Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

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Research Objective

This research project will provide fundamental information on surface-mediated reduction/ precipitation reactions of Tc on Fe^{II}-containing mineral surfaces and the stability of those precipitates under conditions relevant to the vadose zone at the Hanford Site.

Our strategy is to (1) develop a mechanistic description of surface-mediated reduction of Tc^{VII} on Fe^{II}-containing minerals, (2) determine the stability of the precipitated Tc^{IV} solids, and (3) validate our model of Tc attenuation using contaminated Hanford Site sediments. This information will provide crucial support for the development of models of contaminant mobility in the vadose zone. With reliable models, a major cost reduction in remediation efforts may be achieved by targeting those sites that present the greatest environmental threat.

Research Progress and Implications

This report summarizes work after 6 months of a 3-year project. We have made limited progress in the areas of TcO_2(am) solubility studies. TcO_2(am) was prepared from pertechnetate stock solution by hydrazine and microbial reduction using the subsurface dissimilatory iron-reducing bacterium, *Shewanella Putrefaciens*. The amorphous product prepared by both methods was characterized by x-ray absorption spectroscopy and x-ray diffraction. In Figure 1, the near edge structure of the x-ray absorption spectra indicates complete reduction of Tc^{VII} to Tc^{IV} by either method. Note, however, that the amplitude of the x-ray absorption fine structure of the microbially reduced TcO_2(am) is significantly greater than the hydrazine reduced TcO_2(am). This is especially evident in the k^3-weighted EXAFS spectra shown in Figure 2 and in the Fourier transforms of the EXAFS spectra shown in Figure 3. Fits to the EXAFS indicates that the first and second shells in the Fourier transform correspond to oxygen and technetium atoms, respectively. The decreased EXAFS amplitude of the hydrazine reduced TcO_2(am) may result from increased static disorder; however this needs to be confirmed by additional experiments.

Even though the product of the hydrazine and microbial reduction is amorphous collection of the X-ray diffraction spectrum (Fig.4) is still meaningful through analysis of the pair distribution function. From these analyses, the radial distribution of all the atom-pairs in the material can be determined yielding longer-range structural information than can be determined from analysis of the x-ray absorption spectra. By comparing the pair distribution function of TcO_2(am) produced by hydrazine and microbial reduction one can validate the increased static disorder suggested by the x-ray absorption measurements.

Planned Activities

The solubility of TcO_2(am) and possible Tc^{IV}-Fe^{III} oxides will be measured as a function of pH under rigorously controlled redox conditions. The oxidation state of Tc in solution will be determined by a variety of methods, such as solvent extraction techniques, laser photoacoustic spectroscopy (LPAS), UV-Vis-NIR spectrophotometry, and x-ray absorption near edge structure (XANES) analysis. The methods used will depend on the concentration of Tc in solution. Solvent extraction and LPAS will

Figure 1

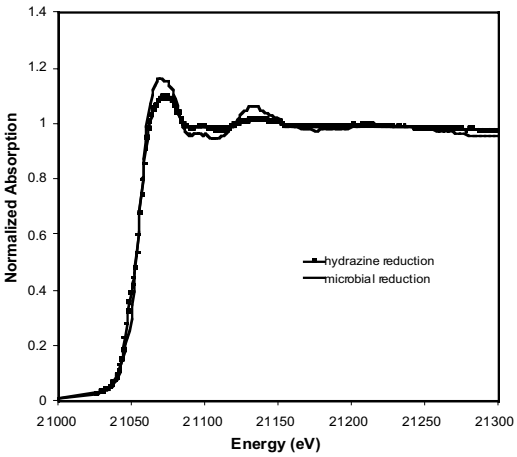


Figure 2

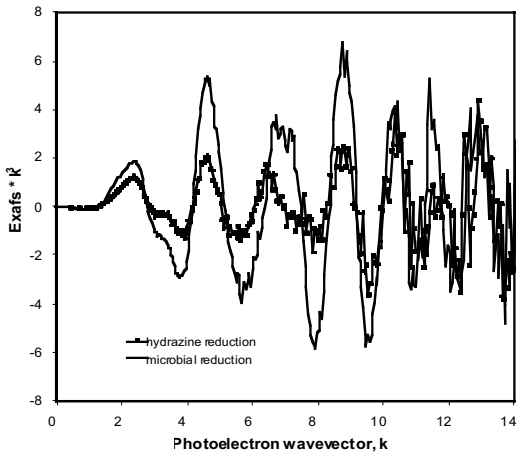


Figure 3

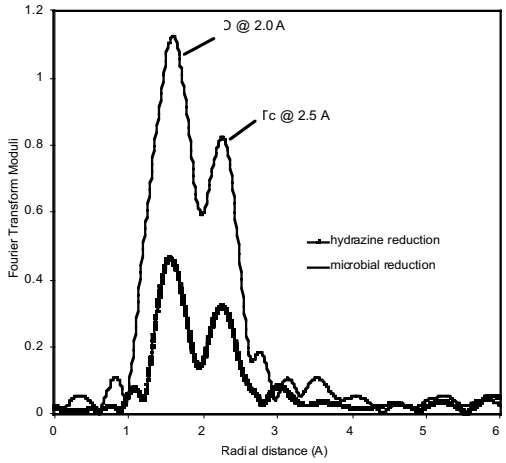
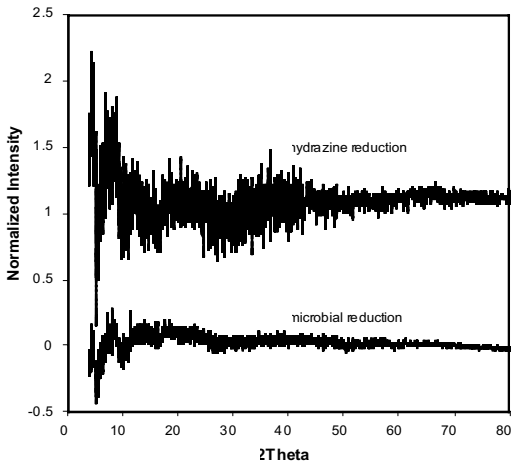


Figure 4



provide oxidation state information at the lowest Tc concentrations, approximately 1 x 10^{-9} M. The solvent extraction process requires acidification of the sample that can potentially change the oxidation state. On the other hand, LPAS requires no alteration to the solution chemistry and distinguishes between the reduced Tc oxidation states. But LPAS is very time intensive. The detection limits for UV-Vis-NIR spectrophotometry and XANES analyses are approximately 1 x 10^{-6} M and 5 x 10^{-4} M, respectively.

Solubility experiments are also planned on Tc-contaminated minerals isolated from vadose zone sediments at Hanford. Ideally, these contaminated sediments will be obtained from the discharge sites associated with the B Plant where the highest Tc contaminated fluids were released. Simulated Tc-contaminated samples will be made with selected Hanford Site sediments that have demonstrated retention of Tc (Plio-Pliestocene and upper Ringold Formation). These sediments will be exposed to TcO_4^- solutions for extended periods of time under saturated and unsaturated conditions in an oxic environment.