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Stability of Intrinsic Pu colloids in the Presence of Montmorillonite at 25 and 80 °C: High-fired and freshly prepared PuO₂ oxides

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1. Introduction

Plutonium (Pu) is one of the dominant long-term dose contributors for any high-level nuclear waste repository because of its toxicity, long half-life (²³⁹Pu half-life = 24.100 yrs.) and current inventory (estimated at >2000 metric tons worldwide) [1]. In an effort to design a long-term barrier system for the safe disposal of nuclear waste, it is important to understand how Pu may migrate in the natural system once it breaches the waste package. Determining the fate and transport of Pu depends not only on the initial chemical form at the source but also the geochemistry and hydrology of the source location and along the down-gradient transport paths. Colloid-facilitated transport of low levels of Pu in both groundwater and surface water has been documented at several DOE sites [2, 3]. Pu sorbed to iron oxide colloids has also been detected over 4 km from its original source in Mayak, Russia [4]. These field studies indicate that the Pu associated with mobile colloids has moved on the scale of kilometers, yet the mechanisms are not well understood. Without a conceptual understanding of the dominant processes and a quantitative understanding of the relevant reaction chemistry, current transport models cannot effectively predict Pu concentrations and transport rates in the field.

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 naturally occurring inorganic, organic or microbial species (called pseudocolloids). At “high” concentrations where actinide ions in solution exceed their solubility, Pu can hydrolyze to form intrinsic colloids (sometimes called eigen-colloids) [5, 6]. In the case of Pu, the solubility-limiting concentration may be as low as $\sim 10^{-10}$ M under ambient conditions [6]. Intrinsic Pu colloid transport will be controlled by the stability (both physical and chemical) of the colloid. In contrast, if Pu is sorbed to inorganic or organic colloids, resulting in the formation of a pseudocolloid, transport will be determined by Pu sorption/desorption rates on the colloidal material. Efforts to model the transport of Pu from a near-field to a far-field environment are currently limited due to the lack of understanding of how intrinsic Pu colloids will persist along a changing geochemical flow path away from a high-level nuclear waste repository where intrinsic Pu colloids are most likely to form [7].

In addition to a broad range of geochemical processes and conditions that can affect the overall stability of intrinsic Pu colloids once they are formed, the initial formation conditions may also play a critical role in their long-term stability (e.g. temperature, pH, isotopic composition). Previous investigations on Pu(IV) colloids show that the ultimate morphology is strongly dependent on the conditions of formation and age of solution [8]. In particular, the degree of crystallinity, which can be affected by aging, temperature and original formation conditions, will affect the stability of intrinsic Pu colloids [9]. Published thermodynamic data for Pu(IV) oxide and hydroxide show a range of $\log_{10}K_{s,0}$ values for PuO₂(hyd) and PuO₂(cr) from -50.2 to -58.8 and -60.2 to -64.0, respectively. These data illustrate how crystallinity can have a significant

impact on the solubility and stability of PuO₂. Radiation effects from ²³⁸Pu have been reported to damage the crystallinity of PuO₂ that can lead to an increased solubility as well [10].

The objective of this work is to 1) better understanding of radionuclide interaction with geomedia (topic P10), and 2) develop new perspectives on colloid-facilitated radionuclide transport (topic P11). In this current study, we investigated the long-term stability of three different forms of intrinsic Pu colloids, all formed under elevated temperature conditions.

- High-fired Pu oxide, 300°C (Wilk#1)
- High-fired Pu oxide, 800°C (Wilk#2)
- 2-yr old aged intrinsic Pu colloids prepared in an acidic solution.

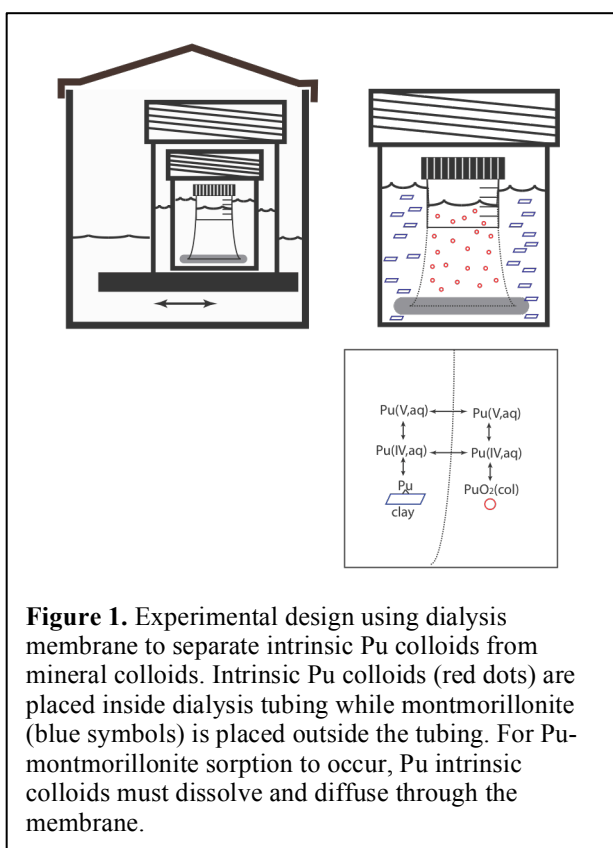
Results from this study are compared to dissolution rates of both fresh and aged colloids prepared in a basic solution and investigated in FY11 and FY12.

