FINAL REPORT
U.S. Department of Energy
DYNAMIC EFFECTS OF TANK WASTE AGING ON RADIONUCLIDE-COMPLEXANT INTERACTIONS

Principal Investigator: Dr. Rebecca M. Chamberlin
Institution: Los Alamos National Laboratory
Collaborators: Prof. Jeffrey B. Arterburn
Institutions: New Mexico State University

Table of Contents

LA-UR-00-5998

Executive Summary

The overall objective of this project was to provide a scientific foundation for safely

processing high organic content nuclear tank wastes for disposal. The harsh chemical and

radiation environment of high-level waste causes "aging" of the organic compounds and

radionuclides, producing new chemical forms of the radionuclides that resist standard

pretreatment methods. Advanced pretreatment techniques are costly to develop and implement,

and unplanned behavior in waste treatment processes (e.g., the release of benzene during

Savannah River's ITP demonstration in 1995) can adversely impact public health, environmental

quality, and the credibility of the Department of Energy. Therefore, it is imperative that the

chemistry and processing behavior of high-level wastes be fully understood.

Key goals of this project were to identify methods to realistically simulate tank waste

aging processes in the laboratory, and then to use those methods to predict how this aging

impacts the DOE's ability to process wastes for geologic disposal. Improved understanding of

radionuclide chemistry in the wastes also supports modeling of contaminant transport from tanks

that have leaked into the subsurface.

The most significant and unexpected result from this project is the identification of a new

reaction pathway that produces intractable chemical forms of technetium-99, similar to

technetium compounds recently discovered in certain Hanford tanks. Although conventional

wisdom suggested that radiation in the tanks was responsible for producing these compounds,

this project provided direct evidence that the compounds are rapidly formed in simulated tank

LA-UR-00-5998

wastes, even when *no radiation field is applied.* Because the reaction is catalyzed by trace amounts of highly reactive metals that form during uranium fission, we predict that this reaction can occur in any alkaline nuclear waste environment that also contains organic compounds. This research also indicates that catalytic metals may exhibit a broader scope of chemical reactivity in tank waste than previously imagined, and that unplanned behavior could occur during waste processing if these chemical effects are not examined in the early stages of process development.

LA-UR-00-5998

Research Objectives

The overall objective of this project was to provide a scientific basis for safely processing complexant-containing tank wastes for disposal. The harsh chemical and radiolytic environment in high-level waste tanks alters both the organic complexants and the metal species, producing radionuclide complexes that resist standard separation methods. Our key goals were 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.

The most significant and unexpected result from this project is the identification of thermal reaction pathways that lead to the reduction of pertechnetate ion ($^{99}TcO_4^-$) in simulated tank wastes. This facile reaction is catalyzed by fission-produced noble metals, and produces hydrous TcO_2 or soluble reduced Tc complexes, depending upon the initial conditions. This reactivity is the first direct evidence that *non-radiolytic* mechanisms are kinetically competent to form the non-pertechnetate species found in complexant-containing Hanford tank supernates (e.g., tanks AN-107, SY-101, and SY-103). Our studies of this reaction have indicated that two major reaction steps are involved: (1) noble metal-catalyzed degradation of the complexants EDTA and HEDTA—and uncatalyzed degradation of other organics—produces hydrogen gas, and (2) hydrogen gas acts as the reducing agent for the catalytic reduction of pertechnetate.

We now believe that the scope of reactivity of fission-product catalysts ruthenium, rhodium and palladium may be broader than previously imagined. While a few researchers have recognized the commercial potential of recovering these industrially important catalysts from nuclear waste, there have been almost no studies of the catalytic activity of Ru, Rh, and Pd in the waste environment. The results of our work contribute to the fundamental understanding of the role of catalysis in tank waste aging and its impact on radionuclide-complexant interactions.

Significance of Project to the EMSP

A half-century of nuclear weapons production in the United States has generated more than 100 million gallons of high-level nuclear waste (HLW), which is currently stored in underground tanks. The Department of Energy is now directing its efforts toward converting the wastes in these temporary storage facilities into stable forms for disposal. The overall DOE scheme for treating tank wastes involves partitioning the waste into a high-level waste stream containing the majority of the problematic radionuclides, and a low-level waste stream containing most of the non-radioactive materials. Ideally the HLW component will quantitatively divert the most highly radioactive (^{137}Cs and ^{90}Sr) and environmentally mobile (^{99}Tc and ^{237}Np) nuclides, and the longest-lived components (actinides such as Pu, Am and Np), into a minimum waste volume.

Remediation approaches for the most problematic radionuclides in alkaline tank supernatants have been developed using relatively simple inorganic waste simulants. Several sorbers with very high affinity and selectivity have been identified for each key radionuclide under these idealized conditions. However, when organic complexants (EDTA, citrate, etc) and their chemical/radiolytic degradation products are present in actual waste samples, even the most efficient sorbers often fail to effectively separate the radionuclide of interest.[1] The potential for

4   LA-UR-00-5998

accidental environmental contamination, instability of final waste forms, or worker exposure is incalculable if these separations methods were implemented into processes used to treat the huge inventory of HLW.

It is now well established that the harsh chemical and radiolytic environment in the high-level waste tanks causes reactions that alter both the organic complexants[2] and the metal species[3] present. A detailed understanding of the complexation reactions of the key radionuclides in tank wastes would obviously allow for reliable, science-based solutions for HLW processing. Conversely, no amount of study will yield effective waste treatment methods if scientists continue to focus on separating species that simply do not exist in real tank wastes.

The results of this EMSP project provide strong evidence that the reactivity promoted by the fission products ruthenium, rhodium and palladium under alkaline tank waste conditions is kinetically competitive with radiolytic and non-catalyzed thermal reactions. In other words, tank waste aging models that do not take catalytic reactivity into account may significantly underestimate processes such as the generation of hydrogen gas and the reduction of pertechnetate ion. We have identified two catalytic processes that significantly alter the composition of tank wastes: Catalytic degradation of EDTA into H_2, CO_2 and low-molecular weight amines, and catalytic reduction of pertechnetate ion using by H_2 gas. Since there are several known reactions that produce H_2 gas in tank wastes,[4] one implication of these results is that pertechnetate reduction can occur even in conditions where catalytic decomposition of complexants is not significant. By extension, we can surmise that *any* Hanford tank that is known to produce H_2 gas will probably also contain non-pertechnetate species of ^{99}Tc.

Another well-documented case where unsuspected catalytic reactivity proved to have devastating effects on waste treatment was during the In-Tank Precipitation demonstration for ^{137}Cs removal at Savannah River Site in November-December 1995.[5] Despite extensive planning and study of this process using surrogate materials, upon scale-up the sodium tetraphenylborate decomposed to liberate benzene in levels above the EPA-permitted amount. The reaction appeared to be catalyzed by trace amounts of various transition metals in the waste, and the copper-catalyzed reaction was extensively characterized. Literature precedent also exists for palladium-catalyzed cleavage of boron-carbon bonds in alkaline solution, but this reaction was apparently not pursued and thus the relative rates of the copper and palladium reactions are not known. The fact that previously-overlooked catalytic reactivity was responsible for a multi-million dollar error at Savannah River is sufficient reason to consider whether fission produced metals might have deleterious effects on other proposed separation methods.

In addition to the direct concern about the disposal of tank wastes, technetium speciation in the waste is of growing concern for Hanford groundwater/vadose zone modeling efforts and protection of the Columbia River. Given that a large number of Hanford tanks are known to have leaked in the past, there is significant interest in characterizing the source-term ^{99}Tc species so that future radionuclide migration can be accurately modeled. By establishing the conditions for catalytic reduction of pertechnetate and the products formed, this project will support the development of ^{99}Tc migration models.

