Pu(IV) Intrinsic Colloid Stability in the Presence of Montmorillonite at 25 & 80 °C

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Chapter 3. Stability of Plutonium(IV) Intrinsic Colloids in the Presence of Montmorillonite at 25 and 80°C

3.1 Introduction

The large volumes of plutonium (Pu) designed for storage in high-level nuclear waste repositories are predicted to be a dominant long-term dose contributor under certain scenarios (Kaszuba and Runde, 1999; Office of Civilian Radioactive Waste Management, 2002). Once it is deposited in the environment, Pu has been shown to migrate in the subsurface associated the colloidal fraction of the groundwater (e.g., Kersting et al., 1999). Colloid-facilitated transport of Pu in both groundwater and surface water has been documented at several DOE sites (Kersting et al., 1999; Santschi et al., 2002). Pu sorbed to iron oxide colloids has also been detected over 4 km from its original source in Mayak, Russia (Novikov et al., 2006). These studies indicate that the Pu associated with mobile colloids has moved on the scale of kilometers. Despite the recognized importance of colloid-facilitated transport of Pu, little is known about the geochemical and biochemical mechanisms controlling its formation and stability over the range in concentrations expected in the environment. For example, how is Pu transported along flow paths that span high Pu concentrations at the source to extremely low concentrations encountered at significant distances down gradient? Without a conceptual understanding of the dominant processes and a quantitative understanding of the relevant reaction chemistry, current transport models cannot effectively predict Pu migration rates.

Pu can be associated with the colloidal fraction of groundwater in two different forms. Pu can migrate as either an 'intrinsic' colloid or sorbed to a naturally occurring inorganic, organic or microbial species. At high concentrations where actinide ions in solution exceed the solubility product, Pu can hydrolyze to form intrinsic Pu(IV) colloids (or sometimes, eigen-colloids) (Kim, 1991; Neck et al., 2007). As an intrinsic colloid, Pu transport will be controlled by the stability (both physical and chemical) of the Pu(IV) intrinsic colloid. At low concentrations Pu tends to sorb to inorganic or organic colloids, resulting in the formation of a pseudocolloid, and transport is determined by the Pu sorption/desorption rates on that colloidal material. Both forms of Pu colloids may exist simultaneously under some subsurface conditions. We currently do not know whether intrinsic colloids, initially formed under high Pu concentrations, will remain stable and migrate down-gradient away from their near-field environment, or if they will dissolve and the aqueous Pu will sorb to organic or inorganic or microbial colloids. Efforts to model the transport of Pu from a near-field environment to lower concentrations in the far-field are currently limited due to the lack of understanding of whether intrinsic Pu colloids will persist along the flow path.

At low Pu concentrations (below solubility), colloid-facilitated transport is likely to be controlled by pseudocolloids. However, the biogeochemical processes controlling Pu transport under these conditions, and the sorption/desorption kinetics in particular, have not been adequately quantified. The identity of naturally occurring inorganic colloids will be a function of the host rock mineralogy. Among the most ubiquitous inorganic colloids are aluminosilicate clays that are commonly observed as mobile colloids due to their inherently small particle size and prevalence as alteration minerals from original host rock material (Kersting et al., 1999). Clays are known to sorb Pu (Bertetti et al., 1998; Keeney-Kennicutt and Morse, 1985; Kozai et al., 1996; Kozai et al., 1993; Lujaniene et al., 2007; Powell et al., 2004, 2005; Powell et al., 2008; Sabodina et al., 2006; Sanchez et al., 1985; Turner et al., 1998). In addition, the proposed use of bentonite within some engineered barrier systems scenarios for high-level nuclear waste repositories provides additional importance to understanding Pu interaction with smectite aluminosilicate clays (Sabodina et al., 2006). Smectite clay may represent a key phase that will control transport of Pu in repository near and far fields.

In Chapter 2, we examined the sorption behavior of Pu in the presence of a common Fe-oxide mineral, goethite at 25 and 80°C at concentrations both above and below solubility. In this chapter, we examine the behavior of Pu in the presence of a common smectite clay mineral, montmorillonite at 25 and 80°C at concentrations both above and below the solubilty of PuO_2 (am,hyd) intrinsic colloids. We designed our experiments to evaluate the stability of intrinsic Pu colloids in the presence of montmorillonite as concentrations decrease, similar to transport along a flow path.

We employed dialysis membranes in an effort to completely segregate intrinsic Pu nano-colloids (2−5 nm) from montmorillonite colloids (>100 nm) and allow aqueous Pu to establish equilibrium between both colloidal phases. Using the dialysis membrane approach, we were able to separate the dissolution of Pu intrinsic nano-colloids from the formation of Pu/clay pseudo-colloids and examine each step indivdually. The kinetics of dissolution of intrinsic Pu colloids in the presence and absence of clay colloids were observed and compared. The results of these efforts provide a clearer understanding of how Pu can migrate over significant temporal and spatial scales.

