Biogeochemical Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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Technetium-99 is an important DOE subsurface contaminant. It is long-lived ($t^{1/2} = 2.13 \times 10^5$ yr), and exists in groundwater as the mobile pertechnetate anion [$Tc(VII)O_4^-$]. Pertechnetate can be immobilized by biotic and abiotic reduction to insoluble $Tc(IV)O_2 \bullet nH_2O$ that exhibits a solubility of 10^{-8} mol/L or less. The half-cell potential for this reaction is "intermediate" in environmental redox space.

Our past NABIR research demonstrated that Fe(II) resulting from the activity of dissimilatory iron-reducing bacteria (DIRB) can reduce and immobilize pertechnetate from high nitrate waters in Hanford and Oak Ridge sediment. The reduction kinetics depend on the biogenic Fe(II) concentration and its molecular and mineralogic environment in the sediment. Ongoing laboratory research is utilizing batch and column experimental systems along with various forms of x-ray, electron, and gamma-ray spectroscopies/microscopies to: (1) quantify the kinetic reactivity of different biotic and abiotic Fe(II) forms to allow rigorous kinetic modeling of parallel reaction/reduction paths; and (2) investigate the oxidation/remobilization reaction with oxygen, and determine the mineralogic, biogeochemical, and microbiologic factors that control it during extended in-ground residence times.

At the 2005 NABIR meeting we will: present quantitative results on the homogeneous reduction rate of Tc(VII) by $Fe(II)_{aq}$ (which is surprisingly significant); identify the nature of mineral products formed using isotopic enrichment with ^{57}Fe and Mössbauer spectroscopy, and high-resolution transmission electron microscopy; and compare these rates to heterogeneous ones with insoluble Fe(II) in different mineralogic states. These results will be complemented with oxidation rate studies of precipitated Tc(IV) resulting from both homogeneous and heterogeneous reduction reactions. It is shown that the molecular/mineralogic environment of Fe(II) has a major influence on both Tc reduction and oxidation rates, albeit for different reasons.