Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

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Research Objective

High-level waste (HLW) has leaked into the vadose zone from buried single-shell tanks at the Hanford Site. Contaminant plumes containing radionuclides are slowly migrating toward the groundwater table. The accepted model of contaminant migration places technetium (Tc) at the leading edge of the plume due to the high mobility of the anionic species, TcO_4^-, in its oxidized state. However, recent drilling and sampling programs at the B-BX-BY and S-SX Hanford Site tank farms have revealed that the Tc distribution within the contaminant plume is more complex than anticipated and some Tc may be retained in the vadose zone as insoluble precipitates. This research project investigates possible mechanisms by which Tc associated with HLW leakages can be attenuated in the vadose zone. It **also** will provide fundamental information on surface-mediated reduction/precipitation reactions of Tc on Fe^{II}-containing mineral surfaces and the stability of Tc precipitates under conditions in the vadose zone at the Hanford Site. This information will provide much needed data for the development of models of Tc mobility in the vadose zone following closure of the tank farms. With reliable models, a major cost reduction in remediation efforts may be achieved by selecting sites that present the greatest environmental threat and designing remediation methods with the greatest efficacy.

Research Progress and Implications

This report summarizes work after 2.5 years of a 3-year study. We hypothesized that if Tc was to be retained in the vadose zone it must be present as a reduced precipitate. To test our hypothesis, we undertook three main tasks: 1) to evaluate the reductive capacity of Hanford formation sediments; 2) to determination of Tc speciation in contaminated Hanford formation sediments; and 3) to conduct solubility experiments under reducing conditions at which Tc^{IV} species are stable in solution.

Reductive Capacity

The reductive capacity of Hanford formation sediments has been evaluated by two methods: using sequential chemical extractions to determine the distribution of Fe^{II} and Fe^{III} species on sediments and using one-dimensional flow experiments to test the capacity of Hanford sediments to reduce pertechnetate. Using the methods of Heron et al. (1994), untreated sediments were compared to sediments that had been pretreated with 4 M NaOH for 200 hr and 450 hr. Although little change was observed between untreated and 200 hr pretreated sediments, the total quantity of Fe^{II} and Fe^{III} species more than doubled from 1260 µg/g to 2720 µg/g between the 200 hr and 450 hr pretreatments. The increase was largely due to an increase in availability of Fe^{III} species. The number of Fe^{II} surface sites was largely independent of pretreatment whereas the number of ion-exchangeable Fe^{II} species actually decreased upon pretreatment probably due to the precipitation of $Fe(OH)_2$.

The flow experiments were designed to simulate the geochemical conditions created by the leakage of HLW into the vadose zone and to test the reactions between pertechnetate and the sediments under caustic conditions. Solutions of oxygen-free 4 M NaOH and known concentrations of pertechnetate were injected into the loaded column and the concentration of Tc in the effluent was measured as a function of time. These experiments demonstrated that 1) the amount of Tc retained is independent of the concentration of Tc injected, 2) the lag in Tc retention observed between 1 and 2 pore volumes likely results from the gradual increase in Fe^{II} concentration as Fe bearing mineral phases dissolve in the presence of 4 M NaOH, and 3) the rate of Tc retention was also found to be weakly dependent on the flow rate through the column. Twelve sediment samples were removed from along the length of the column and subjected to various "oxidative conditions" to determine how tightly Tc was retained on the sediments. These conditions included oxygen-saturated water, 5 M HCl, 0.1 M HNO_3, and 1 M HNO_3. Oxygen-saturated water, 0.1 M HNO_3 and 5M HCl were relatively ineffective at oxidizing and remobilizing the Tc. Only 1 M HNO_3 removed all the retained Tc. The failure of mild oxidative treatments to remove more than 25% of the Tc from the column sediments strongly suggests that Tc is present as reduced species that are relatively insoluble and resistant to re-oxidation.

