determines the relationship between the aqueous concentration (C) and the sorbed concentration (S). The exponent n_1 is the traditional Freundlich exponent while n_{-1} is an empirical exponent proposed by Bar-Tal *et al.* (1990) as an additional fitting parameter. Importantly, if both exponents are set to a value of 1, the equation represents a simple linear adsorption model. This equation is used to define the relationship between the aqueous and sorbed species. However, an equivalent formulation is also used to define the relationship between two sorbed species (e.g. between $Pu(V)_{S1}$ - $Pu(IV)_{S2}$ and $Pu(IV)_{S2}$ - $Pu(IV)_{S3}$ in Figure 1).

Under non-equilibrium and flow-cell conditions, rate-limited adsorption/desorption and advective transport must be included in the model. A kinetic formulation of Equation 1 was combined with an advection term for each reaction shown in Figure 1. For example, the equation describing Pu(V) in the mobile (aqueous) phase of a flow cell has the following form:

$$\frac{dPu(V)_{aq,FC}}{dt} = -k_1 \times Pu(V)_{aq}^{n_1} \times \left(1 - \left(\frac{Q}{K}\right)^{\psi_1}\right) + \frac{F}{V} (Pu(V)_{aq,in} - Pu(V)_{aq}) \quad (2)$$

where

$$Q = \frac{Pu(V)_{S1}^{n_{-1}}}{Pu(V)_{aq}^{n_1}} \quad \text{and} \quad K = \frac{k_1}{k_{-1}} \frac{V}{m}. \quad (3)$$

where F , V , and m are the water flux (L min^{-1}), flow cell volume (L), and solid mass (g), respectively, $Pu(V)_{aq,in}$ and $Pu(V)_{aq}$ are the inflow Pu(V) concentration and the Pu(V) concentration in the flow cell, respectively, k_I and k_{-I} are the forward and reverse adsorption rate constants (min^{-1}), and ψ is a transition state theory (TST)-related parameter. Following from the example of Tinnacher *et al.* (2011), the TST-related parameter was allowed to differ depending on the net direction of the reaction (e.g. ψ_I if $Q < K$ and ψ_{-I} if $Q > K$) (Tinnacher et al., 2011). Equation 2 captures the forward adsorption of $Pu(V)_{aq}$. Similar reactions can be written for each of the 4 reactions included in the Pu model (Figure 1) and, separately, for net forward and reverse reactions. All numerical expressions used in the model are reported in the EA.

3. RESULTS

3.1 Adsorption of Pu(IV) to montmorillonite

The adsorption of Pu(IV) to montmorillonite after a 21 day equilibration period showed a strong pH dependency, with less Pu adsorbed at pH 8 than at pH 4 (Figure EA2; Table 1). Calculated $\log K_d$ (mL g^{-1}) values were 3.9 ± 0.1 and 4.4 ± 0.1 for experiments at pH 8 and 6, respectively. At pH 4, the aqueous Pu concentration was below the limit of detection, leading to an estimated $\log K_d$ of >6.4 based on the detection limit for this experiment (3.9×10^{-14} M). After a 6 month adsorption equilibration period, the $\log K_d$ at pH 8 had increased to 4.7 ± 0.1 .

3.2 Flow cell desorption experiments

A list of adsorption conditions, adsorption $K_{d,s}$, the percent Pu in solution at the end of the adsorption period, and the percent of surface Pu desorbed in each flow cell experiment is given in Table 1. The stirred flow cell experiments were performed to investigate the desorption kinetics of Pu from montmorillonite. In the pH 8 3-week experiment, ^3H was used as a

conservative tracer to test whether ideal mixing conditions were achieved. A plot of the decline in ^3H concentration and an analytical solution for a non-reactive species versus time is shown in Figure EA3. The agreement between the ^3H data and the analytical solution is indicative of ideal mixing in the flow cell. Based on these data, ideal mixing was assumed for all Pu flow cell experiments and modeling described herein.

The concentration of Pu in fractions collected from the pH 8 3-week flow cell experiment is shown in Figure 2A. In the early fractions, much of the Pu in the effluent represents aqueous Pu from the adsorption step, displaced from the cell by the inflow of Pu-free solution. This results in a decline in effluent Pu concentration in the early part of the experiment. To identify when Pu desorption from montmorillonite was measureable in the flow cell effluent, we compared Pu effluent concentrations to the predicted behavior of a non-sorbing tracer (Figure EA4). The deviation from the non-reactive tracer behavior indicates that Pu desorption from the montmorillonite contributed significantly to the overall Pu breakthrough after less than two chamber volumes.

In order to determine if Pu desorption from montmorillonite was rate limited on the timescale of this experiment, changes in flow rate were made to increase the solution residence time in the flow cell. The first flow rate change was from 0.4 mL min^{-1} to 0.2 mL min^{-1} , representing an increase in solution residence time from 50 minutes to 100 minutes. A significant increase in effluent Pu concentration was observed following the change in flow rate (Figure 2A). Decreasing the flow rate from 0.2 mL min^{-1} to 0.04 mL min^{-1} (500 minute; 8.33 hour residence time) also led to a rise in Pu concentration. A further rise in concentration was observed when the flow rate was decreased from 0.04 mL min^{-1} to 0.02 mL min^{-1} (1000 minute; 16.66 hour

residence time). After the initial increases in effluent Pu following each concomitant change in flow rate, there was a steady decrease in the effluent Pu concentration during active flow.

Following the final flow-cell sampling point, the montmorillonite desorption suspension was left to equilibrate for 6 months under no flow (static) conditions. After this time period, the Pu concentration was found to have increased considerably when compared to the final flow cell concentration (final data point in Figure 2A).

To investigate aging of Pu on the mineral surface, an additional flow cell experiment was performed on a montmorillonite sample at pH 8 which had been equilibrated with Pu(IV) for 6 months. The desorption of Pu from the pH 8 6-month experiment is shown in Figure 2B. Although the initial effluent concentration is lower, the pattern of desorption is similar to the pH 8 3-week experiment. The changes in flow rate again lead to increases in the Pu effluent concentration. As in the pH 8 3-week experiment, Pu concentration in the effluent fractions decline as a function of time at any one flow rate and there was a considerable increase in Pu concentration following the static desorption period.

The total amounts of Pu desorbed in the pH 8 3-week and the pH 8 6-month experiments, corrected to account for the initial presence of aqueous Pu in solution, were estimated to be 12.2% and 5.0%, respectively.

Pu oxidation state in the effluent of the pH 8 6-month experiment was assessed after 23 chamber volumes using the LaF_3 precipitation method. This length of time was chosen both to maximize the Pu counts in solution and to try to ensure that the oxidation state of desorbed Pu was measured rather than aqueous Pu following the initial adsorption step (Figure 2B). Pu in solution was $90 \pm 10\%$ Pu(V)/(VI).

The desorption of Pu from montmorillonite in the pH 6 3-week experiment is shown in Figure 2C. The black dashed arrow in Figure 2C identifies an unintentional stop flow event in which the flow was halted for a period of 20 hours. Nevertheless, Pu desorption followed a similar pattern to that observed in the pH 8 3-week experiment, with flow rate decreases resulting in increased effluent Pu concentration. At each flow rate, the Pu concentration increase was also followed by a decline in concentration, although the change in slope was less marked than for both pH 8 experiments. As in both pH 8 experiments, there was a considerable difference in the Pu concentration of the final collected flow cell fraction and that of the aqueous phase at the end of the static desorption period. Pu oxidation state in the effluent was measured after 23 chamber volumes had been passed and was $80 \pm 10 \%$ in the Pu(V)/(VI) oxidation state. The total amount of surface Pu desorbed by the end of the pH 6 3-week experiment was estimated to be 4.2%.

The pH 4 3-week desorption data are shown in Figure 2D. Aqueous Pu concentrations were below the method detection limit in the majority of the collected flow cell effluent fractions as denoted by the horizontal dashed line, and hence, are not shown. However, some Pu was measured in the effluent following the change in flow rate from 0.2 mL min^{-1} to 0.04 mL min^{-1} after 20 chamber volumes (segment iii in Figure 2D). This is consistent with the timing of the highest Pu concentrations observed in the pH 8 3-week, pH 8 6-month and pH 6 3-week experiments and demonstrates that small amounts of Pu were desorbed from montmorillonite at pH 4.

Following the conclusion of the pH 4 3-week experiment, the pH of the influent solution was increased to pH 8 (Segment v on Figure 2D). The change in influent pH led to a significant increase in desorption of Pu from the montmorillonite surface.

