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Project Title: Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste
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1. SPECIFIC DOE PROBLEM BEING ADDRESS. Within the high-level waste investment portfolio DOE has identified a specific need to investigate the fundamental chemistry of technetium and how this relates to potential separation processes.

2. RESEARCH OBJECTIVE. The ultimate goal of this project is to separate technetium from Hanford tank waste. Our prior work with Hanford Site tank waste indicates that the presence of complexants has produced unidentified, reduced technetium species not amenable to current separation technologies, or readily oxidized to pertechnetate. Consequently, we are synthesizing and characterizing some of the major classes of technetium complexes that may be formed under tank waste conditions. These complexes will be used as standards to characterize the non-pertechnetate species in actual wastes and to develop efficient oxidation or separation methods.

3. RESEARCH PROGRESS AND IMPLICATIONS. This report summarizes months 22-30 of a 37 month project. Initially, a series of known dimeric Tc(IV) complexes ($[(L)Tc(\mu-O)_2Tc(L)]^n$) were prepared by the sulfite reduction of pertechnetate under mildly acidic conditions. Ligands examined included EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), DTPA (diethylenetriaminepentaacetic acid) and oxalate. None of these complexes exhibited significant stability under caustic conditions.

Using similar methodology, a second series of complexes were prepared under mildly caustic conditions using ligands such as IDA (iminodiacetic acid), EDDA (ethylenediamine-N,N'-diacetic acid), citrate, and glycolate. Although efforts to grow crystals suitable for x-ray crystallography have thus far been unsuccessful, the properties and structural details of these complexes has been at least partially elucidated using a variety of methods, including; UV-Vis, FT-IR, FT-Raman, NMR, x-ray absorption spectroscopy, and elemental analysis. These complexes typically decomposed within 24 hours in 2 M NaOH but the stability could be somewhat enhanced by mimicking the reducing environment in the tanks with the addition of excess reducing agent and free ligand.

Gluconate is a byproduct of sugar-based denitration processes at Hanford. Using sulfite or stannous chloride as a reductant, it readily forms a stable, reduced technetium complex at base concentrations of at least 2 M NaOH. This complex appears similar to the radiopharmaceutical precursor $[TcO(\text{gluconate})_2]^n$, that is often used as a transfer ligand complex when complexation of the ligand of interest is not competitive with TcO_2 formation and precipitation. Since TcO_2 formation is favored at high base concentrations for the other complexants studied, we have begun

to study the ligand transfer reactions of Tc-gluconate with waste relevant complexants such as EDTA, NTA, EDDA, IDA. Any complexes formed will be examined for waste relevance.

It has previously been determined that at least some of the reduced Tc species in real waste are not retained by the Reillex HPQ resin, nor easily oxidized with peroxide. For this reason, a known quantity of the Tc-gluconate complex in 2.5 M NaOH was contacted with Reillex and the K_d determined. We found that although some of the complex adhered to the resin, a significant portion was not retained. When contacted with excess H_2O_2 , the pink color faded to yellow. This stable yellow species is an unknown reduced Tc-complex that is not retained by Reillex.

In order to obtain greater insight into the nature of the non-perchnetate complexes in actual waste we have tried to separate the species from an actual waste sample of AN-107 using Sephadex[®] G10 size exclusion gel. The total technetium analyses indicated that 60% of the technetium was coming through the column; a percentage consistent with the non-perchnetate content of the AN-107 waste. The small perchnetate anion adheres strongly to the top of the column.

4. PLANNED ACTIVITIES: Future efforts are being directed towards further characterizing these complexes by UV-Vis, FT-IR, FT-Raman, and NMR. We are also preparing a shipment of samples for elemental analysis at Atlantic Microlabs in Georgia. In addition, ten samples were sent for XAS in Feb. and we are awaiting analysis of the data. These samples were of higher purity and concentration than our previous efforts. Preliminary capillary electrophoresis mass spectrometry (CE-MS) experiments with some rhenium and technetium complexes indicate this may be a powerful tool for the analysis of our complexes, as well as those found in real waste. Further experiments are planned.

5. INFORMATION ACCESS: A poster presentation of this work will be made at the EMSP workshop in Atlanta in April and at the American Chemical Society meeting this March in San Francisco. Recent publications dealing with the technetium speciation and separation problems are listed below.

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.

K. R. Ashley, Jason R. Ball, Glenn D. Whitener, Norman C. Schroeder, and Susan D. Radzinski, "Reillex[™]-HPQ Anion Exchange Column Chromatography: Removal of Perchnetate Ion from DSSF-5 Simulant at Various Flow Rates", *SOLVENT EXTR. ION EXCH.*, **17**, 1543 (1999).

K. R. Ashley, Glenn D. Whitener, Norman C. Schroeder, Jason R. Ball, and Susan D. Radzinski "Sorption Behavior of Perchnetate Ion on Reillex[™]-HPQ Anion Exchange Resin from Hanford and Melton Valley Tank Waste Simulants and Sodium Hydroxide/Sodium Nitrate Solutions", *SOLVENT EXTR. ION EXCH.*, **16**, 843 (1998).

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley, Anh P. Truong, and Patrycja A. Szczepaniak, "Technetium Oxidation State Adjustment for Hanford Waste Processing," 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).

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-Perchnetate Species," in preparation.