Autoradiography and scanning electron microscopy (SEM) analysis of the caustically treated sediments were conducted to determine whether reduced Tc precipitate was preferentially associated with specific mineral phases, such as Fe-oxides, or whether it was homogeneously distributed over all mineral surfaces. Figure 1 shows an autoradiographic map of the six sediment samples from the column. The dark spots on the autoradiographic map indicate that the Tc is highly localized and associated with mineral grains. The arrow near Sample 10 points to a region that was selected for SEM analysis. Figure 2a is the SEM image of this area, and it shows two grains several hundred microns in diameter. The bright areas in the backscattered electron (BSE) image of this same region, Figure 2b, indicate concentrations of elements with large number of electrons, such as Fe. Figures 2c and 2d are higher resolution BSE images of the grain on the right in Figures 2a and 2b. The white square in Figure 3d shows the area where an energy dispersive
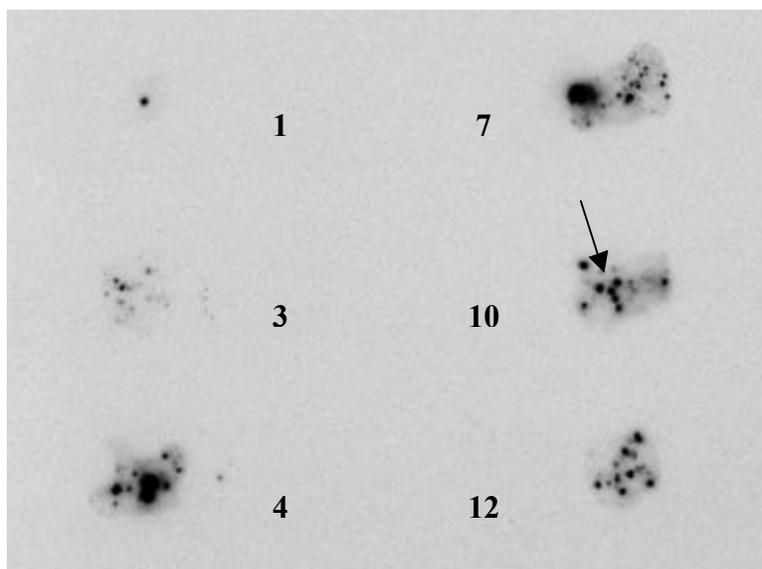

Figure 1. Autoradiographic map of six samples removed from the 1-D column. An arrow shows the location of the SEM studies in Figure 2.
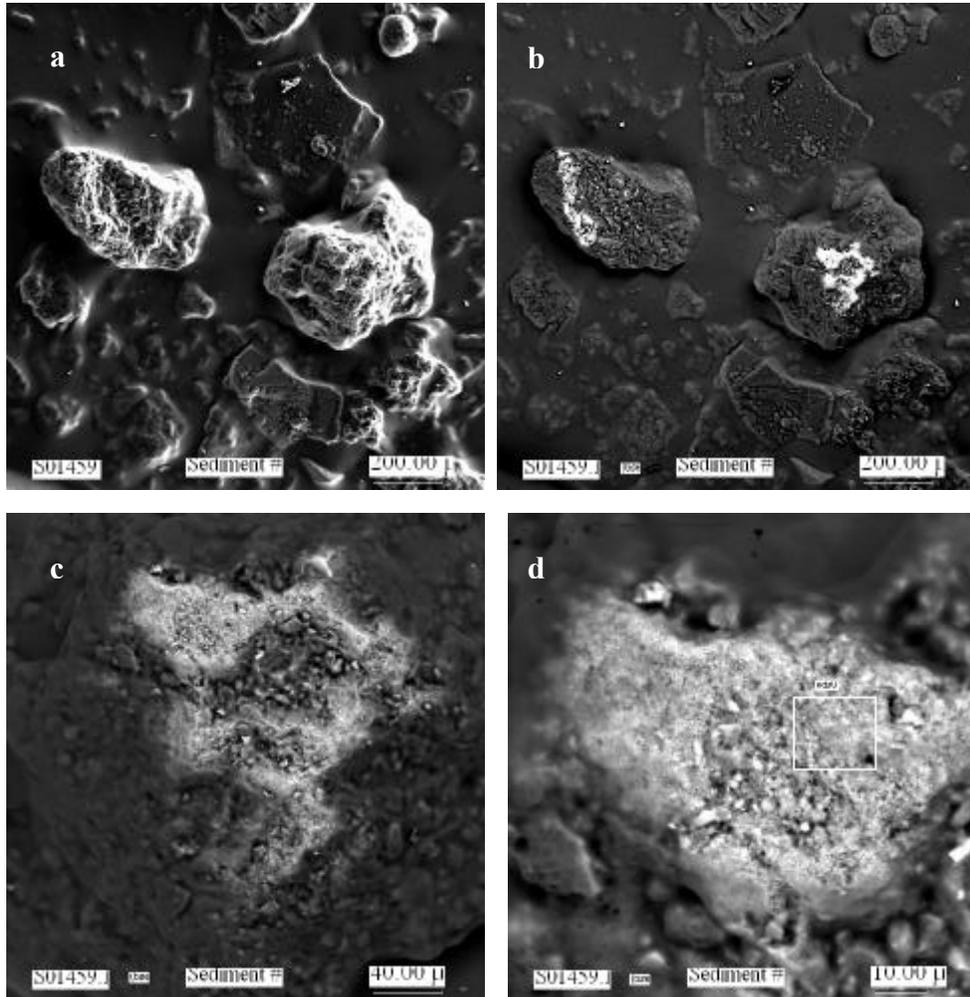
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Figure 2. Scanning electron microscope images of Sample 10, Area 3 (indicated by arrow in Figure. 1). Figure 2b is the backscattered electron (BSE) image of the region shown in Figure 2a. Figure 2c is a high-resolution BSE image of the grain on the left. Figure 2d, at higher resolution, shows the area where an energy dispersive spectrum, displayed in Figure 3, was aacquired.