4. DISCUSSION

4.1 Adsorption of Pu(IV) to montmorillonite

Pu adsorption to montmorillonite showed a pH dependency, with less Pu adsorbed at pH 8 than pH 4 (Figure EA2). A similar increase in Pu(IV) sorption affinity for montmorillonite with decreasing pH has been observed previously (Begg et al., 2014; Boggs et al., 2015). The speciation of solution Pu will change across the large range in pH values used in these experiments and this could lead to differences in sorption behavior. A plot of aqueous Pu(IV) speciation for the current experimental conditions shows that $\text{Pu}(\text{OH})_{4(\text{aq})}$ dominates at pH 8 with a smaller fraction of $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (Figure EA5). The carbonate species is not observed at pH 6 or 4. Thus the presence of a Pu-carbonate complex may contribute to a decrease in Pu sorption at pH 8. For example, Sanchez et al. (1985) found that increasing concentrations of carbonate ligands decreased Pu(IV) and Pu(V) sorption to goethite at pH 8.6. However, Powell *et al.* (2011b) examined Pu(IV) sorption to montmorillonite in 0.01 M NaCl under atmospheric- CO_2 and CO_2 -free conditions (thus limiting the potential for carbonate complexation), yet saw a similar pH dependency in both systems.

Changes in Pu hydrolysis as a function of pH may explain the increased Pu sorption to montmorillonite at pH 4 (Figure EA5). However, Pu(IV) sorption to goethite, gibbsite, hematite and silica has previously been shown to be lower at pH 4 than at pH 8, consistent with expected trends for metal cation surface complexation processes (Begg et al., 2014; Kumar et al., 2012; Romanchuk et al., 2011; Sanchez et al., 1985). This suggests that the predicted aqueous Pu speciation changes do not necessarily cause a substantial increase in overall sorption. We do not think that this pH dependence is due to an experimental artifact (e.g. Pu(IV) colloid formation

caused by pH adjustment). Experiments by Begg *et al.* (2014) for Pu(IV) sorption to goethite, which were performed with the same initial Pu concentration, the same pH adjustment procedure, and the same equilibration period as the current experiments, did not exhibit the same pH dependence observed for montmorillonite in this study.

The change in pH in these experiments may cause physiochemical changes in the montmorillonite that alter its sorption properties. However, Bradbury and Baeyens (2006) observed that Np(V) sorption to montmorillonite as a function of pH followed the same trend as would be expected for surface complexation on a mineral surface (increased sorption as pH increases). It is possible that the pH-dependent redox reactions of Pu may contribute towards the observed sorption behavior. For example, there may be some increased oxidation of Pu(IV) to Pu(V), either in solution or on the mineral surface in experiments with pH values of ≥ 6 . Zavarin *et al.* (2012) studied Pu(V) sorption to montmorillonite across the pH range 3-7. At low ionic strength (0.01 M), Pu(V) sorption and surface-mediated reduction rates increased with decreasing pH, leading to overall sorption behavior consistent with the sorption results presented here. Hence, given the small concentrations of Pu(V) in the initial Pu spike, differences in Pu redox transformation rates as a function of pH may be contributing to the Pu(IV) sorption behavior seen here.

At pH 8, there was an increase in the sorption $\log K_d$ between the 3 week and the 6 month sampling point, from 3.9 ± 0.1 to 4.5 ± 0.1 (Fig. EA2). An increase in Pu(IV) sorption to smectite and illite clays over extended time periods has previously been attributed to the slow adsorption/reduction of trace amounts of Pu(V) present either in the initial Pu(IV) stock, or formed during the spiking of an acidic stock into a circumneutral pH electrolyte (Banik *et al.*, 2016; Begg *et al.*, 2015; Geckeis *et al.*, 2004). However, we cannot rule out contributions from

other aging processes such as Pu(IV) polymerization reactions on the mineral surface, pore diffusion, or stabilization of the Pu-surface complex (Romanchuk et al., 2011; Wong et al., 2015).

4.2 Flow cell desorption experiments

In the flow cell desorption experiments, there was a difference in the total amount of Pu desorbed from the surface as a function of pH (Table 1). More Pu was desorbed at pH 8 than at pH 4, consistent with what might be expected given the Pu adsorption trend. At pH 4, the extent of measurable desorption was minimal. However, when the influent solution was changed to pH 8 (Segment v on Figure 2D), there was a significant increase in Pu desorption from the montmorillonite surface. Thus, the strong association of Pu for the montmorillonite surface at pH 4 is easily undermined by an increase in pH and any associated speciation changes. This result highlights the role of pH in controlling the desorption of Pu, independent of initial adsorption conditions. From a colloid-transport perspective, this stresses the importance of understanding changes in geochemical conditions along transport pathways.

In all flow cell desorption experiments at pH 6 and pH 8, changes in flow rate were followed by an increase in effluent Pu concentration, indicating that Pu desorption was rate-limited for residence times up to 500 minutes (8.33 hours) (Segments ii-iv in Figures 2A, 2B, and 2C). Further, the increase in concentration following the 6 month static desorption period also demonstrates that desorption was rate-limited for the 1000 minutes (16.66 hours) residence time (Segment v in Figures 2A, 2B, and 2C).

After the initial increases in effluent Pu that followed the changes in flow rate, a steady decrease in the effluent Pu concentration during active flow was observed. This behavior was unexpected. If adsorption/desorption was controlled by a single, rate-limited first order reaction,

the effluent concentrations should increase with increased residence time and the slopes should be relatively flat at constant flow rate (see Electronic Annex *One-site first order adsorption model* and Figure EA6). That this is not the case points to the occurrence of multiple reactions during the desorption process that we address with our modeling approach.

Following the 6 month adsorption period at pH 8, there was an increase in the $\log K_d$ compared to the 3 week equilibration period (Figure EA2). Accordingly, in the flow cell experiment, there was a lower initial effluent concentration compared to the 3-week experiment (Figure 2A and 2B). The total amount of Pu desorbed in the pH 8 6-month experiment during the active flow cell portion is less than that desorbed in the pH 8 3-week experiment (Table 1). Thus, the amount of Pu removed from the montmorillonite under equivalent flow cell periods is dependent on the length of the adsorption equilibration period, with less Pu removed after longer initial sorption times. This is consistent with the effect of a surface aging process whereby a change in contaminant surface speciation over time results in a decrease in the availability of the contaminant for desorption (Tinnacher et al., 2011; Wong et al., 2015). However, our experimental approach does not allow us to draw further conclusions about the nature of the aging reaction nor does it indicate whether the aging process had reached completion (i.e. could a longer adsorption period lead to a greater decrease in the extent of desorption?). Despite the differences in the amount of Pu desorbed from montmorillonite in the two pH 8 experiments, the kinetics of desorption in the pH 8 6-month experiment appeared very similar to that observed in the 3-week experiment. The changes in flow rate again led to increases in the Pu effluent concentration, demonstrating that Pu desorption remains rate limited following the extended adsorption period. As in the pH 8 3-week experiment, Pu concentration in the effluent fractions declined as a function of time at any one flow rate. Pu oxidation state in the effluent was

assessed after 23 chamber volumes in the pH 8 6-month and pH 6 3-week experiment. In both experiments, Pu in solution was predominantly in the Pu(V)/(VI) oxidation state, even though Pu(IV) is expected to be the dominant oxidation state on the mineral surface. The Pu(V)/(VI) could be a remnant from the initial Pu(V) in the spike but, given that the measurement was taken after 23 chamber volumes had been flowed, this seems unlikely. It appears more probable that the Pu(V)/(VI) is produced by the oxidation of Pu(IV) on the mineral surface that is then more readily desorbed than the Pu(IV). This is consistent with previous suggestions that the oxidation of Pu(IV) to Pu(V) plays an important role in Pu desorption and fits with our conceptual model (Figure 1) (Kaplan et al., 2006b; McCubbin and Leonard, 1996; McCubbin et al., 2002).

There was a considerable increase in Pu concentration following the 6-month static desorption period in the pH 8 3-week, pH 8 6-month and pH 6 3-week experiments, as can be seen by the last data point in Figures 2A, 2B, and 2C. In both pH 8 experiments, as well as at pH 6, the solution concentration at the 6 month timepoint approaches that measured following the initial *adsorption* period (First data point in Figures 2A, 2B, 2C). Given the loss of Pu during the flow cell experiment and the solid:solution uncertainties associated with the transfer of suspensions for the 6-month static desorption, it is not possible to make quantitative comparisons between the adsorption and desorption K_d s that would allow us to determine whether Pu desorption from montmorillonite is truly reversible under these conditions. Nonetheless, these static experiments demonstrate the slow kinetics of Pu desorption from montmorillonite and the need to perform experiments over long enough timeframes to adequately capture both kinetic and equilibrium reactions.