3.2   *Experimental Approach*

Batch sorption has been the most common method used to measure the affinity of a contaminant for a mineral surface. Traditionally, a known amount of adsorbate is added to a liquid suspension containing a sorbent, and the aqueous concentration of adsorbate is measured after equilibrium is reached. The resulting affinity of the adsorbate for the sorbent is reported using equation 3-1:

$$K_d = (C_{init}-C_{final})/C_{final} \ *V/m \qquad\qquad (3\text{-}1)$$

where C_{init} and C_{final} are initial and final aqueous concentration of adsorbate (mol/L), respectively, V is the volume of liquid (mL), and m is the mass of adsorbent (g). However, if the adsorbate is involved in other processes that also form solid phases (i.e., colloid formation or precipitation), the apparent K_d cannot address the fundamental sorption processes and may lead to a misinterpretation of experimental observations. In order to distinguish between precipitated, colloidal, and sorbed states of Pu, we employed dialysis membranes to segregate pseudocolloids from intrinsic colloids.

Dialysis membranes are commonly used to separate suspended solutes or particles of different dimensions in a liquid mixture. Desirable size separation by dialysis can be achieved by selecting the membrane pore-size molecular weight cutoff (MWCO). For example, membrane pore sizes ranging of 0.5 to 0.6 kilo Daltons (kD) are approximately equivalent to 1 to 2-nm pore sizes. In the case of Pu, dialysis membranes provide a unique function to segregate aquo (<1 nm), intrinsic nano-colloids (2−5 nm), and sorbed pseudocolloids or precipitates (>100-nm mineral phases).

Intrinsic Pu(IV) colloid stability was evaluated using the experimental design shown in Figure 3-1. Briefly, PuO_2 intrinsic colloids are placed inside the dialysis bag. The clay colloids are placed outside the dialysis bag. Thus, the colloidal montmorillonite is isolated from the intrinsic Pu(IV) colloids while exchange of truly aqueous (non-colloidal) ions is permitted. Pu detected outside the dialysis membrane over time represents dissolution of the initial Pu(IV) intrinsic colloids and diffusion across the dialysis membrane. In the presence of montmorillonite, the dissolved Pu can either remain in solution or sorb. The dissolution rate of Pu(IV) intrinsic colloids is expected to be a function of solution pH, temperature, and composition/crystallinity of the colloids. The sorption rate of Pu to montmorillonite is affected by the Pu speciation, solution Eh/pH, ionic strength, and temperature.

This novel experimental design enables us to test the stability of intrinsic colloids relative to adsorbed species on any minerals and over a range of solution conditions. By monitoring solution conditions as a function of time, we are also able to quantify the reaction kinetics as the solution approaches equilibrium. Quantifying the stability of intrinsic colloids is critical to accurately predicting the down-gradient transport behavior of Pu at near-field conditions.

3.3   Materials and Methods

3.3.1   Pu stock solution

Pu stock solutions with two different Pu isotopic ratios were used. A relatively pure alpha-emitting ^{238}Pu stock solution was used in low- and intermediate-Pu-concentration samples. The isotopic ratios in mass percentage for ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu were 76.83%, 21.03%, 2.01%, and 0.142%, respectively. The major isotope contributing to alpha activity in this stock was ^{238}Pu (~99.87% by activity). The second Pu stock solution, used in the high-Pu-concentration experiments, was a ^{242}Pu solution spiked with ~1% of the ^{238}Pu. The mass percentages of the resulting ^{242}Pu stock for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu were 0.75%, 0.21%, 0.13%, 0.04%, and 98.87%, respectively. The major isotopes contributing to alpha activity in this stock were ^{238}Pu (96.75%) and ^{242}Pu (2.93%). Pu stock solutions were purified using AG1x8 100-200 mesh anion exchange resin and filtered through a 3kD MWCO filter. The oxidation state of Pu was confirmed using both UV/VIS and solvent extraction. The aqueous Pu(IV) starting solution was prepared by diluting the stock solution into a pH 8 buffer solution and gradually adding microliters of NaOH (1N or 6N) to adjust pH to ~pH 8.

