Formation and stability of Uranium(VI) Phosphates under Groundwater conditions

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Phosphate addition to uranium-contaminated subsurface environments is a promising approach for *in situ* remediation. Addition of phosphate amendments can result in uranium sequestration in its oxidized +VI state without requiring chemically reducing conditions as needed for *in situ* immobilization via biogeochemical reduction of U(VI) to less soluble U(IV) species. Phosphate addition can be used as a stand-alone process or as a complementary process to bioremediation-based methods. The U(VI)-phosphate-sediment groundwater system is complex owing to the fact that uranium can adsorb to substrate minerals in addition to precipitating in uranyl phosphate solids. Furthermore, the solids that form may be metastable phases instead of those predicted by equilibrium calculations. The conditions that determine the dominant immobilization mechanisms are not well understood, and improvements in our knowledge can enable the design of more efficient remediation strategies.

To gain a better understanding of molecular scale interactions between U(VI) and phosphate, batch precipitation experiments were conducted at various pH conditions with solutions equilibrated with the atmosphere. As would be done in practice, phosphate was added in molar excess to U(VI) [ratio of PO_4^{3-} : U(VI) of 10:1] to enhance the precipitation reactions. Samples collected at various time intervals were used to measure the aqueous phase concentrations of uranium and phosphate using ICP-MS. In the presence of phosphate, more than 90% of uranium was sequestered in the solid phase under acidic conditions (pH= 4, 6) where there otherwise would not have been any uranium precipitation. At higher pH (pH= 7.5), the formation of soluble uranium-carbonate complexes prevented any precipitation. Solids collected on membrane filters were characterized using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray diffraction (XRD). In the presence of phosphate, precipitates of thin 1-5 µm square plates were observed. These analyses suggest the formation of chernikovite [$UO_2HPO_4.4H_2O$], which probably formed as a metastable phase since uranyl phosphate [$(UO_2)_3(PO_4)_2$] is calculated to be the thermodynamically most favorable phase under these conditions. The stoichiometry of the solid was examined by digestion of the solids and corroborates the formation of chernikovite [U(VI) : PO_4^{3-} ratio of ~ 1:1] in the presence of phosphate.

Current experiments are studying the specific effects of dissolved inorganic carbon and common groundwater cations (Na, Ca, Mg etc.) on the formation of precipitates in the presence and absence of phosphate. Ultimately, these experiments on precipitation of uranium-containing solids following homogeneous nucleation will be extended to conditions relevant to field sites by examining precipitation and adsorption in the presence of iron oxides, clays, and actual sediments. These studies will advance our fundamental understanding of molecular-scale mechanisms of uranium immobilization and their impact on uranium fate and transport in the subsurface.