To demonstrate the importance of kinetics when considering adsorption/desorption reactions we consider the maximum potential desorption of Pu from montmorillonite, using the calculated

adsorption K_d values. We predicted the percent Pu that would desorb from each of these samples over a 40 chamber volume desorption flow cell experiment assuming that Pu demonstrated reversible and equilibrium sorption behavior for each chamber volume flowed. In the pH 4 sample, with a log K_d of ≥ 6.4 , no more than 1.6% of the adsorbed Pu would desorb over 40 chamber volumes. In the pH 6 sample, with a log K_d of 4.4, 78% of Pu would desorb over 40 pore volumes. In the pH 8 sample, the 21 day log K_d is 3.9 and leads to 99% of the surface Pu desorbing over 40 pore volumes. Finally, in the pH 8 sample after 6 months' equilibration where the log K_d was 4.5, 54% of the surface Pu desorbs. Comparison with the actual fraction of Pu desorbed over 40 pore volumes in flow cell experiments demonstrates that actual desorption is much lower than predicted by the simple application of an equilibrium K_d . That the calculated values are not achieved experimentally could be due to a combination of hysteresis, irreversibility, or kinetics and highlights the need for detailed desorption data when considering the environmental transport of contaminant species.

4.3 Flow cell modeling approach

We developed a model, based on Tinnacher et al. (2011), to describe the adsorption and desorption of Pu on montmorillonite. In this section we describe the parameters contained within the model's equations and justify how we approached modeling the experimental data. The conceptual model (Figure 1) includes 4 separate reactions each of which may have as many as 6 fitting parameters (i.e. k_1 , k_{-1} , n_1 , n_{-1} , ψ_1 , ψ_{-1} ; Equations (2) and (3)). This leads to as many as 24 fitting parameters for each flow cell experiment. Our approach was to fit the model to the data using the minimum number of constraints necessary to effectively describe the observed sorption/desorption affinities and rates. In addition, where possible, parameters (e.g. equilibrium K) were informed by experiments reported in the literature. In this section, we describe the

literature data and conceptual arguments used to eliminate and/or bracket each of the fitting parameters and ensure that our model honors both the flow cell sorption/desorption data presented here as well as sorption data presented in the literature. Table 2 is a summary of the available literature parameters that provide the necessary constraints to an otherwise over-parameterized problem. In our modeling approach, these values provide soft constraints to the values used to fit the flow cell data.

The Freundlich and empirical exponents, n_x

The Freundlich exponent, n_1 in Equation 1, when restricted to values less than 1, represents non-linear sorption of ions to mineral surfaces. This non-linearity is observed as a decrease in the overall sorption affinity with increasing surface loading and plots as a line with a slope $n < 1$ on a double logarithmic plot (Figure EA7). Conceptually, this is attributed to the presence of a distribution of sites with varying sorption affinities on a heterogeneous surface (Stumm et al., 1992). The empirical exponent, n_{-1} , leads to equivalent non-linear behavior under equilibrium conditions when restricted to values greater than 1. Begg *et al.* (2013) report on the sorption of Pu(V) to montmorillonite at pH 8 over a Pu concentration range of 10^{-16} – 10^{-6} M while Begg et al. (2015) describes Pu(IV) sorption to bentonite at pH 8 over the concentration range 10^{-16} – 10^{-7} M. The studies demonstrate linear sorption behavior for Pu(IV) and Pu(V) for the concentration range of interest to the current work. As a result, there is no justification for including values of n_1 , n_{-1} , n_3 , and n_{-3} other than 1.0 in the present montmorillonite modeling effort at pH 8. By extension, and for simplicity, we also assumed that n_2 , n_{-2} , n_4 , and n_{-4} values are equal to 1.0 and apply the same assumption to the pH 6 and pH 4 data. Initial modeling attempts where these parameters were set to 1.0, provided good fits to the data and gave us no reason to change these values. However, it should be noted that sorption linearity should not be presumed true in all

cases, especially at markedly higher Pu concentrations (Begg et al., 2015; Hixon and Powell, 2014; Romanchuk et al., 2011).

Transition state theory-related fitting parameters, ψ_x

Tinnacher *et al.* (2011) uses a kinetic modeling concept related to transition state theory to account for differences in net adsorption and desorption rates without necessarily implying irreversible sorption behavior. The term (in combination with n_I) is used to explain the slow desorption of Np(V) from the goethite surface that could not be simulated using a simple reversible first order reaction rate. Similarly, we included this term in our approach. The value of ψ in each of the four reactions included in our model depends on the net reaction direction (forward vs reverse) and can be conceptually related to the energies associated with adsorption and desorption reaction intermediates (Tinnacher et al., 2011). In terms of the modeling process, the value of ψ affects the rate of approach to equilibrium.

Values less than $\psi=1$ decrease the rate at which reactions approach equilibrium (See Electronic Annex *Effect of ψ in the approach to equilibrium* and Figure EA8). To first order, the decrease in rate correlates with ψ such that a reduction of ψ from 1 to 0.1 leads to a rate reduction of an order of magnitude. As in the modeling effort of Tinnacher *et al.* (2011), we limit the use of ψ to those occasions in which a simple first order reversible model is ineffective. However, unlike the modeling efforts of Tinnacher *et al.* (2011), ψ terms were not essential to effectively simulate the desorption kinetics observed in most flow cell experiments presented here. Indeed, their impact was rather limited, as we discuss in section 4.4.

Pu adsorption rates, k_1 and k_3

The rate of Pu(IV) adsorption to the montmorillonite surface (k_3 in Figure 1) is fast. Data from Begg *et al.* (2013) for pH 8 indicate that the rate is on the timescale of hours or less. For

Pu(V), results from Powell *et al.* (2011b) and Zavarin *et al.* (2012) indicate that sorption to montmorillonite (k_1) is rapid (<24 h) as well. Given the total timescales of the flow cell adsorption/desorption experiments (weeks to months), the model fit to the flow cell data will likely be insensitive to the forward rate of Pu(IV) and Pu(V) adsorption. Thus, for model fitting purposes, the forward adsorption rates of Pu(IV) and Pu(V) were limited to rate constants that were $>1 \text{ hr}^{-1}$ ($>0.017 \text{ min}^{-1}$) (Table 2).

Surface mediated reduction rate, k_2

The surface mediated reduction of Pu(V) to Pu(IV) has been documented on a variety of minerals, including montmorillonite (Begg *et al.*, 2013; Powell *et al.*, 2006; Powell *et al.*, 2004; Powell *et al.*, 2005; Zavarin *et al.*, 2012). Powell *et al.* (2011b) report pH and time-dependent (from 0 to 91 days) data for Pu(V) sorption on montmorillonite. We applied polynomial fits to the short term (up to 21 days) and long term (up to 91 days) data of Powell *et al.* (2011b) to yield apparent surface mediated Pu(V) reduction rate constants of 2.2×10^{-4} (short term)/ 2.5×10^{-4} (long term), $5.8 \times 10^{-5}/6.0 \times 10^{-5}$, and $5.3 \times 10^{-4}/9.3 \times 10^{-5} \text{ min}^{-1}$ at pH 4, 6, and 8, respectively (Figure EA9). At low pH, the reduction rate is also ionic strength dependent; the rates presented here are based on an ionic strength of 0.01 (Zavarin *et al.*, 2012). Begg *et al.* (2013) compiled apparent surface mediated Pu(V) reduction rate constants for a number of minerals at pH 8 and report a value of $10^{-3} \text{ L m}^{-2} \text{ h}^{-1}$ for SWy-1 montmorillonite. Based on the montmorillonite surface area of $27.2 \text{ m}^2 \text{ g}^{-1}$ and a flow cell montmorillonite concentration of 1 g L^{-1} , this rate constant is equivalent to $4.5 \times 10^{-4} \text{ min}^{-1}$ and is consistent with the rate constants derived from the pH 8 data of Powell *et al.* (2011b) For our modeling purposes, surface mediated reduction rate constants were held to within an order of magnitude of these literature derived rates.

Equilibrium Pu(V) sorption, K_1

First order forward and reverse rate constants for sorption to mineral surfaces can be related to the equilibrium sorption K_d (mL g^{-1}) based on the following relationship:

$$K_d \left(\frac{\text{mL}}{\text{g}} \right) = K_1 \left(\frac{\text{L}}{\text{g}} \right) \times 1000 = \frac{k_1}{k_{-1}} \times \frac{V}{m} \times 1000. \quad (3)$$

As a result, measured K_d s can be used to constrain adsorption and desorption rate constants. Batch sorption data for Pu(V) on montmorillonite has been reported in the literature (Begg et al., 2013; Powell et al., 2011b; Zavarin et al., 2012). However, previous work demonstrates that Pu oxidation state changes on the surface of montmorillonite can make determination of true Pu(V) K_d values difficult (Begg et al., 2013). Np(V), as NpO_2^+ , displays the same di-oxo structure as PuO_2^+ but is not thought to readily reduce on mineral surfaces under oxic conditions (Khasanova et al., 2007). Thus, to circumvent the Pu(V) surface reduction problem, Zavarin *et al.* (2012) use Np(V) sorption data to qualitatively estimate Pu(V) sorption to montmorillonite in the absence of a surface mediated reduction process. We take the same approach here. Np(V) sorption to montmorillonite is reviewed by Turner *et al.* (1998). The pH-dependence and resulting equilibrium log K_d s were estimated at pH 4, 6, and 8 based on Figure 1 in their manuscript (replotted on Figure EA10). The ranges of Np(V) log K_d s (mL g^{-1}) at pH 4, 6, and 8 are 0.7-1.7, 1.0-2.0, and 1.3-2.3, respectively. These K_d ranges are consistent with log Np K_d s calculated from Zavarin *et al.* (2012) at pH 4 (1.4 ± 0.1) and pH 6 (1.3-1.7) (the authors did not have pH 8 data).