LA-UR-00-5998

Background

The overall DOE scheme for treating tank wastes involves partitioning the waste into a high-level waste stream containing the majority of the problematic radionuclides, and a low-level waste stream containing the bulk of the non-radioactive materials. This goal requires efficient separations of these species from tank supernatant solutions containing high alkalinity (pH = 13-14), high ionic strength ($\mu \sim 13$), and a plethora of anions such as nitrate, nitrite, hydroxide, carbonate, phosphate, chloride, and sulfate.[6] While the bulk of the strontium and actinides would normally be insoluble under these alkaline conditions, the presence of complexing agents causes large amounts of these cations to be present in the supernatants. Ironically, the same cation-binding properties that made chelators such as EDTA and citrate useful separation and decontamination agents for nuclear materials production also ensure that they will complicate current efforts to separate the radionuclides during waste processing. Examples of the chelator problems observed in the course of research at LANL include:

> *Technetium.* LANL work with Reillex-HPQ anion exchange resin showed exceptional uptake of the pertechnetate ion (TcO_4^-), with K_d values approaching 1000 from waste simulants. However, the technetium K_d values on Reillex-HPQ for actual waste samples from Hanford Tanks 101-SY and 103-SY were only 4.0 and 5.2 mL/g, respectively. These measurements and other characterization efforts indicated that 60-70% of the technetium in the wastes exists in a form other than pertechnetate. Subsequent studies at PNNL have confirmed the presence of non-pertechnetate species in several organic-containing Hanford tank wastes,[7] and provided additional spectroscopic evidence that dinuclear Tc(IV) complexes are present. Thus, although technetium was originally introduced into the tank wastes as pertechnetate, it is now apparent that extensive thermal and radiolytic digestion of organic complexants produces conditions under which reduction and chelation of the technetium is possible.

> *Strontium.* A series of screening studies measured 1the distribution coefficient (K_d) of strontium from Hanford tank waste simulants onto 120 commercially available or experimental absorbers, including cation exchange and chelating resins, and inorganic sorbers.[1,8] The results repeatedly demonstrated interference by organic complexants. For example, while 15 sorbers showed strontium K_d values greater than 1000 from the inorganic neutralized current acid waste (NCAW) simulant, only two sorbers had K_d > 1000 in a tank 101-SY simulant whose organic complexants had been partially degraded by irradiation.[1a] Sorber performance typically deteriorated by over 90% when organics were present. Similar effects were observed using actual 101-SY and 103-SY waste.

> *Organics:* Organic degradation pathways for complexing agents in tank wastes are varied and complex. For example, when Toste's Complexant Concentrate (CC) simulant containing citrate, NTA, HEDTA, and EDTA was stored in the dark at ambient temperature for 90 days, 95% of the citrate and NTA remained intact, while 73% of the HEDTA and 78% of the EDTA were decomposed by the strongly alkaline medium.[9] However, in a similar CC simulant that was irradiated for 100 hours, only 43% of the citrate, 33% of the NTA, 0.22% of the HEDTA, and 22% of the EDTA remained intact,[10] indicating that the various complexants respond quite differently to thermal and radiolytic

LA-UR-00-5998

degradation. Toste identified over 56 different organic compounds generated in the "dark" experiment and 30 compounds in the irradiated simulant, suggesting that several multi-step decomposition and recombination pathways can operate in the real wastes.

Methods and Results

While the adverse effects of aging on radionuclide partitioning from complexant-containing tank wastes have been extensively documented, the relative effects of thermal and radiolytic aging have not been established. As originally conceived, one major goal of this project was to develop a rapid, reproducible method for simulating the aging of the organic components originally deposited in the waste storage tanks. Considerable effort in other labs has been devoted to the study of radiolytic effects on alkaline waste, but it is clear that radiolysis alone does not account for the organic content of aged tank waste. For example, high concentrations of HEDTA remain in actual waste samples, but high-dose ^{60}Co radiolysis rapidly and completely degrades HEDTA in simulants.[12] Furthermore, absent radiolysis, extensive thermal degradation of EDTA, HEDTA, NTA, and citric acid still occurs in tank waste simulants.[2,9] For these reasons, we believed that a realistic laboratory aging process should produce both thermal and radiolysis-like reactivity, which we endeavored to recreate using microwave, sonochemistry, and high-energy photolytic methods.

A robust method for analyzing the organic content of the wastes and simulants using GC-MS and GC-AED was needed for this study. Procedures for measuring the carboxylate and aminopolycarboxylate organic compounds in the tank wastes have been developed by Toste,[2] with some useful modifications suggested by Comel.[11] We prepared simulants of tank supernates from AN-107 and SY-101 using a combination of analytical data where available, supplemented by the historic analysis of process stream data and tank records compiled by Agnew.[2] These simulants were aged by various methods and their organic content was periodically analyzed. Concurrently, we measured the actual organic content of our Tank AN-107 supernate sample.

Two major issues emerged during this phase of the project. First, it became increasingly clear that the analytical sample preparation methods were causing transformation of the organic compounds in the waste. In support of our observation was a new simulant study by Toste,[12] describing instantaneous "bursts" of NTA degradation (15-30% losses) immediately after adding the complexant to the inorganic matrix. This initial reactivity was followed by negligible thermal degradation after 100 hours at 95 °C (2.6% additional loss). Such reactivity does not fit any reasonable kinetic model and is strongly suggestive of a problem with the analytical method.

The second, more intractable, problem was that of clearly defining the source-term organic content and the aging history of the wastes. An extreme case is the fate of sugar used to reduce the nitrate content of some Hanford wastes prior to tank storage. Under perfectly stoichiometric conditions, sucrose is completely oxidized to carbonate; thus no organic residue would remain. This is the assumption made in Agnew's model of the tank contents.[6] In reality, it is unlikely that perfect stoichiometry was achieved in the denitration process, and therefore some residual organic content should be present. The organic byproduct of sugar denitration can be approximated using gluconate, the monocarboxylic acid derivative of glucose.[1] Either approach may be an oversimplification, and resolution of this question is further hampered by the

LA-UR-00-5998

difficulty of analyzing the hydrophilic sugar by-products in the tank waste matrix. How, then, should the source-term organic be defined for a waste aging experiment? Similarly, how can one simulate the reactivity that occurred *before* a waste stream was neutralized to high pH, concentrated by evaporation, and/or mixed with the contents of another tank – events that typically occurred before the ultimate composition of any given Hanford tank was established.

The combination of these two problems led us to refocus our study of tank waste aging on the observed reduction of $^{99}TcO_4^-$ in complexant-containing supernates. Technetium has a *clearly defined* source term, the fully oxidized pertechnetate anion TcO_4^-, which forms in nitric acid-based plutonium separation processes. Technetium also has a *distinct* end-state after aging: the 50-75% of technetium that exists in reduced form in certain Hanford tank supernates behaves completely unlike pertechnetate in analytical separations, and is therefore easily detected with minimal sample preparation. Formed during long-term storage in waste tanks containing organic complexing agents (*e.g.*, Tanks AN-107, SY-101 and SY-103), these soluble technetium species are poorly characterized except for preliminary spectroscopic evidence of a Tc(IV) metal center.[7] The complexes resist separation by conventional methods such as anion exchange and are difficult to oxidize back to the easily separated pertechnetate ion, so their presence raises concern over the DOE's ability to successfully process the tank waste for disposal.

The mechanism(s) by which the reduced technetium complexes form in tank wastes have not been clearly established. Again, the most obvious source of reactivity is radiolysis, and in fact a concurrent EMSP project at Lawrence Berkeley National Lab recently confirmed the reduction of pertechnetate in tank waste simulants under high-dose ^{60}Co radiation.[13] Hydrous TcO_2 was the most common product of the radiolysis experiments, although pink soluble complexes were formed in the presence of certain organics.

