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The LLNL Subsurface Biogeochemistry of Actinides SFA

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The objective of LLNL's SFA is to *identify and quantify the biogeochemical processes that control the fate and transport of actinides in the environment*. The research approach combines three Thrust Areas: (1) **Fundamental Mechanistic Studies** that identify and quantify biogeochemical processes, (2) **Field Integration Studies** that investigate actinide transport characteristics, and (3) **Actinide Research Capabilities** that provide new opportunities for advancing actinide environmental chemistry. Here, we summarize the accomplishments from 2017 and 2018 and preview our research objectives for the coming years. We quantified the adsorption/desorption behavior of plutonium (Pu) on SWy-1 montmorillonite colloids. A model that incorporates known surface-mediated Pu redox reactions was developed and the resulting rate constants, in part, explain colloid-facilitated Pu transport on decadal timescales. Pu desorption experiments using colloids produced from hydrothermal alteration of nuclear melt glass revealed additional colloid associations that may exacerbate colloid facilitated transport and help explain observations at the Nevada National Security Site. Rates of $\text{NpO}_2(\text{C}_2\text{O}_3)_3^{4-}$ ligand exchange were measured using multinuclear NMR to determine exchange rates of an environmentally-relevant actinide organic ligand. Ligand exchange rates for the geochemically important $\text{NpO}_2(\text{C}_2\text{O}_3)_3^{4-}$ aqueous complex were measured and showed a distinct difference in the pressure dependencies for the uranyl and neptunyl complexes. We explored the redox reactions of PuO_2^{2+} and PuO_2^+ with acetohydroxamic acid and desferrioxamine B. PuO_2^{2+} was instantaneously reduced to PuO_2^+ but weak complexation with hydroxamate limited further reduction to Pu^{4+} . We performed cesium adsorption/desorption ternary (Cs+two minerals) experiments to study long-term sorption reversibility (500 days). The novel experimental approach using dialysis membranes revealed that slow desorption kinetics may play an important role in apparently irreversible Cs sorption. This approach will be applied to study slow desorption kinetics of actinides. The role of structural Fe on Pu(V) surface mediated reduction on montmorillonite was examined. The sorption rate was positively correlated with structural Fe. Comparison to other minerals indicates that surface mediated reduction rates can vary by as much as five orders of magnitude depending on the structure and composition of the surface. We examined U(VI) diffusion through bentonite over six years using a diffusion cell apparatus. Surprisingly, diffusion rates were about two orders of magnitude lower than values obtained in short-term experiments reported in the literature. The results suggest that long-term studies of key transport phenomena may reveal additional processes that can directly impact long-term actinide migration.