An alternative method for isolating Pu(V) sorption from surface mediated reduction on montmorillonite is to use short term (<12 hour) Pu(V)-montmorillonite sorption data. Zavarin *et al.* (2012) report Pu(V) sorption data after 4.5 h at an ionic strength of 0.01 M. This yielded log K_d s of 1.7 at pH 4 and 1.5 at pH 6 (Figure EA11). The values are in good agreement with K_d s

reported for Np(V), providing confidence that they are representative of the Pu(V) adsorption reaction (Zavarin et al., 2012).

Equilibrium Pu(IV) sorption, K_d

Oxidation state changes can also affect determination of Pu(IV) equilibrium adsorption behavior. For example, Pu adsorption experiments performed under oxic conditions have observed that while Pu(IV) tends to dominate on the solid phase, Pu(V) dominates the solution phase (Powell et al., 2011b; Sanchez et al., 1985). Pu(IV) is expected to display a higher sorption affinity for mineral surfaces than Pu(V) if surface reduction processes are ignored (Sanchez et al., 1985). Accordingly, the presence of Pu(V) will lead to a lower apparent Pu(IV) K_d compared to a theoretical sorption experiment in which Pu(IV) was the sole oxidation state on the surface and in the aqueous phase. Thus, all Pu(IV) sorption data taken from oxic batch experiments should be considered a lower limit for the hypothetical pure Pu(IV) sorption. This also points to the fact that sorption/desorption behavior of Pu may differ substantially under anoxic conditions (e.g. deep repository conditions) in which the presence of Pu(V) is likely to be minimized. Pu desorption behavior under anoxic conditions is the subject of future investigations in our laboratory.

Powell *et al.* (2011b) measured Pu(IV) sorption to montmorillonite as a function of pH at time periods of 21, 60 and 91 days under oxic conditions (Figure EA12). Examination of these data lead to pH 4, 6, and 8 log K_d s (mL g⁻¹) of 4.5-5.1, 4.8-5.0, and 4.4-4.7, respectively (Table 2). The values represent our best estimate of pure Pu(IV) sorption. However, the majority of Pu in the aqueous phase was determined to be Pu(V) (Powell et al., 2011b). Thus, the hypothetical pure Pu(IV) sorption K_d s are likely to be higher still.

Pu(IV) sorption can also be estimated using long term (>1 month) Pu(V) sorption data with the assumption that Pu(V) will reduce to Pu(IV) on the surface. Zavarin *et al.* (2012) report Pu(V) sorption data at an ionic strength of 0.01 M, and at 30 days and 60 days. This yielded 30/60-day log K_d s of 3.3/4.7 at pH 4 and 4.0/4.7 at pH 6 (Figure EA13). The K_d increases between 30 and 60 days, indicates that surface mediated reduction of Pu(V) was ongoing. Thus, the higher 60 day value better reflects the behavior of Pu(IV) though it still underestimates the hypothetical pure Pu(IV) sorption K_d (Table 2). Powell *et al.* (2011b) measure Pu(V) sorption to montmorillonite as a function of pH at 60 and 91 days (Figure EA14). Examination of the 60/91-day data leads to pH 4, 6, and 8 log K_d s of 3.6/5.6, 3.8/4.2, and 4.2/4.4, respectively. The values compare well with those of Zavarin *et al.* (2012) and exhibit an increase in K_d with time, indicating the surface mediated reduction of Pu(V) is ongoing on the timescale of months. Finally, in their examination of the linearity of Pu sorption on montmorillonite, Begg *et al.* (2013) measured the sorption of Pu(IV) at 30 days and Pu(V) at 30 days and 1 year in a pH 8 solution of low ionic strength (0.01 M). The 30-day Pu(IV) adsorption log K_d was 4.3 ± 0.1 over the concentration range relevant to our flow cell desorption experiments (10^{-9} to 10^{-14} mol L⁻¹). The Pu(V) sorption K_d was lower than for Pu(IV) at 30 d but when measured at one year was 4.4 ± 0.2 , matching the Pu(IV) value.

4.4 Modeling flow cell data

The pH 8 3-week, pH 8 6-month, and pH 6 3-week flow cell desorption experiment data were fitted with the conceptual model described in Figure 1 and the parameter constraints outlined in the previous section and listed in Table 2. Due to the limited desorption observed in the pH 4 3-week experiment we performed a less extensive modeling of those data. Each simulation included a batch equilibration time (3 weeks or 6 months), the flow cell desorption experiment during which data were actively collected, and, in the case of all but the pH 4 3-week

experiment, a long term static equilibration period (~6 months). Data points were not weighted by their respective error. In all cases, the oxidation state of the Pu stock solution was set to 5% Pu(V) and 95% Pu(IV) to be consistent with the measured value. Details regarding the equilibration period, the flow cell desorption period, and the static desorption period for each experiment are reported in Table EA1. The results of each flow cell experiment are described individually in the following text and Figures. A summary of the fitted parameters is given in Table 3. In general, the consistency of generated model parameters with the available literature data demonstrates that our model can effectively simulate the sorption/desorption behavior of Pu on montmorillonite under ambient (oxic) conditions.

The pH 8 3-week experimental data and model fit are plotted in Figure 3. The model was able to fit the desorption behavior of Pu well (Figure 3a). It effectively replicates the results of the pre-equilibration (first point in Figure 3a), desorption flow cell, and re-equilibration (last point in Figure 3a) data. The ability of the model to fit the data suggests that the desorption behavior is primarily controlled by first order kinetic processes. These processes include adsorption, surface mediated reduction and oxidation, and aging processes on the montmorillonite surface. The inclusion of a kinetic hysteresis effect (ψ) on the third adsorption site (S_3) only noticeably improves the model fit to the data for the 6 month, static desorption data point (Figure 3B). However, this parameter is strongly correlated to the rate constants for reaction 4 (Figure 1), which leads to greater parameter uncertainty as determined by the PEST parameter estimation routine (see uncertainty estimates in Table 3).

Based on the modeling results, four characteristics of Pu sorption/desorption to montmorillonite were evaluated. These are: 1) the Pu(V) adsorption equilibrium $K_d \left(\frac{k_1}{k_{-1}} \times \frac{V}{m} \times 1000 \right)$, 2) the surface mediated Pu(V) reduction rate (k_2), 3) the total Pu adsorption equilibrium

K_d , and 4) the lifetime of Pu on the mineral surface which is controlled, in most instances, by the slow exchange of Pu(IV) from S_3 (k_{-4}). The total Pu adsorption equilibrium K_d ($K_{d,T}$) can be calculated with the following:

$$k_{d,T} = \frac{1 + \frac{1}{K_2} + K_4}{\frac{1}{K_2 K_1} + \frac{1}{K_3}} \times \frac{V}{m} \times 1000 \quad (4)$$

Where $K_x = k_x/k_{-x}$ for the four reactions.

Exclusion or inclusion of ψ at the third surface site for the pH 8 3-week model leads to log Pu(V) K_{ds} of 1.7 ± 0.7 and 1.6 ± 0.6 , respectively, that are consistent with Np(V) batch and short term Pu(V) sorption data described earlier (1.3-2.3, Table 2). Fitted surface mediated reduction rates (-2.4 ± 0.3 and -2.3 ± 0.4 in the absence and presence of ψ , respectively) are higher than the available batch data constraints at pH 8 (-4.0 to -3.3) from the literature but within an order of magnitude of those values. It should also be noted that typically experimental reduction rates are indirectly observed by measuring loss of Pu from solution, so may not represent true reduction rates. Exclusion or inclusion of ψ at S_3 leads to total equilibrium Pu log K_{ds} of 5.1 ± 0.3 and 4.2 ± 0.1 , respectively. Both values broadly agree with the long-term Pu(IV) and Pu(V) sorption data available in the literature (3.9 to 4.7, Table 2). However, it appears that inclusion of ψ at S_3 leads to a better agreement with the literature data, consistent with the better model fit to the 6 month static desorption data point at the end of the flow cell experiment (Figure 3).

