Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

University-Led Research

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Widespread subsurface contamination at DOE sites has resulted from past mining, processing, and waste disposal processes. In situ remediation technologies can sequester uranium on site by transforming uranium to stable, low solubility species. While substantial recent research has investigated biogeochemical U(VI) reduction, this approach may have limited long-term sustainability because of the potential for reoxidation to occur. Phosphate addition is an alternative approach that can enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms are insufficiently understood to design efficient remediation strategies or accurately predict uranium transport in treated systems.

The overall objective of our project is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Specific objectives are to: (1) resolve uncertainty regarding the specific U(VI) phosphate solids that form in homogeneous solutions; (2) determine the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems and the conditions where specific mechanisms dominate; (3) characterize how the interaction of competitive and cooperative reactions controls uranium speciation in sediments; (4) identify chemical divides that separate regimes where specific mechanisms dominate U(VI) speciation in subsurface sediments. In the first six months of this project our team has focused on meeting objectives 1 and 2.

For objective 1 we have investigated homogeneous precipitation of U(VI) phosphates to determine the conditions where specific phases forms. Studies to date have focused on systems lacking simple inorganic electrolyte cations in order to characterize the relative stability and occurrence of chernikovite [$H_3OUO_2PO_4 \cdot 3H_2O$] and uranyl orthophosphate [$(UO_2)_3(PO_4)_2 \cdot 4H_2O$]. Precipitation is initially rapid upon supersaturation and equilibrium is approached within 4 days. Chernikovite forms at all conditions studied; it may co-form with uranyl orthophosphate at pH 4 and high phosphate conditions. Solid characterization by XRD, SEM, EXAFS, and TRLFS is in progress. We plan to explore the effects of electrolyte cations (Na, Ca) and competition with calcium phosphate precipitation over the next six months.

For objective 2 we have investigated U(VI) and phosphate co-sorption on smectite to determine if substantial ternary complexation occurs and to characterize the transition between adsorption and precipitation. Wet chemistry studies show that phosphate has little effect on U(VI) adsorption at pH 4, 6, and 8 prior to the onset of U(VI) phosphate precipitation. Phosphate adsorption is low and these observations suggest that, unlike for iron oxide minerals, little U(VI)-phosphate ternary complexation occurs on smectite. The effect of phosphate on U(VI) adsorption mechanisms and U(VI) phosphate nucleation on smectite is currently being investigated by an integrated series of EXAFS and TRLFS measurements. Over the next six months we plan to determine the effects of Ca on U(VI) adsorption to smectite in the presence of phosphate and extend this work to goethite. Our efforts will then transition to characterizing U(VI)-phosphate reactions in sediments obtained from the Rifle and Hanford IFRCs.