

Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

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Research Objective

In the subsurface environment, the pertechnetate ion, $\text{Tc}^{\text{VII}}\text{O}_4^-$, forms only weak surface complexes with hydroxylated surface sites on clays and Al and Fe^{III} oxides, and consequently, is weakly sorbed by most sediments and subsurface materials. Thus, adsorption of Tc^{VII} onto these surfaces is not a viable mechanism for the attenuation of Tc in unsaturated subsurface environments or the vadose zone. Only the reduction of Tc^{VII} to Tc^{IV} , which results in the precipitation of low-solubility solids, will result in retention of Tc in the vadose zone. Possible reduction mechanisms are 1) homogenous reduction, 2) microbial reduction, and 3) heterogeneous reduction on mineral surfaces. The redox conditions in the vadose zone in the western United States are likely too oxidizing for homogeneous reduction of Tc^{VII} or to support a viable, widely distributed population of Fe-reducing organisms that can reduce Tc directly or indirectly. Thus, the purpose of this research is the investigation of heterogeneous reduction of Tc^{VII} on Fe^{II} -containing mineral surfaces and the stability of the resulting precipitated Tc solids.

Research Progress and Implications

This report summarizes research accomplishments after 1.5 years of a 3-year project. Substantial progress has been made in three areas: solubility studies, characterization of Tc^{IV} solids, and speciation of Tc-contaminated soils from the Hanford Site.

Solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$

Previous $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ solubility studies have had great difficulty in maintaining reducing conditions, resulting in the oxidation of Tc^{IV} species to Tc^{VII} species. Because Tc^{VII} solubility is orders of magnitudes greater than Tc^{IV} , the measured Tc^{IV} in solution in these studies was less than 1% of the total Tc concentration. Solvent extraction techniques can measure the proportion of Tc^{IV} to total Tc in solution with an accuracy of approximately 5%; therefore, the reported Tc^{IV} concentrations are well below the error of the oxidation state measurement. Using 0.02 M hydrazine as a holding reductant, we are able to maintain reducing conditions for up to 65 days under acidic conditions resulting in measured Tc^{IV} to total Tc concentrations of greater than 70% for the data shown in Figure 1. These results give increased confidence in the solubility data and its use for determination of thermodynamic data. The slight increase in solubility under basic conditions (displayed in Figure 1) has significant implications for the very basic radioactive waste stored in double-shell tanks at Hanford. Conducting solubility studies under basic conditions and in the presence of complexing ligands will be the focus of upcoming work.

We conducted X-ray absorption spectroscopic (XAS) investigations on the solution phase at pH 0.9 and the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ solid phase at pH 4.1 at the Stanford Synchrotron Radiation Laboratory. Analysis of the X-ray absorption near edge structure (XANES) revealed that the Tc oxidation state for both samples is Tc^{IV} , which is consistent with the solvent extraction results. In addition, analysis of the extended X-ray absorption fine structure (EXAFS) indicated that the first coordination sphere consists of oxygen atoms for both samples. Fits to the EXAFS of the solution sample at pH 0.9 show that Tc is coordinated by six oxygen atoms at 2.19 Å. This result

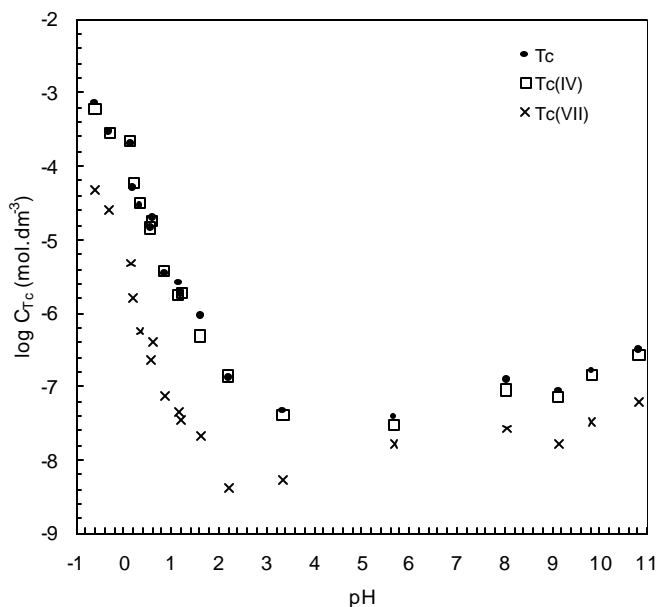


Figure 1. Solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ as Function of pH after 11 Days' Equilibration in Presence of 0.02 M Hydrazine to Maintain Reducing Conditions