The lifetime of Pu on the montmorillonite surface can be related to the rate limiting step in the desorption process. In all model cases, this is the rate of Pu migration from the hypothetical S_3 to the hypothetical S_2 on the montmorillonite surface. In the absence of ψ , this rate constant (log scale) is -5.91 ± 0.23 (Table 3) which leads to a Pu half-life on montmorillonite of 0.6 to 1.8 years based on the error associated with the model value. Inclusion of ψ at S_3 does not lead to a

straight forward half-life calculation and while the resulting rates are slower than in the absence of ψ , they are within an order of magnitude. We stress that this half-life value is used only to illustrate potential desorption timescales, as it is based solely on the rate-limiting reaction as identified in our model. It is likely that in field settings, other factors, including the nature of the Pu-colloid association and the presence of competing immobile mineral surfaces that may enhance desorption from colloids, will also affect Pu transport. Moreover, we acknowledge that there may be some fraction of the sorbed Pu that desorbs more slowly than the fraction desorbed in our experiments. Nevertheless, these desorption rates suggest that Pu may migrate associated with montmorillonite colloids on a timescale of years, or possibly decades, before the majority of surface-bound Pu will desorb. Thus, our modeling fits indicate that the lifetime of Pu sorbed on montmorillonite colloids would be limited, and thus Pu would not be expected to remain on the colloids over long-term, geologic timescales.

pH 8 6-month desorption

The model fit to the pH 8 6-month desorption experiment is plotted in Figure 3. Again, the model, constrained by the parameters in Table 2, effectively replicates the experimental results. The values produced in the 6-month and 3-week equilibrated pH desorption experiments are equal when fitted parameter uncertainties are taken into account (Figure EA15). However, it is not clear whether this would be the case for samples where aging was on the timescales of millennia as might be the case for waste repositories. The inclusion of the kinetic hysteresis effect, ψ term on S_3 , had little effect on the overall fit to the data for the pH 8 6-month data (Figure 3B). Exclusion or inclusion of ψ at the S_3 leads to equivalent Pu(V) log K_{ds} of 2.6 ± 0.5 and 2.5 ± 1.1 , respectively. These values are within error of the 3 week equilibrated model values and still consistent with Np(V) batch data described earlier which we take as analogous to Pu(V)

sorption in the absence of surface reduction processes. Fitted surface mediated reduction rates are equivalent to the 3-week desorption model. Exclusion and inclusion of ψ at S_3 leads to total equilibrium Pu log K_{ds} of 5.5 ± 0.9 and 5.3 ± 1.1 , respectively. The minimum half-life of Pu on the montmorillonite surface following 6 months adsorption results in values of 1.6 to 3.5 years in the absence of ψ at S_3 , apparently slightly longer than the pH 8 3-week model results but statistically equivalent. As modeling of the pH 8 3-week and pH 8 6-month data produces equivalent values for the reaction terms, it suggests that the difference in the amount of Pu desorbed in the pH 8 6-month experiment can be represented by the two aging processes included in our model. This is further demonstration of the importance of appropriate timescales when considering contaminant transport reactions. Moreover, it demonstrates that our model can effectively simulate the sorption/desorption behavior of Pu on montmorillonite under ambient (oxic) conditions on the reaction timescale of months.

pH 6 3-week desorption

The pH 6 3-week desorption data and model fit are plotted in Figure 4. Again, the model effectively replicates the experimental data, successfully accounting for the unintended stop flow event shown in Figure 2C (black arrow). Importantly, unlike the pH 8 3-week data, the inclusion of a kinetic hysteresis effect (ψ) did not lead to noticeable improved fit (data not shown). However, model fitting appeared to be limited by the imposed constraint on the surface mediated Pu(V) reduction rate. Relaxing the constraints on this parameter led to an improvement in fit as seen by the black model line in Figure 4. As in the pH 8 3-week case, modeled surface mediated reduction rates were consistently higher than the rates measured in literature batch experiments. Calculated Pu(V) log K_{ds} were 2.5 ± 0.3 and 2.0 ± 0.8 , using strongly and weakly constrained surface mediated reduction rates, respectively, which are in reasonable agreement with both the

Np(V) (1.0-2.0) and short-term (24 hour) Pu(V) batch data (1.5; Table 2). The total Pu adsorption equilibrium $\log K_{ds}$ (Eq.4) for the two model fits are 5.5 ± 0.5 and 5.5 ± 0.3 , respectively which are in reasonable agreement with those reported by Powell *et al.* (2011b) and others (4.2 to 5.0, Table 2) though they fall at the high end of this range (Zavarin et al., 2012). The minimum Pu half-life on the montmorillonite surface at pH 6, based on the rate-limiting desorption step (migration from S2 to S3), was found to be 0.5 to 1.3 years. Interestingly, despite differences in the amount of Pu desorbed, the model indicates that the overall stability of Pu on montmorillonite at pH 6 is not significantly different from pH 8, suggesting that Pu stability on montmorillonite will not be dramatically affected by pH at circumneutral pH conditions. Comparison of the pH 8 3-week and pH 6 3-week fitted parameters indicates that, within the scale of parameter uncertainty, rate constants at pH 6 and pH 8 cannot be differentiated (Figure EA16).

pH 4 3-week desorption

The low concentration of Pu desorbed in the pH 4 3-week experiment did not warrant a detailed modeling effort. Instead, a limited manual fit was performed in which the forward and reverse surface mediated reduction rates were adjusted along with the rate of Pu migration from S_3 to S_2 (Figure EA17). All other parameter were equal to the fitted constants for the pH 6 3-week experiment. The principle observation from the model result in Figure EA17 is that very little Pu is predicted to desorb from the montmorillonite surface at pH 4, consistent with the experimental data. This low level of desorption was simulated with a slight increase in the surface mediated Pu(V) reduction rate, combined with the decrease in the surface mediated Pu(IV) reoxidation rate and the Pu(IV) migration rate from S_3 to S_2 . The combined parameter adjustment are consistent with the increased rate of surface mediated reduction observed in pH 4

batch data and the increased stability of Pu on montmorillonite as the pH decreases from 8 to 4. The total equilibrium Pu log K_d at pH 4 produced by the model is 6.3, consistent with the batch sorption data reported here. Thus, use of the model helps us to infer that lower Pu desorption at pH 4 compared to pH 8 is the result of the higher apparent K_d s and the slower surface mediated oxidation rates.

Implications of the model for Pu environmental behavior

Recent work has highlighted that most Pu sorption experiments must be performed on a timescale of months for equilibrium to be achieved and to capture processes occurring in groundwater transport scenarios (Begg et al., 2013; Hixon et al., 2013; Huber et al., 2011; Powell et al., 2014; Powell et al., 2011b; Zavarin et al., 2012). As an example, we simulated Pu(V) sorption, with an initial concentration of 1×10^{-10} M, to a 1 g L^{-1} suspension of montmorillonite at pH 8 over a one year time period using the parameters fitted to the pH 8 3-week flow cell data (Figure 5). The simulation results, regardless of the use of ψ on S_3 , suggest that, i) Pu(V) is the dominant oxidation state in the aqueous phase at all times, ii) Pu(IV) is the dominant oxidation state on the solid phase within days of the start of sorption, and iii) equilibrium is only achieved at the timescale of months. All three observations are consistent with batch experimental data in the literature and indicate that our numerical model effectively simulates the kinetics and affinity of Pu(IV) and Pu(V) sorption to the montmorillonite surface under these conditions (Begg et al., 2013; Lu et al., 2003; Powell et al., 2011b; Zavarin et al., 2012).

For each fitted parameter set listed in Table 3, batch sorption was simulated for the cases of Pu(V) adsorption, Pu(IV) adsorption, and Pu(IV) S_3 desorption (Electronic Annex Figures EA18-EA29). The simulations not only support the 3 observations listed above, but also demonstrate that the overall timescales of Pu(V) surface mediated reduction and Pu(IV) aging on the

montmorillonite surface are similar in pH 4, pH 6, and pH 8 simulations. However, an increase in Pu K_d at equilibrium with decreasing pH is observed in the simulations, consistent with our experimental adsorption observations. Furthermore, the contribution of Pu(IV) to the aqueous phase appears to decrease with decreasing pH, which may reflect the weaker sorption of the hydrolyzed Pu(IV) species, and/or Pu(IV) carbonate species, at high pH. The Pu(IV) desorption simulations indicate that true equilibrium will be achieved from the desorption direction over a timescale of months and, in some cases, years. This suggests Pu sorption reversibility experiments will need to be performed over very long timescales if equilibrium is to be achieved.

5. SUMMARY AND CONCLUSIONS

We used batch and flow cell experiments to investigate the adsorption and desorption of Pu on SWy-1 montmorillonite at pH 4, 6, and 8. Both adsorption and desorption behavior showed a pH dependency, with more Pu sorbed at pH 4 ($\log K_d > 6.4$) than pH 8 ($\log K_d 3.9 \pm 0.1$) and, conversely, less Pu desorbed at pH 4 ($< 0.1\%$) than at pH 8 (12.2%). In addition, at pH 8 there was evidence of an aging of Pu on the clay, with more Pu adsorbed after 6 months' equilibration ($\log K_d 4.7 \pm 0.1$) compared to 3 weeks' equilibration ($\log K_d 3.9 \pm 0.1$). Moreover, the extent of desorption was greater in the 3-week sample (12.2%) than in the 6-month sample (5.0%). The desorption of Pu from montmorillonite was rate-limited over the timescale of the 12-day flow cell experiments as indicated by the significant increase in Pu concentration between the final flow cell sample and the end of the 6-month static desorption period.