2. Previous Work

In FY2011 and FY2012, we examined the long-term stability of intrinsic Pu colloids that were prepared in a dilute basic solution. The long-term stability of both freshly prepared and aged (~ 1 year) intrinsic Pu colloids was examined. The intrinsic Pu colloids were prepared by neutralizing Pu(IV) stocks using NaOH solution and adjusting the pH to between 9 and 10. This is the same method used to prepare amorphous PuO₂ for the solubility studies performed by Neck *et al.* (2007). After aging for approximately a week, the intrinsic Pu colloids were centrifuged and the supernatant was removed. A dilution of the intrinsic Pu colloids (3×10^{-5} M) in pH 8 buffer solution was used for stability experiments investigated in FY2011. In FY2012, we repeated some of the experiments with the same intrinsic Pu colloids. However, at that point, the intrinsic Pu colloids had been aged for ~1 year. We did not see any difference in our colloid stability experiments, indicating that sample aging had no effect on intrinsic Pu colloid stability. Complete details for the intrinsic Pu colloid preparation can be found in Kersting *et al.* (2013).

3. Technical Approach

In all of the studies described herein, we used dialysis membranes to test the stability of intrinsic Pu colloids. Dialysis membranes are commonly used to separate suspended solutes or particles of different dimensions in a liquid mixture. Desirable size separation can be achieved by



selecting an appropriate membrane pore-size molecular weight cutoff (MWCO). In our experiments, we used membranes with a MWCO of 0.5 to 6 kilo Daltons (kDa), approximately equivalent to a 1 to 2-nm pore size. This MWCO was found to effectively retain intrinsic Pu colloids. Thus, if intrinsic Pu colloids are placed inside the membrane, any Pu found outside of the membrane could be attributed to the “dissolution” of intrinsic Pu colloids. This dissolution, in turn, reflects the stability of the intrinsic Pu colloids. By monitoring solution conditions as a function of time, we are also able to quantify the rates of intrinsic Pu colloid dissolution. Here and in previous experiment, intrinsic Pu colloid stability was examined at two temperatures: 25 and 80°C.

The design of the intrinsic Pu colloid stability experiments is shown in Figure 1. Briefly, intrinsic Pu colloids in a pH 8 solution are placed inside a dialysis bag. To avoid solubility limited dissolution, an “infinite” sink for dissolved Pu is needed. In our case, this is provided by montmorillonite clay that is placed outside the dialysis bag in a pH 8 buffer solution. The montmorillonite clay and the intrinsic Pu colloids are isolated from each other by the dialysis membrane. Over time, Pu detection outside the dialysis membrane represents dissolution of the intrinsic Pu colloids and diffusion of aqueous Pu across the dialysis membrane. The aqueous Pu that diffuses across the membrane can either remain in solution or sorb onto the montmorillonite. However, the large amount of montmorillonite ensures that the majority of Pu will be sorbed. The stability of intrinsic Pu colloids is expected to be a function of solution conditions, temperature, and composition/crystallinity of the colloids. The sorption rate of Pu to montmorillonite will be affected by the aqueous Pu oxidation state, solution conditions, and temperature. In the experiments described below, only the temperature and the composition/crystallinity of the Pu colloids was varied.

4. Materials

High-fired ²³⁹Pu oxides:

The high-fired Pu oxides were made for this project using reactor fuel grade Pu oxide. The starting material was dissolved in concentrated nitric acid containing a small admixture of HF. After filtering, Pu was converted to the +3 oxidation state using a mixture of hydroxylamine (NH₂OH) and dilute nitric acid. Hydrated Pu(III) oxalate was then precipitated by the addition of oxalic acid or sodium oxalate. The Pu(III) oxalate was precipitated from 3 M nitric acid solution. The precipitate was allowed to digest for 30-60 minutes, filtered, washed with DI water, alcohol, and then dried under vacuum at room temperature. The final step was to calcine the dehydrated precipitates at temperatures of either 300°C (sample Wilk#1) or 800°C (sample Wilk#2) to convert Pu(III) oxalate to PuO₂. More details regarding the preparation and characterization of these high-fired Pu oxides can be found in Isselhardt and Hutcheon (2012[11]). To prepare the samples for our stability experiments, the Pu oxide powders were suspended in Milli-Q water and allowed to settle for 10 minutes prior to discarding supernatants that contained PuO₂ fines. An average particle size of 4 μm was measured by SEM for samples Wilk#1 and Wilk#2. However, Wilk#1 also contained a significant number of smaller particles that were submicron in size (Figure 2a). The Milli-Q water rinse was repeated three times and the final concentration of the two high-fired Pu oxide suspensions was determined using beta liquid scintillation counting (LSC).

Intrinsic Pu colloids prepared in acidic solution: A ²⁴²Pu stock solution that consists of alpha emitters ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, and ²⁴²Pu with activity percentages of 15.8%, 0.062%, 5.0%, and

79.1%, respectively, was purified using an AG1x8 100-200 mesh anion exchange resin column. The intrinsic Pu colloids were prepared by heating 1.6×10^{-3} M Pu(IV, aq) solution in 0.1 M HNO₃ on a hotplate at 60-80 °C for 30 min. The dark brown Pu(IV) solution turned to green immediately upon heating. The formation of intrinsic Pu colloids was confirmed by UV/Vis. The fraction of soluble Pu in the intrinsic Pu colloid solution was determined to be < 0.2% using a 3kDa NMWL (Nominal Molecular Weight Limit) ultracentrifugal filter. After aging for two years, a dilution of the Pu colloids (Pu concentration of 3×10^{-5} M) was made in pH 8 buffer solution and used in our experiments.

