

## Uranyl-chlorite sorption/desorption: Evaluation of different sorption mechanisms

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Sequestration of soluble uranium (U) by clay minerals such as chlorite has been shown to be a major sink for U in contaminated environments such as the Hanford, Washington 300 Area. We have used batch sorption/desorption experiments combined with U L<sub>III</sub>-edge EXAFS spectroscopy to investigate what sorption mechanism(s) dominates uranyl uptake by chlorite (ripidolite CCa-2). Sorption was found to be independent of ionic strength, suggesting a dominantly inner-sphere sorption mechanism. The maximum sorption loading was 0.10 moles U/kg chlorite (~10% U removed from solution) at pH 4, whereas the sorption loading was 2.0 moles U/kg chlorite (nearly 100% removed from solution) at pH 6.5 and pH 10. At a given pH value, the sorption loading was independent of the presence of U(VI)-CO<sub>3</sub> or U(VI)-CO<sub>3</sub>-Ca aqueous complexes. All sorption data were fit well with Langmuir-type isotherms. Addition of 0.1 M HCl resulted in 70-80% desorption of sorbed uranyl. Initial fits of the EXAFS spectra of the sorption samples also indicate that inner-sphere sorption of uranyl dominates uptake. These results suggest that two types of bound uranyl are present, one of which is more tightly bound. This suggestion might be explained by: (1) a mixture of monodentate and bidentate sorption complexes and/or (2) ternary complexes formed through equatorial oxygen atoms. Continued exposure of chlorite to uranyl for two months under simulated weathering conditions resulted in the reduction of U(VI) to U(IV). EXAFS spectra of these samples indicated the presence of 25% U(IV), whereas no U(IV) was detected for the sorption samples. Further, an additional contribution to the spectra was observed that is consistent with the U-U pair correlation in uraninite. These results suggest that long-term exposure of chlorite to uranyl could result in U sequestration as the relatively insoluble UO<sub>2</sub>, versus more transient sorption complexes. Our findings can aid surface complexation modeling of uranyl sorption on clay minerals by providing molecular-level information on how sorption mechanisms change as a function of solution chemistry.

## Uranium(VI)-phosphate interactions at the goethite-water interface

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Interactions of phosphate and uranium at mineral-water interfaces can control the mobility of uranium in subsurface environments. Past mining, processing, and waste disposal activities have left a legacy of uranium-contaminated soil and groundwater. Phosphate addition to subsurface environments can potentially provide long-term *in situ* U(VI) immobilization [1]. In addition to the precipitation of low solubility U(VI)-phosphates, phosphate can also affect U(VI) by enhancing or inhibiting adsorption to iron(III) (oxy)hydroxides. Such surfaces may facilitate the heterogeneous nucleation of U(VI)-phosphate precipitates.

The interactions among phosphate, U(VI), and goethite ( $\alpha$ -FeOOH) were investigated in a series of batch experiments. Combinations of U(VI) and phosphate were selected to probe the influence of solution saturation state on the mechanisms of U(VI) and phosphate removal from solution. To provide insights into the immobilization mechanisms, the solid phases were characterized by scanning and transmission electron microscopy, X-ray diffraction, and X-ray absorption spectroscopy. Dissolved concentrations were interpreted within a reaction-based modeling framework that included dissolution-precipitation reactions and a surface complexation model to account for adsorption [2].

Nucleation of a U(VI)-phosphate phase, most likely (UO<sub>2</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2(s)</sub>, occurred rapidly for initially supersaturated suspensions both with and without goethite. A critical supersaturation index for precipitation was observed. The results suggest that nucleation occurred homogeneously even in the presence of goethite. The U(VI)-phosphate solids precipitated rapidly and persisted for long time-scales even in goethite suspensions for which equilibrium calculations predict immobilization to occur exclusively through adsorption. The goethite surface can act as a sink for dissolved phosphate, which results in higher dissolved U(VI) concentrations than in goethite-free suspensions.

[1] Arey, J.S., J.C. Seaman & P. Bertsch (1999) *Environ. Sci. Technol.* **33**, 337-342. [2] Cheng, T., M.O. Barnett, E.E. Roden & J.L. Zhuang (2004) *Environ. Sci. Technol.* **38**, 6059-6065.