spectrum (EDS) was acquired. The EDS, which gives the elemental composition of the scanned region, is shown in Figure 3. The presence of the elements Si, Al, O, Ca, Na, and K reflect the abundant quartz and feldspar minerals that constitute the Hanford formation sediments. The presence of Fe and Ti in this spectrum indicates the presence of minor amounts of Fe-oxides, perhaps Ti-rich magnetite grains. Note that Tc could not be observed in the EDS spectrum because the Tc K emission is at too high an energy, and the Tc L emission intensity is too weak to be detected at the Tc concentrations present in the sample. However, there is a direct correlation between the dark spots on the autoradiographic map, which indicate the presence of Tc, and high concentrations of Fe in the EDS of the SEM images.
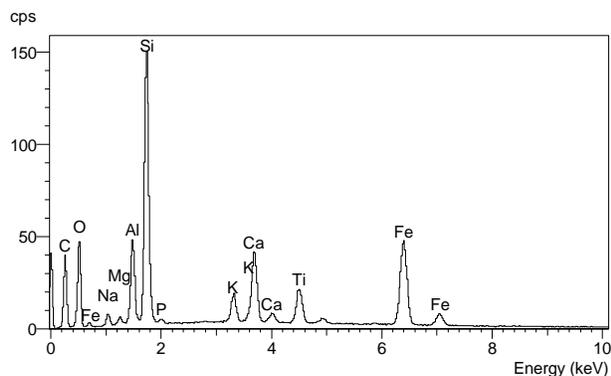
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Figure 3. Energy dispersive spectrum of region indicated by the white box in Fig 7d. The intensity of Fe Ká and Kâ peaks indicate the presence of Fe-rich mineral phases.

The experimental results obtained under this task were critical in directing the research focus of the renewal proposal. We have demonstrated that the reductive capacity of Hanford sediments increases under basic conditions. In addition, we have found a set of experimental conditions that are relevant to the leakages of HLW from waste tanks at the Hanford Site under which pertechnetate is reduced by Hanford formation sediments. Furthermore, we observed evidence of the association of Tc with Fe-oxides that suggests surface-mediated reduction of pertechnetate is the operable mechanism.