Montmorillonite Preparation:

SWy-1 Montmorillonite from the Clay Minerals Society was used in our experiments. Detailed summary on the preparation of the homoionic Na-montmorillonite can be found in Kersting et al. (2012). The prepared clay minerals were then suspended in Milli-Q water and centrifuged to obtain the fraction of particle sizes from 50 nm to 2 microns.

Determinations of Pu concentrations

Two different Pu sources (²⁴²Pu and reactor fuel grade Pu oxide) were used in this study. For the intrinsic Pu colloids made from ²⁴²Pu, alpha liquid scintillation counting (LSC) was used to determine Pu concentrations. The reactor fuel grade Pu oxide contained ²⁴¹Am, the daughter of ²⁴¹Pu, as a predominant alpha emitter. ²⁴¹Am contributed > 90% of the total alpha activity in the samples. Therefore, it was not possible to use alpha LSC to measure Pu concentrations. To solve this problem, we first quantified the Pu isotopic composition of the samples. The reactor fuel grade Pu oxide was dissolved and Pu was isolated from ²⁴¹Am using two AG1x8 resin columns. A NuPlasma HR MC-ICP-MS was used to measure the following Pu isotopic ratios: ²⁴⁰Pu/²³⁹Pu, ²⁴¹Pu/²³⁹Pu, and ²⁴²Pu/²³⁹Pu. Alpha spectrometry was used to measure activity ratio of ²³⁸Pu/²³⁹⁺²⁴⁰Pu. The combination of these data provided an exact Pu isotopic composition of the reactor fuel grade Pu oxide. To measure the rate of reactor fuel grade Pu oxide dissolution, we measured the beta LSC activity to determine ²⁴¹Pu concentration in solution. The Pu isotopic ratios obtained from alpha spectrometry and MC-ICP-MS were used to determine the total Pu concentration. For beta LSC quantification, a ²⁴¹Pu quenching curve was generated from a NIST traceable standard.

Dialysis Experiments

A total of 7 dialysis experiments were successfully performed to investigate the stability of intrinsic Pu colloids in the presence of montmorillonite and compared to the experimental results of previous experiments performed in FY11 and FY12. Experiments were performed at 25°C (4 experiments) and 80°C (3 experiments) to evaluate the effect of temperature on colloid stability. At each temperature, intrinsic Pu colloids were added to the inside of the dialysis bag. The initial Pu concentrations in the dialysis bags were above the solubility of PuO₂(am) at pH 8 reported by Neck et al. (2007). For each experiment, the initial Pu concentration inside the dialysis bag along with other experimental parameters is listed in Table 1.

All batch experiments were conducted in 450-mL Teflon jars with air-tight closures. A volume of 235 mL of pH 8 buffer solution (pH 8, 5 mM NaCl/0.7 mM NaHCO₃) was mixed with 15 mL of montmorillonite stock suspension to yield a 250 mL montmorillonite suspension at a solid to liquid ratio of 1g/L and added to the Teflon jars. A sealed dialysis tube containing 15 mL of an intrinsic Pu colloid suspension was then placed in the 250 mL of montmorillonite suspended in pH8 buffer solution. 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.

Table 1. Conditions of intrinsic Pu colloid stability experiments at 25 and 80 °C.

	Expt	Pu Oxide used	Initial Pu conc. M	Montmorillonite g/L	medium that forms PuO ₂	Temp. when PuO ₂ formed
25 °C	1	formed in dilute acid	3.9×10^{-5}	1	0.1 M HNO ₃	70 °C
	2	Wilk#1	2.1×10^{-7}	1	3 M HNO ₃	300 °C
	3	Wilk#2	2.1×10^{-7}	1	3 M HNO ₃	800 °C
	4	formed in dilute base	1.3×10^{-8}	1 1	pH9 solution	25 °C
80 °C	5	formed in dilute acid	3.4×10^{-5}	1	0.1 M HNO ₃	70 °C
	6	Wilk#1	2.1×10^{-7}	1	3 M HNO ₃	300 °C
	7	Wilk#2	2.1×10^{-7}	1	3 M HNO ₃	800 °C

Note: In this study, experiment #4 used intrinsic Pu colloids prepared in a basic solution to verify that the experimental set-up and conditions in this study are the same as in FY11 and FY12.

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 and analyzed for total Pu. 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). At the termination of the experiments, both the total Pu in the clay suspension and the aqueous Pu were measured. Aqueous Pu was determined by conventional centrifugation of the clay suspension and measurement of the supernatant. Alternatively, aqueous Pu was determined by measuring the filtrate Pu concentration after filtering the suspension through 3kDa pore size centrifugal filters. The pH of the clay suspension was monitored and maintained at pH 8 ± 0.5 at all times.

