

Effect of Mn(II) on the oxidative dissolution of biogenic UO₂.

H. Veeramani¹, J.O. Sharp¹, E. Schofield², K.U. Ulrich³, D.E. Giammar³, J.R. Bargar²; R. Bernier-Latmani¹

¹ Environmental Microbiology Laboratory, Ecole Polytechnique Federale de Lausanne, Switzerland

² Stanford Synchrotron Radiation Laboratory, Menlo Park, CA

³ Dept. of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO

Bioremediation of U(VI) contaminated sites is predicated on the stability and long-term immobilization of the bioremediation product: bacteriogenic uraninite (UO₂). Preventing re-oxidation of UO₂ is an important aspect governing the success of bioremediation. To study processes that can help stabilize bacteriogenic uraninite, *Shewanella oneidensis* MR-1, a free-living gram-negative gamma-proteobacterium, was used to synthesize UO₂ in a simple chemical matrix containing NaHCO₃, PIPES buffer, U(VI), and lactate as an electron donor. The goal of the study was to evaluate the effect of divalent cations on the structure and reactivity of bacteriogenic UO₂. Thus, UO₂ was produced biologically in the presence of Mn(II), a divalent cation ubiquitous in the groundwater.

U(VI) reduction was carried out at two different pH values (6.3 and 8). The rates of reduction were found to be faster at the lower pH. The presence of 1mM or 5mM Mn(II) did not significantly affect U(VI) reduction. A method involving alkaline treatment followed by organic phase separation was developed to separate UO₂ from the biomass in order to perform spectroscopic and reactivity characterization. Characterization techniques included imaging with conventional and scanning TEM, BET determination of surface area, adsorption and dissolution experiments, and synchrotron-based analyses (XANES, EXAFS, WAXS, WANS spectroscopy). BET analysis showed that biogenic UO₂ had a surface area of 51 m²/gram, which is about an order of magnitude greater than the surface area of chemically synthesized UO₂.

Sorption experiments showed uptake of Mn(II) by UO₂ at near neutral and alkaline pH, but rule out significant sorption at and below pH 5. Thus, based on the sorption edge, biogenic UO₂ synthesized in the presence of Mn(II) was subjected to multiple washes using water buffered with MES at pH 5 until no further Mn(II) could be desorbed. A mass balance study (involving acid digestion) and EXAFS measurements indicated that the majority (~92%) of Mn(II) associated with UO₂ was adsorbed and that the remainder was incorporated into the UO₂ crystal structure. To date, oxidative dissolution experiments using air as an oxidant indicate that the presence of Mn(II) does not significantly affect biogenic UO₂ dissolution rates in a bicarbonate-containing matrix at pH 6.3, but that at alkaline pH values, Mn(II) accelerates oxidative dissolution significantly.