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Project Title: **Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste**

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1. 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 (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 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}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 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.

2. RESEARCH PROGRESS AND IMPLICATIONS. This report summarizes months 9-21 of a 36 month project. A series of known technetium complexes were initially prepared using methods similar to those found in the literature. A typical procedure involved the sulfite reduction of pertechnetate under mildly acidic conditions. Each complex was be precipitated and recrystallized from aqueous solutions by the addition of ethanol. These complexes are known to form a dimeric structure $[(L)Tc(\mu\text{-}O)_2Tc(L)]^{n-}$ with the technetium in the +4 oxidation state. Complexes have been successfully prepared using ligands such as EDTA (**ethylenediaminetetraacetic acid**), NTA (**nitrilotriacetic acid**), DTPA (diethylenetriaminepentaacetic acid) and oxalate. None of these complexes exhibited any significant stability under caustic conditions. Further studies need to be performed with these complexes in caustic media when there is a holding reductant and excess ligand present.

Using similar methodology, a second series of complexes were prepared under mildly caustic conditions using ligands such as IDA (iminodiacetic acid), EDDA (ethylenediamine-N,Ní-diacetic acid), citrate, and glycolate. Each complex was initially isolated and recrystallized by ethanol precipitation from water. More recently, it was recently discovered that these complexes could be more highly purified using size exclusion chromatography (Sephadex G10). FT-IR and UV-Vis have been the primary characterization methods thus far. Tc-99 NMR signals have not been observed which is consistent with the presence of a paramagnetic Tc(IV) nucleus. Efforts to grow crystals suitable for x-ray crystallography have thus far been unsuccessful. The glycolate complex showed the highest stability under basic conditions but did decompose over a day in 2 M NaOH. The stability could be somewhat enhanced by mimicking the reducing environment in the tanks with the addition of excess reducing agent and free ligand.

In the presence of IDA, a red and a blue complex (λ_{max} = 507 and 590 nm, respectively) are formed in equilibrium but could be separated and isolated by selective ethanol precipitation or size exclusion chromatography. The infrared spectrum of these complexes indicates coordination of the ligand carboxylate groups to technetium at approximately 1625 cm^{-1}. An observed stretch at ~1085 cm^{-1} is consistent with the presence of a Tc-OH group in each complex.

A red Tc-EDDA complex was also formed with a λ_{max} = 490 nm. The IR spectrum shows carboxylate coordination and Tc-O-Tc bridging stretch at 791 cm^{-1}.

A dark red Tc-citrate complex was also formed with a λ_{max} = 530 nm. This complex is in the process of being characterized.

The deep red Tc-glycolate complex (λ_{max} = 518 nm) is also in the process of being characterized but the infrared spectrum does show carboxyl coordination to Tc at 1650 cm^{-1} and a Tc-OH stretch at 1142 cm^{-1}. A previously proposed ($[Tc(OH)_2glycolate]^{2-}$) prepared by a different method is consistent with these observations.

Recently, an extended series of technetium nitrido complexes have been prepared using $[TcNCl_4]^-$ as a starting material. Substitution of the chlorides for a variety of ligands has been attempted under acidic and basic conditions. For each ligand (EDTA, oxalate, HEDTA, glycolate, citrate, IDA, EDDA), a scarlet red complex is formed in 0.5 M HNO_3, while a bright yellow complex is formed in 0.5 M NaOH. Addition of nitric acid to the yellow complex causes the rapid formation of the red complex and vice-versa. Dimeric red nitrido complexes of EDDA and EDTA with a μ-oxo bridge have been reported in the literature. The red color was attributed to a transition in a linear Tc-O-Tc three-center π-bond system. The yellow complexes may either be dimeric in nature with a bis-μ-oxo bridge, or monomeric. Further characterization is underway.