5. Characterization of intrinsic Pu colloids

Prior to initiating the intrinsic Pu colloid stability experiments, the starting material was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of the high-fired Pu oxide, Wilk#1 and Wilk#2, are shown in Figure 2. Additional images and analysis can be found in Isselhardt and Hutcheon (2012). The predominant morphological structure was a near square platelet with fine porosities observed at higher magnification in both samples (see figures 2b and d). These samples and others investigated in Isselhardt and Hutcheon (2012) suggest a slight decrease in porosity and surface area at higher calcination temperature. The range in particle size of the high-fired Pu oxide was generally from 1 to 10 μm with an average of 4 μm. However, the average size of the individual crystallites in Wilk#1 and Wilk#2 were reported to be 4.5 and 100 nm, respectively.

TEM images of the intrinsic Pu colloids prepared in acidic solution and used in this study are presented in Figure 3. The Pu forms aggregated clusters as seen in Figure 3a that range from 10 to 10's of nanometers. However, high-resolution TEM shows that the clusters are composed of individual nano-colloids, or crystallites (Fig. 3b). The size range of these nano-crystallites was determined to be 2 to 3 nm with an average size of 2.3 nm. Both X-ray EDS analysis and select-area electron diffraction confirmed the formation of an fcc PuO_2 that has a fluorite structure. Clusters of Pu nano-colloids were also observed in the

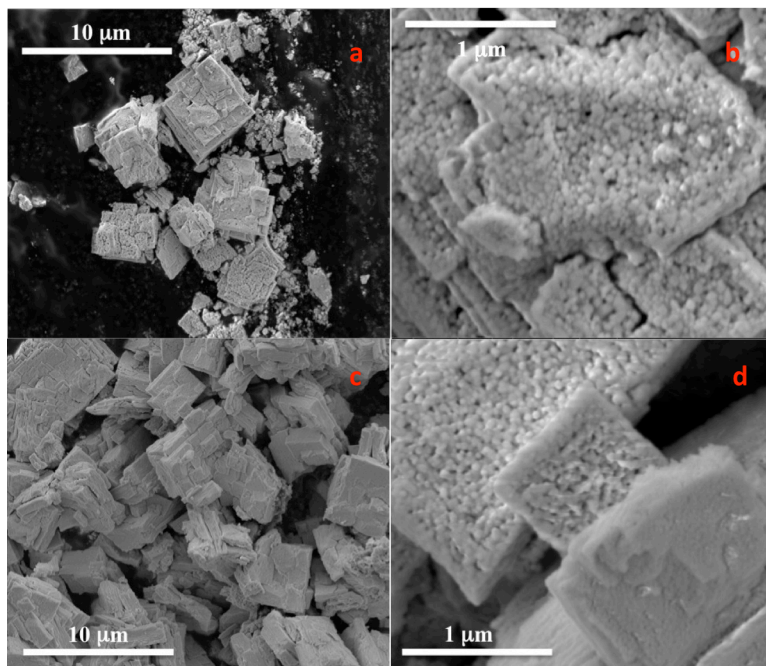


Figure 2. SEM Images of high-fired Pu oxide. Wilk#1 (300°C) is shown in figures a and b and Wilk#2 (800°C) is shown in c and d. Both samples show similar appearance and texture. Notice the fine porous nature of the oxides at high resolution (b and d).

intrinsic Pu colloids prepared in basic solution and used in the FY11 and FY12 study. But in contrast to the colloids prepared in an acidic solution, the colloids prepared in a basic solution do

