

Speciation and dynamics of biologically reduced U(IV) in the Old Rifle, CO, aquifer

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The chemical and physical forms of U(IV), as well as the biogeochemical processes by which they form and transform, profoundly influence the behavior of uranium in reduced sediments. Obtaining this information for sediments biostimulated *in situ*, *i.e.*, in the field, has been one of the most important and difficult scientific challenges in the field of uranium bioremediation. We have used in-well columns to obtain direct access to sediment U(IV) species, evolving microbial communities, and trace and major ion groundwater constituents in the Old Rifle, CO (USA) aquifer. Sediments were examined using x-ray and electron microscopy (XRM and SEM/TEM), x-ray absorption spectroscopy (XAS), and chemical digestions. EXAFS analysis showed that U(IV) occurred predominantly or exclusively as monomeric U(IV) complexes under both metal- and sulfate-reducing conditions, and was associated with biomass or Fe sulfides. Intriguingly, U(IV) was bonded to oxygen atoms, even when associated with iron sulfides. A fraction of these monomeric complexes transformed into uraninite in the aquifer over a subsequent 12 month period. This work establishes the importance of monomeric U(IV) complexes in subsurface sediments at the Old Rifle site and provides a conceptual framework in which previously observed U(IV) reduction products can be related. These experiments also establish that U(IV) species are dynamic in aquifers and can undergo non-oxidative transformation reactions. These new results have important implications for uranium reactive transport models and remediation technologies.

Influence of citric acid, EDTA and fulvic acid on U(VI) sorption onto kaolinite

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Batch sorption experiments were used to investigate U(VI) sorption on kaolinite (2 g/L KGa-1b) as a function of pH (3-10), ionic strength (0.001 - 0.1 M NaNO₃), pCO₂ (0-5%), U(VI) (10⁻⁶ - 10⁻⁴ M U) and organic acid (10⁻⁴ and 10⁻² M citric acid, 10⁻⁴ - 10⁻² M EDTA, and 10 - 20 mg/L fulvic acid). Ligand sorption on kaolinite was also assessed in the absence of U(VI).

In the absence of ligands, U(VI) sorption on kaolinite increases from pH 3 to ~7, plateaus at nearly 100% between pH ~7 - 8.5, and decreases at pH > 8.5. Ionic strength has little effect on U(VI) sorption. Thus, at circumneutral pH, kaolinite could have a strong influence on U(VI) mobility in natural systems. Compared to atmospheric conditions, U(VI) sorption under 0 pCO₂ is slightly enhanced from pH 3 - 7, and unchanged from pH of 7-10, likely due to strong aqueous U(VI)-OH complexes. However, with increased pCO₂, up to 5%, U(VI) sorption diminishes significantly between pH 5-10, due to formation of U(VI)-carbonate aqueous complexes.

Addition of 10⁻⁴ or 10⁻² M citric acid results in decreased U(VI) sorption at all pH values, with up to 50 or 90% reduction in U(VI) sorbed, respectively. Similarly, addition of 10⁻⁴ - 10⁻² M EDTA yields a decrease in sorption of up to ~70% compared to organic-free experiments. TOC analyses of citric acid and EDTA sorption on kaolinite in the presence or absence of U(VI) demonstrate that less than 10% of either ligand is sorbed to the solid surface. Thus, ternary complex formation at the kaolinite surface is unlikely to occur. Instead, U(VI) binds preferentially to organic acids as aqueous complexes. Addition of 10 or 20 mg/L fulvic acid causes an increase in sorption from pH 3 to ~5 respectively, and a decrease from pH ~5 to 10. Up to 40% of 10 mg/L fulvic acid or 20% of 20 mg/L fulvic acid sorbs on kaolinite at low pH, with the amount adsorbed linearly decreasing to ~10% at pH 10. Fulvic acid complexation at the kaolinite surface results in enhanced U(VI) sorption at low pH, likely due to the formation of ligand bridges. However, at high pH, U(VI) sorption is suppressed, presumably due to formation of strong aqueous U(VI)-fulvic acid complexes.

These data suggest that U(VI) sorption on kaolinite could be significant at circumneutral pH, but that organic acids may significantly retard or enhance U(VI) mobility. The data are currently being used to develop surface complexation model parameters describing U(VI) sorption to kaolinite.