Science: Basis for In-Situ Stabilization of U(VI) Using Bacteriogenic Mn Oxides

Experimental: Mn bio-oxides were produced by adding aliquots of Mn(ii) and U(VI) to suspensions of B. subtilis sp. at pH ~7.5. The resulting samples were incubated at room temperature, and the ratio of U/Mn varied between 0.1 to 100. All samples were buffered at pH 7.8 with HEPES.

Mn EXAFS: presence of U(VI) alters structure. Mn bio-oxides show a progressive evolution of structure in the region of ~7-10 Å (highlighted). The sharp positive node at ~8 Å, which is present at low U(VI) (e.g., sample A), indicate a hexagonal layered Mn oxide. With increasing U(VI), this feature disappears. The resulting spectral shape is characteristic of todorokite, a tunnel-structured Mn oxide. Fitting to the EXAFS suggests that the tunnel structure becomes more defined with increasing U(VI).

In-situ SR-XRD: presence of U(VI) alters structure. At low U(VI), the Mn bio-oxides resemble a poorly crystalline hexagonal layered manganese oxide with a prominent 2.5 Å basal plane peak. Increasing U(VI) leads to basal peak broadening and an increase of the basal plane spacing toward 9.8 Å, which is characteristic of both expanded hydrated layer manganates and tunnel manganates such as todorokite. Diffuse scattering at 3.25 Å and 1.9 Å, which are consistent with a todorokite-like tunnel structure containing U, become intense as U(VI) increases. Particle size is estimated to be ~1.2 nm based on the 9.8 Å peak width.

Conclusions: At U(VI) ≤ 4 μM, U(VI) bonds to edges or surfaces of layered Mn bio-oxides. As U(VI) concentration approaches 10 μM, a structural transition to a nano-crystalline tunnel-structured Mn bio-oxide occurs, and U(VI) is increasingly bound at obtuse corner sites in the tunnels. This work strengthens the scientific basis using bacteriological Mn oxidation for enhanced attenuation of U(VI).

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User Support & Activity

The SSRL Environmental Remediation Science Program supports BER ERSD-funded scientists and their collaborators at SSRL through an integrated approach involving direct hands-on support, technique development, education & outreach, and instrument development.

Techniques supported by this program:
- XANES/EXAFS
- X-ray Diffraction (XRD)
- Chemical imaging
- μ-XANES/EXAFS
- μ-XRD

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Eleven BER-ERSD projects conducted research at four SSRL beam stations in FY 05, using 11% of the total time available at these stations. At BL 11-2, which was the station most frequently utilized by ERSD researchers, 26% of the total station time was used by ERSD projects. Support for these activities is also provided by SSRL (DOE-BES) and by the SSRL SMB program (DOE-BER and NIH-NCRR).

Hard X-ray Microprobe

We are commissioning a microprobe optimized for μ-XAS, μ-XRD, and μ-XRF measurements on radionuclides of interest to ERSD researchers including U, Np, Pu, Am, and Cm. This facility will also provide experimental capability for other important metals, including Cr, As, Pb, and Sr. μ-XAS/EXAFS measurements on a 10 μm-diameter Mo wire (20 KeV) show a high degree of reproducibility and low noise, suggesting that the mechanical stability of the system is adequate for planned measurements.