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Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions

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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 method, on the basis of the organic fragmentation and the partitioning behavior of the important radionuclides ^{90}Sr , ^{99}Tc , and ^{239}Pu . 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.

Research Progress and Implications

This report summarizes work carried out at Los Alamos during the first 8 months of a 3-year project. The report reflects only one month of effort by New Mexico State University collaborators, because of delays in allocating funding to that institution.

Laboratory aging of tank waste simulants: 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 do 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.

To date, we have devoted extensive effort toward the organic analysis of complexants in simulants. We established a procedure for formulating and preparing a simulant of any given tank waste supernatant, by combining analytical data and predictive models based on the history of processing at Hanford. Focusing on Hanford Tank SY-101 supernatant, we have developed a method for esterifying the chelators so that they can be separated from the high ionic strength, alkaline simulant matrix by liquid-liquid extraction. Analysis of the chelators by gas chromatography provides quantitative information on changes in the simulant, but newly formed chelators are difficult to identify without further characterization. We are currently setting up an atomic emission detector that will enable identification of these daughter chelators. Some difficulties remain in the analysis. For example, the important parent chelator HEDTA is not detected by our method. New Mexico State chemists will be working on this problem.

Our aging experiments are difficult to interpret but clearly show rapid changes in the organic composition of the simulants upon heating. We are delaying experiments with actual tank wastes

until problems with the analytical method are resolved. Meanwhile we have begun to study the influence of catalytic metals such as rhodium, ruthenium and palladium. These metals are believed to play a significant role in organic reactivity of Savannah River tank wastes, and undoubtedly have an impact on Hanford wastes as well. We are currently testing a hypothesis that catalytic reduction of pertechnetate by hydrogen gas is responsible for formation of intractable technetium species in organic-rich tank wastes.

Effect of individual complexants on radionuclide separation: 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 will be using a combinatorial approach of simultaneously generating multiple chelator fragments in a single solution, and evaluating the most significant chelator-radionuclide interactions through a combination of spectroscopic and radiochemical methods.

We have surveyed the impact of several commercially-available complexants on the partitioning behavior of Sr^{2+} and Ce^{4+} (a Pu^{4+} surrogate) from a simplified simulant. To obtain reliable distribution coefficients, we eliminated the transition metal cations from this simulant to prevent metal hydroxide precipitation. These preliminary experiments showed that radionuclide partitioning onto the chelating resin Diphonix was strongly affected by the parent polycarboxylate chelators EDTA, HEDTA and NTA. However, we have not observed any significant interactions with plausible daughter chelators. Additional chelators will be synthesized at New Mexico State and submitted to Los Alamos for testing.

Planned Activities

Year 1: (a) Analyze organic content and partitioning of Sr, Tc and Pu from actual tank waste samples. (b) Carry out simulant aging experiments and analyze organic content. Repeat selected aging experiments and analyze radiochemical partitioning behavior.

Year 2: (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.

Other Access To Information

Future manuscripts will be posted on the web as they become available (<http://mwanal.lanl.gov/CSTftp/113311/RMChomepage.html>).