Are there also *thermal* (non-radiolytic) mechanisms that lead to technetium reduction in the waste? We endeavored to answer this question by subjecting a ^{99}Tc-containing tank simulant to our battery of aging processes. To our great surprise, we discovered a dramatic transformation that occurs under mild conditions when trace levels of relevant transition metals are present. In reviewing the literature, we found that the potential catalytic reactivity of the noble metals ruthenium, rhodium and palladium has been virtually ignored in the nuclear waste environment. Transition metal-catalyzed reactions are known to interfere with certain waste treatment processes[14] but their impact on aging of the waste itself is completely unknown. Our subsequent studies on catalysis as a source of technetium reduction chemistry and organic destruction in the tank waste environment are summarized below.

Catalytic Reduction of Pertechnetate

To reconstruct the conditions for pertechnetate reduction in alkaline tank wastes, metal salts $RuCl_3$, $RhCl_3$, and $PdCl_2$ in dilute HCl solution were added to a simplified waste simulant containing six organic complexants typical of Hanford tank wastes: ethylenediaminetetraacetic acid (EDTA), hydroxyethyl(ethylenediaminetriacetic acid) (HEDTA), nitrilotriacetic acid (NTA), oxalic acid, citric acid, and glycolic acid. Ammonium pertechnetate (10^{-4} M ^{99}Tc in dilute nitric acid), catalyst metals (0.001 M each), and the six organic complexants (0.050 M each) were combined in 2.5 M sodium hydroxide solution. After heating the mixture at 65°C in

a sealed vial, any precipitates were separated by centrifugation and analyzed radiometrically for ^{99}Tc. The supernate was contacted for 2 hours with the strong-base anion exchange resin Reillex-HPQ, which quantitatively removes TcO_4^- from alkaline solution[15] but rejects most low-valent Tc complexes. Any ^{99}Tc remaining in the post-contact solution was assumed to be a reduced complex, while sorbed ^{99}Tc was reported as pertechnetate. Before thermolysis of the simulant, >99% of the ^{99}Tc activity was recovered as TcO_4^- by sorption onto Reillex-HPQ.

Thermolysis of the waste simulant containing the six organic complexants, and Ru^{III}, Rh^{III} and Pd^{II} as potential catalysts, for 24 hours at 65 °C converted 99% of the ^{99}Tc activity to an insoluble black precipitate. The precipitate resisted dissolution into dilute acid and base, but was readily dissolved by oxidizing solutions such as acidic Ce(IV) or alkaline NaOCl, consistent with the formation of hydrous TcO_2 (eq 1).[16] The ^{99}Tc remaining in solution was all present as pertechnetate. In control experiments omitting either the catalyst metals or organic complexants, over 99% of the Tc activity remained as pertechnetate ion after thermolysis.

$$(1) \quad TcO_4^- \xrightarrow[\text{Ru, Rh, Pd}]{\text{EDTA, HEDTA, etc.}} TcO_2 \cdot xH_2O$$
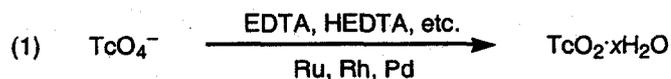
The role of individual noble metals was probed by adding the metals individually and pairwise to the alkaline solution at 0.001 M each. The results in Table 1 show that reduction was 97% complete when ruthenium was the only catalyst present, but that rhodium or palladium alone did not reduce TcO_4^- under these conditions. Surprisingly, any combination of two catalyst metals provided >98% technetium reduction after 4 days. Thus, rhodium and palladium are ineffective catalysts separately, but when combined produce extensive reduction of TcO_4^-, possibly indicating a bimetallic catalyst or a two-step reduction process.

Table 1. Extent of thermal reduction of TcO_4^- in the presence of catalyst metals, using organic complexants (4 days, 65 °C) or hydrogen gas (18 hours, 65 °C) as reducing agent.

Catalyst With complexants	% Reduced no $Fe(NO_3)_3$	% Reduced 0.010 M $Fe(NO_3)_3$
Ru, Rh, Pd	>99	60
Ru, Rh	98	19
Ru, Pd	99	14
Rh, Pd	99	32
Ru	97	3
Rh	0	0
Pd	0	0
No catalyst	0	0
With hydrogen gas	no $Fe(NO_3)_3$	0.010 M $Fe(NO_3)_3$
Ru, Rh, Pd	>99	>99
Ru	98	88
Rh	99	99
Pd	84	84
No catalyst	0	0

LA-UR-00-5998

Hydrogen gas is abundant in complexant-containing tank wastes, and is known to be generated via thermal and radiolytic degradation of waste constituents.[4] Since the yield of $TcO_2 \cdot xH_2O$ decreased from >99% to about 40% when the solution was purged with nitrogen gas, the intermediacy of hydrogen as reductant is probable (eq 2). Accordingly, we measured the ability of hydrogen and the three catalytic metals to reduce TcO_4^- in alkaline solution, in the absence of organic complexants. After 18 hours of 65 °C thermolysis under flowing hydrogen gas, >99% of the pertechnetate was reduced when 0.001 M Rh was present, compared to 0% reduction when the catalyst was absent. Similarly, 84% and 98% of the TcO_4^- was reduced by hydrogen gas in the presence of Pd and Ru, respectively. Rhodium is also the most effective of the three catalysts in the hydrogen reduction of nitrate to nitrite.[14]

$$(2) \quad TcO_4^- \xrightarrow[\text{Ru, Rh, Pd}]{H_2} TcO_2 \cdot xH_2O$$
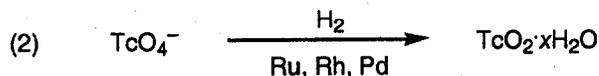
The ratio of pertechnetate to noble metals was also varied to confirm that the reduction with H_2 gas is catalytic, not stoichiometric. Technetium to catalyst ratios between 0.1 and 10 yielded >99% reduction after 18 hours exposure to H_2 gas. When TcO_4^- was present in 100-fold excess, 96% reduction was observed, indicating that the catalysts are capable of performing at least 96 turnovers. Since the catalyst metals are only partially soluble in the alkaline reaction media, the TcO_4^- reduction may be a heterogeneous process. A chemical step involving adsorbed H atoms is implicated in the reduction of aqueous TcO_4^- to $TcO(OH)_2$ at platinum electrodes,[17] so it is plausible that the reductions observed in the our studies are similarly catalyzed via dissociative adsorption of hydrogen onto the metallic elements.

Hydrogen gas may be generated by catalytic or stoichiometric decomposition of the organic complexants in the simulant. The contribution of individual organic species to the reduction was measured by adding each of the six complexants individually (0.050 M) to the simulant containing the three catalysts and TcO_4^- in sodium hydroxide (Table 2). Thermolysis for 4 days at 65 °C yielded >98% pertechnetate reduction using glycolate, HEDTA or EDTA. Other known H_2-generating organics such as formaldehyde and glyoxylate, and the complexant degradation product hydroxyethyliminodiacetic acid (HEIDA) also reduced >98% of the pertechnetate to insoluble $TcO_2 \cdot xH_2O$. In contrast, oxalate, citrate and NTA reduced less than 2% of the pertechnetate under the same conditions.

Table 2. Extent of thermal reduction of TcO_4^- in the presence of individual organic compounds, using a mixture of Ru, Rh, and Pd catalysts (4 days, 65 °C).

| Organic	% Reduced no $Fe(NO_3)_3$	% Reduced 0.010 M $Fe(NO_3)_3$
EDTA	>99	34
HEDTA	>99	32
NTA	2	9
Citrate	2	5
Oxalate	1	3
Glycolate	>99	>99
HEIDA	99	99
Formate	>99	>99
Glyoxylate	>99	>99

LA-UR-00-5998

When $Fe(NO_3)_3$ (0.01 M) was added to the simple sodium hydroxide simulant, the extent of technetium reduction in the HEDTA and EDTA experiments decreased dramatically, from >99% to about 30% after thermolysis for 4 days. With all six original complexants present, the extent of reduction dropped from 99% to 60% in the presence of iron nitrate. This change could arise either from inhibition of the catalyst activity by Fe^{III}, or from competition of nitrate for the H_2 reducing equivalents formed during thermolysis. Iron nitrate did not hinder Tc reduction in the presence of glycolate, formate, glyoxylate or HEIDA, and slightly *increased* the reduction by oxalate, citrate, and NTA. This variability strongly suggests that iron inhibits the degradation of EDTA and HEDTA. Furthermore, when individual catalysts were studied in the presence of iron nitrate, the greatest inhibition was found in the ruthenium experiments (Table 1). The extent of reduction using Ru as the catalyst decreased from 97% to 3%, consistent with competition between Ru and Fe for binding to the complexants.