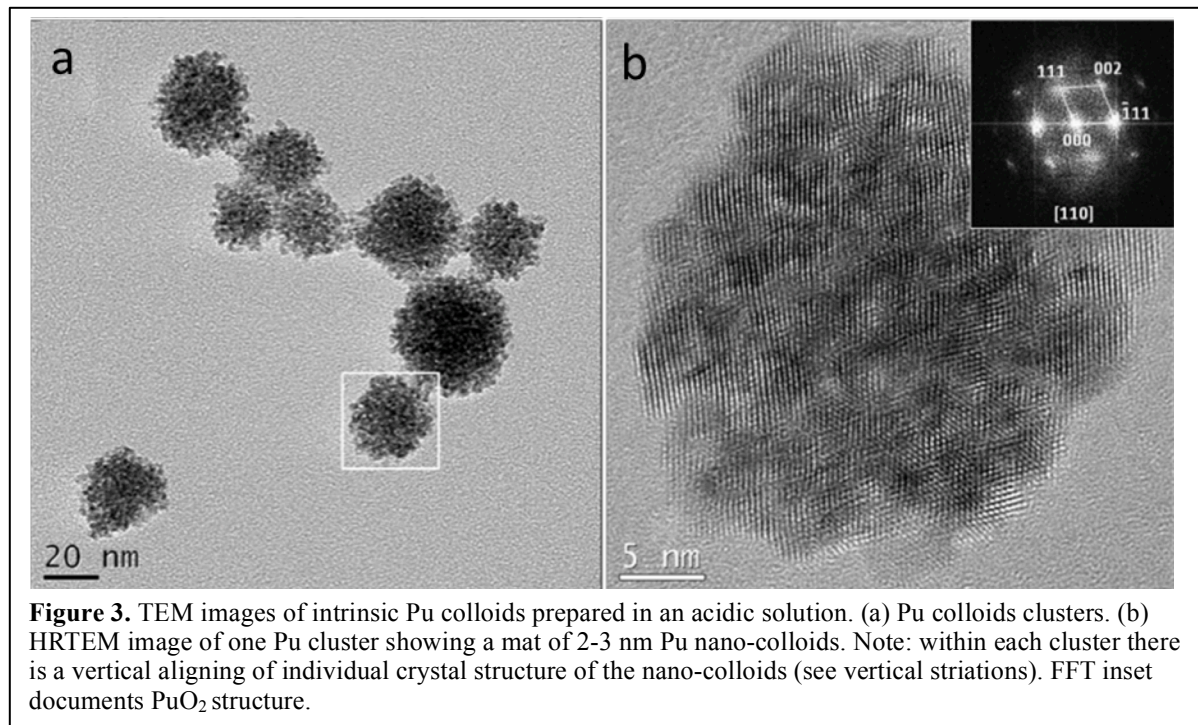


Figure 3. TEM images of intrinsic Pu colloids prepared in an acidic solution. (a) Pu colloids clusters. (b) HRTEM image of one Pu cluster showing a mat of 2-3 nm Pu nano-colloids. Note: within each cluster there is a vertical alignment of individual crystal structure of the nano-colloids (see vertical striations). FFT inset documents PuO_2 structure.

not show a preferred alignment in their clusters, but appear entirely randomly oriented (Figure 4). Neither the freshly prepared nor the aged intrinsic Pu colloids prepared in a basic solution (up

to 1 year) showed preferential alignment of the 2-3 nm nano-colloids. We hypothesize that the heating process used to produce the intrinsic Pu colloids in an acidic solution resulted in the incipient alignment of the crystallites within the clusters. The various intrinsic Pu colloids used in these experiments have different particle sizes and ultimately different surface areas. Due to the health and safety concerns inherent in working with potentially dispersible Pu powders, the high-fired Pu oxides could not be ground to a finer size. The surface area of the various intrinsic Pu colloids was estimated based on the sizes of the crystallites and tabulated in Table 2.

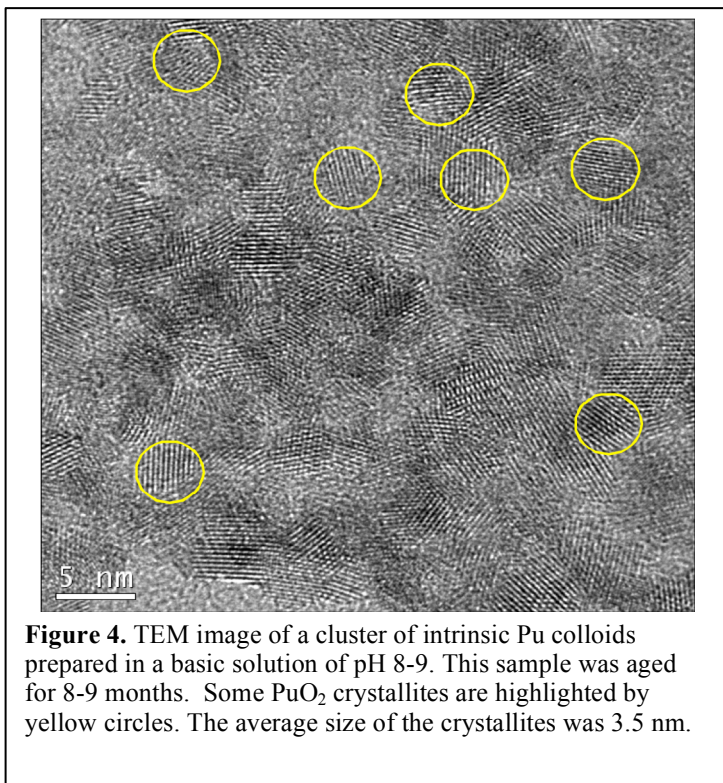


Figure 4. TEM image of a cluster of intrinsic Pu colloids prepared in a basic solution of pH 8-9. This sample was aged for 8-9 months. Some PuO₂ crystallites are highlighted by yellow circles. The average size of the crystallites was 3.5 nm.

Table 2. Estimated Surface Area of Intrinsic Pu colloids and Montmorillonite

Intrinsic Pu colloid / Clay	Ave. Particle Size, (nm)	Ave. Crystallite Size, (nm)	Density, g/cm ³	Surface Area m ² /g
²³⁸ Pu colloid prepared in basic solution	30	3.5	11.5	149.1
²⁴² Pu colloid prepared in acidic solution	50	2.3	11.5	226.8
High-fired ²³⁹ Pu oxide, 300 °C	4000	4.5	11.5	115.9
High-fired ²³⁹ Pu oxide, 800 °C	4000	100	11.5	5.2
Montmorillonite	300	71	2.83	29.9

