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Milestone M4FT-13LL0807071: International Collaboration - Radionuclide Interactions and Transport in Geologic Repository Environments – Pu Interaction with Bentonite

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INTRODUCTION

The focus of this project is to investigate radionuclide interactions with natural and engineered materials, specifically the mineral bentonite that will be used in EU repositories and possibly in US high-level waste repository designs. These experiments are designed to develop a mechanistic understanding of Pu interactions with representative mineral substrates under granitic chemical conditions. The sorption/desorption experiments cover a large range of Pu concentrations and will be compared to sorption/desorption experiment with montmorillonite. The experiments are being coordinated with the Colloid Formation and Migration (CFM) international project led by Karlsruhe Institute of Technology and located at the Grimsel Test Site underground research laboratory in Switzerland. Experiments will be completed by 8/15/2014. Milestone M4FT-13LL0807071 is a progress report on this effort. The research is addressing the following FEPs/needs identified in the R&D Roadmap: 2.2.09.05 - radionuclide speciation and solubility in host rock; 2.2.09.55 - sorption of dissolved radionuclides in host rock; 2.2.09.59 - colloidal transport in host rock.

The bentonite clay used in these experiments was FEBEX bentonite received from the National Cooperative for the Disposal of Radioactive Waste (Nagra), Switzerland that plans to use the clay as a backfill material in its nuclear waste repositories. This clay has been characterized previously and comprised 93±3% montmorillonite, 2±0.5% quartz, 2±1% potassium feldspars, 1±0.7% plagioclase, 2±0.2% cristobalite, 1±0.7% calcite and 1.5±0.1% rhyodacitic rock[1]. Prior to use the clay was Na-homoionized, lightly ground in a mortar and pestle and the resulting material sieved (size fraction <63 µm). The surface area of the clay as used in these experiments was 25.2 ± 1.0 m^2 g^{-1}. In order to ensure consistency with previous montmorillonite adsorption work, experiments were performed in 0.7 mM NaHCO$_3$, 5 mM NaCl buffer solution with a solid: solution ratio of 1 g L^{-1}. All experiments were performed under ambient atmospheric conditions.

ADSORPTION

To compare the rate of adsorption of Pu(V) on bentonite to the rate of Pu(V) adsorption on montmorillonite at pH 8, a time series experiment was performed in triplicate with an initial concentration of 10^{-10} mol L^{-1} Pu(V). The results of this experiment are shown in Figure 1. Here the adsorption of Pu to bentonite is plotted as a function of time along with previously published data for the adsorption of Pu(V) to montmorillonite [2]. The log surface area normalized apparent rate of sorption for bentonite was -3.4 L m^{-2} h^{-1} as compared to the value of -2.8 L m^{-2} h^{-1} for montmorillonite. This similarity in the rate of Pu(V)

adsorption to both clays suggests that the large component of montmorillonite in the bentonite clay is primarily responsible for the uptake of Pu(V) from the aqueous phase.
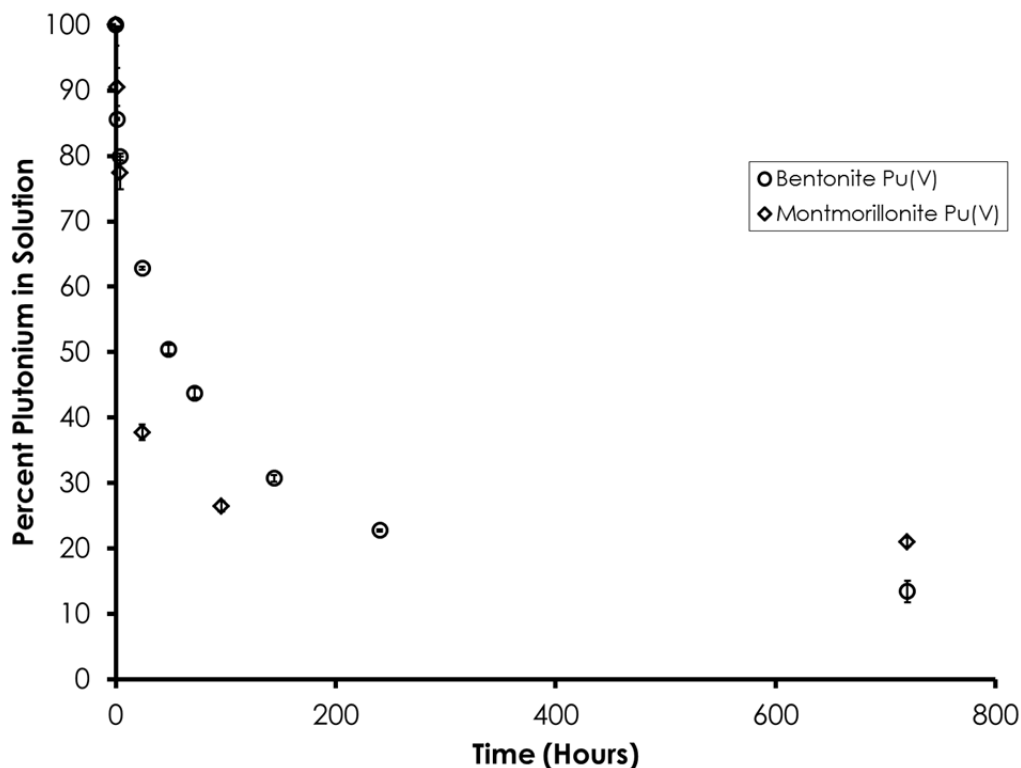

