Plutonium sorption and desorption behavior on bentonite

James D. Begg^{1}, Mavrik Zavarin¹, Scott J. Tumey², Annie B. Kersting¹*

1. Glenn T. Seaborg Institute, Physical & Life Sciences, Lawrence Livermore National Laboratory,
7000 East Avenue, Livermore, CA 94550, USA
2. Center for AMS, Physical & Life Sciences, Lawrence Livermore National Laboratory, 7000 East
Avenue, Livermore, CA 94550, USA

*Corresponding Author: +1 (925) 422 3844 Begg2@llnl.gov

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ABSTRACT

Understanding plutonium (Pu) sorption to, and desorption from, mineral phases is key to understanding its subsurface transport. In this work we study Pu(IV) sorption to industrial grade FEBEX bentonite over the concentration range 10^{-7} - 10^{-16} M to determine if sorption at typical environmental concentrations ($\leq 10^{-12}$ M) is the same as sorption at Pu concentrations used in most laboratory experiments (10^{-7} - 10^{-11} M). Pu(IV) sorption was broadly linear over the 10^{-7} - 10^{-16} M concentration range during the 120 d experimental period; however, it took up to 100 d to reach sorption equilibrium. At concentrations $\geq 10^{-8}$ M, sorption was likely affected by additional Pu(IV) precipitation/polymerization reactions. The extent of sorption was similar to that previously reported for Pu(IV) sorption to SWy-1 Na-montmorillonite over a narrower range of Pu concentrations (10^{-11} – 10^{-7} M). Sorption experiments with FEBEX bentonite and Pu(V) were also performed across a concentration range of 10^{-11} – 10^{-7} M and over a 10 month period which allowed us to estimate the slow apparent rates of Pu(V) reduction on a smectite-rich clay. Finally, a flow cell experiment with Pu(IV) loaded on FEBEX bentonite demonstrated continued desorption of Pu over a 12 day flow period. Comparison with a desorption experiment performed with SWy-1 montmorillonite showed a strong similarity and suggested the importance of montmorillonite phases in controlling Pu sorption/desorption reactions on FEBEX bentonite.

KEYWORDS Plutonium; sorption; desorption; bentonite; montmorillonite; clay

1. INTRODUCTION

Permanent interment in a deep geological repository is seen as the most viable option for radioactive waste disposal in many countries with a civilian nuclear fuel program (IAEA, 1995). Conceptually, the repository scenario comprises a geological barrier (host rock) combined with engineering barriers that aim to contain the radionuclides until they have decayed below harmful levels. The waste itself will likely be contained in steel canisters surrounded by a layer of compacted clay. The efficacy of this disposal option is related to its capacity to confine radioactivity and isolate it from the biosphere (Dozol et al., 1993).

Due to its swelling properties, plasticity, ion exchange and sorption behavior, and sealing capability, bentonite is considered a good candidate for backfill material (Guven, 1990). Traditionally, the term bentonite refers to aluminum phyllosilicate clays derived from the devitrification and chemical alteration of glassy volcanic ash or tuff (Ross and Shannon, 1926). However, the term has been used to describe smectite-rich materials, regardless of origin (Grim, 1968). The smectite mineral group includes a number of 2:1 layer silicates, the most common of which is montmorillonite. Montmorillonites constitute a large proportion of bentonite mineralogy (65-90 wt %) with the result that the two names are often used synonymously, although the former is a clay mineral and the latter a clay rock (Grauer, 1986). Montmorillonite can display significant morphological and chemical differences depending on its provenance (Guven, 1988).

ENRESA, the body responsible for the management of Spanish radioactive waste, has proposed FEBEX bentonite from Cortijo de Archidona in Almeria, Spain for use in its repositories. As a result, the physiochemical properties of this clay rock have been well studied, particularly in an extensive experimental program performed at the National Cooperative for the

Disposal of Radioactive Waste's (Nagra) Grimsel Test Site in Switzerland. The FEBEX bentonite has a high smectite content ($93 \pm 2 \%$) with minor quartz ($2 \pm 1 \%$), plagioclase ($3 \pm 1 \%$), cristobalite ($2 \pm 1 \%$), potassium feldspar, calcite and tridymite as accessory minerals (Missana et al., 2004). The less than $2 \mu\text{m}$ fraction (after Ca homoionization) of this bentonite is composed of $>99\%$ smectite with the structural formula:

$(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{2.78}\text{Fe}^{3+}_{0.33}\text{Fe}^{2+}_{0.02}\text{Ti}_{0.02}\text{Mg}_{0.81})\text{O}_{20}(\text{OH})_4(\text{Ca}_{0.50}\text{Na}_{0.08}\text{K}_{0.11})$ (Fernandez et al., 2004).

Due to their long half-lives and toxicity, the isotopes ^{239}Pu ($2.41 \times 10^4 \text{ y}$) and ^{240}Pu ($6.56 \times 10^3 \text{ y}$) are expected to contribute significantly to the total hazardous inventory in a waste repository scenario (Schwenk-Ferrero, 2013). Despite several decades of study, our understanding of how Pu migrates in subsurface environments is far from complete due to the wide array of factors which can significantly influence its mobility. These include Pu redox processes (Choppin, 1991; Sanchez et al., 1985), colloid-facilitated transport processes (Kersting et al., 1999; Novikov et al., 2006), solubility effects (Efurd et al., 1998; Neck et al., 2007), sorption/desorption rates and affinities for natural mineral surfaces (Powell et al., 2004; Zavarin et al., 2012), and interactions with natural organic matter (including bacteria) (Icopini et al., 2009; Zhao et al., 2011). Pu exhibits a complex redox chemistry in natural waters with four oxidation states (VI, V, IV, III) potentially stable and with each oxidation state displaying a unique solubility (Neck et al., 2007) and mineral sorption affinity (Begg et al., 2013; Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Silva and Nitsche, 1995). Pu(IV) and Pu(V) are the more common species under mildly oxic environmental conditions and also represent the oxidation states with the lowest (Pu(V)) and highest (Pu(IV)) affinities for mineral surfaces (Choppin, 2007; Kaplan et al., 2007; Silva and Nitsche, 1995).

