Reduction of TcO_4^{-2} by Biogenic Fe(II) in Sediments from DOE's Oak Ridge and Hanford Sites

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Technetium-99 is an important subsurface contaminant at DOE Sites, including Hanford, Oak Ridge, and Savannah River. At Hanford, it is the most important risk-driving contaminant, and its subsurface inventory and mobility is key to all long-term site assessments and risk analyses. ^{99}Tc is persistent with a long half-life (2.3×10^5 years) and often exists in the subsurface as the mobile, pertechnetate [$Tc(VII)O_4^{2-}$] anion. ^{99}Tc can be immobilized from water by reduction of $Tc(VII)\ O_4^{2-}$ to insoluble Tc(IV) oxides, and this reductive process may be manipulated for remedial purposes. This research is investigating the role of mineral-bound, biogenic Fe(II) in the heterogeneous reduction of Tc(VII) in the absence and presence of NO_3^-, a key DOE co-contaminant.

Last year, we reported that $Tc(VII)O_4^{2-}$ is rapidly reduced to Tc(IV) by biogenic Fe(II) produced by metal-reducing bacteria (*Shewanella putrefaciens*) in both Oak Ridge and Hanford sediments. Surprisingly, $Tc(VII)O_4^{2-}$ was quantitatively reduced even in the presence of high concentrations of NO_3^-, which are present in most DOE groundwater plumes. The reaction of NO_3^- with biogenic Fe(II) and Tc(IV) is kinetically inhibited. This work has lead to the development of kinetic models that describe the reduction rate of $Tc(VII)O_4^{2-}$ as a function of biogenic Fe(II) concentration. Research over the past year has developed a mechanistic basis for these models by identifying and characterizing the forms of biogenic Fe(II) that are most reactive with $Tc(VII)O_4^{2-}$. This task has been accomplished by using FRC sediments that have been biologically and abiotically reduced, treated with various chemical agents to remove hypothesized reactive Fe(II) phases, and respiked with various concentrations of specific Fe isotopes (^{56}Fe and ^{57}Fe) to allow the monitoring of specific Fe(II) pools. These materials have been studied both before and after reaction with $Tc(VII)O_4^{2-}$, and the results have provided intriguing insights on the reactivity of various Fe(II) forms (adsorbed surface complexes on Fe(III) oxides, exchangeable Fe(II) on phyllosilicates, structural Fe(II) in phyllosilicates, and other unique biotic phases) with $Tc(VII)O_4^{2-}$. Specific reactive Fe(II) phases have been identified and monitored after reaction with $Tc(VII)O_4^{2-}$ using wet chemical techniques, analytical transmission electron microscopy, variable temperature ^{57}Fe Mossbauer spectroscopy, and x-ray absorption spectroscopy. An exciting result has been the finding that metal-reducing bacteria generate an apparently unique surface phase in the FRC sediment that is quite reactive with Tc(VII). It exhibits a distinct Mossbauer signal, but has not yet been definitively identified. Additional studies this year will target the identification of this phase and characterize mineralogic and chemical factors controlling the oxidation rate of $Tc(IV)O_2 \bullet nH_2O$ from Oak Ridge and Hanford sediments.