Catalyst inhibition by iron may be important in real nuclear wastes, where first-row transition metals are typically present at 0.01 - 0.05 M levels. Nonetheless, preliminary experiments confirm that catalytic degradation of complexants is still viable in the Hanford tanks. For example, in a simulant of tank 101-SY containing the catalyst metals (10^{-4} M each) and iron salts at 0.015 M, over 65% of EDTA was degraded to low molecular-weight species after 90 days at room temperature, as determined by GC-MS analysis. An identical simulant lacking the catalysts showed only 2% EDTA decomposition under the same conditions. Separate studies showed that anions such as nitrate and sulfate, and cations such as aluminum, have little or no effect on the reductions.

Even if catalytic degradation of complexants is slowed by tank waste constituents such as Fe^{III}, Table 1 shows that the technetium reduction by H_2 gas remains remarkably efficient. During the 18-hour reduction with hydrogen gas, the catalytic activity of ruthenium was only slightly decreased by iron nitrate (88% versus 98%), and the rhodium and palladium reactions were unaffected. Thus, as long as any thermal or radiolytic mechanism for hydrogen production is operative in tank waste, catalytic pertechnetate reduction can still occur. In a simulant of Hanford tank AN-107 containing 0.001 M catalysts, pertechnetate was appreciably reduced (11%) after 4 days at 65 °C. Given that the Hanford tank wastes are radiolytically self-heating and have been stored for decades, catalytic reduction of pertechnetate is clearly a kinetically viable process in the tanks.

Finally, we note that the reduced technetium observed in actual wastes from Hanford tanks AN-107, SY-101 and SY-103 exists in a soluble form, while the conditions described above produced only insoluble $TcO_2 \cdot xH_2O$. If Tc reduction is slower in tank waste, complexation may become competitive with precipitation, or slow leaching of $TcO_2 \cdot xH_2O$ by complexants may occur. Preliminary experiments also indicate that gluconate, which is believed to be present in some Hanford tanks as a byproduct of sugar-based denitration processes, efficiently traps reduced technetium and prevents precipitation. In a noble metal-catalyzed reduction experiment with 0.050 M gluconate, greater than 99% of ^{99}Tc activity remained in solution after 24 hours at 65 °C, but only 24% of the soluble ^{99}Tc sorbed onto Reillex-HPQ as TcO_4^-. The remaining 76% of the soluble technetium is most likely a non-sorbing gluconate complex of the type $[TcO(gluconate)_2]^{n-}$, similar to widely-used technetium radiopharmaceutical precursors (eq 3).[18] This assignment is supported by the close similarity between the UV-vis absorption spectrum of

the gluconate-containing simulant and our independently synthesized Tc-gluconate complex. Preliminary EXAFS results also corroborate this assignment.

(3) $\quad TcO_4^- \xrightarrow[\text{Ru, Rh, Pd}]{\text{gluconate}} [TcO(gluconate)_2]^{n-}$
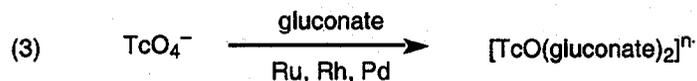
In summary, we have shown that the chemical environment of complexant-rich tank wastes is sufficient to cause catalytic reduction of $^{99}TcO_4^-$, even in the absence of radiolysis. The transformation appears to involve a two-step process of complexant degradation to generate H_2, followed by catalytic reduction of pertechnetate to hydrous TcO_2 or soluble complexes. Because the fission product metals rhodium, ruthenium and palladium are essentially non-radioactive and are present in low concentrations in nuclear waste,[19] they have not been considered important analytes in the past. Given the accumulating evidence that fission product catalysis can dramatically impact the safe treatment and disposal of nuclear wastes, we conclude that further study of their abundance, distribution and reactivity in the waste is urgently needed.

*Catalytic Transformations of Organic Complexants*

The observed quantitative reduction of pertechnetate ion, TcO_4^-, by organic complexants in the presence of catalytic amounts of fission product noble metals inspired mechanistic studies directed towards understanding the details of this significant transformation. We have focused our studies on three important mechanistic questions:

- Can catalytic transfer hydrogenation from organic complexants and their degradation products effectively reduce other chemical species?
- How are the metal catalysts involved in the mechanism of chelate degradation?
- Are other post-degradation pathways available for continued structural modification of the organic components?

Previous investigations by Ashby et. al. have identified the formation of hydrogen from formaldehyde in simulated alkaline tank waste mixtures.[20] Formaldehyde is known to be produced by the radiolysis of EDTA, NTA, and IDA, and therefore is expected to be a component of the waste. At high concentrations of formaldehyde a Cannizzaro reaction which produces formate and methanol has been observed. Small amounts of hydrogen can be produced by an alternative reaction pathway, which involves protonation of the hydride produced from the Cannizzaro intermediate at low formaldehyde concentrations. These studies also evaluated hydrogen production from other organic components at 120° C for time periods from 12-70 days, and found the relative scale of H_2 production: glycolate > HEDTA > >> EDTA, glycine, IDA and NTA.

One important difference between the scale of hydrogen production ability described by Ashby, and the ability of organic complexants to reduce pertechnetate ion in the presence of Ru, Rh, and Pd is that EDTA gave complete reduction of TcO_4^- in our experiments. Glycolate, HEDTA, HEIDA, glyoxylate, and formate were also highly effective for Tc reduction. Our mechanistic studies have used a minimalist experimental design to further investigate the possibility of

hydrogen transfer chemistry from organic complexants catalyzed by the fission product noble metals. In order to determine if a catalytic system for transfer hydrogenation was produced under the reaction conditions, we carried out reactions in the presence of cinnamate as a hydrogen acceptor, and then analyzed product mixtures for the presence of hydrocinnamic acid (eq 4). Reactions were carried out using 2.5 M NaOH to simulate typical waste tank conditions. The ratio of the three metal catalysts ($RuCl_3$, $RhCl_3$, and $PdCl_2$)/cinnamic acid/potential organic H-donors was 1/10/40 respectively. The individual organic components HEDTA, EDTA, IDA, formate, glycolate, gluconate, and glycine were investigated. The reactions were heated at 65° C for 16 hours, and worked up by acidification with hydrochloric acid followed by extraction into ether, and product analysis using 1H-NMR.
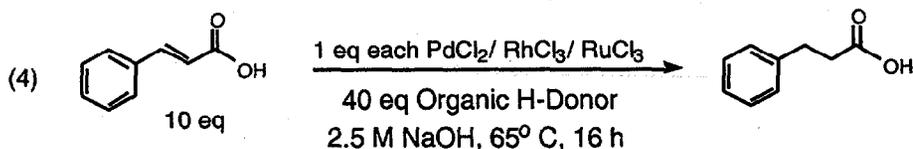
The following relative scale of cinnamic acid reduction was observed: formate > gluconate > HEDTA > glycolate >>> EDTA, IDA, and glycine. The reductions involving formate gave quantitative yields of hydrocinnamic acid, while only traces were produced from EDTA, IDA, and glycine. The strong hydrogen-donating ability of formate is potentially significant, considering the common occurrence of this compound as a component of tank waste. Reaction mixtures containing formate and the individual metal catalyst $PdCl_2$ also gave complete reduction of cinnamic acid. This reaction also occurs under the more strongly alkaline conditions in 5 M NaOH. A variety of other α,β-unsaturated carboxylic acids, and α-keto carboxylates were also reduced under the standard reaction conditions (eq 5-7). Catalytic transfer hydrogenations involving formate are well-known in alcohol solvents, but have not previously been reported in alkaline aqueous medium.
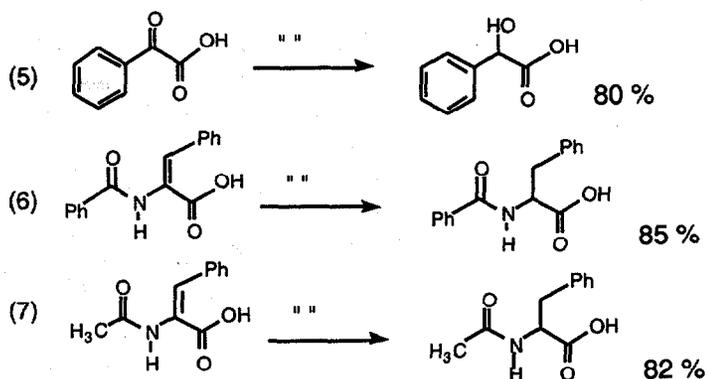
Although we observed that EDTA was not an effective hydrogen donor for the catalytic transfer hydrogenations under the relatively short time periods investigated, these results do not exclude the possibility of a metal-mediated degradation process capable of generating hydrogen. Several catalytic turnovers are required in order to observe significant amounts of the reduced

