The Role of Biogeochemical Dynamics in the Formation of U(VI) Solids under Oxic Conditions

Tracy Letain,[1] Carrie Gillaspie,[3,4] Sue B. Clark,[3,4] Terry C. Hazen,[1] Heino Nitsche[2,5] (PI)

[1]Center for Environmental Biotechnology, Lawrence Berkeley National Laboratory, Berkeley, CA;
[2]Nuclear Sciences Division, Lawrence Berkeley National Laboratory, CA;
[3]Chemistry Department, Washington State University, Pullman, WA;
[4]Center for Multiphase Environmental Research, Washington State University, Pullman, WA;
[5]Department of Chemistry, University of California at Berkeley

To assist the U.S. Department of Energy (DOE) with long-term stewardship issues associated with bioremediation of uranium (U), the overall goal of this work is to define the mechanisms by which microorganisms facilitate the formation of insoluble hexavalent U solid phases. Under anoxic conditions, microbial reduction of U(VI) to U(IV) can potentially decrease groundwater U contamination by lowering solubility and by slowing migration through the soil. However, such biological alteration must be considered temporary unless long-term anoxia can be maintained. When oxic conditions return, U(IV) will likely oxidize to U(VI), which is generally more soluble and potentially more mobile. For example, in U ore deposits in which uraninite (consisting of reduced, tetravalent U as UO_{2+x}) is the parent material, exposure to oxidizing conditions results in alteration to U(VI) minerals, with the U(VI)-phosphates frequently defining the boundaries of the ore body. Of the U(VI)-containing minerals, these U(VI)-phosphates are of interest because they are the least soluble of the U(VI) solids found in nature. Additionally, U(VI) solids such as metaschoepite have been observed as the products of the oxidation and corrosion of spent nuclear fuel, in which U is present in the reduced form.

Microorganisms present in soils may play a role in the formation of U(VI)-phosphate solid phases. However, the role of microorganisms in transformation and precipitation of actinide-containing minerals is not well understood. Bacteria are believed to influence actinide geochemistry through various mechanisms that are a part of the biogeochemical cycle of U. Our research links important geochemical and microbiological aspects of this problem, providing a fundamental basis for predicting the complex and dynamic interplay of biological treatment strategies.

We are investigating the role of model microorganisms such as *Bacillus sphaericus* and *Shewanella putrefaciens* on U(VI) sorption, solid phase formation, and transformation. These species are commonly found in soils as well as microbial consortia isolated from the NABIR Field Research Center at Oak Ridge National Laboratory. Data will be presented on the relative abilities of these bacteria to sorb U over a wide pH range, with special attention to the sorption behavior at low concentrations of U ($\leq 10^{-6}$ M), such as would be commonly found in the environment. We observe maximum sorption between pH 5 and 6. Cell-surface functional groups responsible for U interaction are identified using TRLFS (Time-Resolved Laser-induced Fluorescence Spectroscopy) and EXAFS (X-ray Absorption Fine Structure Spectroscopy). This information can then be used to design remediation systems that stimulate biological activity to favor the formation of U(VI)-phosphate phases. We are also investigating the impact of these bacteria on the transformation of the U(VI) oxide hydrates (e.g., metaschoepite, $[(UO_2)_8O_2(OH)_{12}]\cdot 12H_2O$) to U(VI) phosphates such as metaautunite, $Ca[(UO_2)(PO_4)]_2\cdot 6H_2O$. The abiotic transformation pathway of metaschoepite to metaautunite has been previously elucidated by Sowder (1998) and indicates that dissolution and reprecipitation of the U crystal structure is required, thus presenting a potential kinetic barrier for nucleation and reprecipitation. Our current biotic studies suggest that the bacterial surfaces may serve as nucleation sites, possibly via the surface sorption sites identified by TRLFS.