Iron Reduction and Radionuclide Immobilization: Influence of Natural Organic Matter and Reaction-Based Modeling

William D. Burgos[1] (PI), Brian A. Dempsey[1], Je-Hun Jang,[1] Gour-Tsyh (George) Yeh,[2] and Eric E. Roden[3]

[1]The Pennsylvania State University; [2]University of Central Florida; [3]The University of Alabama

The objectives of our research are to evaluate the potential for humic substance addition to stimulate in situ Fe(III)-reducing activity and U(VI) bioimmobilization, and to construct and validate a comprehensive reaction-based model to simulate these processes. To achieve these objectives we have been conducting research in a variety of areas including (1) kinetic measurements of biological Fe(III) reduction in natural sediment columns for reaction-based reactive transport modeling, (2) construction of reaction-based reactive transport models, (3) kinetic measurements of concomitant Fe(III) and U(VI) reduction in natural sediments, (4) abiotic reduction of U(VI) by sediment-associated Fe(II), (5) complexation of U(VI) by humic substances using dialysis and ultrafiltration techniques, (6) impact of humic substances of biological U(VI) reduction, and (7) sorption of U(VI) on specimen ferric oxides. Our poster presentation will focus on this last research element.

Studies were conducted to investigate the precipitation of U(VI) oxides and the sorption of U(VI) onto hydrous ferric oxide (HFO) or hematite at pH 5.9 to 7.8, ambient PCO2, 0.1 mM Fe(III), U(VI) to Fe(III) molar ratios from 0.001 to 70, and for reaction times from 15 min to 48 days. "Dissolved" U(VI) was measured using Kinetic Phosphorescence Analysis (KPA) after filtration using 0.2 µm pore-size filters. "Total" U(VI) was measured using KPA after dissolution of solids in 0.5N HNO_3 or $NaHCO_3$. Complete recovery of U(VI) was demonstrated. Ferric oxide precipitates were characterized using Fe-57 Mössbauer Spectroscopy.

Sorption onto HFO decreased with time for conditions that were undersaturated with respect to U(VI) oxides. The decreased sorption coincided with conversion of some HFO to hematite, and the conversion to hematite was catalyzed by U(VI). Based on data from 48 days, the slope of the sorption isotherm at pH 7.8 first decreased and then increased with increasing dissolved U(VI). This indicated that sorption of $(UO_2)^3(OH)_5^+$ became a significant process at the higher concentration, which is consistent with the EXAFS observation of polymeric sorbed U(VI) species by other investigators. Accordingly, sorption was modeled assuming both monomeric and polymeric surface species. Sorption resulted in between 50 and 99% sorption of U(VI), corresponding to significant retardation of U(VI) in groundwater. Due to the change from monomeric to polymeric sorption mechanisms, mobility of U(VI) in oxic groundwater is predicted to be greatest for intermediate U(VI) concentrations at alkaline pH.

Two different U(VI) oxide phases were formed. Fast precipitation at high U(VI) concentrations resulted in a solid with solubility consistent with schoepite, using solubility and complexation constants reported by Langmuir. Slower precipitation of U(VI) oxide with solubility about four times lower than "schoepite" was observed for lower U(VI) concentrations. The development of precipitates over time and the lower solubility for the highest total U(VI) conditions were consistent with slow Ostwald ripening. These results are significant in terms of retardation or precipitation of U(VI). The results also indicate that hydrolysis constants reported by Langmuir are more consistent with experimental data than hydrolysis constants reported by Grenthe.