Speciation of Hanford Formation Sediments

To determine the speciation of the Tc in the vadose zone, and especially whether Tc is associated with Fe-oxides, Tc-contaminated samples were obtained from three boreholes drilled in the SX tank farm in the 200 West Area at the Hanford Site. The horizons were selected for either autoradiography or x-ray absorption spectroscopy (XAS) analysis. Samples from five horizons from the 299-W23-19 borehole (B8809) adjacent to Tank SX-115 were selected for autoradiography experiments because the radioactivity was exclusively due to ^{99}Tc, and therefore, there would be no interference from other radionuclides such as [137]Cs. Only one horizon, which consisted of a very fine sand, showed evidence of nonuniform Tc distribution, suggesting an association of Tc with a particular mineral phase. Unfortunately, efforts to isolate and identify the composition of these sediment grains using scanning electron microscopy were unsuccessful due to the small size of the soil particles.

Since the oxidation state of Tc is the dominant factor in predicting the mobility of Tc in the vadose zone, samples with high Tc concentrations were selected from two boreholes adjacent to tank SX-108 for Tc K-edge XAS studies on beamline 11-2 at the Stanford Synchrotron Radiation Laboratory. Through analysis of the x-ray absorption near edge structure (XANES) portion of the XAS spectrum, the oxidation state of Tc in the samples can readily be determined. The selected samples contained significant Tc contamination in both the water and acid extracts suggesting that Tc was predominantly present as pertechnetate. The samples were analyzed both "as-received" and "water-washed." Ideally, the as-received samples should contain Tc as pertechnetate whereas the water-washed treatment would remove the highly soluble pertechnetate, leaving any insoluble reduced Tc^{IV} species behind. Unfortunately, even sample 4A/B/C, the horizon with the highest Tc contamination, contained insufficient Tc for bulk XAS

analysis. Therefore, a fraction of this sample and sample 15A from the slant borehole were prepared for micro x-ray fluorescence mapping on the PNC-CAT beamline at the Advanced Photon Source.

The micro x-ray fluorescence technique uses an x-ray beam a few microns in diameter that is rastered over the surface area of the sample. The energy of the x-ray beam is sufficient to excite x-ray fluorescence from elements of interest in the sample. The fluorescence spectrum is collected as a function of x-y position providing an elemental map of the sample. Comparison of the Tc distribution to other elements may reveal associations between Tc and other mineral phases; for example, Fe-oxides. The results of micro x-ray fluorescence mapping for samples 15A and 4A/B/C are shown in Figure 4. The elemental maps for Fe, Mn, and Ti are strongly correlated in both samples whereas the elemental maps for Fe and Ca are inversely correlated.
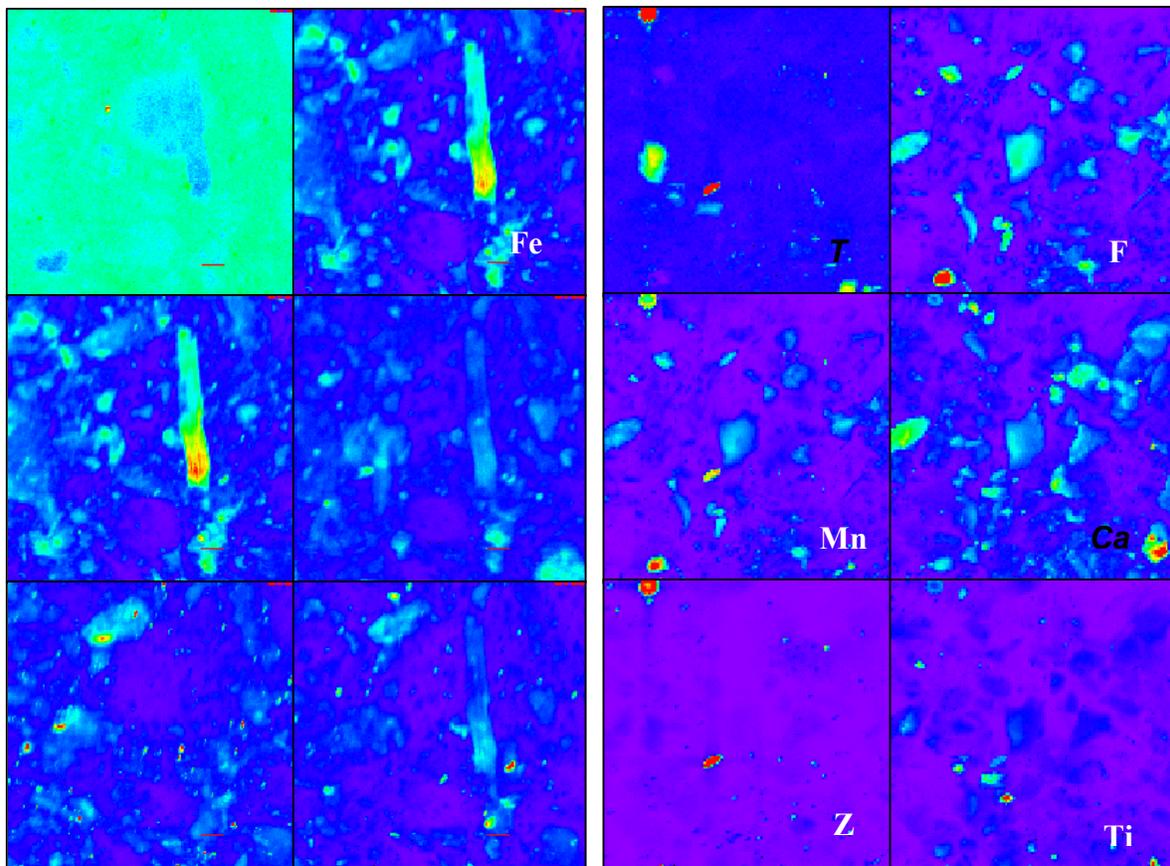

