Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

LLNL SFA (Laboratory Research Manager: Annie B. Kersting)

A.B. Kersting (PI), M. Zavarin, J. Begg, P. Zhao, P. Huang, Z. Dai, R. Tinnacher, R. Kips, H. Mason, S.A. Carroll, R. Maxwell, R. Williams, S. Tumey - *LLNL*; B.A. Powell, J. Wong - *Clemson U.*

The challenge in predicting the mobility and transport of plutonium (Pu) is determining the dominant geochemical processes that control its behavior in the subsurface. The reaction chemistry of Pu (*i.e.*, aqueous speciation, solubility, sorptivity, redox chemistry, and affinity for colloidal particles, both abiotic and microbially-mediated) is particularly complicated. Its migration is known to be oxidation-state dependent and facilitated by transport on particulate matter (*i.e.*, colloidal particles). Despite the recognized importance of colloid-facilitated transport, little is known about the geochemical and biochemical mechanisms controlling Pu-colloid formation and association.

The objective of this program is the identification and quantification of the biogeochemical processes that control the fate and transport of Pu at picomolar to attomolar (10^{-12} – 10^{-18} mol/L) concentrations. Our program is composed of five research elements that are aligned with processes likely to affect Pu transport at environmentally relevant concentrations: 1) Binary sorption to low-site-density, high-affinity surface sites (*e.g.*, surface defects), 2) Stabilization of Pu surface complexes on mineral colloids by natural organic matter, 3) Surface precipitation of Pu polymers (nanocolloids), 4) Co-precipitation with colloids as a result of mineral alteration, and 5) Direct and indirect microbial interactions.

This overview poster highlights this year's results and ongoing effort. They include

- Binary sorption affinity and reversibility. Np(V), Pu(V) and Pu(IV) sorption affinity, reversibility, and morphology on goethite from attomolar to micromolar concentrations was examined. Higher affinities were observed at picomolar concentrations for Np but not Pu. At high concentrations, Pu(IV) and Pu(V) form 2-5 nm PuO_2 and/or Pu_4O_7 nano-colloids. Binary sorption experiments have been extended to other minerals (montmorillonite, bentonite). Sorption/desorption kinetics, reversibility, and stability of the various forms of Pu on mineral surfaces are the focus of ongoing research.
- Pu stabilization by ternary complexes. The influence of natural organic matter on Pu mobility is dependent on behavior and character of the organic ligand. Ternary surface-NOM-Pu surface complexes can form at low pH values where the ligand strongly sorbs. Conversely, at neutral pH values ligand complexation results in higher aqueous Pu concentrations and the potential mobilization of Pu. Stability constants describing humic and fulvic acid complexation with Pu have been determined and formation of ternary complexes on model minerals (goethite, gibbsite) is being investigated.
- Characterization of Pu-contaminated samples from the field. We have developed and tested the use of NanoSIMS imaging for Pu analysis. Sub-micrometer-scale Pu distribution on Hanford sediments located 60 feet beneath a disposal crib has been completed and mineral associations (e.g. Pu-Fe associations) identified. Characterization effort is being expanded to other field sites.
- Development of NMR capability for paramagnetic actinides. We have benchmarked the use of NMR (using Ni and Cu) to probe the surface configuration of paramagnetic species by exploiting the strong response of NMR signals to the presence of paramagnets. This capability is being extended to actinides and will provide a unique facility for probing actinide behavior at the mineral-water interface.
- Ab initio modeling of monomeric adsorption processes. We completed ab initio simulations to model the structure of the hydrated Pu monomer under neutral solution conditions ($Pu(OH)_4$). Successful representation of the tetrahydroxy species is our starting point for examining the monomeric adsorption of Pu on mineral surfaces (goethite, corundum).