6. Technical Results and Discussion

Intrinsic ²³⁸Pu colloids prepared in a basic solution

As mentioned previously, the stability of intrinsic Pu colloids prepared in a basic solution (both freshly prepared and aged up to 1 year) was studied in the presence of montmorillonite at 25 and 80°C in FY11 and FY12 (Kersting et al., 2012). Colloid stability at three different intrinsic Pu colloid concentrations (10⁻¹¹, 10⁻⁹ and 10⁻⁷ M) was examined. These intrinsic ²³⁹Pu colloids were aged for 1 month to >1 year prior to use in the stability experiments. No difference in behavior was observed between the fresh and aged samples. The results are briefly summarized here to facilitate comparison with the results from this study. Figure 5a and 5b shows the percentage of intrinsic Pu colloids that dissolved and diffused across the dialysis membrane over time at 25 and 80°C, respectively. At both temperatures, the intrinsic Pu colloids dissolve, diffuse across the dialysis membrane, and sorb to montmorillonite. However, the reaction kinetics are significantly

faster at 80°C than at 25°C. Over the 100 days of these experiments, samples with initial Pu concentrations below the solubility of amorphous PuO₂ as determined in Neck et al. (2007) (10⁻¹¹ M and 10⁻⁹ M) dissolved much more than samples with an initial Pu concentration above the solubility of amorphous PuO₂ (10⁻⁷ M). Thus, the dissolution of intrinsic Pu colloids prepared in a basic solution is relatively fast and appears to follow the solubility behavior of amorphous PuO₂. The experimental results suggest that intrinsic Pu colloids prepared in a basic solution are relatively unstable and unaffected by the aging process.

Interestingly, as a consequence of the experimental design, we could also determine the affinity of Pu for the montmorillonite surface at 25 and 80°C. Based on our measurement of total and aqueous Pu in the montmorillonite suspension, the Pu K_d (mL/g) at 80°C was found to be significantly higher than at 25°C. This indicates that Pu has a higher affinity for montmorillonite at elevated temperatures.

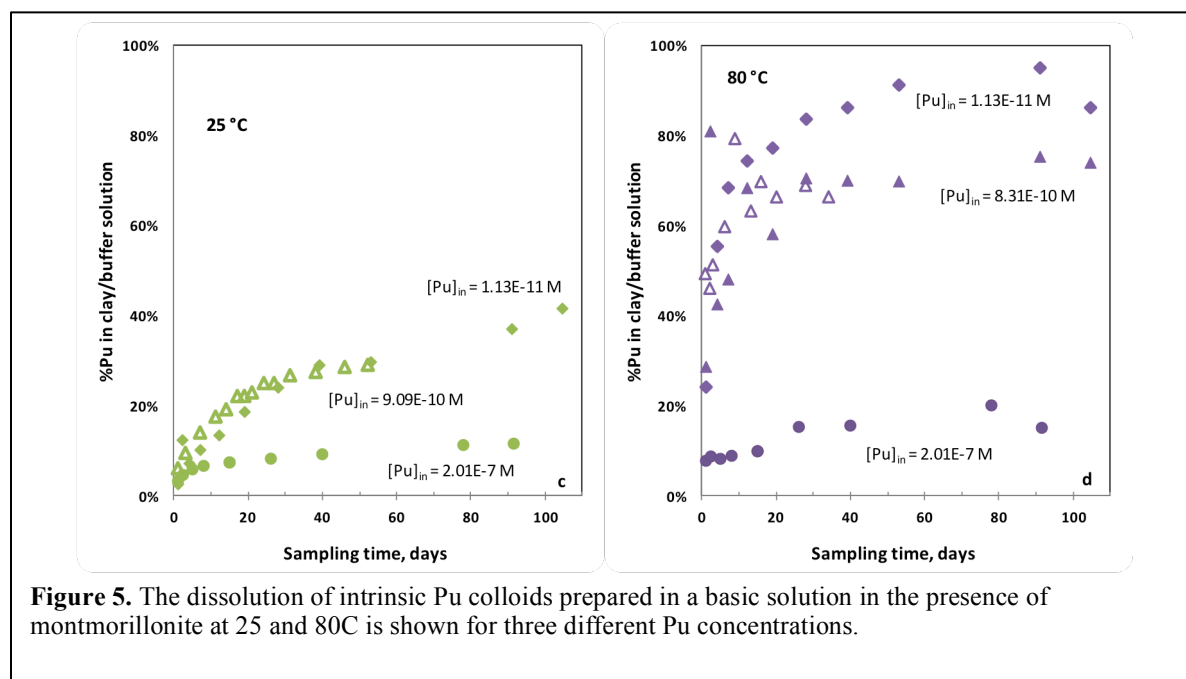
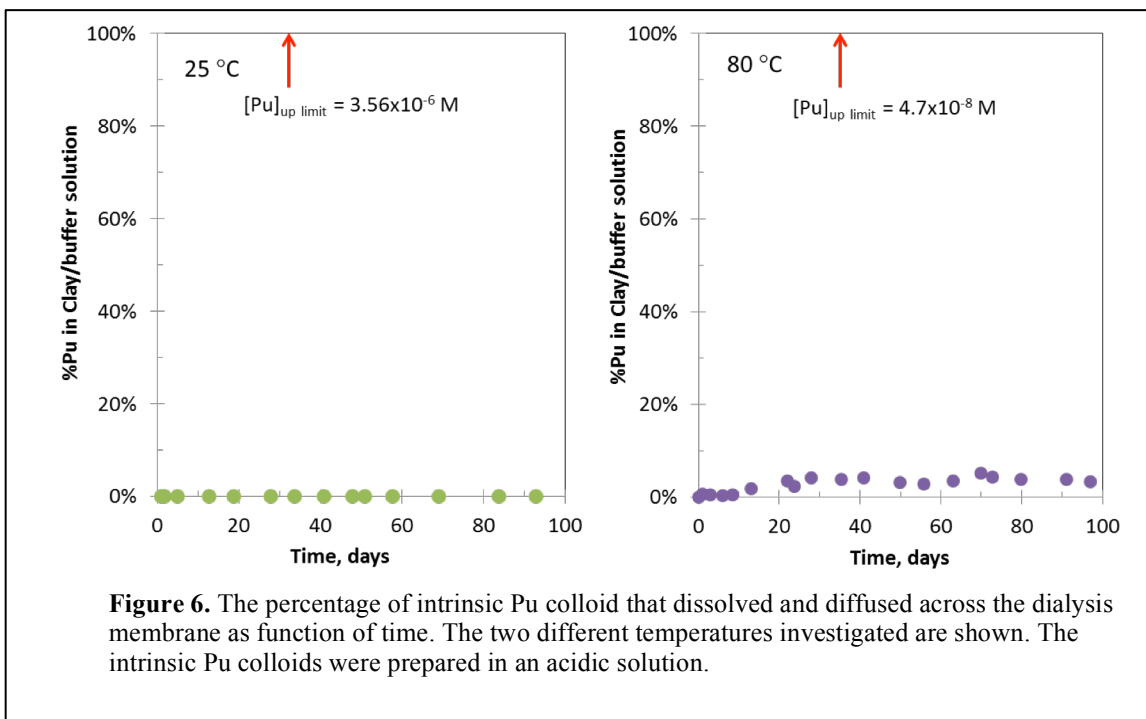


