

Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions
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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 methods for preparing 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. Complexant-containing waste simulants are aged by various chemical processes and compared to samples of actual Hanford tank waste. This work will help to identify important aging processes in the tanks and provide the basis for developing successful treatment strategies.

2. RESEARCH PROGRESS AND IMPLICATIONS.

This report summarizes work completed after 2.5 years of a 3-year project. Earlier in the project, we prepared, artificially aged, and analyzed simulants of tank AN-107 and SY-101 supernates, based on analytical data and historical records. During this phase of the project, it became clear that published analytical sample preparation methods were causing transformation of the organic compounds. Also, significant and unresolvable ambiguities in defining the source-term organic content of the wastes became apparent. The combination of these two problems led us to refocus our study of tank waste aging on the $^{99}\text{TcO}_4^-$ (pertechnetate) reduction that occurs in complexant-containing supernates. The reduced complexes of technetium that form as these wastes age are resistant to both conventional partitioning methods and to oxidative treatments. The mechanism(s) for pertechnetate reduction are unknown but could be radiolytic or thermal in origin.

Catalytic Reduction of Pertechnetate

The fission product metals ruthenium, rhodium, and palladium are well-known as potent catalysts, but their impact on nuclear waste aging has been overlooked. We prepared simplified simulants containing pertechnetate ion (0.1 mM), typical waste relevant organic complexants (50 mM each of EDTA, NTA, HEDTA, citrate, glycolate, and oxalate) and catalytic metals (1.0 mM each of Ru, Rh, Pd) in 2.5 M NaOH. Thermolysis of this simulant for 24 h at 65_C converted 99% of the ^{99}Tc activity to an insoluble black precipitate identified as hydrous TcO_2 . In control experiments omitting catalytic metals or organic complexants, no reduction was observed. Probing the role of individual noble metals revealed that only ruthenium was an effective catalyst alone, but any combination of

two catalytic metals produced extensive reduction of TcO_4^- in 4 days. When the organics were probed individually under these conditions, glycolate, HEDTA and EDTA yielded >98% TcO_2 . The addition of $\text{Fe}(\text{NO}_3)_3$ caused a substantial inhibition of the technetium reduction in the HEDTA and EDTA experiments, seemingly due to catalyst inhibition by Fe(III).

Hydrogen is a likely source of reducing equivalents and is known to be generated in complexant-containing tank wastes via thermal and radiolytic degradation of organic waste constituents. Complexant-free simulants were heated for 18 hours under flowing hydrogen gas, yielding >85% reduction of the pertechnetate using any of the three metal catalysts. Simulants containing gluconate, a byproduct of sugar-based denitration processes at Hanford, trapped the reduced technetium as a soluble complex before TcO_2 precipitation could occur. The complex identical to the widely-used technetium radiopharmaceutical precursor $[\text{TcO}(\text{gluconate})_2]^{3-}$ by UV-Vis.

In summary, we have shown that the chemical environment of complexant-rich tank wastes is sufficient to cause catalytic reduction of TcO_4^- , even in the absence of radiolysis. The transformation appears to involve a two-step process of complexant degradation to generate H_2 , followed by catalytic reduction of pertechnetate to hydrous TcO_2 or soluble complexes. Given the evidence that fission product catalysis can dramatically impact the safe treatment and disposal of nuclear wastes, we concluded that further study of their abundance, distribution and reactivity in the waste is needed.

Catalytic Transformations of Organic Complexants

The Tc results led us to focus on the mechanism of chelator degradation, and how degradation products might effectively reduce other chemical species. In order to determine if hydrogen transfer was occurring under our reaction conditions, we prepared a typical basic simulant that containing the three metal catalysts, one complexant, and cinnamic acid as a hydrogen acceptor. Proton NMR was used to analyze for hydrogenated cinnamic acid after thermolysis. The following relative scale of cinnamic acid reduction was observed: formate > gluconate > HEDTA > glycolate >>> EDTA, IDA, and glycine.

We next aimed to identify metal-mediated processes for EDTA degradation. Labeling the C-1 or C-2 position of the acetate groups with ^{13}C provided a direct NMR probe of intermediates and final products. In a standard 2.5 M NaOH simulant, no degradation of C-2 labeled ^{13}C -EDTA was observed in 5 days of thermolysis. However, partial degradation was noted when 1.0 mM NaNO_3 was added. At high nitrate concentrations (100 mM), significant ^{13}C -formate was observed, along with ^{13}C -carbonate. This indicates inhibition of transfer hydrogenation at high nitrate concentrations.

Simulants prepared at 5.0 M NaOH did not show any degradation of ^{13}C -EDTA, even in the presence of nitrate. At a lower concentration of 0.5 M NaOH, ^{13}C -formate is the major product, along with a small amount of carbonate, ethylenediaminetriacetic acid (^{13}C -EDA₃), and N,N'-ethylenediaminediacetic acid (^{13}C -EDA₂). The latter two likely degrade at a faster rate than the starting EDTA, and are presumably transiently formed in 2.5 M NaOH. The observation of formate is consistent with the slower rate of conversion of formate to carbonate at the lower pH. The reaction of C-1 labeled ^{13}C -EDTA was also investigated at 2.5 M NaOH in the presence of nitrate. Only a decrease in the carboxylate signal over time was observed, consistent with a decarboxylation process, releasing ^{13}C -CO₂. This confirmed that the α -carbon of the acetic acid group serves as the exclusive source of carbonate.

Collectively, these observations support a process for EDTA degradation under alkaline conditions where three "hydride equivalents" are produced for each N-substituted acetic acid group that undergoes conversion to carbonate and carbon dioxide. Because only the initial EDTA breakdown step is slow, once the process is initiated it is possible to rapidly form 12 hydride equivalents, presumably leading to H₂ gas release or metal reduction. We are also examining an N-methylation reaction of amines in the presence of formate and formaldehyde, which may have broad relevance for the chemistry of organic amines in the waste.

3. **PLANNED ACTIVITIES:** Year 3: Studies of the catalytic reactions will be closed out, with an emphasis on clearly establishing the relevance of the reactions to actual Hanford tank wastes.

4. **INFORMATION ACCESS:** Six manuscripts are either submitted or in preparation. Preprints may be obtained by contacting the Principal Investigator.