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Project Title: **Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions**

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Graduate Students: Two graduate students at New Mexico State University are partially or wholly supported by this project.

Summary/Progress Report

1. RESEARCH OBJECTIVE

The overall objective of this project is to provide a scientific basis for safely processing complexant-containing high-level tank wastes for disposal. Our key goals are to identify a means to prepare *realistic* complexant-containing tank waste simulants, and to use those simulants to determine the relative importance of organic complexants and their breakdown products on the partitioning of important radionuclides. These goals will be accomplished by artificially aging complexant-containing tank waste simulants using microwave, ultrasound, and photolysis techniques. The simulants will be compared to samples of actual Hanford tank wastes to determine the most realistic aging methods, on the basis of the organic fragmentation and the partitioning behavior of important radionuclides. Also, we will use our simulant aging process to investigate the relative effects of chelator degradation products on the partitioning of important radionuclides from the waste. Using NMR-active labels in the chelators, we will use a combinatorial approach of generating multiple chelator fragments in a single experiment and then determining which fragments have a negative effect on the separations chemistry. Our successful completion of this goal will specifically identify the most problematic organic fragments in complexant-containing waste and provide the basis for developing successful treatment strategies for these wastes.

2. RESEARCH PROGRESS AND IMPLICATIONS.

This report summarizes work carried out at Los Alamos National Laboratory and New Mexico State University during the first 1.5 years of a 3-year project.

A key problem in developing treatment schemes for nuclear tank wastes is that samples of the wastes are exceedingly difficult to obtain, transport and handle in the laboratory. Although simulated wastes are a safe and inexpensive means for other researchers to become involved in tank waste remediation studies, freshly prepared simulants may not reproduce the partitioning behavior of actual tank waste samples. Therefore, one of our goals is to devise a method for preparing a realistic tank waste simulant that truly behaves like actual tank waste.

Thermal reduction of pertechnetate under tank waste conditions: A key issue in producing a realistic simulant is reproducing the separations behavior of technetium-99. Technetium is known to be converted from pertechnetate ($TcO_4^{\tilde{n}}$) to reduced species (possibly Tc(IV) coordination

complexes) during storage of high-organic content alkaline wastes. The process responsible for pertechnetate reduction is unknown but could be radiolytic or thermal in origin. We prepared simplified simulants containing pertechnetate ion, complexants (EDTA, NTA, HEDTA, citrate, glycolate, and oxalate) and catalytic fission product metals (Ru, Rh, and Pd), along with representative transition metals (Fe, Ni) in sodium hydroxide. After 24 hours heating to 64_C in a sealed vessel, significant technetium reduction was apparent in the simulants that contained *both* complexants and catalytic fission product metals. Palladium appears to be especially effective in promoting technetium reduction. Further studies are in progress to determine the mechanism and products of the thermal reduction processes.

Impact of chelators and fragments on radionuclide partitioning: Over 50 chelator decomposition products have been previously identified in aged tank wastes, most of which are potential chelators themselves. Reconstructing the radionuclide speciation from a simple inventory is impossible because known stability constants for the metal-ligand combinations are limited. We surveyed the impact of several commercially available complexants on the partitioning behavior of Sr^{2+} from a simplified simulant. These preliminary experiments showed that radionuclide partitioning onto the chelating resin Diphonix was strongly inhibited by the parent polycarboxylate chelators EDTA, HEDTA and NTA, but not by citric acid or by degradation products such as iminodiacetic acid (IDA). Complexant effects on actinide partitioning from alkaline wastes were measured indirectly by exploiting the high solubility of actinyl ions in Me_4NOH solution. Anion exchange separation of uranyl ion from alkaline solution was hindered by the strong complexants EDTA and HEDTA, while fragments such as IDA had little effect. These results may indicate that complete organic destruction is not required for successful pretreatment of Hanford tank wastes.

Tank AN-107 organic analysis, and effects of treatment on strontium partitioning: Samples of AN-107 tank waste supernate were esterified using thionyl chloride/methanol and analyzed by gas chromatography and online atomic emissions spectroscopy. Ten complexant molecules dominate the organic content of AN-107 waste, most of which are the known parent chelators mentioned above. Distribution coefficients for ^{99}Tc on Reillex-HPQ and for ^{90}Sr on Diphonix resins were low for untreated AN-107 samples, but increased steadily after protracted oxidation by persulfate or ozone. The residual organic content of these treated waste samples will be analyzed to determine which chelators are most effectively degraded by the oxidative treatments.

Chelator degradation during NMR labeling experiments: ^{13}C-labelled EDTA and NTA were synthesized from bromoacetic acid (containing ^{13}C in either the carboxylate or methylene position) and the appropriate amines. These NMR-active compounds were used to investigate thermal degradation of the complexants under simulated waste conditions, especially during the esterification procedure used to analyze tank waste constituents. Acidification of the simulants followed by thionyl chloride/methanol esterification produced several new compounds which would appear as artifacts in GC analysis; iron(III) is particularly effective in promoting this reaction. Similarly, neutralizing a waste simulant to pH 1-2 and heating at 90_C for 6 hours produced *complete* degradation of both EDTA and NTA to other products. Although neutralization of the Hanford tank wastes prior to vitrification is not a preferred option, the effectiveness of acidic thermolysis in organic destruction may warrant further consideration of such approaches.

3. PLANNED ACTIVITIES. Year 2: (a) Correlate Sr and Tc partitioning results for AN-107 waste with the extent of organic destruction achieved by various oxidative pretreatment methods.

(b) Determine mechanism of thermal pertechnetate reduction process. Year 3: (c) Analyze mechanisms and outcomes of organic transformations using GC/MS and NMR methods. (d) Analyze key radionuclide-chelator complexes in aged simulants using heteronuclear shift correlation NMR experiments.

4. INFORMATION ACCESS

Several manuscripts will be submitted by the end of fiscal year 1999. Preprints may be obtained by contacting the Principal Investigator.