Biogeochemistry of Technetium: Effects of Enzymatic Metal Reduction on Speciation and Potential for Transport and Remediation in Porous Subsurface Media

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Development of remedial measures for technetium (Tc) and other contaminants that are transported in aerobic groundwaters as oxyanions will require a fundamental understanding of the mechanisms of microbial and abiotic reduction and the factors controlling the effects of these processes on form and mobility. The effect of electron donor on the rate and extent of pertechnetate ion [$Tc(VII)O_4$] reduction by the subsurface metal-reducing bacterium *Shewanella putrefaciens* CN32 was determined, and the aqueous and solid phase reduction products formed in the presence and absence of inorganic and organic complexing ligands (bicarbonate, DTPA, EDTA, citrate) were evaluated through a combination of high resolution transmission electron microscopy, X-ray absorption spectroscopy and thermodynamic calculations. The kinetics of these reactions were contrasted to Tc(VII) reduction by $Fe(II)_{aq}$ and Fe(II) sorbed on goethite.

When H_2 served as the electron donor, dissolved Tc(VII) was rapidly reduced to amorphous Tc(IV) hydrous oxide, which was largely associated with the cell periplasm and the outer cell surface in unbuffered 0.85% NaCl and with extracellular particulates (0.2 – 0.001 μm) in bicarbonate buffer. The reduction rate was much lower when lactate was the electron donor, with extracellular Tc(IV) hydrous oxide also the dominant solid-phase reduction product. In bicarbonate systems, soluble (< 0.001 μm) electronegative Tc(IV) carbonate complexes were also formed that exceeded Tc(VII) in electrophoretic mobility. Thermodynamic calculations indicated that NaCl solutions without complexing ligands were oversaturated with respect to Tc(IV) hydrous oxide which would be present from pH 4 to 9 and at Eh values <50 mV, and that negatively-charged aqueous Tc(IV) carbonate species would dominate in carbonate solutions from pH 5.5 to 10.5 and at Eh values <200 mV. Thus, carbonate complexes may represent an important pathway for Tc transport in anaerobic subsurface environments where it has generally been assumed that Tc mobility is controlled by low solubility Tc(IV) hydrous oxide and adsorptive, aqueous Tc(IV) hydrolysis products. The presence of organic complexing ligands during microbial reduction of Tc(VII) in NaCl resulted in the formation of aqueous complexes of Tc(IV,V) and investigations are underway to further define their chemical speciation and potential for transport in groundwaters.

In abiotic experiments, Tc(VII) was reduced slowly in the presence of Fe(II) in water, but was rapidly reduced to Tc(IV) by Fe(II) sorbed on goethite. At higher sorbed Fe(II) concentrations (near saturation), the rate of Tc(VII) reduction exceeded direct microbial reduction even with H_2 as the electron donor, suggesting that sorbed Fe(II) resulting from biogenic processes may be an important reducing agent for Tc(VII) in groundwater systems. The effective redox potential and kinetics of electron transfer for biogenic Fe(II) will depend specifically on the chemical/ mineralogic environment in which the Fe(II) resides. Investigations are underway to determine the relative importance of direct and indirect reductive processes for Tc(VII) in static and advective experimental systems.