Figure 1 Sorption of Pu(V) to FEBEX bentonite (circles) and SWy-1 Na-montmorillonite (diamonds) plotted as percentage of Pu removed from solution vs. time. Initial Pu concentrations were 10^{-10} M for bentonite and 10^{-9} M for montmorillonite. Error bars for bentonite are 1σ of triplicate experiments and are 1σ values calculated from parallel quadruplicate experiments for montmorillonite.

A Pu(IV) adsorption isotherm was performed with bentonite at pH 8. Previous work with Pu(IV) and Pu(V) adsorption to montmorillonite has shown that Pu(V) adsorption behavior will converge with that of Pu(IV) over sufficient timescales [2, 3]. The Pu adsorption experiment was performed with initial Pu(IV) concentrations ($[Pu]_{initial}$) ranging from 10^{-7} – 10^{-16} mol L^{-1}. As previous work has highlighted the need for long equilibration periods when performing Pu adsorption studies, Pu(IV) was equilibrated for 120 days in these experiments [2, 4]. Pu in solution was measured using liquid scintillation counting (LSC) for experiments with $[Pu]_{initial}$ 10^{-7} – 10^{-11} mol L^{-1} and at the Center for Accelerator Mass Spectrometry (CAMS) at LLNL for experiments with $[Pu]_{initial}$ 10^{-11} – 10^{-16} mol L^{-1}.

The Pu(IV) sorption isotherm is shown in Figure 2. Pu(IV) sorption was broadly linear at $[Pu]_{initial}$ ranging from 10^{-7} mol L^{-1} to 10^{-16} mol L^{-1} after 120 days' equilibration. The slope of the plot of log[Pu] in solution against log[Pu] on solid was 1.06 (R^2 0.998). The K_d values ranged from 21000 – 79000 mL g^{-1}. Also plotted in Figure 2 is the equivalent Pu(IV) montmorillonite adsorption isotherm for $[Pu]_{initial}$ 10^{-7} mol L^{-1}

– 10^{-13} mol L^{-1} following 30 days' equilibration. The slope of the plot of log[Pu] in solution against log[Pu] on solid for montmorillonite was 1.04 (R^2 0.997) while K_d values ranged from 8900 – 27000 mL g^{-1}. The similarity of the Pu(IV) bentonite and montmorillonite isotherms further suggests that the montmorillonite in the bentonite is largely responsible for controlling the adsorption of Pu in these experiments.
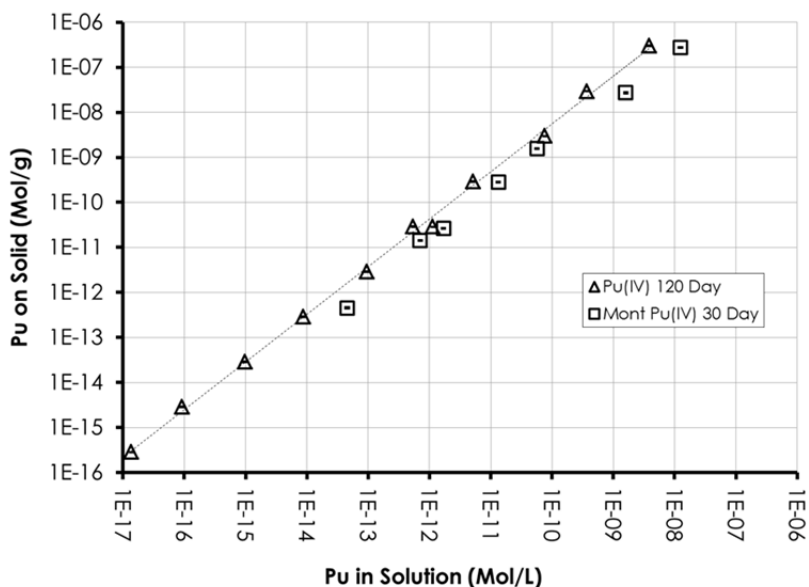

Figure 1 120 day Pu(IV) sorption isotherm for FEBEX bentonite (1 g L^{-1}; triangles) and 30 day Pu(IV) sorption isotherm for Na-montmorillonite (1 g L^{-1}; squares) in 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at pH 8.