The intrinsic PuO$_2$ nano-colloids were prepared by neutralizing Pu(IV) stocks using NaOH solution and adjusting the pH to between 9−10. This is the same method used to prepare amorphous PuO$_2$ for the solubility studies used by Neck et al. (2007). After aging for more than a week, the Pu colloids were centrifuged at an RCF of 9168 for 1 hour, and the supernatant was removed. The Pu colloid particle size cut-off based on centrifugation was 14 nm. However, the fundamental particle size of intrinsic Pu nano-
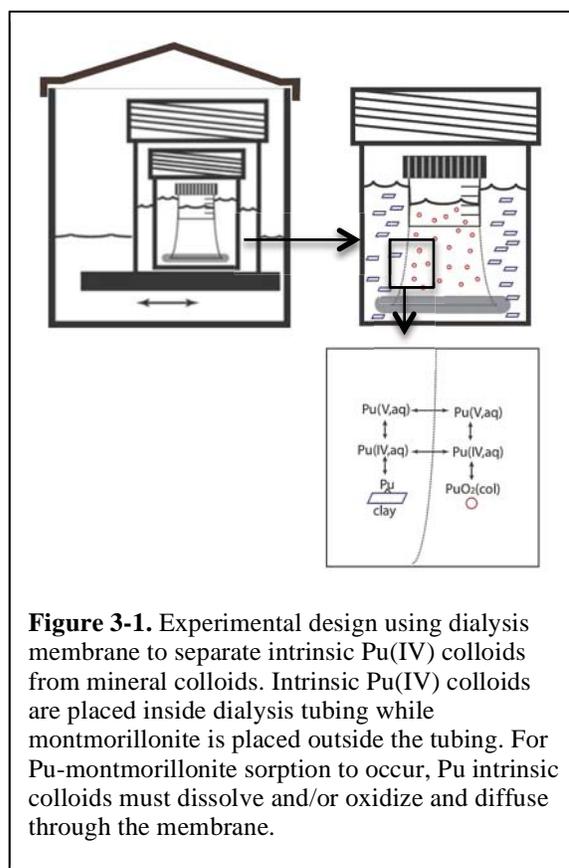
Figure 3-1. Experimental design using dialysis membrane to separate intrinsic Pu(IV) colloids from mineral colloids. Intrinsic Pu(IV) colloids are placed inside dialysis tubing while montmorillonite is placed outside the tubing. For Pu-montmorillonite sorption to occur, Pu intrinsic colloids must dissolve and/or oxidize and diffuse through the membrane.
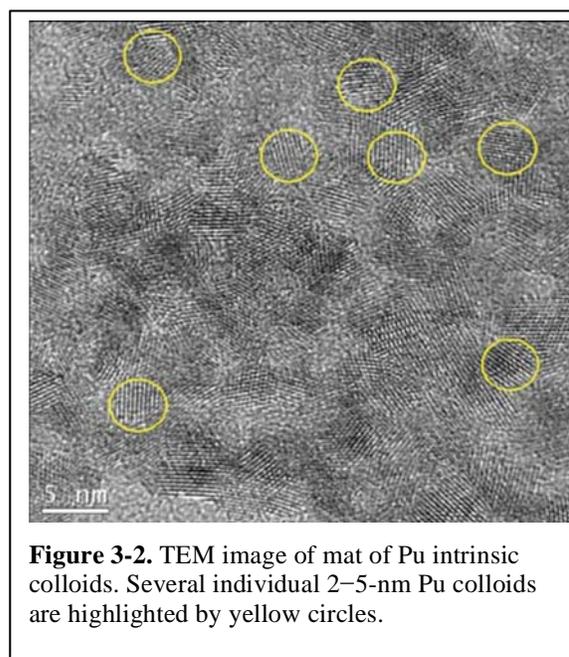
Figure 3-2. TEM image of mat of Pu intrinsic colloids. Several individual 2−5-nm Pu colloids are highlighted by yellow circles.

colloids prepared in this study is much smaller, on the order of 2−5 nm (Figure 3-2). The Pu colloids were re-suspended in Milli-Q water. The Pu colloid starting solutions were prepared by adding a spike of Pu colloids into the pH 8 buffer solution without further pH adjustment. The concentration of soluble Pu in the Pu colloid starting solutions, measured in 3kD MWCO filtrate by LSC, were 1~3% of the total colloid concentration.

3.3.2   Montmorillonite

SWy-1 montmorillonite (Clay Minerals Society) was pre-treated using 1 mM HCl (to dissolve any carbonate minerals) followed by addition of 0.1% of H_2O_2 (to oxidize organic contaminants and reduced metals (e.g., Fe^{2+}). The treated montmorillonite was centrifuged to remove excess liquid, and the wet paste was transferred to a 6−8-kD MWCO dialysis tube suspended in 0.01 M NaCl solution to produce a homoionic Na-montmorillonite. The clay minerals were dialyzed for seven days, and the NaCl solution was changed at least once per day. The clay minerals were then suspended in Milli-Q water and centrifuged to obtain the fraction of particle sizes from 50 nm to 2 microns. The wet solids were dried at 40°C until a constant weight was obtained. A stock montmorillonite suspension was made by mixing 4 g of dried montmorillonite in 400 mL of pH 8 buffer solution (10 g/L). The surface area of montmorillonite measured by N_2(g)-BET was 31.45 ± 0.17 m^2/g, which is comparable to the reported value of 31.8 m^2/ g (Clay Minerals Repository).

3.3.3   Batch dialysis experiments

A total of 14 dialysis experiments were performed to test the experimental design and quantify the stability of intrinsic Pu(IV) colloids in the presence of montmorillonite (Table 3-1). The experiments were performed at two temperatures, 25°C (7 experiments) and 80°C (7 experiments), to evaluate the effect of temperature on intrinsic colloid stability. At each temperature, Pu was initially added either as an aqueous phase (to test simple diffusion and sorption of Pu) or as an intrinsic colloid (to test intrinsic colloid dissolution, diffusion and sorption of Pu). The initial Pu concentrations bracketed the PuO_2(am, hyd) solubility (~5×10^{-9} M) (Neck et al., 2007). In addition, montmorillonite-free solutions (spiked blanks) with initial Pu concentrations below and near PuO_2(am, hyd) solubility were used for comparison with sorption experiments and evaluation of Pu loss to container walls and the dialysis membrane.