Capillary electrophoresis mass spectrometry (CE-MS) has been used to analyze some of our rhenium and technetium complexes. The $Re_2(\mu\text{-}O)_2(EDTA)_2$ and $Re_2(\mu\text{-}O)_2(NTA)_2$ samples were run at pH 5, as expected these complexes behaved as anions at this pH. At 1 mmolar concentration the samples show some instability, with the NTA complex being less stable than the EDTA complex. The NTA sample actually shows enhanced stability in the presence of the EDTA complex. This is because the EDTA complex appears to convert to two major and 1 minor species when diluted. This process is apparently releasing some free EDTA that can complex Re released from the NTA complex.

We analyzed eight samples by EXAFS and XANES at Stanford Accelerator Center. David Blanchard, our PNNL collaborator, performed this work. The samples were Tc-EDDA (**1**), Tc-IDA (**2**, red product), Tc-IDA, (**3**, blue product), Tc-IDA (**4**, red product with holding reductant, HSO_3^-, and excess IDA), Tc-IDA (**5**, blue product with holding reductant, HSO_3^- and excess IDA), Tc-nitrido-IDA, **6**, Tc-nitrido-EDDA, **7**, Tc-EDDA (**8**, with holding reductant, HSO_3^-, and excess EDDA). All the samples are dissolved in water except for Tc-nitrido-EDDA, which is in 0.05 M NaOH. All the samples were approximate 1 x 10^{-3} M. Samples **1**, **3**, **5** and **8** look like Tc(IV) species. Samples **1**, **5** and **8** were stable while **3** showed some decomposition. The stability of **5** relative to **3** was apparently due to the excess reductant and IDA present; a situation not unlike a Hanford tank waste environment where complexant concentrations are large relative to technetium and radiolysis maintains a reducing environment. Samples **2** and **4** were stable and appear to be Tc(V) species. The Oxidation State of **6** and **7** are unclear at this point; however **7** appeared to decompose. It should be noted that those samples that showed decomposition did not appear to be forming pertechnetate on the time scale of this experiment, three weeks. However, samples **1**, **2**, and **3**, at 5 x 10^{-5} M, decomposed to pertechnetate within 24 hours during an attempted analysis by capillary electrophoresis mass spectrometry. Lastly the X-ray absorption fine structure spectroscopy (EXAFS) suggested that the red IDA complex is monomeric, the blue IDA complex is dimeric, and the Tc-EDDA is a polynuclear complex.

3. PLANNED ACTIVITIES: Future efforts are being directed towards fully characterizing these complexes. Pure samples have already been prepared using size exclusion chromatography and are awaiting FT-Raman analysis at the CMR building here at LANL. In addition, samples are being prepared for shipment to Atlantic Microlabs in Georgia for elemental analysis. We also have time scheduled in July at the synchotron facility at Stanford for x-ray absorption analysis in collaboration with David Blanchard from PNNL.

4. INFORMATION ACCESS: A talk on this work will be presented at the EMSP symposium at the American Chemical Society meeting this August in New Orleans. Recent publications dealing with the technetium speciation problem are listed below.

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley, Anh P. Truong, and Patrycja A. Szczepaniak, ìTechnetium Oxidation State Adjustment for Hanford Waste Processing,î in *Science and Technology for Disposal of Radioactive Tank Waste,* N. J. Lombardo and W. W. Schulz, eds., Plenum Publishing Corporation, New York, NY, (1998).

K. R. Ashley, G. D. Whitener, N. C. Schroeder, J. R. Ball, and S. D. Radzinski, in Progress in Metal Ion Separation and Preconcentration, ACS Symposium Series 716, A. H. Bond, M. L. Dietz, and R. D. Rogers, Eds., American Chemical Society, Washington, D C., 1999, p. 219.

Norman C. Schroeder**,** Susan D. Radzinski**,** Kenneth R. Ashley, Anh P. Truong, Glenn D. Whitener, "Feed Adjustment Chemistry for Hanford 101-SY and 103-SY Tank Waste: Attempts to Oxidize the Non-Pertechnetate Species," in preparation.

Norman C. Schroeder, Jason R. Ball, and Susan D. Radzinski Kenneth R. Ashley Kenneth R. Ashley, "Reillexô-HPQ Anion Exchange Column Chromatography: Removal of Pertechnetate from DSSF-5 Simulant at Various Flow Rates," submitted to Solvent Extraction and Ion Exchange.