Figure 5. The dissolution of intrinsic Pu colloids prepared in a basic solution in the presence of montmorillonite at 25 and 80C is shown for three different Pu concentrations.

Stability of intrinsic ²⁴²Pu colloids prepared in an acid solution

These intrinsic Pu colloids were aged for about two years before being used in this study. The initial Pu concentration inside the dialysis bags was 3.9×10⁻⁵ and 3.4×10⁻⁵ M in the 25°C and 80°C experiments, respectively. The maximum possible Pu concentration in the montmorillonite suspension, assuming complete dissolution of the intrinsic Pu colloids, would be 3.56×10⁻⁶ and 4.7×10⁻⁸ M, respectively. The experiments were run for three months. Figure 6 plots the percentage of intrinsic Pu colloids that dissolved and diffused across the membrane as a function of time. For the experiment at 25°C, there was no detectable Pu in the montmorillonite suspension. The method detection limit was 1×10⁻⁹ M, which is < 0.03% of the total Pu in the system. For the experiment at 80°C, less than 5% of the intrinsic Pu colloids dissolved and diffused into the montmorillonite suspension. Clearly, intrinsic Pu colloids prepared in an acidic solution are much more stable than intrinsic Pu colloids prepared in a basic solution. It is possible that the alignment of the crystal structure seen in the Pu crystallite clusters result in a

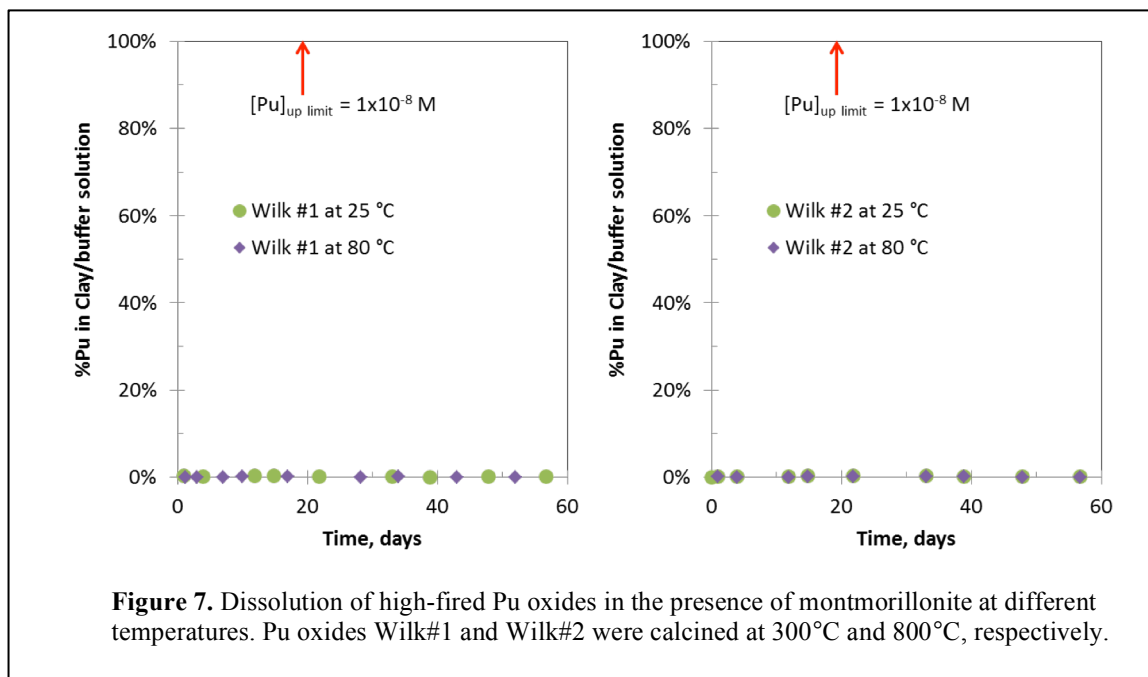
more stable structure. It is also possible that the higher dissolution rates observed in the intrinsic ^{238}Pu colloids prepared in a basic solution may have been, in part, the result of greater radiation damage resulting from the short-lived ^{238}Pu isotope contained in this preparation (compared to



the intrinsic ^{242}Pu colloids prepared in an acidic solution [10].

