

FY03 Annual Report for EMSP Project 81921
Tc Chemistry in HLW: Role of Organic Complexants

1. Research Objective

Tc complexation with organic compounds in tank waste plays a significant role in the redox chemistry of Tc and the partitioning of Tc between the supernatant and sludge components in waste tanks. These processes need to be understood so that strategies to effectively remove Tc from high-level nuclear waste prior to waste immobilization can be developed and so that long-term consequences of Tc remaining in residual waste after sludge removal can be evaluated. Only limited data on the stability of Tc-organic complexes exists and even less thermodynamic data on which to develop predictive models of Tc chemical behavior is available. To meet these challenges we are conducting a research program to study to develop thermodynamic data on Tc-organic complexation over a wide range of chemical conditions. We will attempt to characterize Tc-speciation in actual tank waste using state-of-the-art analytical organic chemistry, separations, and speciation techniques to validate our model. On the basis of such studies we will develop credible model of Tc chemistry in HLW that will allow prediction of Tc speciation in tank waste and Tc behavior during waste pretreatment processing and in waste tank residuals.

The research has two integrated experimental components, 1) highly controlled laboratory studies to acquire data on Tc-organic complexes needed in order to create a predictive model of Tc chemistry, and 2) Tc speciation in actual tank waste samples using state of the art separations and organic characterization techniques. Our initial laboratory studies have focused on organic complexants that have been identified as capable of forming stable complexes with Tc(IV) under basic conditions. The results from tank waste speciation studies will guide the design of future laboratory experiments. This interplay will aid in the design of more realistic and complex laboratory experiments from which a model can be developed.

2. Research Progress and Implications

Solubility experiments. Based on the recent EMSP results (Schoeder et al. 2000; Shuh et al. 2000) and literature data (Peretukhin et al. 1996; Erikson et al. 1992) we have initiated solubility studies of Tc(IV) in the presence of bicarbonate, carbonate, EDTA, citrate, and gluconate over a wide range of pH conditions. The experimental method for the solubility studies is similar for each ligand and is briefly summarized below. Our bicarbonate/carbonate experimental studies are nearly complete and will be interpreted using Pitzer ion interaction model, whereas the EDTA, citrate, and gluconate experimental studies are in progress. The results for each of these ligands are summarized in Figure 1 below. Experimental studies of formate, oxalate and glycolate ligands have just been initiated.

All experiments and sample preparations are conducted in an atmosphere-controlled chamber under an Ar atmosphere. Deionized, distilled and degassed water is used in all cases. Steady state Tc concentrations are approached from the undersaturation direction.

$\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ precipitate is prepared individually for each sample by $\text{Na}_2\text{S}_2\text{O}_4$ reduction of pertechnetate stock solution under basic conditions. The black precipitate forms quickly and is allowed to mature in the mother liquid for 72 hrs. The precipitate is washed using near neutral aqueous solution and then equilibrated with 20 ml of pH adjusted aqueous solution, 0.02 M hydrazine (holding reductant), and the ligand of interest for at least 3-days prior to initial sampling.