To better understand Pu interactions with montmorillonite, we developed a model that could effectively simulate the sorption/desorption behavior of Pu on montmorillonite under ambient (oxic) conditions. Further, by modeling multi-month, sorption-desorption experiments,

794 our aim was to begin to systematically address field-scale contaminant transport concerns. The
795 model demonstrated that slow Pu desorption behavior is controlled by a combination of rate
796 limited redox and non-redox aging processes occurring on the surface of montmorillonite. From
797 an experimental standpoint, it is clear that most Pu sorption experiments must be performed on a
798 timescale of months for equilibrium to be achieved and to capture processes occurring in oxic
799 groundwater transport scenarios. In the context of waste repository scenarios, the effects of long
800 aging periods (millennial timescales) and the potential for truly irreversible sorbed Pu fractions
801 needs to be considered further.

802 The slow rate constants produced by the model (Table 3) may, in part, explain the surprisingly
803 long Pu travel times and distances observed at the Mayak site and, in particular, the NNSS, NV.
804 With Pu desorption rates on timescales of months to years, it may be possible to explain the
805 observation of trace level Pu in downgradient wells from highly contaminated sites at the NNSS
806 as a result of colloid-facilitated transport of Pu sorption and slow desorption behavior on
807 montmorillonite. Importantly, our results also imply that migration of Pu adsorbed to
808 montmorillonite colloids at longer (e.g. >50 year) timescales may not be possible. However,
809 because our desorption experiments only accessed 12.2% or less of the adsorbed Pu, we have not
810 fully explored the presence of irreversible sorption processes. A small fraction of the adsorbed
811 Pu may have been irreversibly sorbed to montmorillonite and our experimental method did not
812 effectively probe the reversibility of the entire adsorbed Pu pool. Furthermore, at geologic
813 timescales, additional phenomena such as mineral recrystallization, coprecipitation, or other
814 processes may have an effect on the reversibility of Pu associated with clay particles. These
815 additional processes could lead to colloid facilitated transport at longer timescales. As a result,

additional exploration of longterm processes and their impact on colloid facilitated transport are warranted.

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REFERENCES

- Banik, N. I., Marsac, R., Lützenkirchen, J., Diascorn, A., Bender, K., Marquardt, C. M., and Geckeis, H., 2016. Sorption and redox speciation of plutonium at the illite surface. *Environmental Science & Technology* **50**, 2092-2098.
- Bar-Tal, A., Feigenbaum, S., Sparks, D. L., and Pesek, J. D., 1990. Analyses of Adsorption Kinetics Using a Stirred-Flow Chamber: I. Theory and Critical Tests. *Soil Sci. Soc. Am. J.* **54**, 1273-1278.
- Begg, J. D., Zavarin, M., and Kersting, A. B., 2014. Plutonium desorption from mineral surfaces at environmental concentrations of hydrogen peroxide. *Environmental Science & Technology* **48**, 6201-6210.
- Begg, J. D., Zavarin, M., Tumey, S. J., and Kersting, A. B., 2015. Plutonium sorption and desorption behavior on bentonite. *Journal of Environmental Radioactivity* **141**, 106-114.
- Begg, J. D., Zavarin, M., Zhao, P., Tumey, S. J., Powell, B., and Kersting, A. B., 2013. Pu(V) and Pu(IV) sorption to montmorillonite. *Environmental Science & Technology* **47**, 5146-5153.
- Boggs, M. A., Dai, Z., Kersting, A. B., and Zavarin, M., 2015. Plutonium(IV) sorption to montmorillonite in the presence of organic matter. *Journal of Environmental Radioactivity* **141**, 90-96.
- Bradbury, M. H. and Baeyens, B., 2006. Modelling sorption data for the actinides Am(III), Np(V) and Pa(V) on montmorillonite. *Radiochim. Acta* **94**, 619-625.
- Burke, I. T., Boothman, C., Lloyd, J. R., Livens, F. R., Charnock, J. M., McBeth, J. M., Mortimer, R. J. G., and Morris, K., 2006. Reoxidation behavior of technetium, iron, and sulfur in estuarine sediments. *Environmental Science & Technology* **40**, 3529-3535.
- Choppin, G. R., 1991. Redox speciation of plutonium in natural waters. *Journal of Radioanalytical and Nuclear Chemistry-Articles* **147**, 109-116.
- Cvetkovic, V., Painter, S., Turner, D., Pickett, D., and Bertetti, P., 2004. Parameter and model sensitivities for colloid-facilitated radionuclide transport on the field scale. *Water Resources Research* **40**, n/a-n/a.

Doherty, J., 2004. *PEST, Model independent Parameter Estimation, User Manual*. Watermark Numerical Computing.

EPA, 1996. Drinking water regulations and health advisories. In: Agency, E. P. (Ed.).

Felmy, A. R., Moore, D. A., Rosso, K. M., Qafoku, O., Rai, D., Buck, E. C., and Ilton, E. S., 2011. Heterogeneous reduction of PuO₂ with Fe(II): Importance of the Fe(III) reaction product. *Environmental Science & Technology* **45**, 3952-3958.

Geckeis, H., Schafer, T., Hauser, W., Rabung, T., Missana, T., Degueldre, C., Mori, A., Eikenberg, J., Fierz, T., and Alexander, W. R., 2004. Results of the colloid and radionuclide retention experiment (CRR) at the Grimsel Test Site (GTS), Switzerland - impact of reaction kinetics and speciation on radionuclide migration. *radiat* **92**, 765-774.

Hamilton-Taylor, J., Kelly, M., Mudge, S., and Bradshaw, K., 1987. Rapid remobilization of plutonium from estuarine sediments. *Journal of Environmental Radioactivity* **5**, 409-423.

Hixon, A. E., Arai, Y., and Powell, B. A., 2013. Examination of the effect of alpha radiolysis on plutonium(V) sorption to quartz using multiple plutonium isotopes. *Journal of Colloid and Interface Science* **403**, 105-112.

Hixon, A. E., Hu, Y. J., Kaplan, D. I., Kukkadapu, R. K., Nitsche, H., Qafoku, O., and Powell, B. A., 2010. Influence of iron redox transformations on plutonium sorption to sediments. *radiat* **98**, 685-692.

Hixon, A. E. and Powell, B. A., 2014. Observed changes in the mechanism and rates of Pu(V) reduction on hematite as a function of total plutonium concentration. *Environmental Science & Technology* **48**, 9255-9262.

Hu, Q. H., Zavarin, M., and Rose, T. P., 2008. Effect of reducing groundwater on the retardation of redox-sensitive radionuclides. *Geochemical Transactions* **9**, 12-12.

Huber, F., Kunze, P., Geckeis, H., and Schafer, T., 2011. Sorption reversibility kinetics in the ternary system radionuclide-bentonite colloids/nanoparticles-granite fracture filling material. *Applied Geochemistry* **26**, 2226-2237.

Kaplan, D. I., Demirkanli, D. I., Gumapas, L., Powell, B. A., Fjeld, R. A., Molz, F. J., and Serkiz, S. M., 2006a. Eleven-year field study of Pu migration from PuIII, IV, and VI sources. *Environmental Science & Technology* **40**, 443-448.

Kaplan, D. I., Powell, B. A., Demirkanli, D. I., Fjeld, R. A., Molz, F. J., Serkiz, S. M., and Coates, J. T., 2004. Influence of oxidation states on plutonium mobility during long-term transport through an unsaturated subsurface environment. *Environmental Science & Technology* **38**, 5053-5058.

Kaplan, D. I., Powell, B. A., Duff, M. C., Demirkanli, D. I., Denham, M., Fjeld, R. A., and Molz, F. J., 2007. Influence of sources on plutonium mobility and oxidation state transformations in vadose zone sediments. *Environmental Science & Technology* **41**, 7417-7423.

Kaplan, D. I., Powell, B. A., Gumapas, L., Coates, J. T., Fjeld, R. A., and Diprete, D. P., 2006b. Influence of pH on plutonium desorption/solubilization from sediment. *Environmental Science & Technology* **40**, 5937-5942.

Keeney-Kennicutt, W. L. and Morse, J. W., 1985. The redox chemistry of Pu(V)O₂⁺ interaction with common mineral surfaces in dilute solutions and seawater. *Geochimica Et Cosmochimica Acta* **49**, 2577-2588.

Kersting, A. B., 2013. Plutonium transport in the environment. *Inorganic Chemistry* **52**, 3533-3546.

Kersting, A. B., Efur, D. W., Finnegan, D. L., Rokop, D. J., Smith, D. K., and Thompson, J. L., 1999. Migration of plutonium in ground water at the Nevada Test Site. *Nature* **397**, 56-59.

Khasanova, A. B., Kalmykov, S. N., Perminova, I. V., and Clark, S. B., 2007. Neptunium redox behavior and sorption onto goethite and hematite in the presence of humic acids with different hydroquinone content. *Journal of Alloys and Compounds* **444-445**, 491-494.