All batch experiments were conducted in 450-mL Teflon jars with air-tight closures. 225 mL of pH 8 buffer solution (pH 8, 5 mM NaCl/0.7 mM $NaHCO_3$) was mixed with 25 mL of montmorillonite stock suspension to yield a 250-mL montmorillonite suspension at a solid to liquid ratio of 1g/L. A sealed dialysis tube containing 30 mL of either aqueous Pu(IV) or intrinsic PuO_2 nano-colloids was then placed in the 250 mL pH buffer solution with or without (spiked blanks) montmorillonite. The 450-mL Teflon jars were submerged in 1-L Teflon containers filled with Milli-Q water to minimize evaporative losses and provide secondary containment to the radioactive samples. Over the course of the experiment, the 25°C samples were placed on a top-loading orbital shaker, and the 80°C samples were submerged in a heated water bath (Innova 3100) and shaken at an orbital speed of 100 rpm.

Each experiment was sampled as a function of time over a three-month period. At each sampling interval, aliquots of the montmorillonite suspension were collected, centrifuged and analyzed for total Pu, Pu in the supernatant, and pH. The montmorillonite concentration in the suspension was also measured based on light scattering at a wavelength range of 300−500 nm using UV-VIS spectrometry (Cary 500, Varian).

Table 3-1. Experimental conditions for Pu(IV) samples at 25 and 80 °C.

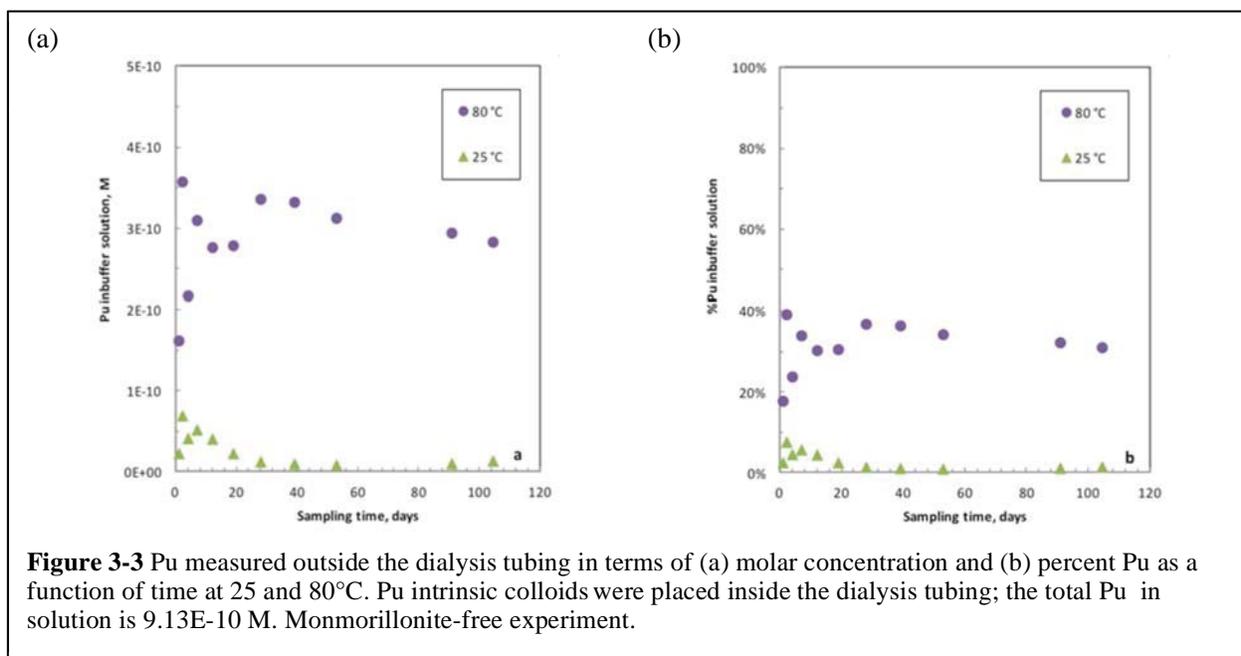|	Expt	Pu colloids	Swy-1 Montmorillonite	Expt	Pu(IV, aq)	Swy-1 Montmorillonite
		mol/L	g/L		mol/L	g/L
	1	1.13E-11	1	9	5.93E-12	1
25 °C	2	9.09E-10	1	10	6.20E-10	1
	3	2.01E-7	1	11	6.52E-12	0
	4	9.13E-10	0			
	5	1.14E-11	1	12	5.93E-12	1
80 °C	6	8.31E-10	1	13	6.20E-10	1
	7	2.01E-7	1	14	6.52E-12	0
	8	9.13E-10	0			

Pu concentrations listed above were calculated respect to total volume of 280 mL. The initial Pu concentratons inside the dialysis membranes were ~9 times higher than listed values.