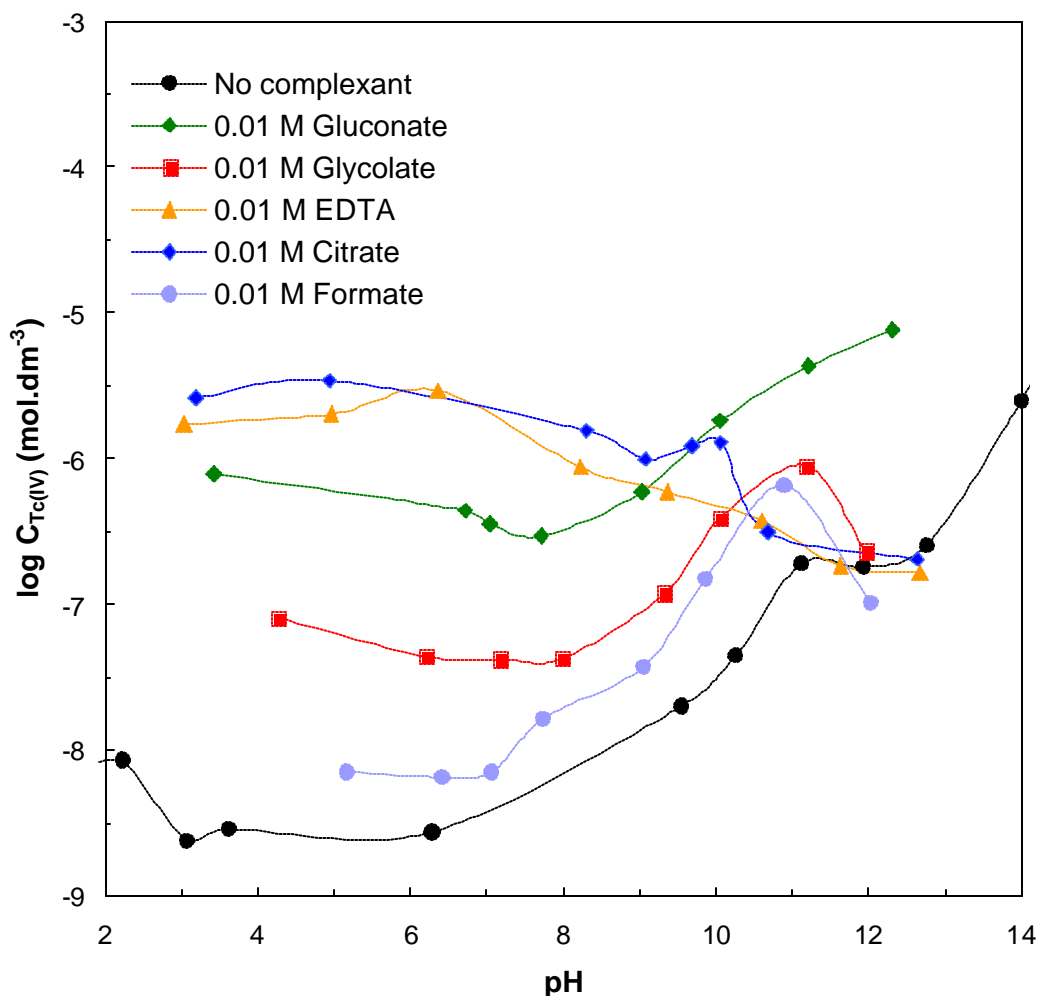


Figure 1. Summary of results for $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ solubility experiments. At pH greater than 12, conditions expected for HLW tanks, the only gluconate results in increased solubility of $\text{Tc}(\text{IV})$ species.

Electrospray mass spectroscopy. Electrospray ionization mass spectrometry (ESI/MS) has been used for the analysis of complex, polar, and labile molecules since it was introduced by Yamashita and Fenn (1984). Recently, there has been increasing applications for the analysis of smaller molecules. We have developed ESI/MS for the analysis of metal-organic complexes (e.g., $\text{Cu}(\text{EDTA})$) (Campbell et al. 1994, 1993). In

addition, we have developed capillary electrophoresis mass spectrometry for the separation and analysis of Co(II)EDTA and Co(III)EDTA (Peterson et al. 1998).

We have examined a series of metal organic species including Cu-DTPA, Cu-EDTA, Cu-NTA, Ni-EDTA, Fe-DTPA, and Fe-EDTA using ESI/MS to provide a proof of principle for use of ESI/MS for the analysis of metal-organic species. The intact metal-organic species provided intense $(M-H)^-$ species in the negative ion mode. The results clearly indicate that ESI/MS can be applied to the analysis of the intact metal-organic species listed above. To extend that application, K_4ReO_2 -NTA and K_4ReO_2 -oxalate were synthesized and then examined using ESI/MS in the negative ion mode. Re complexes are similar to technetium complexes but are not radioactive. Therefore, no specific safety requirements or decontamination procedures are required. We have used direct injection of the Re complexes into a HP 5989B MS Engine electrospray mass spectrometer operated in the negative ion mode. Presently, we are interpreting the mass spectral data. These spectra were easy to interpret and concentrations were at fairly low levels. The concentration required to obtain a spectrum of ReO_2 -oxalate was approximately 100 fold higher concentration than that of the Cu and Fe complexes. The mass spectrum is still being interpreted. It is possible that the Re complex is not stable under these ionizing conditions. Additional research is required in this area. In addition, other Re complexes (less oxygenated) will be synthesized and examined using electrospray mass spectrometry.

References

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