# 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 reduction to insoluble $Tc(IV)O_2 \bullet nH_2O$. 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 sediments. The global biological reduction of Mn(III/IV) oxides that were present in both sediments was a prerequisite for Tc(VII) reduction as these phases oxidize Tc(IV). The reduction kinetics depended on the biogenic Fe(II) concentration and its molecular and mineralogical environment in the sediment. The reduction rate was rapid in batch systems with half-lives ranging from hours to several days. A kinetic model was developed from extensive reduction data sets that described the rate of Tc(VII) reduction as a function of Fe(II) concentration and speciation.

Newly initiated research is investigating the oxidation/remobilization reaction with oxygen, and quantifying mineralogical, biogeochemical, and microbiological factors that may control it during extended in-ground residence times. Biotic, biogenic, and abiotic $Tc(IV)O_2 \bullet H_2O$ phase assemblages are being generated in model systems and Oak Ridge and Hanford sediments using knowledge from our first three years of research; the oxidation kinetics of Fe(II) and Tc(IV) in these are being studied in batch and column systems before and after (1) geochemical aging and (2) biogeochemical transformation by Fe(II) oxidizing, $NO_3^-$ reducing bacteria. Spectroscopic and microscopic techniques are being used to define Fe and Tc speciation, and their physical locations and forms, as a basis for interpretation of oxidation rate. A linked equilibrium/kinetic biogeochemical transport model will be applied to identify the reaction network, and to quantify the interdependent kinetic reactions involved in the oxidation process. Initial results have shown that insoluble $Tc(IV)O_2 \bullet H_2O$ oxidizes relatively rapidly in bioreduced Oak Ridge sediment. However, the oxidation rate and extent depended on biogenic Fe(II) concentration and its biogeochemical speciation. Slow rates of Fe(II) oxidation consistent with what may happen in the field yielded a large residual Tc(IV) concentration that was resistant to further oxidation.