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ABSTRACT TITLE: Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

ABSTRACT: Phosphate addition is an in situ remediation approach being considered by the DOE 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 in treated systems. 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 identify the U(VI)-phosphate precipitates that form from homogeneous solutions, characterize the cooperative and competitive effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, and then investigate how phosphate affects U(VI) speciation and fate in sediments from the Rifle and Hanford sites.

Batch experiments were performed to determine the products of U(VI)-phosphate precipitation in homogeneous systems and the resulting equilibrium solubility of those solids as a function of groundwater composition. In the absence of groundwater cations (e.g., Na\(^+\) and Ca\(^{2+}\)) metastable chernikovite \([\text{H}_3\text{O} \text{(UO}_2\text{(PO}_4\text{)} \cdot 3\text{H}_2\text{O}}]\) forms instead of the thermodynamically stable uranyl orthophosphate \([\text{(UO}_2\text{(PO}_4\text{)} \cdot 4\text{H}_2\text{O}}]\). Sodium and calcium addition affect U(VI)-phosphate precipitation, with the former inducing the precipitation of Na-autunite \([\text{Na(UO}_2\text{(PO}_4\text{)} \cdot 3\text{H}_2\text{O}}]\) whereas calcium causes U(VI) removal through both autunite \([\text{Ca(UO}_2\text{(PO}_4\text{)} \cdot 11\text{H}_2\text{O}}]\) precipitation and adsorption onto or incorporation into calcium phosphates.

Separate batch experiments have been conducted to investigate how phosphate affects U(VI) adsorption and precipitation in the presence of montmorillonite and goethite. For both systems, supersaturation is required before the nucleation and precipitation of Na-autunite initiates. The critical supersaturation needed for Na-autunite precipitation on goethite was twice that for montmorillonite. Before the onset of precipitation, U(VI) binding is through adsorption processes. Phosphate has a negligible effect on macroscopic U(VI) adsorption to montmorillonite at pH 4, 6, and 8 despite evidence from EXAFS and TRLFS spectroscopies for ternary complexation. In contrast, phosphate enhances U(VI) adsorption to goethite at pH 4 but suppresses adsorption at pH 8; the former is attributed to U(VI)-phosphate ternary complexation and the latter to surface site competition between U(VI) and phosphate.

Our efforts are currently transitioning to batch and column studies of U(VI)-phosphate reactions in sediments from the Rifle site in Colorado. Batch studies in artificial Rifle groundwater show negligible U(VI) sorption except above $10^{-5}$ M initial U(VI). The addition of phosphate reduces U(VI) sorption. Studies of U(VI) speciation and the origin of this inhibitory effect are ongoing. Column experiments have also been initiated to examine the influence of phosphate on U(VI) transport, again in artificial groundwater. Following uranium loading, half of the columns then received artificial groundwater amended with phosphate and the other half received phosphate-free solutions. Flow rates were set to provide environmentally relevant seepage velocities. Periodic stopped flow events are being performed...
to assess the effects of intraparticle diffusive transport on overall U(VI) mobility. After reaction, columns will be sampled along their length and characterized to determine U speciation and micro-scale spatial distribution. Similar studies are planned for sediments from the Hanford site.