Stability of high-fired Pu oxides

Two high-fired Pu oxides, calcined at 300°C and 800°C, respectively, were used in these stability experiments. The initial high-fired Pu oxide concentrations inside the dialysis bags were 2.1×10^{-7} M for all experiments at 25°C and 80°C. The maximum possible Pu concentration in the montmorillonite suspension, assuming complete dissolution of the high-fired Pu oxides, would be 1.2×10^{-8} M. These experiments have been running for three months and are ongoing. Plotted in Figure 7 is the percentage of high-fired Pu oxide that has dissolved and diffused across the membrane as a function of time. For experiments at both 25 and 80°C, there was no detectable Pu in the montmorillonite suspension. The method detection limit was 5×10^{-11} M, which is < 0.5% of total Pu in these experiments. These results indicate that both the 300°C and 800°C high-fired Pu oxides are quite stable over the three month period investigated.



In comparing all the experiments to date, it is apparent that Pu oxides produced in a variety of different ways leads to a wide range of intrinsic Pu colloid stability. The intrinsic Pu colloids prepared in a basic solution are the least stable. Their stability is also temperature-dependent, with significantly faster dissolution observed at 80°C compared to 25°C. The high-fired Pu oxides are the most stable; at both temperatures examined to date, both the 300°C and 600°C calcined Pu oxides were stable with no detectable dissolution after 60 days. TEM and SEM analyses indicate that the calcined Pu oxides are morphologically distinct from the intrinsic Pu colloids prepared in acidic and basic solutions. Although it is not possible to directly compare dissolution rates between the different Pu oxides because the surface areas of the intrinsic Pu colloids and high fired Pu oxides are difficult to estimate, general observations can be made. It does not appear that aging makes a difference in the stability of the intrinsic Pu colloids, as no difference in dissolution rates were observed between the freshly precipitated and aged intrinsic Pu colloids prepared in a basic solution. Although intrinsic Pu colloids prepared in basic and acidic solutions both have an fcc crystal structure, those prepared in an acidic solution appear to have a more crystalline structure and some long range order among the aggregated ~2.5 nm Pu crystallites. This suggests a more crystalline and stable structure resulting in slower dissolution compared to the more disordered intrinsic Pu colloids prepared in a basic solution. It is also possible that elevated temperatures helped to stabilize the intrinsic Pu colloids prepared in an acidic solution. The intrinsic Pu colloids prepared in a basic solution were kept at 25°C while the intrinsic Pu colloids prepared in an acidic solution were heated during preparation. Thus, the greater stability of intrinsic Pu colloids prepared in an acidic solution may, in part, be the result of sample heating.

7. Conclusions and Future Work

In this study, we have examined the stability of three different types of intrinsic Pu colloids and Pu oxides in the presence of montmorillonite at 25 and 80°C under atmospheric conditions. Several conclusions can be drawn:

- Intrinsic Pu colloids made in dilute basic solution 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 intrinsic Pu colloids is slower than at 80°C. Nevertheless, formation and dissolution of intrinsic Pu colloids appears to be a reversible process. Pu dissolution rates and the affinity for montmorillonite increase with temperature. The reversible nature and relatively fast dissolution rates of intrinsic Pu colloids precipitated in a basic solution suggests that these types of colloids are not very stable and their presence downstream of a nuclear waste repository setting is unlikely.
- In contrast, intrinsic Pu colloids produced from acidic solution and Pu oxides calcined at 300 and 800°C are stable over the 3 months investigated. Under these formation conditions, intrinsic Pu colloids and/or Pu oxides may play an important role in the migration of intrinsic Pu colloids away from nuclear waste repository setting.
- How Pu oxides are formed impacts their ultimate chemical stability. Heat may play an important role in enhancing the stability of intrinsic colloids by increasing its crystallinity. Importantly, the results described here suggest that repository scenarios that include higher heat loading may result in stabilization of Pu oxide phases, which can lead to greater migration of intrinsic Pu colloids. However, the repository temperature history, combined with the predicted timing of canister failure and re-saturation of the repository near field will all play a role in the evolution of any specific repository scenario and the potential for Pu mobilization.

In FY14, we will expand the range of conditions under which intrinsic Pu colloid and high-fired Pu oxide stability is examined. Specifically, the behavior of Pu across a range of ionic strength is essential to extend our studies to Salt Repository scenarios. The role of alpha-recoil effects on destabilization of oxide phases will also be examined. Finally, the effect of iron oxides, which are more relevant for Salt Repository scenarios than clays, in accelerating intrinsic Pu colloid and high-fired Pu oxide dissolution will be examined. The ultimate goal of these experiments is to provide guidance regarding the potential of colloid-facilitated actinide transport to each of the generic repository scenarios under investigation.

8. Acknowledgments

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