3.4   Results and Discussion

3.4.1   Stability of Pu intrinsic colloids in the absence of clay at 25 and 80°C

Prior to performing the dialysis experiments outlined in Table 3-1, spiked blanks containing ^{3}H and aqueous Pu(V) were used to test the experimental design and determine diffusion rates of ^{3}H and Pu(V) through the dialysis membranes at 25 and 80°C (data not shown). Pu(V) was used instead of Pu(IV) to reduce the likelihood of Pu sorption to container walls. The diffusion of both ^{3}H and Pu(V) was rapid, and steady state was achieved within five hours at both temperatures. The diffusion rate across the membrane of both the ^{3}H and aqueous Pu(V) appeared to be slightly slower at 80°C than that at 25°C. This was most likely a function of mixing rates at the two temperatures and temperature-dependent behavior of the dialysis membrane material (regenerated cellulose). However, at both temperatures, diffusion was determined to be fast enough that it would not be rate limiting when evaluating colloid stability on the scale of days.

PuO_2 intrinsic colloid stability in the absence of montmorillonite (i.e., montmorillonite-free spiked blanks) is presented in Figure 3-3. The initial Pu concentration in the dialysis bag was 7.8E-9 M, which is at the solubility limit of colloidal Pu. However, the concentration of the Pu colloids with respect to total solution volume (255 mL) is 9.13E-10 M (Table 3-1). This is below the solubility of Pu colloids (Neck et al., 2007), suggesting that the intrinsic colloids should dissolve over time. However, the results presented in Figure 3-3 are inconclusive. Figure 3-3a indicates that Pu concentrations outside of the dialysis membrane increase at early time (days), but then decreases at later times (weeks−months) at both 25 and 80 °C. Sorption to container walls and membrane material appear to be affecting the long-term behavior of Pu. Figure 3-3b indicates that approximately 6% and 37% (25 and 80°C, respectively) of the total PuO_2 resides in solution outside the dialysis membrane at early time. Base on this early time data, it appears that the dissolution rate of Pu colloids is much higher at 80°C than that at 25°C. It suggests that Pu intrinsic colloids tested in this study will not be stable at Pu concentrations below their solubility and intrinsic colloid formation appears to be reversible. However, the stability of PuO_2 intrinsic colloids is a function of its morphology, crystallinity, and aging, and further investigations on Pu colloids stability are continuing by evaluating different formations of the Pu oxide. We are also conducting additional experiments to quantify the sorption of aqueous Pu onto the dialysis membranes and container walls.
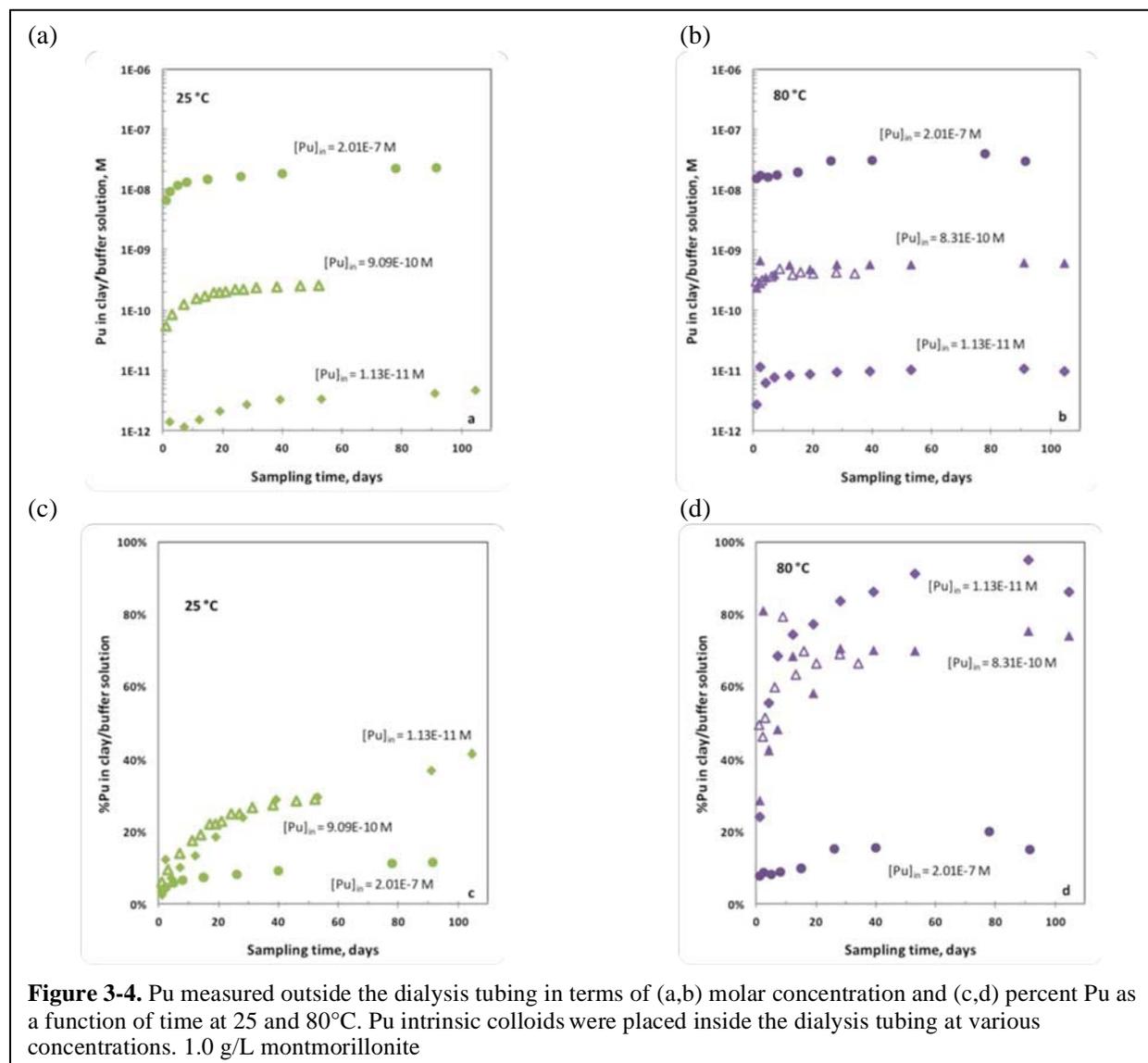
Figure 3-3 Pu measured outside the dialysis tubing in terms of (a) molar concentration and (b) percent Pu as a function of time at 25 and 80°C. Pu intrinsic colloids were placed inside the dialysis tubing; the total Pu in solution is 9.13E-10 M. Monmorillonite-free experiment.

