## Biogeochemical controls on the product of microbial U(VI) reduction

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Biologically mediated immobilization of radionuclides in the subsurface is a promising strategy for the remediation of U-contaminated sites. During this process, soluble U(VI) is reduced by indigenous microorganisms to sparingly soluble U(IV). The crystalline U(IV) phase uraninite, or UO<sub>2</sub>, is the preferable end-product of bioremediation due to its relatively high stability and low solubility in comparison to the noncrystalline biomass-associated non-uraninite U(IV) species. However, non-uraninite U(IV) species have been reported to be a predominant U(IV) product formed under field relevant conditions. Therefore the goal of this study was to delineate the biogeochemical conditions that promote the formation of non-uraninite U(IV) versus uraninite, to decipher the mechanisms of its preferential formation and to apply this knowledge to environmentally relevant cases. Batch experiments as well as biofilm reactors were set up to test the influence of biogeochemical conditions on U(IV) product formation. U(IV) products were analyzed with X-ray absorption spectroscopy (XAS), scanning transmission X-ray microscopy (STXM) and various wet chemical methods. As a result of batch experiments, we report an increasing fraction of non-uraninite U(IV) species with decreasing initial U concentration. Additionally, the presence of several common groundwater solutes (sulfate, silicate and phosphate) promote the formation of non-uraninite U(IV). Our experiments revealed that the presence of specific solutes promotes the formation of bacterial extracellular polymeric substances (EPS) and increases bacterial viability, suggesting that the formation of non-uraninite U(IV) is due to a biological response to the presence of these solutes during U(VI) reduction. Ongoing biofilm studies focus on the characterization and origin of U(IV) species formed under field relevant conditions, i.e., in the flow-through systems, under alternating redox regimes with controlled biotic and abiotic processes.

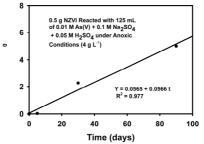
## Arsenic immobilization and transformation by zerovalent iron

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## **Introduction and Experiments**

Both graular [1] and nanosized zerovalent iron (NZVI) [2] are effective in removing arsenic from water. Granular ZVI also has been used as permeable reactive barrier media to intercept and remove As from contaminated groundwater at a smelting site [3] and as a filter material for removing As from Bangladesh tube well water [4]. This study focus on As removal mechanisms by NZVI. Batch tests were conducted using 25-nm NZVI to remove As(V) and As(III) under anaerobic conditions as a function of time and pH with or without phosphate and silicate. Minerals were identified.



**Figure 1.** Plot of pseudo-second order removal kinetics for As(V) in the long term test.

## **Results and Discussion**

Both As(V) and As(III) removal increased with increasing time to approach a steady state after 4-5 days in the short-term test. There was generally more removal of As(III) than As(V). Complete or near complete removal of As(V) and As(III) was achieved at pH levels less than 10. Competition of phosphate and silicate against As(V) and As(III) was observed at alkaline pHs. New solid phases formed such as parasymplesite in the As(V) system and vivianite in the phosphate system. This study demonstrated that As(V) removal involves both solid precipitation and adsorption; whereas, As(III) removal only involves surface adsorption.

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[2] Kanel et al. (2005) Environ. Sci & Technol. 39, 1291-1298.
[3] Beak & Wilkin, (2009) J. Contam. Hydrol 106, 15-28.
[4] Leupin & Hug (2005) Water Res. 39, 1729-1740.