Mineral-colloid facilitated transport is thought to be a significant contributor to Pu migration in the subsurface (Kersting et al., 1999; Novikov et al., 2006; Santschi et al., 2002). One of the concerns with the use of bentonite as a backfill material in a repository is that it can form colloids, which may enhance the migration of radionuclide species that are sorbed to them (Geckeis et al., 2004). As a result, attention has been focused on the interaction between Pu and bentonite colloids (Huber et al., 2011; Missana et al., 2008). Previous work on FEBEX bentonite has shown that colloids with a hydrodynamic size of 250 ± 50 nm have an XRD pattern consistent with an aluminum-rich dioctahedral smectite with no significant impurities (Missana et al., 2004).

The sorption of Pu species to Khakassiya bentonite and SWy-1 montmorillonite has been found to exhibit pH and ionic strength dependency, indicating that both ion-exchange and surface complexation processes are occurring (Sabodina et al., 2006; Zavarin et al., 2012). However, surface complexation processes will dominate at neutral to alkaline pHs. Smectite minerals have been shown to have a high sorption affinity for Pu. For example, Pu(V) partitioning to Yucca Mountain tuffs found a ubiquitous and preferential association of Pu with smectite minerals (Vaniman et al., 1995). Further, Pu(IV) K_d values from 10,000 to 40,000 L kg⁻¹ (log K_d 4.0 to 4.6) have been reported for smectite-rich sediments from Lithuania in the pH range 5 to 12 (Lujanienė et al., 2007). Missana *et al.* (2008) studied the sorption of Pu(IV) to FEBEX bentonite *colloids* (>99% smectite) at pH 9.5 and reported log K_d values of 5.37 ± 0.18 . Pu(IV) sorption to FEBEX bentonite *colloids* under anaerobic conditions at pH 9.6, resulted in log R_d values (a term equivalent to K_d but without the assumption of equilibrium) of 5 and 5.9 after one and three weeks of sorption time, respectively (NAGRA, 2006). The increase in R_d

values with time was attributed to the presence of a small amount (~ 5 %) of Pu(VI) in the spike solution which was slowly reduced to Pu(IV) on the mineral surface (NAGRA, 2006).

In a recent study, we examined the long term sorption behavior of Pu(IV) and Pu(V) on SWy-1 Na-montmorillonite under aerobic conditions. After 30 d equilibration, calculated $\log K_d$ values for Pu(IV) and Pu(V) were 4.25 ± 0.15 and 3.57 ± 0.18 , respectively (Begg et al., 2013). However, following one year of equilibration, calculated $\log K_d$ values in the Pu(V) experiments had increased to 4.32 ± 0.15 , similar to those calculated for Pu(IV) after 30 d. The convergence of K_d values for Pu(IV) and Pu(V) was attributed to the slow reduction of Pu(V) on the montmorillonite surface causing increased uptake of Pu(V). This finding highlights the need to ensure that experimental studies used to inform predictive transport models accurately encapsulate long term environmental behaviors.

Several recent studies have indicated that actinide concentration can affect their sorption to mineral surfaces (Hixon and Powell, 2014; Missana et al., 2008; Snow et al., 2013). In the case of Pu(IV), its low solubility at circumneutral pH means that sorption may demonstrate an apparent concentration dependence as solubility limits are reached. For example, the study of Pu(IV) sorption to bentonite colloids (>99% smectite) showed that sorption was linear for initial Pu concentrations of $1 \times 10^{-8} - 1 \times 10^{-7}$ M but at higher concentrations precipitation of Pu was evidenced by a sharp increase in the isotherm slope (Missana et al., 2008). Concentration dependent sorption behavior may also be observed at low actinide concentrations: work with goethite and Np(V) found that K_d values differed by an order of magnitude at solution concentrations below 10^{-11} M compared to higher concentrations (Snow et al., 2013). This behavior was attributed to the existence of different adsorption sites on the mineral having different adsorption affinities for Np. These examples of concentration dependent behavior of

actinides indicate that there may be a difference between the sorption behavior of Pu at the concentrations found in contaminated subsurface waters ($10^{-12} - 10^{-20}$ M) (Dai et al., 2005; Kersting et al., 1999; Novikov et al., 2006; Penrose et al., 1990) and concentrations typically used in laboratory experiments ($10^{-7} - 10^{-11}$ M Pu). Although a primary assumption of reactive transport models, the validity of extrapolating Pu-mineral sorption behavior from relatively high concentration laboratory experiments to the low concentrations found in many field settings has not been widely tested.