Figure 4. X-ray microprobe elemental maps for samples 15A , left, and 4A/B/C, right. Warm tones indicate high concentrations of the element indicated. The apparent Tc concentrations in sample 4A/B/C are actually due to interference from Zr.

The Fe-Mn-Ti correlation is likely due to the presence of titanomagnetite and Fe-Mn oxide grains. The inverse correlation with Ca probably reflects the presence of feldspars and calcite grains. A detailed analysis of the Tc "hot spots" in sample 4A/B/C using micro-XANES indicated that the apparent Tc signal was due to interference from Zr; the Tc K-edge at 21044 eV and the Zr L_{III}-edge at 22230 eV are too close in energy to be completely resolved.

Efforts to characterize the Tc in contaminated Hanford formation sediments from the tank farm drilling program have been unsuccessful although the reported Tc concentrations should have been sufficient for the experimental techniques we are using. We are currently reviewing the sampling protocols at the drill site and our sample preparation methods to determine if either, or both, of these processes are removing Tc from the samples before analysis. We are hopeful that the drill cores from the B-BX tank farm will provide sediment samples that will permit direct determination of the Tc speciation.

Solubility of Reduced Tc Species

The solubility of reduced Tc species was determined under a wide range of pH conditions and in the presence of high concentrations of chloride and bicarbonate/carbonate. We conducted solubility studies of TcO_2(am) as a function of pH from 6 M HCl to pH5 and as function of chloride concentration from 0.001 to 5 M NaCl. In addition, we have conducted these experiments under carefully controlled reducing conditions such that the preponderance of Tc is present in solution in the reduced Tc^{IV} oxidation state. The oxidation state determination based on solvent extraction techniques has been verified by analysis of the XANES portion of the x-ray absorption spectra and UV-Vis spectroscopy, where the solution concentrations are high enough. Powder x-ray diffraction and analysis of the EXAFS portion of the x-ray absorption spectra were used to characterize the solid phase in equilibrium with the solution phase.