13   LA-UR-00-5998

hydrocinnamic acid in these experiments. The pertechnetate reduction experiments used a large excess of EDTA relative to TcO_4^-, therefore only a fraction of the available EDTA was required to elicit complete reduction. We next directed our investigation to identify possible metal-mediated processes for EDTA degradation. Carbon-13 labeling provides a convenient NMR handle that can be easily monitored during a chemical process to identify changes in substitution or oxidation state of the labeled carbon atom. By using ^{13}C-labeled EDTA, we hoped to be able to directly detect the intermediates and identify the final products formed by metal-mediated degradation, without needing additional derivatization procedures.

We synthesized EDTA that was ^{13}C-labeled at either the C-1 carboxyl, or the C-2 position of the acetate groups, from the reaction of ethylenediamine with commercially available C-1 or C-2 ^{13}C-labeled bromoacetic acid. The reactions were carried out using 1.0 mM ^{13}C-EDTA in 2.5 M NaOH, combined with 1.0 mM mixtures of each of the metal chlorides $PdCl_2$, $RuCl_3$, and $RhCl_3$. An equimolar ratio of metals to labeled ligand was chosen to enhance the possibility of metal mediated processes, and to ensure our ability to observe the reactions of the ^{13}C-labeled ligand. The heterogenous reaction mixtures were heated at 65° C with magnetic stirring for time periods up to 5 days. Samples were filtered, the volume reduced *in vacuo*, and then diluted with D_2O for ^{13}C-NMR analysis.

No apparent degradation of the C-2 ^{13}C-EDTA was observed in the simple simulant matrix after 5 days, however we found that partial degradation did occur in the presence of added nitrate ion. Reactions conducted with 1.0 mM $NaNO_3$ converted C-2 ^{13}C-EDTA into ^{13}C-carbonate. When the reaction was carried out at higher nitrate concentration, using 100 mM $NaNO_3$, ^{13}C-formate was produced as the major product along with ^{13}C-carbonate. No other ^{13}C-labeled compounds were evident in these samples. Control experiments without the metals showed no evidence of degradation even after 10 days at 100° C. Additional control experiments in which ^{13}C-formate was added to the metal complexes and 1 mM $NaNO_3$ in 2.5 M NaOH demonstrated the rapid and complete conversion of formate to carbonate in 18 hours at 65° C. The fate of the incipient hydride produced in this step has not been defined at this time, although it appears likely that hydrogen gas is evolved. The observation of ^{13}C-formate in the reaction with 100 mM $NaNO_3$ is consistent with some inhibition of the transfer hydrogenation step by the high nitrate concentration. This result also indirectly argues against the possibility of nitrate reduction by the formate to carbonate transfer hydrogenation reaction.

When the analogous reactions with C-2 ^{13}C-EDTA were carried out under more strongly basic conditions using 5 M NaOH, 1.0 mM $NaNO_3$, $PdCl_2$, $RuCl_3$, and $RhCl_3$, no degradation was observed. This observation should be placed in perspective by noting that our control experiments have shown the catalytic formate to carbonate conversion does occur at the higher base concentration. Therefore, the initial metal-mediated degradation of EDTA is apparently inhibited at higher pH. We then investigated the reaction carried out under less basic conditions, at 0.5 M NaOH. Degradation was observed under these conditions to produce ^{13}C-formate as the major product, a small amount of carbonate, along with two other products: ethylenediaminetriacetic acid (^{13}C-EDA3), and N,N'-ethylenediaminediacetic acid (^{13}C-EDA2). It is important to note that these two degradation products were *not* observed in 2.5 M NaOH. This suggests that they continue to react under the more strongly basic conditions at a faster rate than the starting material EDTA, and are not allowed to build up in concentration. The

observation of formate as the major product 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. Monitoring the reactions of C-1 ^{13}C-EDTA using 2.5 M NaOH, 1.0 mM NaNO$_3$, 1.0 mM PdCl$_2$, RuCl$_3$, and RhCl$_3$, with ^{13}C-NMR showed a continuous decrease in the carboxylate signal over time, which was not accompanied by the appearance of any new signals. This result is consistent with a decarboxylation process, which releases ^{13}C-CO$_2$. This experiment confirms that the α-carbon of the acetic group serves as the exclusive source of the final product carbonate.

Collectively, these observations support a process for EDTA degradation under alkaline conditions, which is summarized in Scheme 1. In this scheme three "hydride equivalents" are produced for each N-substituted acetic acid group that undergoes conversion to carbonate and carbon dioxide. Under the experimental conditions investigated the "hydride equivalents" are presumably converted to hydrogen gas. This scheme emphasizes the tremendous potential reducing ability of EDTA in the presence of fission product noble metals. The experimental

Scheme 1. Proposed Pathway for Alkaline Pd/Rh/Ru Mediated Degradation.
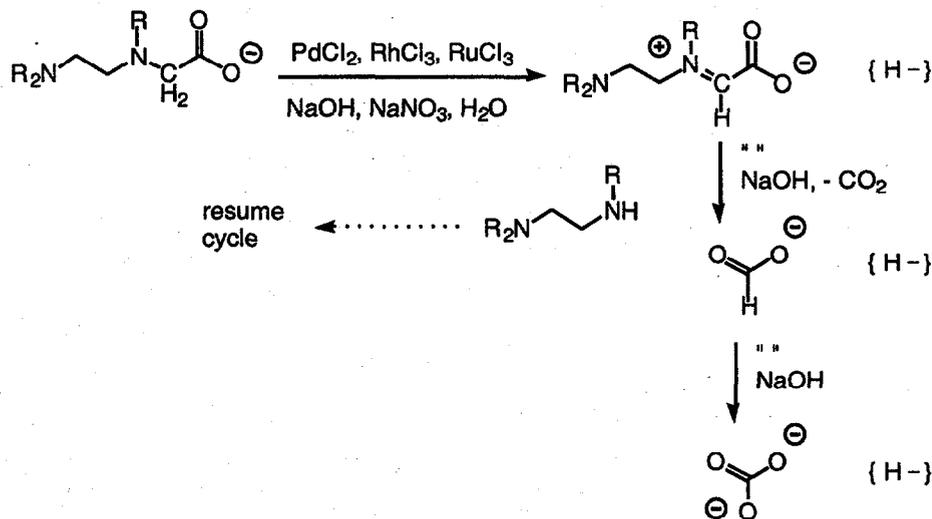

results suggest that the first step in this process of EDTA degradation is slow at high pH, while the subsequent steps occur more rapidly in the presence of added base. The ethylenediamine fragment EDA$_3$ resulting from the conversion of one N-substituted acetic acid group to formate is proposed to resume the cycle at a faster rate than EDTA at high pH, producing in turn EDA$_2$, then EDA, and finally ethylene diamine. Each EDTA is capable of generating 12 "hydride equivalents" by this process. This pathway is consistent with the results of the metal catalyzed pertechnetate ion reduction, where limited amounts of EDTA degradation were accompanied by complete reduction of pertechnetate.

