Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

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Phosphate addition is an in situ remediation approach that may enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms upon phosphate addition are insufficiently understood to design efficient remediation strategies or accurately predict U(VI) transport. The overall objective of our project is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Our research approach seeks to determine the U(VI)-phosphate precipitates that form from homogeneous solutions, characterize the effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, and investigate how phosphate affects U(VI) speciation and fate in field sediments.

Our initial studies investigated the products of U(VI)-phosphate reactions in the absence and presence of sorbing mineral phases. In homogeneous systems, autunites form even when other U(VI) phosphates are more thermodynamically stable. In the presence of Ca, U(VI) may also sorb to or coprecipitate with calcium phosphates. In heterogeneous systems, phosphate has no macroscopic effect on U(VI) adsorption to a smectite clay despite LIFS and EXAFS spectra showing a clear change in surface speciation. In contrast, phosphate enhanced U(VI) adsorption to goethite at pH 4 but suppressed adsorption at pH 6 and 8. For both smectite and goethite, autunites precipitated at high phosphate and U(VI) concentrations but only after a critical supersaturation was exceeded.

Our current activities focus on U(VI)-phosphate reactions in Rifle and Hanford site sediments. Synthetic groundwaters designed to match the major element compositions at the sites were employed for both sediment types. Batch studies show little to no U(VI) sorbs to Rifle sediments except at high (1 mM) phosphate concentrations. The addition of phosphate to the influent of columns of Rifle sediments results in substantial sustained decreases in effluent U(VI) concentrations. Sequential extractions of sediments from the columns confirmed the accumulation of uranium with time and observed a gradual shift of solid-associated uranium to less mobile species. EXAFS and LIFS analysis of these sediments suggested that U(VI) was immobilized by both precipitation of an autunite mineral and adsorption. Batch studies of Hanford sediments showed distinct behavior from the Rifle sediment system. Substantial U(VI) adsorption occurred and was enhanced by phosphate addition, with an autunite-type precipitate forming at initial U(VI) and phosphate concentrations above 25 μM and 100 μM, respectively. Ongoing column experiments are investigating U(VI) retention in Hanford sediments in the presence of phosphate.