Pu desorption reactions have been far less well studied than sorption reactions. This is problematic because application of thermodynamic equilibrium parameters in field transport models which incorrectly represent desorption processes are likely to be flawed (Artinger et al., 2002). One of the pertinent issues for Pu, especially given the evidence that its mobility may be enhanced by mineral-colloid facilitated transport, is whether there is equality in sorption and desorption behavior (Kersting et al., 1999). Differences in behavior may be caused by aging processes, hysteresis effects, and irreversible sorption, amongst others (Tinnacher et al., 2011). A study of Pu(IV) sorption to Callovo-Oxfordian argillite found that after seven days' desorption, Pu K_d values were of the same order of magnitude as they were following a seventy four day adsorption period, indicating sorption reversibility (Latrille et al., 2006). Similarly, Lu *et al.* (2003) investigated Pu interaction with montmorillonite and found that with a 20 day adsorption period and a 32 day desorption period, similar K_d values were obtained for both adsorption and desorption steps.

The aim of the current work is two-fold: to provide information on Pu sorption/desorption to/from industrial grade FEBEX bentonite, a potential repository backfill material, and to determine if the linearity observed for Pu(V) sorption to a pure Na-montmorillonite (Begg et al.,

2013) extends to Pu(IV) sorption to a multi-component clay rock material. We investigate the sorption behavior of Pu(IV) to FEBEX bentonite across a wide range of initial concentrations ($10^{-7} - 10^{-16}$ M) over a 120 d period. In addition, we perform long term (10 month) sorption experiments with Pu(V) to compare with the slow apparent rates of reduction previously observed for Pu(V) on montmorillonite (Begg et al., 2013). The results of these experiments demonstrate the apparent control that the montmorillonite component in bentonite exerts on the sorption behavior of Pu, provides long term sorption data for industrial grade FEBEX bentonite, and validates the extrapolation of Pu(IV) experiments performed at concentrations of $10^{-9} - 10^{-11}$ M Pu to much lower concentrations typically found in the environment at timescales relevant for groundwater transport.

2. MATERIALS AND METHODS

2.1 Bentonite Preparation

Unless stated otherwise, all solutions were prepared using ultrapure water (Milli-Q Gradient System, >18 M Ω ·cm) and ACS grade chemicals without further purification. The FEBEX bentonite was ground in a mortar and pestle and sieved to <63 μ m to minimize clay heterogeneity. The clay was then homo-ionized in 1 M NaCl solution for 7 days and dialyzed in MQ H₂O to remove excess salts. As experiments were performed to characterize the behavior of Pu in the presence of bulk bentonite, no further treatment was performed. A portion of the bentonite suspension was dried, the clay lightly ground, and its surface area measured (N₂(g)-BET Quadrasorb SI). The surface area of the prepared bentonite was 25.2 ± 1.0 m² g⁻¹.

The solids were re-suspended in a 0.7 mM NaHCO₃, 5 mM NaCl buffer solution (pH 8) to make a suspension with a bentonite concentration of ~ 5 g L⁻¹. This buffer solution was chosen so as to allow comparison with previous experiments performed with SWy-1 Na-

montmorillonite (Begg et al., 2013). Gravimetric analysis of the dried mass of the solid in triplicate 5 mL aliquots of the suspension returned a standard error of 1.2%, indicating homogeneity in the stock suspension and providing confidence in the amount of solid added to experiments. The stock suspension was allowed to equilibrate under aerobic conditions for several days prior to the start of sorption experiments.

2.2 Pu Stock Solutions

Three different Pu stock solutions were used in the sorption experiments in order to facilitate measurement over the wide range of Pu concentrations investigated. A ^{242}Pu stock (15.8% ^{238}Pu , 5.1% $^{239+240}\text{Pu}$, 79.1% ^{242}Pu by activity) and a ^{238}Pu stock (98.8% ^{238}Pu , 0.11% ^{241}Pu , and 0.1% ^{239}Pu by activity) were used in experiments with initial concentrations of $10^{-7} - 10^{-11}$ M. A New Brunswick Laboratory (NBL) Pu reference material CRM-137 (33.5% ^{238}Pu , 35.3% ^{239}Pu , 31.3% ^{240}Pu by activity) was used in experiments with initial Pu concentrations $\leq 10^{-11}$ M. A table of the different stocks used, including their oxidation state, where measured, is given in Supplementary information Table S1.

The Pu stock solutions were purified using anion exchange resin (BioRad AG 1×8 , 100-200 mesh) pre-conditioned with 8 M HNO_3 . Prior to loading on the resin, Pu was reacted with NaNO_2 to reduce it to Pu(IV). The Pu was loaded on the resin in 8 M HNO_3 , washed with 3 column volumes of 8 M HNO_3 , and then eluted in 1 M or 0.1 M HCl (Powell et al., 2011a). For experiments using Pu(IV), the oxidation state of the Pu stocks was checked with a LaF_3 precipitation method (Kobashi and Choppin, 1988) and found to be at least $\geq 92\%$ Pu(III)/(IV) (Table S1). Subsequent stock dilutions were made using 0.1 M HCl , with select analysis indicating that this did not significantly alter the oxidation state of the Pu. For experiments starting with Pu(V), the Pu(IV) stripped from the columns was converted to Pu(VI) either

electrochemically (^{242}Pu stocks) or by heating in HNO_3 (^{238}Pu stocks), adjusting to pH 3 with NaOH, spiking with 0.05 M hydrogen peroxide and gently heating to produce Pu(V). To remove any Pu(VI) remaining in solution, the stocks were diluted in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution to achieve a circumneutral pH and contacted with 10 g/L high surface area SiO_2 , which will preferentially adsorb Pu(VI), before being phase separated for use in experiments (Orlandini et al., 1986). Pu(V) stocks were <3 % Pu(III)/(IV) by LaF_3 precipitation. Final Pu concentration in the stock solutions was determined by liquid scintillation counting (LSC; Packard Tri-Carb TR2900 LSA and Ultima Gold cocktail).