In order to evaluate the effect of further lowering of pH on the degradation of C-2 labeled ^{13}C-EDTA, we carried out reactions in 2.5 M HNO_3, with 1.0 mM $PdCl_2$, $RuCl_3$, and $RhCl_3$. The acidic reaction mixtures were homogenous, and experiments were conducted using NMR tubes heated from 65° - 100° C, and monitored over time. Under the acidic conditions degradation of EDTA was rapid and complete. N,N'-Ethylenediaminediacetic acid (EDA2) was formed as a major product, along with glycolic acid, glyoxylic acid, and formic acid. The concentration of EDA2 did not change significantly with continued heating up to 6 days. With increasing reaction time the glycolic acid, glyoxylic acid, are converted to formic acid and then removed under the acidic conditions by forming CO_2. In contrast to the rapid reaction of the catalytic system, control reactions of ^{13}C-EDTA carried out in 2.5 M HNO_3 excluding the metals showed no degradation even after 10 days at 100° C. The overall process for the observed degradation under acidic conditions is represented in Scheme 2. The precise role of the metals in this process has not been defined at this time. One possible route for the first step in the degradation of EDTA is represented in Scheme 3.

Scheme 2. Proposed Pathway for Acidic Pd/Rh/Ru Mediated Degradation.
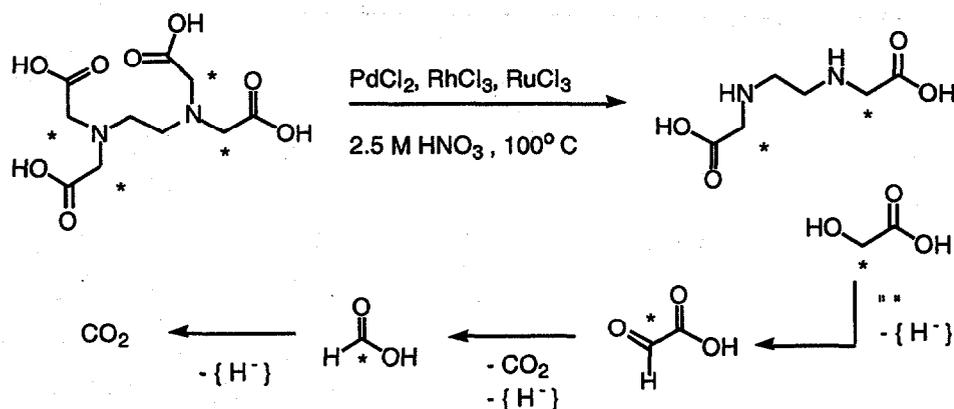
Scheme 3. Possible Mechanism for Acidic Pd/Rh/Ru Mediated Degradation.
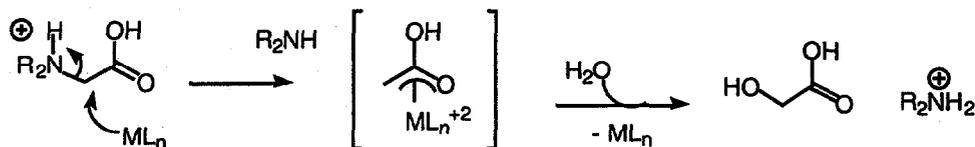
The catalytic reaction of several other ^{13}C-labeled organic compounds was also investigated in 2.5 M HNO_3. The catalyzed degradation of C-2 ^{13}C-glycine resulted in conversion to glycolic acid, and formic acid. Extended reaction times also resulted in the conversion of these compounds to CO_2. The catalyzed reaction of C-2 ^{13}C-glycolic acid in 2.5 M HNO_3 produced formic acid after 1.5 hours at 100° C, which was subsequently converted completely to CO_2 within 42 hours. The catalyzed reaction of N-(^{13}C-Me)-IDA in 2.5 M HNO_3 rapidly produced N-(^{13}C-Me)-glycine after 1 day at 65° C. After increasing the temperature to 100° C resulted in complete conversion to N-methylglycine after 1 day. With continued heating for 4 more days

only a trace of the N-methylglycine remained. The catalytic reaction of C-2 ^{13}C-labeled nitrilotriacetic acid (NTA) in 2.5 M HNO_3 was also investigated, producing IDA and large amounts of glycolic acid, and a small amount of formic acid after 18 hr at 65° C.

The observed rapid metal-catalyzed reactions of organic compounds in acidic solution are relevant for the nuclear waste storage tanks for several reasons. Large amounts of the process waste now stored was initially strongly acidic. Efforts to adjust the overall pH of the heterogenous mixtures by addition of acid or base without rapid effective mixing may lead to significant local deviations in pH, providing "hot spots" for potential reactivity. Further, potential waste treatment procedures involving acidification may be accompanied by large amounts of hydrogen produced by the metal-catalyzed pathway.

The diverse chemical composition of the tank waste may bring about a variety of chemical modifications of organic complexants. The simultaneous presence of formate and formaldehyde together provides the potential for N-methylation of amines. The Eschweiler-Clarke procedure has been used extensively throughout the last century to N-methylate amines.[2122] The procedure typically uses an excess of aqueous formaldehyde and formic acid. Although the strongly alkaline conditions of the waste simulant are very different from any of the reported applications of the Eschweiler-Clarke procedure, we decided that further investigation of this possibility was warranted.

We conducted initial experiments using 2.5 M NaOH, 0.1 M ^{13}C-formaldehyde, 0.1 M formate, and 0.4 M glycine at 65° C. The reaction was monitored by ^{13}C-NMR, and was found to produce N-(^{13}C)-methylglycine and N,N-di-(^{13}C)-methylglycine. Similarly, the reaction of 0.3 M EDA_2 with 0.6 M formate, and 0.6 M ^{13}C-formaldehyde in 2.5 M NaOH at 65° C gave N,N'-di(^{13}C)-methylethylenediaminediacetic acid, and was complete within 3 hours (Scheme 4).

Scheme 4. N-Methylation of EDA_2 with Formate/Formaldehyde.
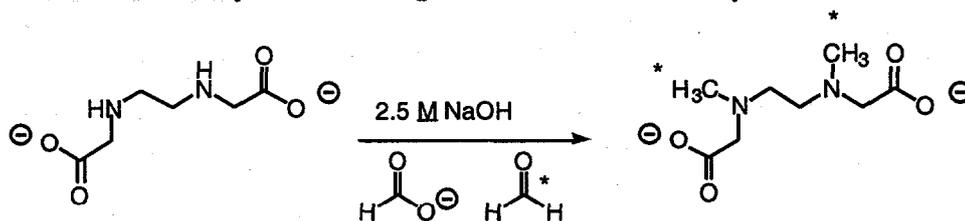
Other secondary amines reacted analogously, *e.g.*, IDA was converted to N-methyl-IDA, and N-methylglycine gave N,N-dimethylglycine. No methylation of an amide nitrogen was observed in the attempted reaction of N-Benzoylglycine. This reaction results in the rapid N-methylation of primary and secondary amines, and may have broad relevance for the chemistry of organic amines in the waste tanks.

