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ABSTRACT TITLE: Quantifying Plutonium Sorption Affinities and Desorption Rates from Mineral Surfaces: A Numerical Approach to Modeling Batch/Flow-Cell Experimental Data and Implications to Field-Scale Plutonium Transport

ABSTRACT: The Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) at Lawrence Livermore National Laboratory ("Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales") is focused on identification and quantification of the biogeochemical processes that control the fate and transport of Pu at environmentally relevant (10^{-12} – 10^{-18} mol/L) actinide concentrations. The first of five program elements is focused on quantifying affinities and rates of binary sorption/desorption to mineral surfaces at environmentally relevant Pu concentration. Experiments are performed using batch/flow cell experimental techniques combined with LLNL's unique capability in measuring actinide concentrations at ultralow ($<10^{-14}$ mol/L) concentrations by AMS and characterizing the morphology of Pu associated with mineral surfaces (TEM/NMR). To date, we have examined Np(V)-goethite, Pu(IV/V)-goethite, and Pu(IV/V)-montmorillonite sorption isotherms over a ten order of magnitude Pu/Np concentration range. We have also used dynamic flow cell sorption/desorption experiments to quantify the kinetics of these reactions. A simple yet flexible numerical model has been developed to simulate the known Pu redox transformations occurring on the surface of minerals and quantify the various sorption, desorption, and redox transformation data collected to date. The model is based on our early efforts focused on modeling Np(V) sorption behavior on goethite [1]. However, the model was expanded to account for the surface-mediated Pu redox processes identified on mineral surfaces. In the case of Pu(V) interaction with goethite, we were able to fit our pH 8 batch sorption experiments and adsorption/desorption flow cell data, including the transient stop flow events, simultaneously. The simulated affinities and sorption/desorption rates are consistent with previous surface mediated reduction rates reported in the literature and measured aqueous and sorbed Pu oxidation states. Importantly, a kinetic hysteresis effect was essential to fitting the surface mediated redox reactions. The inclusion of this effect in the numerical model is consistent with the hysteresis term used in the earlier Np(V) model [1]. However, the hysteresis effect for Pu is much more pronounced and leads to desorption rates on the timescale of years. The rate limiting step in Pu desorption appears to be the slow oxidation of Pu(IV) on the mineral surface to Pu(V). The slow desorption rates suggest that observed colloid facilitated radionuclide transport may occur as a result of the relative stability of adsorbed Pu(IV). Similar behavior was observed in the case of Pu-montmorillonite experiments as a function of pH and actinide concentration.

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Reference:

[1] R.M. Tinnacher, et al., Geochim. Cosmochim. Acta 75, 6584 (2011).