2.3 Plutonium Batch Sorption Experiments

Sorption experiments were performed over a wide range of initial Pu(IV) concentrations (10^{-7} – 10^{-16} M). In the following description we use the nominal terms *high concentration* to refer to experiments initially spiked to Pu concentrations of 10^{-7} – 10^{-11} M and *low concentration* for experiments initially spiked to Pu concentrations of 10^{-11} – 10^{-16} M. The two types of experiments were performed in separate laboratories in order to minimize any potential contamination of the *low concentration* samples.

All Pu(IV) and Pu(V) batch sorption experiments were performed under air in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution (pH 8) with 1 g L^{-1} FEBEX bentonite. These experimental conditions were chosen to achieve consistency with previous experiments using SWy-1 Na-montmorillonite (Begg et al., 2013). Pu(IV) and Pu(V) aqueous speciation for initial Pu concentrations of 10^{-10} M in the buffer solution were calculated using the Geochemist's Workbench family of codes and thermodynamic data from Guillaumont *et al.* (2003). The results are shown in Supplementary Information (SI) Figure S1. Batch experiments were conducted in either 50 mL Nalgene Oak Ridge polycarbonate centrifuge tubes (*high concentration*) or 500 mL

Nalgene bottles (*low concentration*). Higher volumes were required in *low concentration* experiments to achieve the low detection limits afforded by accelerator mass spectrometry (AMS). Pu(IV) sorption experiments were performed at *low concentrations* and *high concentrations*, while Pu(V) experiments were performed only at *high concentrations*. For Pu(IV) experiments, where the Pu stock was in 0.1 M HCl, dilute NaOH was added to the samples immediately prior to spiking in order to neutralize the acidity associated with the Pu(IV) spike. This was not necessary for Pu(V) experiments where the pH of the stock was circumneutral. Bentonite blanks (with no Pu) and Pu spiked blanks (with no bentonite; select concentrations) were run in parallel. The results of the mineral free experiments are included in the SI. The pH of each experiment was checked (Orion 920A with calibrated electrode) and adjusted to $\text{pH } 8.0 \pm 0.2$ using dilute NaOH or HCl within 10 minutes of spiking. Measurement of pH over the course of the experiments indicated that the drift in pH was less than 0.2 pH units. Samples were placed on an orbital shaker at 125 rpm at room temperature for the duration of the experiment. Experiments were kept in the dark in order to minimize photo-catalyzed reactions that may directly or indirectly affect the redox speciation of Pu (McCubbin and Leonard, 1996; Powell et al., 2005).

At each time point, samples were centrifuged to achieve a 50 nm size cut off. No further attempts at size fractionation were made. We note that centrifugation can potentially remove not only Pu sorbed on bentonite but also any Pu precipitates with a particle size greater than 50 nm. Thus, the apparent sorption determined based on centrifugation could, in fact, represent a combination of Pu sorption, Pu precipitation, as well as Pu surface precipitation on the bentonite particle surfaces. However, in the *low concentration* experiments, we consider the formation of Pu precipitates and/or polynuclear species to be thermodynamically unfavorable. For *high*

concentration samples, aliquots of both the suspension and the supernatant were removed and counted via LSC. In *low concentration* experiments, aliquots of supernatant were acidified to 2% HNO₃ and analyzed using AMS (10-MeV tandem accelerator at the Center for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratory, CA). AMS is an ultra-sensitive analytical technique that can quantify long-lived radionuclides at ultra-low concentrations and routinely achieves instrumental backgrounds of 10⁵ atoms for actinide elements (Marchetti et al., 2005). AMS analysis has been reported previously and included isotope dilution using a non-isobarically interfering isotope of ²⁴²Pu (99.99% ²⁴²Pu) (Marchetti et al., 2005).

2.4 Plutonium Desorption Flow Cell Experiments

A stirred flow cell experiment was performed at pH 8 to examine the desorption of Pu(IV) from bentonite. The flow cell set up was similar to that described previously for Np(V) and goethite and Pu(IV) and goethite (Begg et al., 2014; Tinnacher et al., 2011). The flow cell was made of Teflon®, with a 20 mL hemispherical chamber and fitted with a 100 nm pore size Millipore polycarbonate filter. A diagram of the flow cell is shown in SI Figure S2. Prior to use, the cell was washed with 10% HCl and MQ water. To sorb Pu on the clay, Pu(IV) at 3×10^{-10} M was equilibrated with 1 g L⁻¹ bentonite for 21 days. After this equilibration period, an aliquot of the spiked suspension was centrifuged (25 000 × g, 2 h; 50 nm cut-off) and the concentration of the Pu in the supernatant measured. A 20 mL aliquot of bentonite suspension was loaded into the flow cell with a stir bar included to ensure ideal mixing conditions. In previous flow cell work with SWy-1 Na-montmorillonite, ³H was used as a conservative tracer to test if ideal mixing conditions existed. A plot of the decline in ³H concentration and a theoretical non-reactive

species is shown in SI Figure S3. The similarity between the calculated and observed curves demonstrates that the flow cell experiment is ideally mixed when the stir bar is operational.

Atmosphere-equilibrated, Pu free, 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at pH 8 was flowed through the cell at an initial 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. Periodic pH measurements of the effluent were performed to ensure that the experiment remained at pH 8. Collected fractions were acidified with 2% HNO₃ prior to Pu analysis. Pu concentration in the effluent fractions was determined via liquid scintillation counting. The total timescale of the flow cell experiment was 12 days.