In summary, the results described in this section have identified several important chemical processes of organic compounds that are relevant for nuclear waste storage tanks. Fission-produced noble metals Pd/Rh/Ru are very effective catalysts for transfer hydrogenation under

alkaline conditions from formate, glycolate, and gluconate. The initial step of the metal-mediated degradation of EDTA is relatively slow under alkaline conditions, however subsequent steps involving its degradation products occur rapidly to release the tremendous reducing power of EDTA, generating 12 "hydride equivalents" by this process. The metal-mediated degradation of EDTA is much faster under acidic conditions, producing effective H-donors glycolic acid and formic acid. Large amounts of hydrogen could potentially be released by this mechanism if the tank waste is acidified for pretreatment. Primary and secondary amines are rapidly N-methylated in the presence of formaldehyde and formate under alkaline conditions. This reaction may be significant for the formation of N-methylamine derivatives under the conditions at which the tank waste is stored

Relevance, Impact and Technology Transfer

a. How does this new scientific knowledge focus on critical DOE environmental management problems?

The above narrative describes in detail how the fission-product catalyzed reactivity discovered in this project relates to DOE environmental management problems. Key points of relevance are: (1) The project defined a viable pathway to the generation of intractable non-pertechnetate species which are known to exist in certain Hanford tanks; (2) Technetium(IV/V) gluconate complexes and hydrous technetium(IV) oxide were identified as likely species to exist in Hanford wastes, thus enabling advanced treatment technologies to be developed; (3) New, non-radiolytic pathways for hydrogen gas generation in tank wastes were discovered, which potentially impact tank safety models and/or processing schemes; (4) More broadly, the project served to focus increased attention on the role of trace catalytic metals in the nuclear waste environment. It is clear as a result of these studies, coupled with the results of the Savannah River ITP process demonstration, that catalysis must be considered when planning nuclear waste treatment strategies.

b. How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?

This project provided direct evidence that catalytic reactivity in tank wastes has a significant impact on waste chemistry. It is reasonable to assume that the Savannah River ITP benzene problem would have been avoided if the $500M process development efforts had included adequate consideration of the impact of chemical catalysis. Current and future process development efforts could suffer similar setbacks, resulting in added cost and time as well as further eroding DOE-EM credibility, if the waste management community fails to recognize the potential for catalytic reactivity in other systems.

c. To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?

The reactivity studies were carried out in solutions designed to mimic nuclear waste environments whenever possible, to ensure that the results are immediately relevant and applicable to current problems such as the existence of non-pertechnetate species in Hanford tanks. However, the general approach used can, in principle, be applied to other waste management problems, such as examining the robustness of new separation processes. Also, we have deliberately published (or planned publication of) our results across a broad range of chemistry journals in order to draw attention to this work from several scientific disciplines, including organic synthesis, radiochemistry, and environmental science.

d. What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?

This project, in conjunction with concurrent EMSP projects led by other PI's, reaffirms LANL's role as a national leader in the chemistry of technetium in nuclear waste, while also affirming LANL's commitment to educating the next generation of scientists through collaboration with NMSU. We are particularly pleased to have involved a number of minority and female students in this research program. The results of this work are being disseminated in prominent chemistry journals and to individuals affiliated with the DOE complex, and we expect that this work will provide a new perspective on waste management problems at Hanford, Savannah River, and possibly other sites.

e. Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment or expertise has been developed?

Although large-scale trials are not relevant to the results of this work, it is clear that the role of catalysis must be considered when planning large-scale trials of *other* waste separation and pretreatment technologies.

f. How have the scientific capabilities of collaborating scientists been improved?

The project work was divided such that NMSU focused on organic analyses, aging studies and reaction mechanisms of the complexants in the simulants, while LANL focused on technetium reactivity, radionuclide partitioning, and actual tank waste studies. However, the relatively close proximity of the two laboratories enabled frequent informal exchanges and a greater cross-fertilization between the traditionally distinct fields of synthetic chemistry and radiochemistry.

g. How has this research advanced our understanding in the area?

As described in other sections, this research has clearly identified a major class of reactivity in tank waste environments.

h. What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?

None, although the scope of the catalysis problem would be greatly clarified by further scientific studies, as detailed in the "future work" section below.

LA-UR-00-5998

i. Have any other government agencies or private enterprises expressed interest in the project?

No.

Project Productivity

As described in previous pages, the project results in the area of fission-product catalysis could not have been foreseen at the start of the project. Coincidentally, the role of metal catalysis in the decomposition of tetraphenylborate during the ITP demonstration at Savannah River highlighted the importance of understanding catalysis in the tank waste environment. The decision to pursue this timely and significant topic, as well as the fact that the project was funded at only 60% of the requested level, dictated that some of the original project goals be abandoned. The payoff of this redirection is more than sufficient to justify this decision.

Personnel Supported:

Personnel receiving direct financial support from this EMSP project were: Rebecca M. Chamberlin (PI, LANL), Jonathan G. Bernard (postdoc, LANL), Eve Bauer (technician, LANL), Anicele M. Gonzalez (graduate student, NMSU), Madhavi Pannala (technician, NMSU).

Personnel contributing to this project but supported by other institutional or fellowship funds were: Jeffrey B. Arterburn (co-PI, NMSU), Douglas E. Berning (postdoc, LANL) Monique P. Richards (undergraduate student, LANL), and David M. Liepman (undergraduate student, LANL).

Publications:

"Palladium Catalyzed Transfer Hydrogenation in Aqueous Alkaline Medium" Arterburn, J. B.; Pannala, M.; Gonzalez, A. M.; Chamberlin, R. M. *Tetrahedron Letters*, **2000**, *41*(41), 7847-7849.

"Catalytic Reduction of Pertechnetate ($^{99}TcO_4^-$) in Simulated Alkaline Nuclear Wastes" Bernard, J. G.; Bauer, E.; Richards, M. P.; Arterburn, J. B.; Chamberlin, R. M. *Radiochim. Acta*, **2001**, in press.

"Catalytic Degradation of EDTA in Simulated Nuclear Waste; Analysis of the Degradation Pathway using Carbon-13 NMR" Arterburn, J. B.; Gonzalez, A.; Pannala, M.; Chamberlin, R. M. To be submitted to *Chem. Commun.*

"Impact of Chemical Catalysis on the Non-Radiolytic Aging of Technetium-99 in Alkaline Nuclear Waste" Bernard, J. G.; Berning, D. E.; Bauer, E. ; Liepman, D. M.; Arterburn, J. B.; Chamberlin, R. M. To be submitted to *Environ. Sci. Technol.*

"Anion Exchange and Complexation of the Uranyl Ion in Strongly Alkaline Solution." Bauer, E.; Chamberlin, R. M. To be submitted to *Solvent Extr. Ion Exchange.*

"A General Method for the Synthesis of Labelled *N*-Methyl Amines" Arterburn, J. B.; Pannala, M.; Gonzalez, A.; Chamberlin, R. M. To be submitted to *J. Labeled Compounds Radiopharm.*

Interactions

a. Participation/presentations at meetings, workshops, conferences, seminars, etc. This research was presented, and continues to be presented, at a variety of prominent venues including EMSP Workshops, American Chemical Society meetings, and Gordon Research Conferences.

b. Consultative and advisory functions to other laboratories and agencies, especially DOE and other government laboratories. The PI was contacted twice by the National Academy of Sciences regarding service on study groups for DOE-EM issues; however, it was determined that participation in an EMSP project might be construed as a conflict of interest.

c. Collaborations. The PI is currently collaborating with Dr. David Shuh (LBNL) and Dr. Carol Burns (LANL) on the continuation of their EMSP project on the fundamental chemistry of technetium. In addition, the PI is collaborating with Dr. Benjamin Warner (LANL) on an LDRD-funded study of actinide-mediated catalysis, which may have related implications for waste management.

Transitions: To our knowledge, no technologies have been developed directly from this research to date.

Patents: None.

Future Work: Numerous avenues of future research are suggested by the results of this project. The broad scientific questions include: How significant are catalytic reactions in the overall problem of radionuclide complexation and separation from high-level waste? What hidden dangers do these catalysts present in developing separations for tank wastes? What opportunities exist for harnessing the catalytic reactivity in support of waste treatment? The PI would be pleased to accept future funding to pursue these topics.

