Identifying Molecular Scale Mechanisms Controlling Actinide Transport

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The Subsurface Biogeochemical Research Scientific Focus Area at Lawrence Livermore National Laboratory is focused on identifying and quantifying the biogeochemical processes that control the fate and transport of Pu and other actinides at environmentally relevant concentrations (1E-12 - 1E-18 mol/L). We are taking advantage of LLNL's unique capabilities in (1) measuring actinide concentrations at ultralow concentrations (<1E-14 mol/L) by AMS (2) characterizing the morphology of Pu associated with mineral surfaces and microbes by TEM and SEM, and (3) investigating the structure and reaction kinetics of actinide complexes by NMR. Additional capabilities at Clemson University (e.g. FTIR) are employed to elucidate the nature of ternary actinide-organic-mineral complexes.

Recent flow cell sorption/desorption experiments have been used to quantify reaction kinetics. Both equilibrium isotherm data and desorption kinetic data indicate that Pu sorption behavior at environmentally relevant trace concentrations (1E-15 M) is equivalent to observations at higher concentrations (1E-10 M). Rate data are being used to assess the stability and migration potential of Pu under environmentally relevant timescales and distances.

Unique longterm (~3 year) nuclear melt glass alteration experiments are examining secondary mineral formation (including colloids) across a range of temperature (25 - 200 °C) and the association of Pu with colloids. Follow-on experiments are investigating the nature of these Pu associations (e.g. coprecipitation, sorption).

The stability of Pu on colloids and mineral surfaces is dependent on its redox state. Recent studies examined the role of trace peroxide in surface water and groundwater on the mobilization of Pu. Fenton reactions lead to oxidation (and mobilization) of Pu. However, these reactions are pH dependent, transient, and their effectiveness is dependent on the nature of mineral surface to which Pu is sorbed.

NMR has proved to be a unique tool for exploring reaction kinetics (and surface structure) of actinide complexes. Recent investigation of the Np(VI) tris-carbonato complex has identified proton-enhanced and proton-unenhanced ligand exchange pathways that parallel those of U(VI). These experiments are revealing previously unknown patterns in reaction kinetics among the actinides.

Ternary sorption studies (actinide-NOM-mineral) have been performed to examine the role of organic matter in actinide transport. Column studies using radiolabeled NOM and hematite colloids in the presence of either Th(IV) or Pu(IV) have shown that NOM coatings on colloid surfaces can prevent aggregation and enhance transport of colloid bound Pu/Th. Specific binding of the NOM to mineral surfaces has been characterized using ATR-FTIR spectroscopy.

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