Coupled Biogeochemical Processes Governing the Stability of Bacteriogenic Uraninite and Release of U(VI) in Heterogeneous media: Molecular to Meter Scales

John Bargar, Rizlan Bencheikh-Latmani, Daniel Giammar, Allen Pope, Eleanor Schofield, Bradley Tebo, Kai-Uwe Ulrich, Harish Veeramani
Attending co-PI: Rizlan Bencheikh-Latmani
Environmental Microbiology Laboratory
Ecole Polytechnique Federale de Lausanne (EPFL)
Centre Est (CE) 1 644, Station 6
Lausanne, 1015 Switzerland
Phone: +41 21 693-5001; Fax: +41 21 693-6205
Email: rizlan.bencheikh@epfl.ch

Bacteriogenic UO_2 will be an important if not dominant source of mobile U(VI) at DOE sites where subsurface reductive bioremediation of U(VI) has been conducted. The chemical stability of bacteriogenic UO_2 is the seminal issue governing the success of its use as an "*in-situ* waste form" in the subsurface. It is likely that important groundwater cations, Ca^{2+}, Mg^{2+}, as well as Fe^{2+} and Mn^{2+} may be incorporated in bacteriogenic UO_2, modifying its structure, particle size, stability, and oxidation kinetics. The goal of this research is to evaluate this hypothesis and identify the conditions (within the subset considered) under which biogenic UO_2 is most resistant to re-oxidation by O_2 and MnO_2 and Mn(II)-oxidizing bacteria.

We have characterized the local and long-range atomic structures of solid-phase bacterial U(IV) products produced by *Shewanella sp.* strain MR-4 grown aerobically and exposed to U(VI) under anaerobic conditions. Samples were prepared as functions of reaction time and Ca^{2+} concentrations and measured under *in-situ* conditions using extended x-ray absorption fine structure (EXAFS) spectroscopy and synchrotron-based wide-angle x-ray scattering (WAXS). Both techniques indicate the dominant products to be UO_{2+x} with particle sizes in the range of 2 to 5 nm, consistent with previous reports (Suzuki et al, 2002). Ca K-edge EXAFS and lattice parameter measurements will be used to test the hypothesis that Ca^{2+} is incorporated into the UO_{2+x} lattice and to assess other potential modes of Ca^{2+}-UO_{2+x} interaction. Structural information from these studies will be compared to the stability and dissolution kinetics of these materials in order to elucidate the relationship between structure and reactivity of this complex natural material.

In addition to U(IV) of biogenic origin, U(IV) oxide was synthesized abiotically by reducing a U(VI) solution with hydrogen at low pH and precipitating a U(IV) oxide upon addition of strong base. The composition and crystalline structure of the abiotically synthesized U(IV) oxide were characterized as above, and the products were found to be UO_{2+x}. Dissolution experiments using continuously-stirred flow-through reactors evaluated both the equilibrium solubility of the U(IV) oxide as a function of pH under anoxic conditions as well as the rate of dissolution as a function of pH, low levels of dissolved oxygen, and the presence of dissolved carbonate.

Furthermore, soil samples from the Old Rifle Field site were collected for the enumeration of heterotrophic and Mn(II)-oxidizing bacteria. Viable cell counts and numbers of Mn(II)-oxidizing bacteria were determined on 10 different soil samples using MPN and direct plate counts with three different media ranging from complex organic to oligotrophic. The MPN count for Mn oxidizing bacteria ranged from $4.0 \cdot 10^3$ to $6.9 \cdot 10^4$ MPN/gram with the average for all soil samples coming to about $2.2 \cdot 10^4$ MPN/gram or roughly 0.1% of the total viable population. Seventeen Mn(II)-oxidizing isolates from the plates were subcultured for purification and characterization. A few strong Mn(II) oxidizers representative of the Rifle site will be used in future studies to investigate the mechanisms and kinetics of UO_2 oxidation by Mn(II)-oxidizing bacteria.