is significant because definitive identification of the existence of a “bare” Tc^{4+} ion species at low pH is critical to correct thermodynamic modeling of the solubility data, especially in light of recent work by others suggesting the presence of mixed chloride species like TcOCl^+ under highly acidic conditions. Fits to the solid phase data at pH 4.1 indicate the presence of two coordination shells: six oxygen atoms at 2.01 Å and one Tc atom at 2.55 Å, which is consistent with previous results for the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ solid phase. Fourier transforms of the EXAFS are shown in Figure 2.

A review of previous $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ solubility studies suggests that the measured solubility depended on the process used to generate the solid phase. Differences of an order of magnitude in Tc solubility have been observed when the solubility of electrochemically deposited $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ was compared to chemical reduction of pertechnetate, yet both materials are X-ray amorphous. We undertook a limited study of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ precipitates formed by chemical reduction using hydrazine, sodium dithionite, and microbial reduction using the dissimulatory iron-reducing bacteria *Schewanella Putrifaciens* and compared the diffuse X-ray scattering patterns and EXAFS. Although the samples are largely amorphous, diffraction peaks are clearly apparent in the pattern in Figure 3(a). These patterns have not been matched to any known Tc structure, and further analysis is in progress. Fourier transforms of the EXAFS of the samples are shown in Figure 3(b). Fits to the EXAFS indicate that variations in the amplitudes of the transform are due to variation in the disorder associated with each sample. Variation in disorder is also evident in minor transform peaks between 3 to 4 Å apparent radial distance. Surprisingly, the microbially reduced $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ appears to have the highest degree of order. Future work will entail a thorough analysis of the diffuse X-ray scattering data including calculation of the

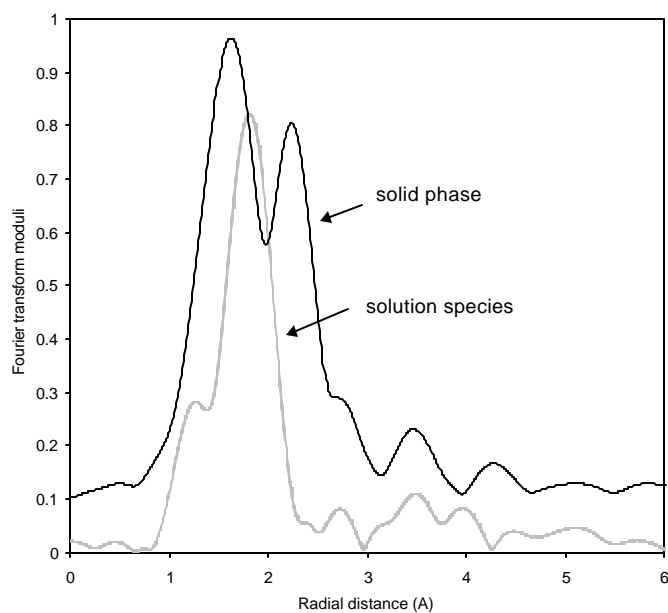


Figure 2. Fourier Transform of Tc K-Edge EXAFS for Solution and Solid Phase Samples

