Influence of Natural Organic Matter on the Subsurface Fate and Transport of Plutonium

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This task within the Transuranic Subsurface Transport SFA is focused on understanding the role of natural organic matter on the fate and transport of plutonium. The task is guided by the hypotheses that NOM can increase Pu mobility by *1) forming NOM coatings on colloids which stabilize Pu surface complexes and 2) formation of aqueous Pu-NOM complexes which prevent sorption of Pu.*

Aqueous stability constants describing complexation of Pu(IV), Th(IV), and Np(V) with IHSS Leonardite Humic Acid and IHSS Suwannee River Fulvic Acid were determined using a combined ultrafiltraton/competitive ligand exchange technique. The stability constants were determined using a four site model of the humic acid and fulvic acid (noted as HL1, HL2, HL3, and HL4) with discrete pKa values of 3, 5, 7, and 9, respectively. The stability constants for Pu(IV) and Th(IV) binding with humic acid were:

$$Pu^{4+} + HL3 + 2H_2O \leftrightarrow Pu(OH)_2L3^+ + 3H^+ \qquad \log K = 6.76$$
$$Th^{4+} + HL3 + 2H_2O \leftrightarrow Th(OH)_2L3^+ + 3H^+ \qquad \log K = 3.58$$

Binding of Pu(IV) was approximately 3 orders of magnitude stronger than Th(IV) indicating that Th(IV) makes a relatively poor choice as an analog for Pu(IV) despite common usage. This was verified by comparison with other common Th(IV) and Pu(IV) organic ligand complexes. Complexation with fulvic acid was examined based on dissolution of PuO_2(s) nanoparticles. Suspensions of PuO_2(s) were prepared in 5mgC/L and 50 mgC/L fulvic acid across the pH range 3 to 9. The aqueous concentration of Pu continuously increased over a 90 day period. Since equilibrium has not yet been achieved, stability constants have not yet been determined. Dissolution rates ranging from 0.5 to 2.0 μg_{Pu}/L/day were determined across the pH range 4 to 7.5.

The influence of organic ligands on sorption of Pu(IV) to gibbsite and goethite was monitored using citric acid, desferrioxamine B, fulvic acid, and humic acid. These ligands were selected to represent a range of molecular weights and sources of NOM. Batch sorption experiments of Pu in the presence of these ligands indicate sorption at low pH values may be due to the formation of ternary surface complexes. For example, sorption of Pu(IV) to gibbsite in the presence of humic acid at pH 4 and 6 was greater than sorption in the absence of humic acid. Furthermore, greater sorption was observed at pH 4 as compared with pH 6. In the absence of humic acid sorption is expected to increase with increasing pH. Thus, humic acid appears to facilitate formation of a ternary surface complex. Modeling the pH 4 and 6 sorption isotherms using the aqueous stability constants listed above yielded a ternary surface complexation constant of:

$$\equiv AlOH + Pu^{4+} + 2H_2O + 2HL3 \Leftrightarrow \equiv AlOH_2(HL3)_2Pu(OH)_2^{3+} + H^+ \qquad \log K = 36.8\ (0.4)$$

Although the ternary surface complexes above indicate the potential for decreased mobility of Pu, batch sorption experiments also indicate that the relatively small siderophores, citric acid and DFOB, reduce sorption most effectively. Citric acid and DFOB decreased the fraction of sorbed Pu when compared with the binary system for all pH values studied. Using continuously stirred flow-through batch reactors, complete desorption of Pu from goethite has been achieved. These results have been verified by observing transport of Pu through a sediment column in the presence of DFOB. Therefore, the presence of DFOB and other small molecular weight, chelating ligands in an environmental system would likely lead to increased mobility of plutonium. However, even in the presence of NOM, Pu sorption increases as the pH is raised, indicating competition between aqueous Pu-NOM complexes and Pu hydrolysis products which generally exhibit strong sorption.