Feedback: Site representatives should be encouraged to take the initiative in contacting EMSP PI's about the relevance of their work. Also, projects that are funded at levels significantly lower than requested in the proposal should be given a detailed rationale for the funding decrease and guidance on which aspects of the project should be eliminated.

LA-UR-00-5998

Literature Cited

1. (a) Marsh, S. F.; Svitra, Z. V.; Bowen, S. M. "Effects of Aqueous-Soluble Organic Compounds on the Removal of Selected Radionuclides from High-Level Waste. Part I: Distribution of Sr, Cs, and Tc onto 18 Absorbers from an Irradiated Organic-Containing Leachate Simulant for Hanford Tank 101-SY." Report LA-12862 (1995).

(b) Marsh, S. F.; Svitra, Z. V.; Bowen, S. M. "Effects of Aqueous-Soluble Organic Compounds on the Removal of Selected Radionuclides from High-Level Waste. Part II: Distribution of Sr, Cs, Tc, and Am onto 32 Absorbers from Four Variations of Hanford Tank 101-SY Simulant Solution." Report LA-12943 (1995).

(c) Marsh, S. F.; Svitra, Z. V.; Bowen, S. M. "Effects of Aqueous-Soluble Organic Compounds on the Removal of Selected Radionuclides from High-Level Waste. Part III: Distribution of Sr, Cs, Tc, Pu, and Am onto 33 Absorbers for Four Variations of a 3:1 Dilution of Hanford Complexant Concentrate Simulant. Part IV: The Effects of Varying Dilution Ratios on the Distributions of Sr, Cs, Tc, Pu, and Am onto 12 Absorbers from Hanford Complexant Concentrate Simulant Solution." Report LA-13000 (1995).

2. (a) Toste, A. P.; Lechner-Fish, T. J.; Hendren, D. J.; Scheele, R. D.; Richmond, W. G. *J. Radioanal. Nucl. Chem. Art.* **1988**, *123*, 149-166.

(b) Toste, A. P.; Osborn, B. C.; Polach, K. J.; Lechner-Fish, T. J. *J. Radioanl. Nucl. Chem., Articles* **1995**, *194*, 25-34.

3. (a) Schroeder, N. C.; Radzinski, S. D.; Ball, J. R.; Ashley, K. R.; Cobb, S. L.; Cutrell, B.; Whitener, G. "Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using Reillex™-HPQ Resin," Report LA-UR-95-4440, 1995.

(b) Worl, L. A.; Bowen, S. M.; Berg, J. M.; Padilla, D. D.; Cisneros, M. R. "Actinide Removal from Hanford Supernatant Tank Waste," Report LA-UR-95-3743.

4. (a) Barnabas, F.; Cerny, E.; Jonah, C. D.; Meisel, D.; Sauer, M. C., Jr. *Radiat. Phys. Chem.* **1995**, *46(1)*, 57-60.

(b) Samuels, W. D.; Camaioni, D. M.; Babad, H. *Technol. Programs Radioact. Waste Manage. Environ. Restor.* **1994**, *1*, 399-403.

(c) Ashby, E. C.; Doctorovich, F.; Liotta, C. L.; Neumann, H. M.; Barefield, E. K.; Konda, A.; Zhang, H. M.; Hurley, J.; Siemer, D. D. *J. Am. Chem. Soc.*, **1993**, *115*, 1171-1173.

5. Barnes, M.J.; Walker, D.D.; Crawford, C.L.; Swingle, R.S.; Peterson, R.A.; Hay, M.S.; Fink, S.D. "Decomposition of Tetraphenylborate In Tank 48H." Report WSRC-TR--96-0113, Westinghouse Savannah River Co., May, 1996.

6. (a) Agnew, S. F. "Hanford Defined Wastes: Chemical and Radionuclide Compositions," Report LA-UR-94-2657, August 1994.

(b) Hohl, T. M. "Synthetic Waste Formulations for Representing Hanford Tank Waste," Report WHC-SD-TI-549, Rev. 0, May 1993.

7. (a) Schroeder, N. C.; Radzinski, S. D.; Ashley, K. R.; Truong, A. P.; Szczepaniak, P. A. Technetium Oxidation State Adjustment for Hanford Waste Processing. In *Science and Technology for Disposal of*

Radioactive Tank Wastes; Schulz, W. W., Lombardo, N. J. Eds.; Plenum Press: New York, 1998; pp 301-320.

(b) Blanchard, D. L., Jr.; Brown, G. N.; Conradson, S. D.; Fadeff, S. K.; Golcar, G. R.; Hess, N. J.; Klinger, G. S.; Kurath, D. E. Technetium in Alkaline, High-Salt Radioactive Tank Waste Supernate: Preliminary Characterization and Removal. Report PNNL-11386, Richland, WA, January 1997.

8.   (a) Marsh, S. F.; Svitra, Z. V.; Bowen, S. M. "Distributions of 15 Elements on 58 Absorbers from Simulated Hanford Double-Shell Slurry Feed (DSSF)." Report LA-12863, November 1994.

(b) Marsh, S. F.; Svitra, Z. V.; Bowen, S. M. "Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY." Report LA-12654 (Rev.), August 1994.

9.   Toste, A. P.; Lechner-Fish, T. J. *Waste Management* **1993**, *13*, 237-244.

10.   Toste, A. P. *J. Radioanal. Nucl. Chem., Articles* **1992**, *161*, 549-559.

11.   Comel, A.; Guiochon, G. *J. Radioanal. Nucl. Chem.* **1994**, *181*, 373-384.

12.   Toste, A. P. *J. Radioanal. Nucl. Chem.* **1999**, *239*, 433-439.

13.   Lukens W.W., Allen P.G., Bucher J.J., Edelstein N.M., Shuh D.K. *Abstr. Papers Amer. Chem. Soc.*, **1999**, *218*, 199 NUCL.

14.   (a) King, R. B.; Bhattacharyya, N. K.; Smith, H. D.; Wiemers, K. D. *Environ. Sci. Technol.* **1996**, *30*, 1292-1299.

(b) King, R. B.; Bhattacharyya, N. K.; Smith, H. D.; Wiemers, K. D. *Environ. Sci. Technol.* **1997**, *31*, 984-992.

(c) Crawford, C. L.; Barnes, M. J.; Peterson, R. A.; Wilmarth, W. R.; Hyder, M. L. *J. Organometal. Chem.* **1999**, *581*, 194-206.

15.   Ashley, K. R.; Whitener, G. D.; Schroeder, N. C.; Ball, J. R.; Radzinski, S. D. *Solvent Extr. Ion Exch.* **1998**, *16*, 843-859.

16.   Lieser, K. H. *Radiochim. Acta*, **1993**, *63*, 5-8.

17.   Mazzocchin, G. A.; Magno, F.; Mazzi, U.; Portanova, R. *Inorg. Chim. Acta*, **1974**, *9*, 263-268.

18.   Liu, S.; Edwards, D. S. *Chem. Rev.*, **1999**, *99*, 2235-2268.

19.   *Nuclides and Isotopes: Chart of the Nuclides*, 15th ed., General Electric Nuclear: San Jose, CA, 1996.

20.   *Emerging Technologies For Hazardous Waste Management*; Ashby, E. C.; Barefield, E. K.; Liotta, C. L.; Neumann, H. M.; Doctorovich, F.; Konda, A.; Zhang, K.; Hurley, J.; Boatright, D.; Annis, A.; Pansino, G.; Dawson, M.; Juliao, M., Eds.; American Chemical Society: Washington, D.C., 1994, pp 249-284.

21.   (a) Eschweiler, W. *Chem. Ber.* **1905**, *38*, 880.

(b) Pine, S. H.; Sanchez, B. L. *J. Org. Chem.* **1971**, *36*, 829.