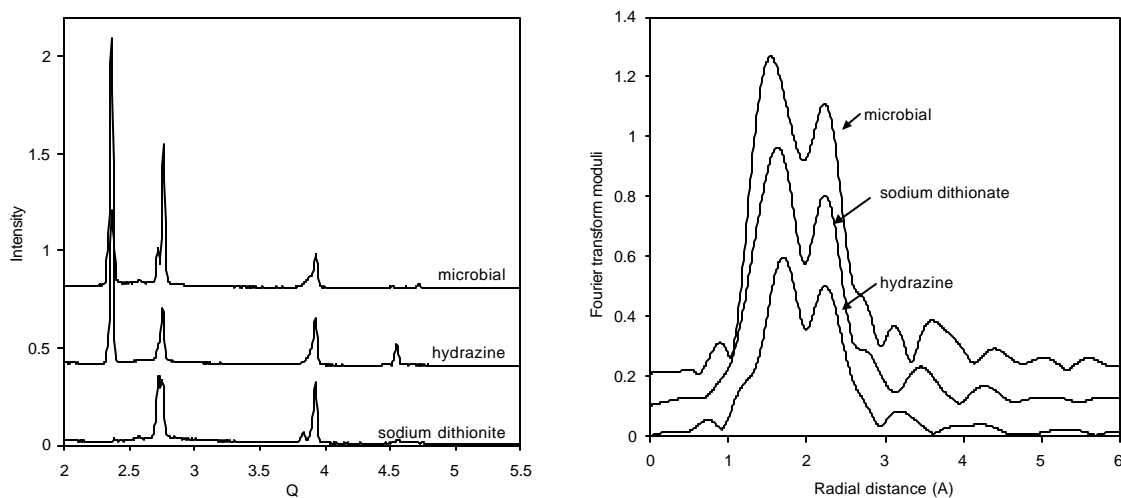


Figure 3. (a, left) A portion of the diffuse X-ray scattering pattern in Q-space showing diffraction peaks in the three $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ “amorphous” precipitates using different reductants. (b, right) Fourier transform of the EXAFS of the same three samples. The transforms are offset vertically and have not been corrected for phase shift.

pair distribution function, identification of the crystalline component possibly using Reitveld analysis of the diffraction data, and solubility studies on each of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ samples to determine whether the apparent variation in disorder is reflected in the measured solubility products.

Autoradiography of Tc-Contaminated Hanford Soils

We obtained Tc-contaminated samples from a borehole in the 200 West Area of the Hanford Site for autoradiography experiments. Autoradiography relies on the decay of radionuclide to expose a film plate indicating the spatial location of the radionuclide, which then can be isolated for further analysis. Samples from six intervals from the 299-W23-19 borehole were selected for autoradiography experiments because the contamination is exclusively due to ^{99}Tc , thus reducing the interference of other radionuclides such as ^{137}Cs . Initial results indicate that Tc is not homogeneously distributed but is associated with individual soil grains, as shown in Figure 4. The next step is to isolate and identify the soil grains with localized Tc concentrations using scanning electron microscopy. The association of Tc with a specific mineral grain may reveal the role of mineral interactions in the attenuation of Tc in the vadose zone.

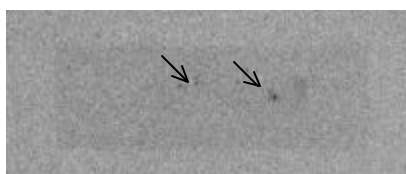


Figure 4. Autoradiography Image of Sleeve 33G Showing Localized Tc, Indicated by Arrow

Planned Activities

In addition to extending the work presented above, the following projects will be initiated:

X-Ray Absorption Spectroscopy of Tc-Contaminated Soils

The oxidation state of Tc is most likely the dominant factor in predicting the mobility of Tc in the vadose zone. We will conduct a thorough analysis of the XANES, the oxidation state of Tc-contaminated samples obtained from two boreholes in the 200 West Area of the Hanford Site, in June 2001. Both untreated samples and water-washed samples from the SX-slant borehole will be analyzed. It is anticipated that the untreated samples will contain all Tc species present, whereas the water-washing treatment is likely to remove highly soluble Tc(VII) species and leave insoluble reduced Tc species behind. The identification of reduced Tc species has significant implications for the mobility of Tc in the vadose zone.

Heterogeneous Precipitation of Tc on Fe^{II}-Containing Minerals

We will determine the distribution, composition, and speciation of Tc precipitates or co-precipitates formed on Fe-oxide surfaces using high spatial resolution chemical imaging and spectroscopic techniques including autoradiography and scanning electron microscopy. Selected

samples with Tc-precipitates will be sent to Stanford Synchrotron Radiation Laboratory or to the Advanced Photon Source for high spatial resolution XANES analysis using focused beam capabilities.

Information Access

1999-2000 Progress Report. <http://www.osti.gov/em52/2000projsum/70177.pdf>

Poster Board EMSP Workshop, April 2000.

http://www.osti.gov/em52/NWS2000_Posters/id70177.pdf