Understanding the Subsurface Reactive Transport of Transuranic Contaminants at DOE Sites

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Our primary hypothesis is that Np and Pu can interact with surfaces in fundamentally different ways than other metals, metalloids, and oxyanions – namely by reductive surface precipitation from undersaturated solutions. We are testing our hypotheses by studying the sorption of Pu and Np and their analogues to representative heterogeneous subsurface materials from Savannah River Site (SRS).

The sorption of Np(V), the dominate oxidation state of Np in the environment, onto sand from the SRS does not occur under any environmentally relevant conditions. In contrast, Np(V) is sorbed onto clay substrate under slightly basic conditions. XPS and EDS spectroscopy were used to probe the specific minerals that the Np(V) is associated with, and invariably the Np(V) is found associated with Fe minerals. In addition, the transport of Np(V) has been shown to be mitigated by the precipitation of U(VI) minerals that act as carriers for Np(V).

Th(IV) [as an analogue for Pu(IV)] transport experiments are being conducted using columns packed with SRS geomedia. At low pH (pH=4) and high ionic strength (I=0.1 M) conditions, Th(IV) transport is strongly retarded by the soil. However, a decrease in ionic strength to I=0.001 M caused colloids to be released from the geomedia. In addition to colloids, high concentrations of Th(IV) were also detected in the effluent samples immediately after the change in solution chemistry. However, after measuring dissolved and total Th(IV) concentrations, it was determined that colloid-facilitated transport was not the predominant cause for peaks in Th(IV) concentration up to ten times that of the influent solution. Instead, a drop in pH caused by the change in solution chemistry was responsible for the peaks in Th(IV) concentration. Depending on the surface charge of the geomedia, fluctuations in ionic strength can cause pH fronts to occur, producing dramatic effects on the transport of strongly actinides that can cause effects more pronounced than conventional colloid-facilitated transport.

The Advanced Light Source-Molecular Environmental Sciences (ALS-MES) Beamline scanning transmission X-ray microscope (STXM) successfully imaged and conducted near-edge X-ray absorption fine structure (XAFS) spectroscopy studies on sets of particulates derived and prepared from several sources within the project. One of the most interesting results supported by the STXM experiments, in addition to laboratory studies, was that U interactions with the non-hydrophobic components of the humic acids studied were more important than anticipated. Additional STXM experiments on particulates obtained from column experiments provided information about elemental associations and the presence of C on the particles. Upcoming STXM experiments will continue these investigations and will initiate new experiments as beamtime permits. Hard X-ray XAFS studies were also conducted on representative U, Np, and Pu materials obtained from selected materials from the sorption experiments.