Microbial Reduction and Immobilization of Uranium in Fe(III)- and Mn(IV)-Containing Sediments

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Solid and liquid wastes discharged to the ground over a 40-year period constitute a major environmental problem at Department of Energy (DOE) sites nationwide. Uranium is the most common radionuclide in soils, sediments and groundwater at these sites and therefore is of particular environmental concern.

Dissimilatory iron-reducing bacteria (DIRB) can utilize ferric iron associated with aqueous or solid phases as a terminal electron acceptor coupled to the oxidation of H_2 or organic substrates. DIRB are also capable of reducing other metal ions, including contaminants such as U(VI), Tc(VII) and Cr(VI), significantly altering their solubility and mobility.

The focus of this research project is on laboratory investigations of coupled microbiological-geochemical transformations of U(VI) species in the presence of reactive solid phases (synthetic and naturally-occurring) containing Fe- and Mn-oxides and humic acid-facilitated microbial metabolism and reduction of metals. This research is evaluating three hypotheses pertaining to redox disequilibria, microbial U reduction and nucleation for precipitation of U(IV) solids, and humic acid acceleration of microbial reduction of Fe oxides. These processes are of particular concern for the effective in-situ reduction and long-term stability of contaminants.

To probe these complex processes, the reduction of U(VI) by the subsurface bacterium *Shewanella putrefaciens* CN32 was investigated in the presence of goethite under conditions where the aqueous composition was controlled to vary U speciation and solubility. Uranium(VI) as the carbonate complexes $UO_2(CO_3)_3^{4-}{}_{(aq)}$ and $UO_2(CO_3)_2^{2-}{}_{(aq)}$, in the absence or presence of goethite [_-$FeOOH_{(s)}$], was reduced by the bacteria to U(IV). Uranium(VI) in PIPES buffer that was estimated to be initially present predominantly as the U(VI) mineral metaschoepite [UO_3•$2H_2O_{(s)}$] was also reduced by the bacteria in the absence of presence of goethite. Anthraquinone-2,6-disulfonate (AQDS), a humic acid analog that can be reduced to dihydroanthraquinone (AH_2DS) by CN32, had a slight moderating effect on U reduction in either buffer. In contrast, only ~30% of the U(VI) associated with a synthetic metaschoepite was reduced by the organism in the presence of goethite with 1 mM lactate as the electron donor, possibly due to the formation of a layer of $UO_{2(s)}$ or $Fe(OH)_{3(s)}$ on the surface of the metaschoepite that physically obstructed further bioreduction. However, increasing the lactate to a non-limiting concentration (10 mM) increased the nominal reduction of U(VI) from metaschoepite to greater than 80%, indicating that the hypothesized surface-veneering effect was electron donor dependent. Uranium(VI) was also reduced by bacterially-reduced AQDS in the absence of cells, and by Fe(II) sorbed to goethite in abiotic control experiments. In the absence of goethite, uraninite was a major product of direct microbial reduction and reduction by AH_2DS. These results indicate that DMRB, via a combination of direct enzymatic or indirect mechanisms, can reduce U(VI) to insoluble U(IV) in the presence of solid Fe oxides. Current research is probing the microbial reduction of U(VI) in the presence of Mn oxides.

Preliminary results have demonstrated that biogenic uraninite (UO_2) is oxidized by pyrolusite (β-MnO_2) and that the presence of the oxide significantly decreases the rate of microbial reduction of U(VI). Additional experiments are underway to identify and quantify the coupled microbial and geochemical processes in these systems.