- Kirsch, R., Fellhauer, D., Altmaier, M., Neck, V., Rossberg, A., Fanghanel, T., Charlet, L., and Scheinost, A. C., 2011. Oxidation state and local structure of plutonium reacted with magnetite, mackinawite, and chukanovite. *Environmental Science & Technology* **45**, 7267-7274.
- Kobashi, A. and Choppin, G. R., 1988. A study of techniques for separating plutonium in different oxidation states. *Radiochim. Acta* **43**, 211-215.
- Kumar, S., Kasar, S. U., and Tomar, B. S., 2012. Interfacial sorption/desorption studies of Pu(IV) on silica and alumina surfaces. *radiat* **100**, 885-892.
- Lu, N., Cotter, C. R., Kitten, H. D., Bentley, J., and Triay, I. R., 1998. Reversibility of sorption of plutonium-239 onto hematite and goethite colloids. *radiat* **83**, 167-173.
- Lu, N. P., Reimus, P. W., Parker, G. R., Conca, J. L., and Triay, I. R., 2003. Sorption kinetics and impact of temperature, ionic strength and colloid concentration on the adsorption of plutonium-239 by inorganic colloids. *radiat* **91**, 713-720.
- Lujaniene, G., Benes, P., Stamberg, K., and Sciglo, T., 2012. Kinetics of plutonium and americium sorption to natural clay. *Journal of Environmental Radioactivity* **108**, 41-49.
- McBeth, J. M., Lear, G., Lloyd, J. R., Livens, F. R., Morris, K., and Burke, I. T., 2007. Technetium reduction and reoxidation in aquifer sediments. *Geomicrobiology Journal* **24**, 189-197.
- McCubbin, D. and Leonard, K. S., 1996. Photochemical dissolution of radionuclides from marine sediments. *Marine Chemistry* **55**, 399-408.
- McCubbin, D., Leonard, K. S., and Emerson, H. S., 2002. Influence of thermal and photochemical reactions upon the redox cycling of Pu between solid and solution phases in seawater. *Marine Chemistry* **80**, 61-77.
- Montero, P. R. and Sanchez, A. M., 2001. Plutonium contamination from accidental release or simply fallout: study of soils at Palomares (Spain). *Journal of Environmental Radioactivity* **55**, 157-165.
- Moon, H. S., Komlos, J., and Jaffe, P. R., 2007. Uranium reoxidation in previously bioreduced sediment by dissolved oxygen and nitrate. *Environmental Science & Technology* **41**, 4587-4592.
- Möri, A., Alexander, W. R., Geckeis, H., Hauser, W., Schäfer, T., Eikenberg, J., Fierz, T., Degueldre, C., and Missana, T., 2003. The colloid and radionuclide retardation experiment at the Grimsel Test Site: influence of bentonite colloids on radionuclide migration in a fractured rock. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **217**, 33-47.
- Morris, K., Butterworth, J. C., and Livens, F. R., 2000. Evidence for the remobilization of Sellafield waste radionuclides in an intertidal salt marsh, West Cumbria, UK. *Estuarine Coastal and Shelf Science* **51**, 613-625.
- Nelson, D. M. and Lovett, M. B., 1978. Oxidation state of plutonium in the Irish Sea. *Nature* **276**, 599-601.
- Newsome, L., Morris, K., and Lloyd, J. R., 2014. The biogeochemistry and bioremediation of uranium and other priority radionuclides. *Chemical Geology* **363**, 164-184.
- Nitsche, H. and Edelstein, N. M., 1985. Solubilities and speciation of selected transuranium ions. A comparison of a non-complexing solution with a groundwater from the Nevada Tuff Site. *radiat* **39**, 23-33.
- Novikov, A. P., Kalmykov, S. N., Utsunomiya, S., Ewing, R. C., Horreard, F., Merkulov, A., Clark, S. B., Tkachev, V. V., and Myasoedov, B. F., 2006. Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia. *Science* **314**, 638-641.
- Orlandini, K. A., Penrose, W. R., and Nelson, D. M., 1986. Pu(V) as the stable form of oxidized plutonium in natural waters. *Marine Chemistry* **18**, 49-57.
- Powell, B. A., Dai, Z. R., Zavarin, M., Zhao, P. H., and Kersting, A. B., 2011a. Stabilization of plutonium nano-colloids by epitaxial distortion on mineral surfaces. *Environmental Science & Technology* **45**, 2698-2703.

944 Powell, B. A., Duff, M. C., Kaplan, D. I., Fjeld, R. A., Newville, M., Hunter, D. B., Bertsch, P. M., Coates, J.
 945 T., Eng, P., Rivers, M. L., Serkiz, S. M., Sutton, S. R., Triay, I. R., and Vaniman, D. T., 2006.
 946 Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain tuff.
 947 *Environ. Sci. Technol.* **40**, 3508-14.

948 Powell, B. A., Fjeld, R. A., Kaplan, D. I., Coates, J. T., and Serkiz, S. M., 2004. Pu(V)O₂⁺ adsorption and
 949 reduction by synthetic magnetite (Fe₃O₄). *Environmental Science & Technology* **38**, 6016-6024.

950 Powell, B. A., Fjeld, R. A., Kaplan, D. I., Coates, J. T., and Serkiz, S. M., 2005. Pu(V)O₂⁺ adsorption and
 951 reduction by synthetic hematite and goethite. *Environmental Science & Technology* **39**, 2107-
 952 2114.

953 Powell, B. A., Kaplan, D. I., Serkiz, S. M., Coates, J. T., and Fjeld, R. A., 2014. Pu(V) transport through
 954 Savannah River Site soils - an evaluation of a conceptual model of surface- mediated reduction
 955 to Pu (IV). *Journal of Environmental Radioactivity* **131**, 47-56.

956 Powell, B. A., Kersting, A. B., Zavarin, M., and Zhao, P., 2011b. Development of a Composite Non-
 957 Electrostatic Surface Complexation Model Describing Plutonium Sorption to Aluminosilicates.
 958 Lawrence Livermore National Laboratory, Livermore, California.

959 Romanchuk, A. Y., Kalmykov, S. N., and Aliev, R. A., 2011. Plutonium sorption onto hematite colloids at
 960 femto- and nanomolar concentrations. *radiat* **99**, 137-144.

961 Sabodina, M. N., Kalmykov, S. N., Sapozhnikov, Y. A., and Zakharova, E. V., 2006. Neptunium, plutonium
 962 and Cs-137 sorption by bentonite clays and their speciation in pore waters. *J. Radioanal. Nucl.*
 963 *Chem.* **270**, 349-355.

964 Saiers, J. E. and Hornberger, G. M., 1996. The role of colloidal kaolinite in the transport of cesium
 965 through laboratory sand columns. *Water Resources Research* **32**, 33-41.

966 Sanchez, A. L., Murray, J. W., and Sibley, T. H., 1985. The adsorption of plutonium IV and V on goethite.
 967 *Geochimica et Cosmochimica Acta* **49**, 2297-2307.

968 Santschi, P. H., Roberts, K. A., and Guo, L. D., 2002. Organic nature of colloidal actinides transported in
 969 surface water environments. *Environmental Science & Technology* **36**, 3711-3719.

970 Smith, D. K., Finnegan, D. L., and Bowen, S. M., 2003. An inventory of long-lived radionuclides residual
 971 from underground nuclear testing at the Nevada test site, 1951-1992. *Journal of Environmental*
 972 *Radioactivity* **67**, 35-51.

973 Smith, S. C., Douglas, M., Moore, D. A., Kukkadapu, R. K., and Arey, B. W., 2009. Uranium Extraction
 974 From Laboratory-Synthesized, Uranium-Doped Hydrous Ferric Oxides. *Environmental Science &*
 975 *Technology* **43**, 2341-2347.

976 Stumm, W., Sigg, L., and Sulzberger, B., 1992. *Chemistry of the Solid-Water Interface: Processes at the*
 977 *Mineral-Water and Particle-Water Interface in Natural Systems*. Wiley.

978 Tinnacher, R. M., Zavarin, M., Powell, B. A., and Kersting, A. B., 2011. Kinetics of neptunium(V) sorption
 979 and desorption on goethite: An experimental and modeling study. *Geochimica Et Cosmochimica*
 980 *Acta* **75**, 6584-6599.

981 Turner, D. R., Pabalan, R. T., and Bertetti, F. P., 1998. Neptunium(V) sorption on montmorillonite: An
 982 experimental and surface complexation modeling study. *Clays and Clay Minerals* **46**, 256-269.

983 Wendling, L. A., Ma, Y. B., Kirby, J. K., and McLaughlin, M. J., 2009. A Predictive Model of the Effects of
 984 Aging on Cobalt Fate and Behavior in Soil. *Environmental Science & Technology* **43**, 135-141.