3. RESULTS AND DISCUSSION

3.1 Pu(IV) Sorption to Bentonite

The sorption of Pu(IV) to bentonite was studied over an initial Pu concentration range of 10⁻⁷ – 10⁻¹⁶ M. The resulting sorption isotherm after 120 d equilibration is shown in Figure 1. To determine if sorption equilibrium was achieved in the experiment, samples at 10⁻¹⁰ and 10⁻⁷ M were sampled after 67 d, 100 d and 120 d. The results of this sampling are shown in the inset in Figure 1. The similarity in the aqueous Pu concentrations at 100 d and 120 d versus 67 d indicate that sorption equilibrium was reached by 120 d. The slow approach to sorption equilibrium is consistent with previous studies on Pu(IV) sorption to clay and may reflect the presence of small amounts of Pu(V) in the initial stock solution, although we cannot discount other aging processes such as Pu polymerization/precipitation reactions, particularly in the higher concentration sample (Begg et al., 2013; NAGRA, 2006). Sorption of pure Pu(IV) to bentonite should be followed by oxidation of some fraction of Pu(IV) and a decrease in K_d over time. However, the presence of Pu(V) in the Pu(IV) spike masked any decrease in K_d as a function

time due to Pu(IV) oxidation. A similar observation was made by (Powell et al., 2011b) for Pu(IV) sorption to montmorillonite. Moreover, unintended changes in Pu oxidation state may be exacerbated when an acidic Pu(IV) stock is spiked into a circumneutral pH solution under oxic conditions. In the supplemental information, Figure S4 shows oxidation state analysis of a parallel experiment where a mineral-free, pH 8 solution was spiked with a >97% Pu(III)/(IV) stock solution (4.48×10^{-7} M) to a concentration of 3×10^{-10} M. Both LaF₃ and solvent extraction analysis of the aqueous Pu indicate that 1 h after spiking, approximately 30% of the Pu(III)/(IV) had been oxidized to Pu(V)/(VI). LaF₃ analysis over 6 d showed no appreciable change in Pu oxidation state from the 1 h values while no significant Pu was lost from solution over this short time period.

After 120 d equilibration, the sorption of Pu(IV) to bentonite was broadly linear over the orders of magnitude concentration range tested (Figure 1). Our results show that on timescales of months, Pu(IV) exhibits similar apparent sorption behavior to bentonite at the higher concentrations used in typical laboratory experiments ($10^{-7} - 10^{-11}$ M) as it does at concentrations typically found in contaminated environments ($\leq 10^{-12}$ M). This result complements previously published linear sorption behavior observed for Pu(V) on SWy-1 Na-montmorillonite over a similar Pu concentration range (Begg et al., 2013). A log-log slope for Pu(IV) sorption to bentonite was calculated and found to be 1.06 ± 0.01 (1 S.E.). A value greater than 1 suggests that surface precipitation (or, indeed, bulk precipitation in our case) of Pu may be occurring (Dzombak and Morel, 1993). The expected concentration range for Pu(IV) intrinsic colloid formation at pH 8 is highlighted in blue in Figure 1 (Neck et al., 2007). Based on thermodynamic considerations, the highest two concentrations used in the current isotherm experiment should lead to Pu(IV) precipitation and colloid formation (Neck et al., 2007). The isotherm slope also

suggests that polymerization/ surface precipitation processes may be occurring in the two highest Pu concentration samples (initial Pu(IV) 10^{-7} and 10^{-8} M). This is consistent with Pu-goethite sorption data of Kersting *et al.* (2011) that exhibited substantial Pu precipitation effects only above 10^{-8} M Pu. Although the effects of precipitation/polymerization appear to be relatively small when examined across 10 orders of magnitude in Pu concentration and on a log scale, they nonetheless affect the apparent sorption behavior of Pu at the two highest Pu concentration samples (initial Pu(IV) 10^{-7} and 10^{-8} M). Accordingly, we recommend that future experiments investigating Pu(IV) environmental adsorption behavior are performed at concentrations $<10^{-9}$ M.

As the isotherm slope is close to unity, sorption can be considered Langmuirian in behavior. However, unlike traditional Langmuir plots which exhibit a flattening of the isotherm as mineral surface sites become saturated, the data remain largely linear at higher concentrations. Previously, Missana and Garcia-Gutierrez (2007) calculated the strong site concentration on bentonite colloids to be 6.1×10^{-8} mol m^{-2} . Given that the experiments were performed with 1 g L^{-1} clay with a surface area of 25 $\text{m}^2 \text{g}^{-1}$ this would suggest a strong site concentration of 1.54×10^{-6} mol L^{-1} which exceeds the highest Pu concentration used (10^{-7} M). As a result, strong site saturation effects are not expected or observed in our experiments. Indeed, we suggest that polymerization/precipitation/surface precipitation effects will become prominent before saturation of strong sites occurs.

Previous work with Pu(IV) and hematite has identified a concentration dependence to the rate of Pu(IV) sorption over a 2 d period (Romanchuk et al., 2011). A one-step, fast adsorption was seen in experiments with 10^{-14} M Pu compared to a two-step adsorption (fast initial sorption followed by slower uptake) at 10^{-10} M Pu. The fast sorption step was attributed to the adsorption

of monomeric Pu(IV) while the slower step was hypothesized to be caused either by diffusion to micropores or by the formation of polymeric Pu(IV) species (Romanchuk et al., 2011). Our current work with clays indicates that regardless of initial sorption rates, the apparent extent of Pu(IV) sorption to bentonite appears broadly independent of initial concentration for the 10^{-7} – 10^{-16} M range on timescales relevant to groundwater transport scenarios. However, there are indications of Pu polymerization/ precipitation reactions in our highest concentration samples and the importance of such reactions is acknowledged.