3.4.2   Dissolution of Pu intrinsic colloids in the presence of clay at 25°C and 80 °C.

The dissolution of PuO_2 intrinsic colloids and sorption of Pu to montmorillonite were examined using three different initial colloidal Pu concentrations (10^{-11}, 10^{-9} and 10^{-7}M) (Table 3-1) that bracket the range of stability identified in Neck et al. (2007). The Pu concentration in the clay suspension is plotted as a function of time and temperature in Figure 3-4. This measurement includes both the aqueous and sorbed Pu. Depending on the initial temperature and Pu concentration, aqueous Pu concentratons were between 1 and 15% of the total Pu in the suspensions. Figure 3-4 shows the total concentration of Pu outside the dialysis bag as both a concentration and a percentage. For all three initial Pu concentrations and both temperatures, the Pu concentrations initially increase rapidly and then gradually reach a plateau. Although the intrinsic colloids dissolved at both temperatures, the intrinsic colloids dissolved at a faster rate at 80°C than at 25°C. Figure 3-4b shows that the dissolution at 80°C reached a plateau within ~80 days. However, intrinsic Pu colloids continue to dissolve during the period (90−104 days) at 25°C, but at a slower rate than in the first few weeks (Figure 3-4a). After 100 days, the total concentration of Pu dissolved at 25°C is less than at 80°C for a given Pu concentration. This demonstrates that the rate of Pu colloids dissolution increases with increasing temperature. When the concentration of PuO_2 colloids is below its solubility (10^{-11} M), we would expect that the intrinsic colloids dissolve than when the total Pu concentration exceeds the solubility (10^{-7} M) of Pu colloids. This is what we observed at eleveated temperature. At room temperature, the dissolution rate is may be too slow to observe the total dissolution within our 100 day time frame. When the initial concentratons of Pu approached or exceeded solubility (10^{-9} and 10^{-7} M), a much smaller fraction of intrinsic colloids dissolved. (Figure 3-4).

By comparing the behavior of intrinsic Pu colloids in the presence versus the absence of clay colloids (Figure 3-5), it is clear that the dissolution of the intrinsic colloids is facilitated by the presence of clay. Montmorillonite provides a "sink" for aqueous Pu which creates a strong gradient for the dissolution of colloidal Pu. Pu sorption onto montmorillonite results in the formation of Pu-montmorillonite pseudocolloids. Thus, the results indicate that Pu-montmorillonite pseudocolloids may be more stable

than Pu intrinsic colloids when concentrations drop below Pu solubility. At higher temperatures, the rate of dissolution is increased.

Figure 3-4. Pu measured outside the dialysis tubing in terms of (a,b) molar concentration and (c,d) percent Pu as a function of time at 25 and 80°C. Pu intrinsic colloids were placed inside the dialysis tubing at various concentrations. 1.0 g/L montmorillonite

3.4.3   Aqueous Pu(IV) sorption onto montmorillonite at 25 °C and 80 °C

To test our experimental design and evaluate how the initial state of Pu (colloidal versus aqueous) affects sorption kinetics on montmorillonite, dialysis experiments were performed using aqueous Pu(IV). In this case, the kinetics of Pu sorption to montmorillonite may be controlled by Pu(IV) diffusion across the membrane and/or Pu(IV) sorption onto the clay. However, based on the ^{3}H and Pu(V) spiked blank experiments, diffusion rates for our experimental design are very fast (hours).