985 Wong, J. C., Zavarin, M., Begg James, D., Kersting Annie, B., and Powell Brian, A., 2015. Effect of
 986 equilibration time on Pu desorption from goethite. *radiat* **103**, 695-705.

987 Zavarin, M., Powell, B. A., Bourbin, M., Zhao, P., and Kersting, A. B., 2012. Np(V) and Pu(V) ion exchange
 988 and surface-mediated reduction mechanisms on montmorillonite. *Environmental Science &*
 989 *Technology* **46**, 2692-2698.

990 Zavarin, M., Roberts, S. K., Hakem, N., Sawvel, A. M., and Kersting, A. B., 2005. Eu(III), Sm(III), Np(V),
 991 Pu(V), and Pu(IV) sorption to calcite. *radiat* **93**, 93-102.

992 Zhao, P., Begg, J. D., Zavarin, M., Tumey, S. J., Williams, R., Dai, Z. R., Kips, R., and Kersting, A. B., 2016.
993 Plutonium(IV) and (V) Sorption to Goethite at Sub-Femtomolar to Micromolar Concentrations:
994 Redox Transformations and Surface Precipitation. *Environmental Science & Technology* **50**,
995 6948–6956.

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TABLES

Table 1. Extent of adsorption and desorption in flow cell experiments

pH	Adsorption time	Kd at start of flow cell (ml/g)	% Pu unsorbed at start of flow cell	% Surface Pu desorbed
8	3 weeks	8.8×10^3	10.1	12.2
8	6 months	2.9×10^4	3.3	5.0
6	3 weeks	2.5×10^4	3.9	4.2
4	3 weeks	2.5×10^6	<0.05	<0.1

23 Table 2. Model parameter constraints based informed by literature data.

$K_1 * 1000$ log(mL/g)	k_1 log(min ⁻¹)	k_{-1}^n log(min ⁻¹)	k_2 log(min ⁻¹)	$K_3 * 1000^o$ log(mL/g)	k_3 log(min ⁻¹)	k_{-3}^n log(min ⁻¹)
pH 8						
1.3 – 2.3 ^g	>-1.8 ^d	-0.6	-4.0 – -3.3 ^e -3.3 ^f	3.9 ^a 4.7 ^b 4.4 – 4.7 ^e 4.4 ^k 4.4 ^l 4.3 ^m	>-1.8 ^c	-2.7 -3.5 -3.2 – -3.5 -3.2 -3.2 -3.1
pH 6						
1.0 – 2.0 ^g	>-1.8 ^d	-0.8 – 0.2	-4.2 ^e	4.4 ^a	>-1.8 ^c	-3.2
1.3 – 1.7 ^h		-0.5 – -0.1		4.8 – 5.0 ^e		-3.6 – -3.8
1.5 ⁱ		-0.3		4.7 ^j 4.2 ^k		-3.5 -3.0
pH 4						
0.7 – 1.7 ^g	>-1.8 ^d	-0.5 – 0.5	-3.6 ^e	>6.4 ^a	>-1.8 ^c	-5.2
1.4 ^h		-0.2		4.5 – 5.1 ^e		-3.3 – -3.9
1.7 ⁱ		-0.5		4.7 ^j 5.6 ^k		-3.5 -4.4

24 a = this paper, 21 day equilibration; b = this paper, 6 month equilibration; c = Begg et al. (2013);
 25 d = Powell et al. (2011b), Zavarin et al. (2012); e = Powell et al. (2011b); f = Begg et al. (2013);
 26 g = Turner et al. (1998); h = Zavarin et al. (2012) Np(V) data; i = Zavarin et al. (2012) 4.5 h
 27 Pu(V) data; j - Zavarin et al. (2012) 60 day Pu(V) data; k = Powell et al. (2011b) 91 day Pu(V)
 28 sorption; l = Begg et al. (2013) 1 year Pu(V) data; m = Begg et al. (2013) 30 day Pu(IV) data; n =
 29 calculated based on K_x and k_x ; o = estimated from batch Pu(IV) or longterm Pu(V) sorption
 30 experiments.
 31

32 Table 3. Flow cell data fitting results. 2SD errors reported

		pH 8	pH 8	pH 8	pH 8	pH 6	pH 6	pH 4
		3-week data	3-week data	6-month data	6-month data	3-week data	3-week data	3-week data
		no psi	psi	no psi	psi	no psi	no psi ^b	no psi
k ₁	log(min ⁻¹)	-1.58 +- 0.41	-1.70 +- 0.54	-1.00 +- 0.36	-1.21 +- 0.80	-1.21 +- 0.19	-1.27 +- 0.51	-1.27
k ₋₁	log(min ⁻¹)	-0.31 +- 0.53	-0.31 +- 0.31	-0.60 +- 0.28	-0.69 +- 0.80	-0.68 +- 0.28	-0.24 +- 0.62	-0.24
K ₁ *1000	log(mL/g)	1.7 +- 0.7	1.6 +- 0.6	2.6 +- 0.5	2.5 +- 1.1	2.5 +- 0.3	2.0 +- 0.8	
k ₂	log(min ⁻¹)	-2.42 +- 0.30	-2.28 +- 0.41	-2.36 +- 0.45	-2.28 +- 0.21	-3.24 +- 0.12	-2.72 +- 0.37	-2.54 ^a
k ₋₂	log(min ⁻¹)	-4.09 +- 0.15	-3.90 +- 0.13	-3.82 +- 0.31	-3.84 +- 0.72	-4.52 +- 0.27	-4.21 +- 0.15	-4.51 ^a
k ₃	log(min ⁻¹)	-1.67 +- 0.31	-1.75 +- 0.28	-1.65 +- 0.32	-1.72 +- 1.10	-1.24 +- 0.21	-1.16 +- 0.19	-1.16
k ₋₃	log(min ⁻¹)	-3.31 +- 0.16	-3.20 +- 0.12	-3.48 +- 0.23	-3.51 +- 0.39	-3.69 +- 0.19	-3.55 +- 0.10	-3.55
K ₃ *1000	log(mL/g)	4.6 +- 0.3	4.5 +- 0.3	4.8 +- 0.4	4.8 +- 1.2	5.4 +- 0.3	5.4 +- 0.2	
k ₄	log(min ⁻¹)	-4.17 +- 0.04	-3.83 +- 0.24	-4.77 +- 0.10	-3.44 +- 0.66	-4.05 +- 0.11	-3.94 +- 0.06	-3.94
k ₋₄	log(min ⁻¹)	-5.91 +- 0.23	-4.74 +- 0.43	-6.26 +- 0.17	-4.75 +- 0.59	-5.78 +- 0.23	-5.76 +- 0.12	-6.36 ^a
ψ ₋₄	log(ψ ₋₄)	1	-1.92 +- 0.70	1	-1.92*	1	1	1
Residuals		3.3	2.7	6	5.8	3.6	2.2	
Net Kd ^c	log(mL/g)	5.1 +- 0.3	4.2 +- 0.1	5.5 +- 0.9	5.3 +- 1.1	5.5 +- 0.5	5.3 +- 0.5	6.3

^a Values adjuted by hand to achieve a reasonable fit to the flow cell data. All other value taken direction from the fit to the pH 6 data.

^b Fit performed with weaker constraints on the surface mediated redox rate constants.

^c Based on Equation 4.

FIGURES

CAPTIONS

Figure 1. Conceptual model used for the simulation of Pu desorption kinetics from montmorillonite. In this model, sites 1, 2, and 3 represent unique states of adsorbed Pu and not necessarily unique surface sites.

Figure 2. Pu aqueous concentration in the flow-cell effluent representing desorption from montmorillonite: (A) desorption at pH 8 following 3 week adsorption period; (B) desorption at pH 8 following 6 month adsorption period; (C) desorption at pH 6 following 3 week adsorption period; (D) desorption at pH 4 following 3 week adsorption period. Vertical dashed lines represent changes in influent flow-rate. Flow rates and residence times: (i) 0.4 mL min^{-1} , 50 minutes; (ii) 0.2 mL min^{-1} , 100 minutes; (iii) 0.04 mL min^{-1} , 500 minutes; (iv) 0.02 mL min^{-1} , 1000 minutes; (v) 0 mL min^{-1} , 6 months (Figures A, B, and C), 0.04 mL min^{-1} at pH 8 (Figure D). Errors bars represent 2σ % from LSC counting statistics.

Figure 3. Model fits (red lines) to 3-week equilibrated (circles) and 6 month equilibrated (triangles) pH 8 data in the (A) absence and (B) presence of a kinetic hysteresis parameter (ψ) for the third surface site.

Figure 4. Model fits to 3-week equilibrated pH 6 data generated with strict (red line) and loose (black line) constraints to the surface mediated reduction rate parameter.

Figure 5. Simulated Pu (V) adsorption to 1 g/L montmorillonite using *pH 8 3-week* parameters (A) excluding and (B) including ψ on S_3 . In this model, sites 1, 2, and 3 represent unique states of adsorbed Pu and not necessarily unique surface sites.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5