

Stabilization of Pu Surface Complexes on Mineral Colloids by Natural Organic Matter

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The LLNL SFA has been examining the influence of natural organic matter (NOM) on Pu sorption to minerals. The major objectives have been to determine the affinity of Pu for NOM, identify the conditions that lead to the formation of ternary Pu-NOM-mineral complexes, and quantify the stability and mobility of those complexes.

We determined thermodynamic data for Pu-NOM complexes by determining stability constants for Th(IV)-, Np(V)-, and Pu(IV)-HA (humic acid) complexes using a discrete pKa approach. Comparison of Th(IV)-HA and Pu(IV)-HA complexes to others actinide-ligand complexes revealed a consistent pattern in which Pu(IV) complexes are nearly four orders of magnitude more stable than their Th(IV) counterparts.

Pu sorption to montmorillonite, gibbsite and goethite in the presence of desferrioxamine B (DFOB), HA, fulvic acid (FA), HA and citric acid (CA) was examined. When compared to the binary Pu-mineral systems, the addition of CA, FA, HA decreased the sorption of Pu(IV) at circumneutral pHs. A similar effect was observed with the addition of DFOB to gibbsite and goethite. In contrast, when Pu(IV) was equilibrated with DFOB prior to addition of montmorillonite, a significant increase in Pu(IV) sorption was observed. However, when DFOB was equilibrated with montmorillonite prior to addition of Pu(IV), Pu(IV) sorption was equivalent to the binary system. X-ray diffraction and TEM revealed that DFOB accumulated in the interlayer of montmorillonite. The irreversible nature of DFOB accumulation in the montmorillonite interlayer leads to an apparent dependence of Pu sorption on the order of addition. The results highlight the importance of siderophores/hydroxamate ligands as Pu complexants and the unique intercalation mechanism that can lead to irreversible Pu sorption to layered clays.

The effect of NOM on Pu adsorption/desorption kinetics was also investigated. In goethite suspensions at low pHs, we found that FA coatings slowed Pu adsorption kinetics, while aqueous FA accelerated Pu surface reactions. Independent of the initial form of FA, FA increased Pu sorption in low-pH environments and stabilized Pu on the mineral surface above a solid concentration of $\sim 0.20 \text{ mg TOC g}_{\text{goethite}}^{-1}$. Furthermore, the presence of FA led to surface complexes on the goethite surface that appeared to be less reversible than the simple binary complexes. Thus FA and other NOM may increase Pu colloid facilitated transport by 1) enhancing the Pu sorption to colloids and 2) enhancing the stability and mobility of the colloids. Alternatively, NOM could decrease Pu mobility through enhanced retention on a host rock.