The Effect of Natural Organic Matter on Plutonium Sorption to Goethite
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The effect of natural organic matter (NOM; citric acid, Deferoxamine B (DFOB), Suwannee River fulvic acid, and Leonardite humic acid) on plutonium sorption to goethite was studied using batch sorption experiments at 5 mgC·L⁻¹ and 50 mgC·L⁻¹ NOM, 10⁻¹⁰ M plutonium, and 0.1 g·L⁻¹ goethite concentrations. Aqueous concentrations of both plutonium and NOM in the bulk solution were monitored by liquid scintillation counting (LSC) in order to understand the extent of NOM and plutonium sorption to goethite and possible ternary complex formation. This was made possible through the utilization of radiolabeled NOM where possible. Commercially available ¹⁴C-citric acid was purchased, while fulvic acid and humic acid were labeled with tritium as a part of this study using tritiated NaBH₄ to reduce NOM ketones to secondary alcohols while minimally affecting structure or reactivity. DFOB could not be labeled by the same mechanism, as it lacks ketones, and no radiolabeled DFOB is commercially available. Therefore DFOB sorption was determined by total organic carbon analysis in a separate plutonium free experiment.

These data indicate that NOM type, NOM concentration, and system pH have significant impacts on plutonium sorption, as well as the underlying sorption mechanisms. All the NOM studied reduced plutonium sorption from near pH 4 to the point of zero charge of goethite (~ pH 8). Citric, fulvic, and humic acids decreased aqueous plutonium concentrations below pH 4 presumably through ternary complex formation with the goethite surface or, in the case of humic acid, by incorporation into coagulating NOM complexes. In systems above pH 8, competition between Pu(IV) hydrolysis and complexation by NOM was apparent and resulted in an increase in sorption and a decreased solubilizing effect of the NOM.

Mechanisms for ternary complex formation were characterized by Fourier transform infrared (FTIR) spectroscopy in the absence of plutonium. For this study, high concentrations of NOM (2.5 g·L⁻¹) were mixed for several days with goethite and the pH regularly adjusted to ~ 4.5. The solid fraction of these suspensions were lyophilized and the powder was analyzed by attenuated total reflectance FTIR spectroscopy. Citric and fulvic acids demonstrated clear surface interactions with goethite near pH 4.5 whereas no DFOB interactions were observed. The observation of no/limited DFOB interactions with goethite is consistent with batch sorption data at all the pHs studied. Spectra indicate significant homoaggregation of humic acid and little goethite surface interaction near pH 4.5. These data augment that of the batch sorption experiments in determining the mechanisms of plutonium removal from the bulk aqueous solutions either by 1) binary sorption to the goethite surface 2) NOM assisted sorption to the goethite surface 3) incorporation into an NOM aggregate. These data also indicate that plutonium sorption to goethite can be either enhanced by formation of ternary surface complexes at low pH or reduced via formation of soluble plutonium-NOM complexes. The former has implications for colloid facilitated transport of plutonium where the NOM may stabilize iron mineral colloids and also provide strong association of plutonium with the colloids.

Extended x-ray absorption fine structure (EXAFS) spectroscopy was used to study the coordinating environment of plutonium sorbed to goethite under conditions suggested by batch sorption and FTIR spectroscopic data to result in ternary complex formation. EXAFS data support the formation of a ternary, goethite-plutonium-citrate, complex near pH 4.