At the Pu(IV) concentrations substantially below solubility of PuO_2(am, hyd.) (i.e. 5.93E-12 M, Table 3-1), potential precipitation of PuO_2(am, hyd) or formation of colloidal PuO_2 is essentially eliminated. Therefore, quantitative diffusion of Pu(IV) and sorption to montmorillonite is expected. This is

experimentally in the 80°C data (Figure 3.6b). At 25°C, only 60% of the Pu(IV) is associated with montmorillonite at 100 days (Figure 3-6a). Nearly complete loss of Pu from the aqueous phase in the absence of clay at 25°C spiked blank solutions suggests that sorption to container walls and dialysis membrane effectively competes with montmorillonite for the sorption of Pu.

At Pu(IV) concentrations that approach PuO_2(am, hyd.) solubility, formation of colloidal PuO_2 cannot be ruled out. Indeed, after termination of sorption experiments, the Pu(IV) solution inside the dialysis tubes was analyzed for both aqueous and colloidal Pu species and Pu colloids were detected. A more detailed understanding of conditions under which colloidal Pu may form is warranted.

The kinetics of aqueous Pu(IV) sorption to montmorillonite at 25°C are faster than that in the colloidal PuO_2 experiments (Fig. 3-4c). Therefore, we conclude that PuO_2 dissolution is the rate limiting step in our
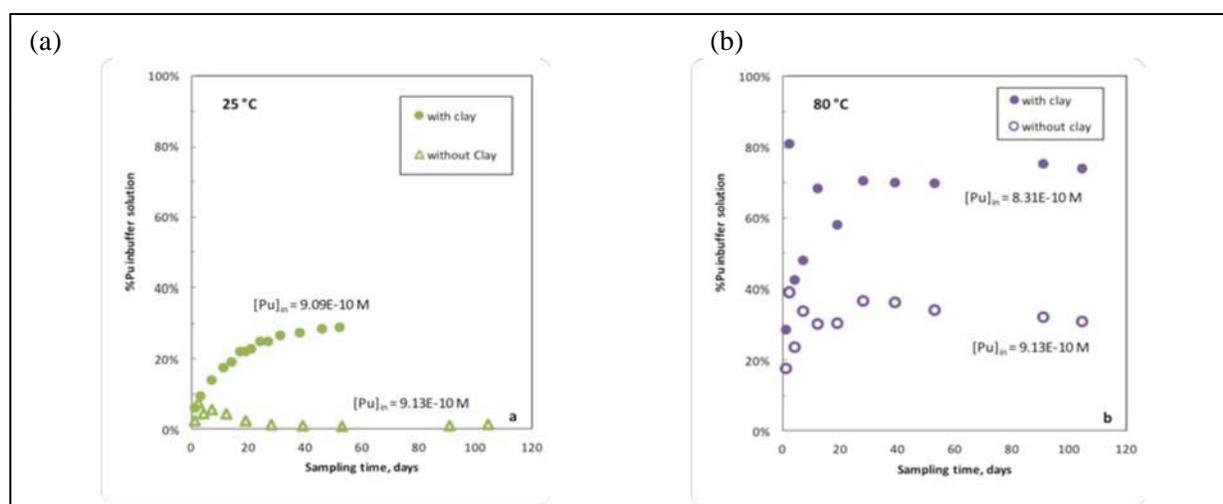
Figure 3-5. Pu measured outside the dialysis tubing at (a) 25°C and (b) 80°C as a function of time. Pu intrinsic colloids were placed inside the dialysis tubing. Comparison of montmorillonite-free (open circles) and 1.0 g/L montmorillonite (filled circles) experiments.
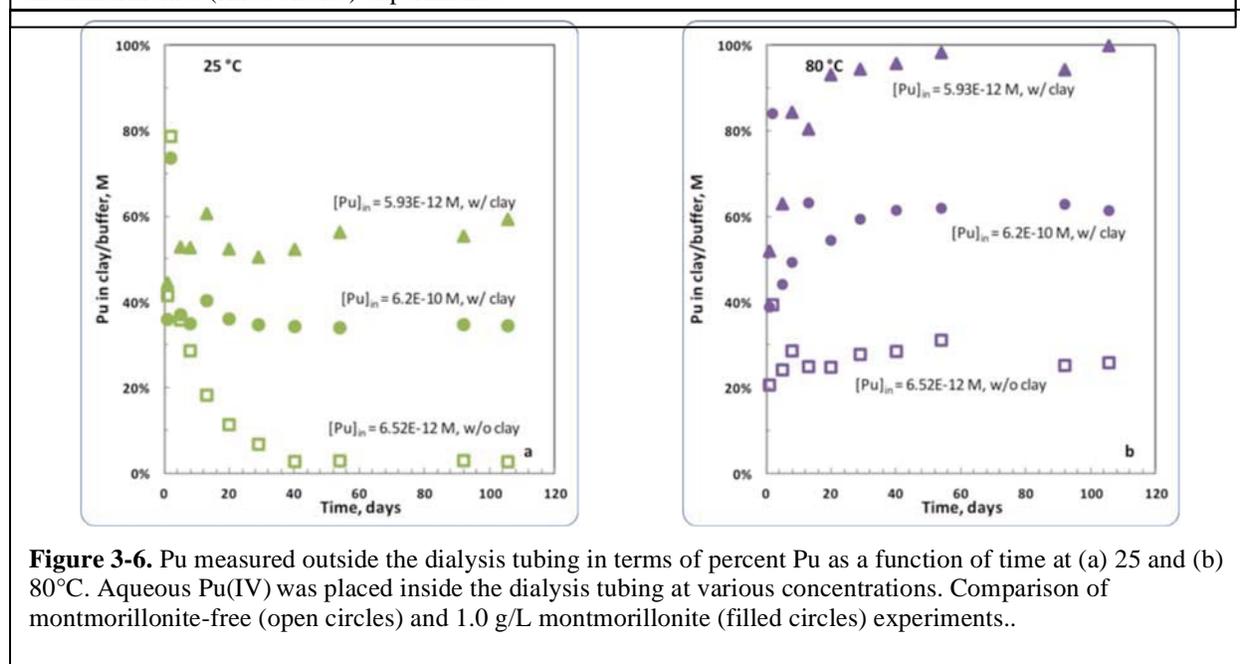
Figure 3-6. Pu measured outside the dialysis tubing in terms of percent Pu as a function of time at (a) 25 and (b) 80°C. Aqueous Pu(IV) was placed inside the dialysis tubing at various concentrations. Comparison of montmorillonite-free (open circles) and 1.0 g/L montmorillonite (filled circles) experiments..

