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Actinide Mobility at the Ravenglass Site: The Role of Iron and Redox Cycling

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The LLNL BioGeoChemistry of Actinides SFA is investigating actinide migration behavior at the Ravenglass saltmarsh, 10 km south of the Sellafield site, U.K. Since 1952, authorized liquid radioactive effluents (e.g. Am, Cs, Np, Pu, and U) have been discharged from Sellafield into the Irish Sea. The released radionuclides have been re-dispersed along the North-East Irish sea coast including the Ravenglass estuary, a low energy intertidal saltmarsh. Despite periodic study over the past several decades, biogeochemical controls on long-term radionuclide distribution and retention at Ravenglass remain uncertain. Recent work indicates redox conditions shift from aerobic at the sediment surface, to Fe(III) reducing within 12 cm at depth. Shifting redox profiles at this site have the potential to impact the long-term stability of redox active actinides (i.e. Pu, Np, U) and influence actinide release rates into the Irish Sea.

At the Ravenglass site, we are determining actinide desorption behavior from sediments under anoxic and oxic conditions. Currently we have completed Ravenglass sediment desorption experiments (30 cm core, 6 layers) in artificial seawater under anoxic conditions. Analyses to determine the actinide content in the desorbed solutions are currently underway. Follow-on desorption experiments under oxic conditions have begun.

A central hypothesis to our research is that Pu can be stabilized by redox and non-redox mineral alteration processes that lead to Pu incorporation into secondary mineral phases. Minerals of interest include Fe(II)/(III) phases which will likely be subject to dissolution and recrystallization in this dynamic biogeochemical setting. We have monitored the fate of Pu(IV) during the alteration of Pu-doped ferrihydrite to goethite (FeOOH) and hematite (Fe₂O₃). Upon transformation, goethite showed a higher extent of Pu-incorporation than hematite. We have also started similar experiments with magnetite Fe(II/III)₃O₄. Upon synthesis, 98% of Pu remains associated with the magnetite phase. We are currently monitoring the affinity of Pu to the magnetite phase over time and Pu desorption during surface oxidation.

Finally, we are investigating the role of reduced and oxidized forms of humic acid (HA) on Pu sorption/desorption to goethite. In batch systems, both forms of HA demonstrate a similar apparent effect on Pu adsorption. The aggregation of Pu-goethite-HA ternary complexes may enhance the stability of Pu in sediments. However, the redox transformation of both the goethite surface and Pu sorbent in the presence of HA remains unknown. Ongoing research is attempting to disentangle the effect of redox transformations of Pu and iron oxide surfaces in the presence of reduced organic matter.