Log K_d values from the Pu(IV) bentonite sorption isotherm at 120 d range from 4.3 – 4.9. There was a slight increase in calculated log K_d values as a function of Pu(IV) concentration. We attribute this to Pu(IV) intrinsic colloid formation and/or other precipitation processes at the higher concentrations, as discussed previously, rather than the result of concentration-dependent, high sorption affinity sites on the clay (that would exhibit an inverse relationship between K_d and Pu(IV) concentration). The log K_d values observed in this experiment are lower than values for Pu(IV) sorption to bentonite colloids of 5-5.9 measured by Geckeis *et al.* (2004) and 5.39 ± 0.18 measured by Missana *et al.* (2008). However, these previous experiments were performed at pH 9.5 – 9.6, used bentonite colloids of ~200 - 280 nm (which are expected to be entirely composed of montmorillonite) and were performed under anaerobic conditions (Huber et al., 2011). The K_d values observed here likely reflect the contribution of Pu(V), which sorbs weakly to montmorillonite and reduces slowly to Pu(IV) under aerobic conditions (Zavarin et al., 2012). Anaerobic conditions expected in certain repository scenarios are likely to promote greater Pu(IV) stability relative to the aerobic conditions examined herein.

Also shown in Figure 1 is the 30 d sorption isotherm for Pu(IV) on SWy-1 Na-montmorillonite previously reported in Begg *et al.* (2013). Comparison of the Pu(IV) sorption

isotherms for montmorillonite and bentonite shows they are very similar in terms of slope and the extent of Pu sorption. These results show that Pu sorption by a bulk bentonite (92% montmorillonite) is comparable to sorption to pure montmorillonite. However, a slightly higher sorption affinity of Pu(IV) for bentonite than montmorillonite is observed and is more marked at the two highest Pu concentrations. Given that the current work suggests that sorption equilibrium is not achieved until after 67 d (Figure 1 inset), we suggest that this difference is in part due to the different equilibration period in the two experiments: 30 d for montmorillonite and 120 d for bentonite. Indeed, interpolation of bentonite K_d values for the experiment at 10^{-10} M Pu(IV) suggests a 30 d log K_d of 4.1 compared to 4.3 in the equivalent montmorillonite experiment.

3.2 Pu(V) Sorption to Bentonite

The sorption rate of Pu(V) to FEBEX bentonite was studied in triplicate over a 30 day period using an initial concentration of 10^{-10} M (Figure 2). Also plotted in Figure 2 is the sorption of Pu(V) to SWy-1 Na-montmorillonite at an initial concentration of 10^{-9} M reported previously (Begg et al., 2013). Both sorption plots show a similar time dependence, suggesting that the montmorillonite component of the bentonite controls the sorption of Pu(V). The sorption of Pu(V) by bentonite shows an initial rapid uptake with $49.5\% \pm 0.7\%$ removed in the first 48 h. This is followed by a slower uptake over the rest of the experiment with $13.4 \pm 1.6\%$ Pu remaining in solution at 30 d. Applying the first order rate model previously used to describe Pu(V) sorption to SWy-1 montmorillonite to the bentonite-Pu(V) sorption data leads to a surface area normalized sorption rate of $10^{-3.5} \text{ L m}^{-2} \text{ h}^{-1}$ which compares quite favorably with $10^{-2.8} \text{ L m}^{-2} \text{ h}^{-1}$ calculated for montmorillonite (Begg et al., 2013).

The long-term (greater than 30 d) sorption of Pu(V) to bentonite was also studied over an initial concentration range of $10^{-7} - 10^{-11}$ M Pu. Samples were analyzed after 30, 120 and 300 d.

At 30 days, the isotherm appears linear on a log-log plot with slope of 0.92 ± 0.03 (Figure 3). However, the slope of 0.92 indicates that sorption is, in fact, non-linear and appears to exhibit a Freundlich behavior (i.e. $S = K_f C^n$ with $n = 0.92$). However, as these data do not reflect an equilibrium state and sorption is affected by surface mediated reduction rates, the apparent non-linearity most likely reflects a concentration dependence on the surface mediated reduction of Pu(V). This is consistent with the findings of Hixon and Powell (2014) who observed a concentration rate dependence for Pu(V) reduction on hematite between 10^{-8} and 10^{-6} M. At 120 d, the isotherm is truly linear with a log-log slope of 1.03 ± 0.03 . Further, the position of the isotherm has shifted between the two time points, indicating that sorption of Pu from the aqueous phase has continued over the time period between 30 d and 120 d. At 300 d, the isotherm is linear (1.02 ± 0.001), with a further small shift in position relative to the 120 d isotherm.

The Pu(V) sorption data for 30 d and 300 d is compared to the 120 d Pu(IV) sorption data in Figure 4. Over the course of the experiment, the position of the Pu(V) sorption data moves towards the 120 d Pu(IV) sorption data. This observation is consistent with the idea that kinetically limited reduction of Pu(V) on the mineral surface is responsible for the slow, continued uptake of Pu(V) (Begg et al., 2013). Log K_d values for Pu(V) sorption to bentonite after 300 days were 4.42 ± 0.03 . The similarity of the K_d values of both Pu(IV) and Pu(V) over these long timescales demonstrates a convergence of the sorption behavior of Pu on bentonite regardless of initial oxidation state.

