

# **Environmental Management Science Program**

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## **Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste**

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### Research Objective

The ultimate goal of this proposal is to separate technetium from Hanford tank waste. Our recent work has shown that a large portion of the technetium is not pertechnetate ( $\text{TcO}_4^-$ ) and is not easily oxidized. This has serious repercussions for technetium partitioning schemes because they are designed to separate this chemical form. Rational attempts to oxidize these species to  $\text{TcO}_4^-$  for processing or to separate the non-pertechnetate species themselves would be facilitated by knowing the identity of these complexes and understanding their fundamental chemistry. Tank characterization work has not yet identified any of the non-pertechnetate species. However, based on the types of ligands available and the redox conditions in the tank, a reasonable speculation can be made about the types of species that may be present. Thus, this proposal will synthesize and characterize the relevant model complexes of Tc(III), Tc(IV), and Tc(V) that may have formed under tank waste conditions. Once synthesized, these complexes will be used as standards for developing and characterizing the non-pertechnetate species in actual waste using instrumental techniques such as capillary electrophoresis electrospray mass spectrometry (CE-MS), x-ray absorbance spectroscopy (EXAFS and XANES), and multi-nuclear NMR (including  $^{99}\text{Tc}$  NMR). We will study the redox chemistry of the technetium complexes so that more efficient and selective oxidative methods can be used to bring these species to  $\text{TcO}_4^-$  for processing purposes. We will also study their ligand substitution chemistry which could be used to develop separation methods for non-pertechnetate species. Understanding the fundamental chemistry of these technetium complexes will enable technetium to be efficiently removed from the Hanford tank waste and help DOE to fulfill its remediation mission.

### Research Progress and Implications

This report summarizes the first 8 months of a 3-year project. Our efforts have so far been directed at the synthesis and characterization of technetium and rhenium complexes. The initial development work has been made using rhenium, the chemical analogue of technetium, which also forms dinuclear m-oxo complexes. This is allowing more rapid development of this program because the concerns of working with radioactivity is eliminated. The techniques developed with the rhenium analogues are then transferred to the technetium work. Complexes synthesized to date have been  $[(\text{HEDTA})\text{Re}(\text{m-O})_2\text{Re}(\text{HEDTA})]_2^-$ ,  $[(\text{NTA})\text{Re}(\text{m-O})_2\text{Re}(\text{NTA})]_2^-$ ,  $[(\text{tetn})\text{Re}(\text{m-O})_2\text{Re}(\text{tetn})]_4^+$  (tetn = triethylenetetraamine), and  $[(\text{C}_2\text{O}_4)_2\text{Re}(\text{m-O})_2\text{Re}(\text{C}_2\text{O}_4)_2]_2^-$ . These complexes have been synthesized at pH 4 using  $\text{ReOCl}_5$ - or  $\text{ReCl}_6$ - as starting materials. The complexes are very water soluble and difficult to isolate. We have studied the reactivity of these complexes in sodium hydroxide solutions, conditions similar to the Hanford tank waste. Rapid scanning UV-VIS experiments suggest that the complexes oxidize quickly to a Re(IV)/Re(V) complex and slowly to a Re(V)/Re(V) species and eventually to  $\text{ReO}_4^-$ . The oxidation is promoted by higher base concentrations and the extent of exposure to air. The order of reactivity is oxalate > NTA > EDTA. The  $[(\text{HEDTA})\text{Tc}(\text{m-O})_2\text{Tc}(\text{HEDTA})]_2^-$  complex has been synthesized from pertechnetate at pH 4. We have measured the distribution coefficient (Kd) of this complex between Reillex-HPQ anion exchange resin and solutions of the complex that range in pH from 1-14. In the presence of nitrate the complex fails to sorb on the resin at any pH. Without nitrate present the complex does sorb. At pH < 2 the sorption is low because

the complex is neutral. Above pH 2 sorption does occur as the complex deprotonates to form initially a 2-, then 3- and 4- anionic species. The maximum sorption,  $K_d$  values  $> 300$  mL/g, occur at pHs between 5-9. Above pH 10 the  $K_d$  values decrease as the complex begins to oxidize. As with the rhenium complexes, we speculate that a Tc(V)/Tc(V) species is forming which then oxidizes to pertechnetate. However, this is occurring at a slower rate compared to the rhenium complexes.

This project is collaborating on the purchase and assembly of a capillary electrophoresis mass spectrometry (CE-MS) instrument. The HP engine mass spectrometer has been delivered and is currently being assembled. The capillary electrophoresis section of the instrument will be interfaced with the MS through an Analytica electrospray source. The estimated sensitivity of the CE/MS unit is at the attomole to picomole level which would make it possible to detect  $< 10^{-8}$  M of a non-pertechnetate species in a mL of waste. We are using the rhenium and technetium complexes that we synthesize as standards to help develop capillary electrophoresis mass spectrometry (CE-MS) as a method for characterizing the technetium species in actual wastes. Capillary electrophoresis has been shown to provide separation efficiencies above 106 theoretical plates, allowing separation of complex mixtures before introduction into the mass spectrometer for analysis. Total sample usage is very small ( $\sim 1$  nL), making this type of instrument attractive for use with radioactive samples.

Our collaborator, Dave Blanchard, at PNNL has studied the XAS spectra of  $[\text{TcO}_2(\text{en})]^+$  (en = ethylenediamine) and  $\text{NH}_4\text{TcO}_4$  under acidic conditions and compared the spectra to the non-pertechnetate Tc species present in tank waste and to the  $[(\text{HEDTA})\text{Tc}(\text{m-O})_2\text{Tc}(\text{HEDTA})_2]$ -complex prepared by the LANL group. The data are currently being analyzed. A paper is being prepared for publication with the results of an X-ray Absorption Near Edge Spectroscopy (XANES) analysis of the Tc in samples of waste from Hanford tanks AN-107, AW 101, SY-101, and SY-103. Both pertechnetate and non-pertechnetate Tc species are present in all untreated samples. Pertechnetate is almost completely removed by contacting the waste samples with Reillex-HPQ anion exchanger. The highest concentration of the non-pertechnetate was found in waste with the highest organic complexant concentration, suggesting the presence of a Tc species complexed or bound to complexants or complexant fragments. The XANES of the Tc in these treated samples (which varies from 20% to 80%, depending on the tank) is consistent with a Tc(IV) species bound to complexants or complexant fragments through oxygen linkages. Spectra of one of the wastes (SY-103) before and after aging for approximately 4 months shows an increase in the fraction of pertechnetate present, indicating oxidation of the non-pertechnetate to pertechnetate.

## Planned Activities

We will finish synthesizing the first series of polyaminopolycarboxylate and aminopolycarboxylate rhenium complexes that will give us complexes containing donor atoms sets ranging from four oxygens through four nitrogens. We will make the corresponding technetium complexes. All complexes will be examined for their reactivity in basic solution. The complexes will be used for the XAS, XANES, and CE/MS work. This work will occur through the summer and into the start of the next fiscal year.

## Other Access To Information

N.C. Schroeder, S.D. Radzinski, K.R. Ashley, A.P. Truong, and P.A. Szczepaniak, "Technetium Oxidation State Adjustment for Hanford Waste Processing," accepted for publication in *Science and Technology for Disposal of Radioactive Tank Waste*, N.J. Lombardo and W.W. Schulz, eds., Plenum Publishing Corporation, New York, NY, (1997)