dialysis system at room temperature.

The kinetics of aqueous Pu(IV) sorption to montmorillonite at 80°C, however, are very similar to what we observed in the colloidal PuO_2 experiments. On the timescale examined here, it appears that dissolution of colloidal PuO_2 at 80°C is fast.

3.4.4   Temperature effects on the sorption K_d

In all Pu-montmorillonite sorption experiments, both aqueous and total Pu was measured in the clay suspensions. These data are used to evaluate the sorption of Pu on montmorillonite (Figure 3-7) as a function of temperature. The results indicate that the affinity of Pu for montmorillonite increases with temperature. As a result, the K_d increases with temperature.

This result suggests that sorption of Pu on montmorillonite clay minerals is endothermic. In fact, we also observed this endothermic character in our previous Pu-goethite sorption experiments (see Chapter 2 of this report). Investigations that evaluate the temperature effects on actinides sorption onto minerals are scarce. However, this type of thermodynamic data is important to help us understand behavior of actinides interactions with minerals at near-field conditions near radiological waste repositories.
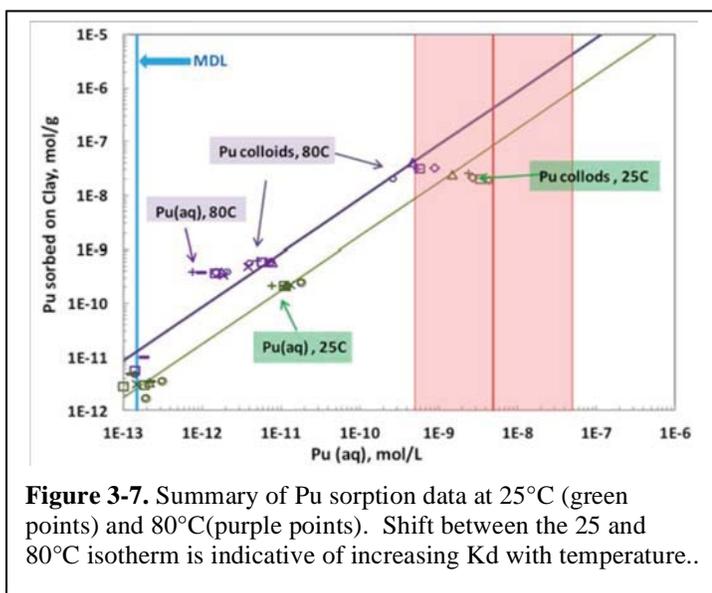
Figure 3-7. Summary of Pu sorption data at 25°C (green points) and 80°C(purple points). Shift between the 25 and 80°C isotherm is indicative of increasing Kd with temperature..

3.5   Conclusions

In this study, we have examined the stability of Pu intrinsic colloids in the presence of montmorillonite at 25 and 80 °C under atmospheric conditions. Dialysis membranes were used to segregate Pu intrinsic nano-colloids (2−5 nm) from montmorillonite colloids (>100 nm) and allow Pu aquo (<1 nm) species to establish equilibrium between both colloidal phases. Intrinsic Pu colloids were found to dissolve quickly, particularly when a strong thermodynamic gradient is provided (i.e., Pu sorption to montmorillonite). At 25°C, the dissolution of colloidal Pu is the rate limiting step in the dissoluton-sorption process. Nevertheless, formation and dissolution of intrinsic PuO_2 colloids appears to be reversible. Pu colloid dissolution rates and the affinity for montmorillonite increase with temperature. The formation of Pu-montmorillonite pseudocolloids is favored over Pu intrinsic colloids at both temperatures. The reversible nature and relatively fast dissolution rates suggest that migration of Pu intrinsic colloids may be limited. However, the nature and form of Pu colloids and its associated stability can vary depending on the conditions under which they were formed.   As a result, while these data suggest that migration of Pu intrinsic colloids may be limited, a broad survey of Pu colloid stability as a function of aging and crystallinity is warranted.

3.6 References

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