By assuming that the slow uptake of Pu from solution seen in the Pu(V) isotherm was due to the slow reduction of Pu(V) on the clay surface, the data from the 30 d, 120 d, and 300 d time points were used to estimate the apparent reduction rate. By using these last three data points, we hope to better isolate the reduction process from the early time sorption of Pu(V) (Begg et al.,

2013). Apparent first order reduction rates were calculated from the slope of the plot of $\ln(C)$ versus time. The average surface normalized apparent reduction rate for these experiments was $10^{-5.3 \pm 1.3} \text{ L m}^{-2} \text{ h}^{-1}$. Interestingly, when the same calculation was applied to the Pu(IV) data collected at 10^{-10} M for 67, 100 and 120 d, the calculated rate was $10^{-4.7 \pm 0.7} \text{ L m}^{-2} \text{ h}^{-1}$. The similarity between the values further suggests that the long term uptake observed in Pu(IV) experiments was due to reduction of residual Pu(V) in solution.

The oxidation state of Pu in solution was monitored for bentonite experiments performed at 10^{-10} M and 10^{-8} M Pu(V) using LaF_3 precipitation (SI Figure S5). In both experiments, the percentage of Pu(V)/(VI) in solution declined between 30 and 120 days. At 300 d, the percent Pu(V)/(VI) in solution was ~ 33 at both 10^{-10} M and 10^{-8} M , respectively. In contrast, in mineral free Pu(V) experiments, LaF_3 analysis showed that the Pu remaining in solution after 300 days was dominated by Pu(V)/(VI) ($96 \pm 10\%$ and $75 \pm 18\%$ for experiments at 10^{-10} and 10^{-8} M , respectively). This difference in oxidation state indicates that interaction of Pu(V) with mineral surfaces results not only in surface mediated reduction of Pu(V) but also leads to a difference in oxidation state distribution in solution. This change in the oxidation state of solution Pu in the presence of bentonite indicates that a solid:solution sorption equilibrium is established with respect to both Pu(V) and Pu(IV) under the present experimental conditions. This is in accordance with the recently proposed model for Pu(V) oxidation state distribution in the solid/aqueous phase following sorption on Savannah River sediments (Powell et al., 2014).

3.3 Desorption of Pu From Bentonite

A flow cell experiment was performed to investigate the desorption of Pu from bentonite. Prior to desorption, Pu(IV) at an initial concentration of $3 \times 10^{-10} \text{ M}$ was equilibrated with 1 g L^{-1} bentonite in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution at pH 8 for 21 days under aerobic

conditions. After this period, the calculated $\log K_d$ for Pu(IV) sorption was 4.1, which is consistent with the sorption behavior of the Pu(IV) isotherm experiment performed at 10^{-10} M (4.4 at 67 d, 4.8 at 120 d).

The desorption of Pu from bentonite is plotted in terms of the cumulative fraction of total Pu desorbed in Figure 5. Also included in this plot are the data from a parallel experiment at pH 8 performed with SWy-1 Na-montmorillonite. Much (but not all) of the sharp increase in the cumulative desorbed Pu between 0 and ~ 2.5 chamber volumes (cv) in both plots represents removal of aqueous Pu remaining in solution following the sorption period. This Pu is displaced from the flow cell over the course of several cv (i.e. tailing). Comparison of a theoretical non-reactive tracer dilution curve under the initial flow conditions with the observed Pu concentrations in the bentonite experiment shows that the two curves begin to deviate within 1.2 cv (SI Figure S6). The deviation demonstrates an excess of Pu in the effluent from that which would be expected by dilution alone, indicating that Pu desorption from bentonite contributes significantly to the overall Pu breakthrough after just one chamber volume.

Both the shape of the plots and the final amounts of Pu desorbed are very similar for FEBEX bentonite and SWy-1 montmorillonite. This behavior is not unexpected in the context of the similarity of Pu sorption behavior between bentonite and montmorillonite. This plot further suggests that it is the montmorillonite component of the FEBEX bentonite that is controlling the desorption behavior of Pu in this experiment. The slope of the cumulative desorption plot for both bentonite and montmorillonite continues to rise over the duration of the experiment, indicating that Pu is still being desorbed from the mineral surfaces at the termination of the flow period.

We calculated an apparent $\log K_d$ at the end of the flow cell experiment of 6.0 based on the Pu concentration in the final effluent fraction, accounting for the net removal of 16.5 % of the Pu from the system (Figure 5), and assuming no change in solid: solution ratio. This K_d value is much larger than the values in the Pu(IV) sorption experiments after 120 d equilibration (4.3 – 4.9). This indicates that on the timescale of the flow portion of the experiment (chamber residence time < 1 d) desorption of Pu appears to be rate limited. Following the cessation of the 12 d flow cell desorption experiment, the Pu-bentonite suspension was allowed to equilibrate under no-flow conditions (0.0 mL min^{-1}) for two months. After 60 d, the $\log K_d$ was calculated to be 4.8, which is in good agreement with the 120 d sorption K_d values. This similarity indicates Pu-bentonite sorption reversibility over extended time periods. The slow approach to apparent desorption equilibrium in these experiments (i.e. on timescales greater than 1 d) is consistent with previous work looking at Pu desorption from montmorillonite, bentonite colloids and argillites (Huber et al., 2011; Latrille et al., 2006; Lu et al., 2003). The slow desorption kinetics observed here highlight the need to consider both desorption rates and desorption equilibrium conditions when predicting Pu transport.

