

Poster #21-43

Redox Transformations of U, Hg, and As in Iron Oxide and Clay Systems

Maxim Boyanov^{1,2*}, Drew Latta^{1,3}, Michelle Scherer³, Bhoopesh Mishra^{1,4}, Brittany Huhmann^{3,5}, Anke Neumann^{3,6}, Edward O'Loughlin¹ and Kenneth Kemner¹

¹Argonne National Laboratory, Argonne, IL

²Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

³The University of Iowa, IA

⁴University of Leeds, Leeds, UK

⁵Massachusetts Institute of Technology, MA

⁶Newcastle University, Newcastle, UK

Contact: mboyanov@anl.gov; mboyanov@ice.bas.bg

BER Program: SBR

Project: Argonne National Laboratory SFA

Project Website: https://doesbr.org/documents/ANL_SFA_flyer.pdf
<https://www.anl.gov/bio/project/subsurface-biogeochemical-research>

Reactive Transport Models (RTMs) are often employed to predict the cycling of elements and the dispersal of contaminant plumes in natural environments. While RTMs can be based on *assumed* reaction pathways and empirical parameters, the transferability and the robustness of the model increase with the availability of mechanistic information that allows for the assignment of the *actual* reaction pathways, including the reactive species, products, and kinetics of the transformations operable in the system. Because model predictions are used to guide policy, improvement of RTMs translates directly into improved management and cost decisions.

The Argonne Subsurface SFA continues to provide the mechanistic understanding of processes needed for the improvement of RTMs. In the context of pollutant dispersal in groundwater, we studied the transformations of several dissolved contaminants (U, Hg, and As) in contact with reduced subsurface minerals (iron oxides and Fe-containing clays). In reactions of U^{VI} with reduced SWy-2 or NAu-1 clays we find that electron transfer occurs under the studied conditions (2-100 g/L clay loading, 250 μM U^{VI}, 2 mM bicarbonate, pH 7.2). However, the extent of U reduction and the reaction products depend on the type and amount of added clay. Using synchrotron x-ray spectroscopy (U L_{III}-edge XANES and EXAFS) we find that despite the stoichiometric excess of Fe^{II} in the system, U^{VI} is reduced to U^{IV} (uraninite) only at high solids loadings, whereas a mixed-valence U^V-U^{VI} oxide is stabilized at lower loadings. The results suggest that clay surfaces do not have sufficient high affinity sites for U^{IV} complexation that could prevent uraninite formation and that the formation of the mixed-valence U^V-U^{VI} oxide is controlled by the reducing capacity in the system. In reactions of Hg^{II} with reduced clays (4 g/L SWy-2 or NAu-1, pH 7.2 MOPS) the results of Hg L_{III}-edge XANES and EXAFS show that Hg^{II} is reduced to elemental Hg⁰, independent of Hg concentration (0.1, 0.25, 0.5, and 1.0 mM), the presence of Cl⁻ anions (0, 1, 10 mM), or the presence of a humic acid (0, 10, 20, 50, and 100 mg/L SWHA). Reduction to Hg⁰ was also observed in the pH range 5.0-9.0. In reactions of As^V with the reduced iron oxide magnetite, the results of As K-edge EXAFS spectroscopy indicate that co-precipitation of dissolved As^V with magnetite leads to the formation of a stable, incorporated As^V species. The formation of such species may play a significant role in controlling As mobility in natural systems.