Our solubility measurements are in good agreement with those reported in the literature in the pH range from 1 to 5 as shown in Figure 5. At acidities less than pH = 1, there is increasing discrepancy. At a given pH, increased solubility is observed with increased chloride concentration. Models of Tc solubility based on the existing thermodynamic data are in good agreement at low chloride concentrations and at pH greater than 1 but fail to predict the observed Tc solubility at high chloride concentration. EXAFS analysis of the solution species indicates that $TcCl_6$ species dominate at pH less than or equal to zero. Unfortunately, the concentration of Tc species is not sufficient for EXAFS analysis at higher pH, where mixed hydroxychloride Tc complexes and Tc hydrolysis products are thought to exist. Characterization of the solid phase by EXAFS analysis across the pH range indicates the stability of TcO_2(am) as the solubility
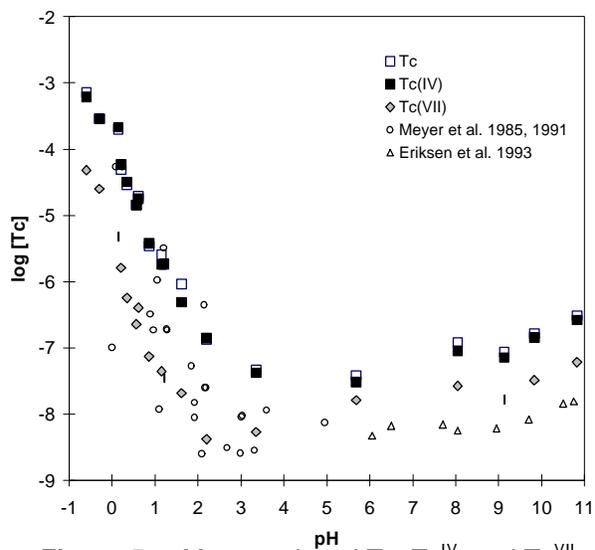
Figure 5a. Measured total Tc, Tc[IV], and Tc[VII] in solution in contact with TcO$_2$(am). The reported Tc[IV] data of Meyer and Eriksen are shown for comparison.
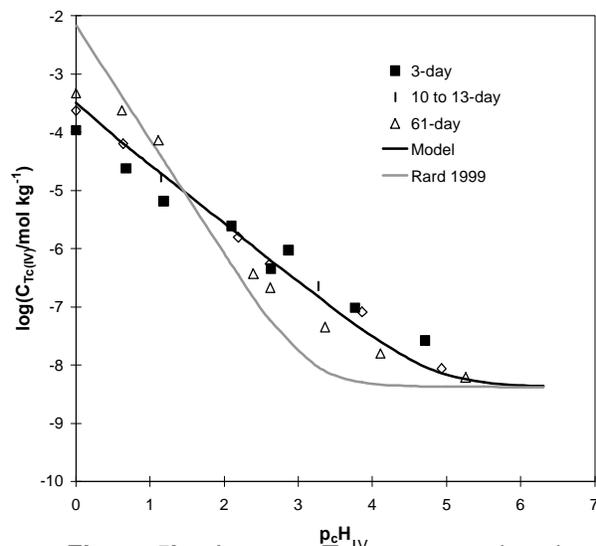
Figure 5b. Aqueous Tc[IV] concentrations in contact with TcO$_2$(am) in 2.5 M NaCl solution. The dashed line represents the predicted Tc concentration based on the existing thermodynamic data (Rard 1999). The solid line represents our improved model.

limiting phase. Analysis of the powder x-ray diffraction data from the solid sample indicates that solid phase is amorphous across the pH range. Solubility studies under alkaline conditions and in the presence of carbonate have just been initiated.

Planned Activities

Future experimental work includes batch experiments of Tc(VII) sorption/reduction on hematite, magnetite, biotite, and hornblende; micro-XANES analysis of sediments from column experiments; and solubility experiments in the presence of carbonate at constant ionic strength. Future data analyses include thermodynamic modeling of the solubility data and interpretation of the column studies, which then will be incorporated into journal publications.

Information Access

Journal Articles

Hess NJ, Y Xia, DA Moore, and D Rai. 2002. Thermodynamic model for the solubility of TcO$_2$· nH$_2$O in acidic solutions and high NaCl concentrations. To be submitted to *Journal of Solution Chemistry.*

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Presentations

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