Oxidation state analysis using LaF_3 precipitation was performed on flow cell effluent during the flow period, after remnant aqueous Pu from the sorption step had been removed from the cell. The analysis indicated that the desorbed Pu was predominantly in the Pu(V)/(VI) oxidation state ($90 \pm 10\%$). This would suggest that in the short term, desorption of Pu(V) from the mineral surface is favored over Pu(IV). Further, given that Pu(IV) was initially adsorbed on the bentonite and is expected to be favored on the mineral surface, this result also suggests that the oxidation of Pu(IV) to Pu(V) is important for the desorption of Pu. However we cannot verify this without direct oxidation state analysis of Pu on the mineral surface. If Pu(IV) oxidation is involved in the

desorption reaction, Pu desorption rates may be substantially lower under anoxic conditions where Pu(IV) oxidation is inhibited. Such an inhibition may further exacerbate mineral-colloid facilitated transport under anoxic repository conditions. Interestingly, oxidation state analysis of the Pu supernatant after the 2 month post flow cell equilibration period indicated that the aqueous Pu was predominantly Pu(IV). This suggests that changes in Pu oxidation state are responsible for differences in short term and long term desorption behavior of Pu from bentonite.

4. CONCLUSIONS

We investigated the sorption behavior of Pu(IV) to FEBEX bentonite over the concentration range $10^{-7} - 10^{-16}$ M to determine if Pu sorption behavior at concentrations used in typical laboratory experiments ($10^{-7} - 10^{-11}$ M) was comparable to typical environmental concentrations ($\leq 10^{-12}$ M). On the timescale of months, the affinity of Pu(IV) for bentonite appears to be independent of concentration. However, slight non-linear behavior suggests that polymerization/precipitation reactions contribute to the apparent sorption at Pu(IV) concentrations $\geq 10^{-8}$ M. The sorption behavior of Pu(IV) to FEBEX bentonite is very similar to that previously observed for Pu(IV) sorption to colloidal SWy-1 Na-montmorillonite.

Pu(V) sorption to bentonite is also linear. However, Pu(V) sorption exhibits a much more significant time-dependence. The time-dependence is indicative of rate limited reduction of Pu(V) on clay minerals. The reduction rate constants determined based on these data agree with previously published reduction rates of Pu(V) on SWy-1 montmorillonite. The favorable comparison between Pu(IV) and Pu(V) behavior in the presence of FEBEX bentonite and SWy-1 Na-montmorillonite highlights the dominant role of montmorillonite phases in controlling Pu sorption/desorption reactions on FEBEX bentonite. By extension, this also suggests that the

accessory minerals in the bentonite do not significantly alter the sorption/desorption behavior of Pu.

The kinetics of desorption are of key importance for predicting the mobility of Pu in groundwater environments, especially if Pu is associated with colloidal mineral phases. The observation that after 2 months of desorption the K_d value was similar to the K_d value observed after 21 d sorption indicates rate-limited yet truly reversible Pu sorption under these experimental conditions. These experiments were performed under aerobic conditions and Pu(IV) reoxidation appears to play an important role in the observed desorption behavior. Aerobic conditions may not be present in all nuclear waste repository scenarios (e.g. Duro et al., 2014). As a result, future work should build on these results by examining Pu sorption/desorption behavior across a wider range of geochemical conditions.

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LIST OF FIGURE CAPTIONS

Figure 1. 120 d Pu(IV) sorption isotherm for FEBEX bentonite (1 g L^{-1}) in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution at pH 8 (open black diamonds). Inset shows time series data for experiments at 10^{-7} and 10^{-10} M initial Pu(IV) to indicate apparent adsorption equilibrium at 120 d. Also shown are data for 30 d Pu(IV) adsorption isotherm for SWy-1 Na-montmorillonite (1 g L^{-1}) in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution at pH 8 (closed black diamonds) (Begg et al., 2013). Lines are shown to guide the eye only. Blue shaded area represents expected concentration for Pu(IV) colloid formation (Neck et al., 2007). Error bars, based on LSC counting uncertainties (1σ) for bentonite experiments and 1σ for quadruplicate montmorillonite experiments, are within range of the symbols used.

Figure 2. Sorption of Pu(V) to FEBEX bentonite (1 g L^{-1} ; open red triangles) and SWy-1 Na-montmorillonite (1 g L^{-1} ; closed red triangles) plotted as percentage of Pu removed from solution vs time. Initial Pu concentrations were 10^{-10} M for bentonite and 10^{-9} M for montmorillonite. Error bars are based on 1σ for triplicate bentonite experiments and 1σ for quadruplicate montmorillonite experiments and where not visible are within range of symbols used.

Figure 3. Pu(V) sorption isotherm for FEBEX bentonite (1 g L^{-1}) in 0.7 mM NaHCO_3 , 5 mM NaCl buffer solution at pH 8. Different symbols represent sampling at different time points: 30 d (open red triangles), 120 d (open blue triangles), 300 d (open green triangles). Lines are to guide the eye only. Error bars based on LSC counting uncertainties (1σ) are within range of symbols used.

Figure 4. Sorption of Pu(V) to FEBEX bentonite (1 g L^{-1} , pH 8) at 30 d (open red triangles) and 300 d (open green triangles), compared with Pu(IV) sorption to FEBEX bentonite (1 g L^{-1} , pH 8) at 120 d (open black diamonds). Lines are to guide the eye only. Error bars based on LSC counting uncertainties (1σ) are within range of symbols used.

Figure 5. Cumulative fraction of Pu removed from bentonite (open black diamonds) and montmorillonite (closed black diamonds) for the flow cell experiments. Error bars based on LSC counting uncertainties (1σ) are within range of symbols used.

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5