DESORPTION

A flow-cell experiment was used to characterize Pu(IV) desorption from bentonite and to compare it with previously determined Pu(IV) – montmorillonite desorption behavior. Prior to the desorption step, Pu(IV) was equilibrated with bentonite at pH 8 for 21 days. Desorption experiments were performed in a 20 mL stirred cell fitted with a 100 nm filter and a stir bar to ensure ideal mixing conditions. An aliquot of adsorption suspension was placed in the flow cell and atmosphere-equilibrated Pu-free 0.7 mM NaHCO₃, 5 mM NaCl buffer solution at pH 8 flowed through the cell at an initial rate of 0.4 mL/min (average retention time of ~ 50 minutes). Effluent fractions were collected over time, acidified with 2% HNO₃ and Pu concentration determined via LSC. In order to evaluate the kinetics of the desorption process, the flow rate was changed approximately every 10 pore volumes to flow rates of 0.2, 0.04, and 0.02 mL min^{-1}.

The results from both the bentonite and the montmorillonite flow cell experiments at pH 8 are shown in Figure 3. The results show that there is measurable desorption of Pu from bentonite over the duration of the flow cell experiment. In the first flow regime (0.4 mL min^{-1}), differences between the two systems are likely due to poor mixing in the bentonite cell caused by a non-rotational stir bar. This was rectified after

1.8 pore volumes. Further divergence between the two systems is also seen towards the end of the flow cell experiment (0.04 mL min^{-1}). Nonetheless, the desorption profiles for bentonite and montmorillonite are very similar, indicating that, as with the adsorption experiments, the same processes are responsible for the desorption of Pu from the two clays.
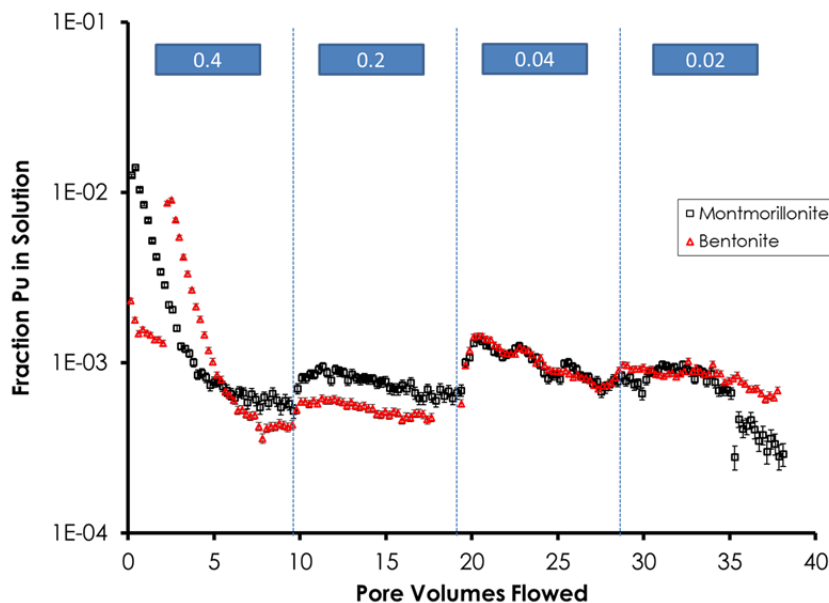
Figure 3 Results from Pu(IV) - montmorillonite (squares) and Pu(IV) - bentonite (triangles) desorption flow-cell experiments. Data points represent the fraction of the total system Pu in the collected effluent. Experiments performed in a 20 mL cell with 1 g L$^-$ clay at pH 8. Montmorillonite experiments were spiked with [Pu]$_{initial}$ 1 × 10^{-10} M, bentonite experiments spiked with [Pu]$_{initial}$ 3 × 10^{-10} M. Influent solution was Pu-free 0.7 mM NaHCO$_3$, 5 mM NaCl buffer. Influent flow rates were 0.4, 0.2, 0.04 and 0.02 ml min^{-1} and are shown on the plot. Changes in flow rate are denoted by vertical dashed lines. Error bars based on propagation of % 2s liquid scintillation counting uncertainties.

SUMMARY

From our work to date we can conclude that:

- Adsorption behavior of Pu(V) on bentonite is similar to montmorillonite suggesting that our understanding of the simple binary Pu-montmorillonite system can provide insight for the more complex multi-component mineralogy of bentonite clay.
- The Pu(IV) sorption isotherm for bentonite is broadly linear over a large range in Pu concentration ([Pu]$_{initial}$ ranging from 10^{-7} mol L^{-1} to 10^{-16} mol L^{-1}) suggesting that the process controlling sorption at extremely low concentrations is the same as at higher concentrations.
- The desoption behavior of the bentonite and montmorillonite are very similar, indicating that, as with the adsorption experiments, the same processes are responsible for the desorption of Pu from the two materials.

ACKNOWLEDGEMENTS

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