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Hanford Tank Safety Project

Complex Concentrate Pretreatment FY 1986 Progress Report

September 1986

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under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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On the cover:

An aerial photograph of the SY waste tank farm under construction (circa 1975) on the Hanford site in southeastern Washington State. Tank 241-SY-101 is the tank in the foreground to the right.

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Summary

After of the transuranic elements are removed from complex concentrate waste by the TRUEX process, the remaining waste will be grouted for final storage. The purpose of this project, conducted at the Pacific Northwest Laboratory (PNL), is to support a future decision to grout the complexant waste without destroying the organic contents. In work performed this year^(a), it has been demonstrated that grouts with acceptable parameters for the Transportable Grout Facility can be made using actual waste. The acceptability of these grouts from a regulatory view seems to be less of a problem than was thought at this time last year. None of the organics found in the waste are included on the U.S. Environmental Protection Agency's Hazardous Chemicals List.

To date, 75.1% of the organic content of the waste from Tank 107AN has been identified. In addition to the major complexants identified in the waste, several classes of organics have been found; they include carboxylic acids and alkanes. Only the complexing and chelating agents are known to have strong complexant strengths. Most of the organics other than the major complexants, i.e., chelator fragments, were also found in the synthetic waste, which was made with EDTA, HEDTA, NTA, and citrate. This important finding indicates that the bulk of the decomposition products found in the waste from Tank 107AN probably came from the chemical decomposition of the major complexants used in B-Plant.

Initially, acceptable grout samples were difficult to make even from synthetic TRUEX waste. The first samples were made with the full complement of organics, which had not previously hampered the making of acceptable grouts. It was realized, however, that during the TRUEX process, virtually all of the inorganic carbon is removed as $\text{CO}_2(\text{g})$. After the carbonate was replaced, acceptable grouts were easily made. Therefore, carbonate, as Na_2CO_3 , or other additives must be added to the TRUEX waste before it is sent to the Transportable Grout Facility.

Two potential problems with the processing of the complex concentrate wastes were identified during the use of the TRUEX process on samples of several milliliters. One was the amount of foam that is generated during acid addition to the alkaline waste. Some of this foam appears to be of a waxy nature but does redissolve when the waste is strongly acid. The second potential problem is that noticeable amounts of NO_x gases are generated. No quantitative measure of the NO_x gas generation was made. The problem relates to processing the waste in B-Plant where there are no facilities to handle NO_x gases.

(a) The work was performed and the report written in FY 1986. It is being published in 1991 because of its relevance to the Tank Waste Safety Program.

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1.0 Introduction

Nuclear fuel reprocessing activities at the Hanford Site have generated wastes which are stored in large underground tanks. Some of these wastes contain high concentrations of organic complexants. According to the reference plan, as outlined in the Hanford Waste Management Technology Plan, the wastes that contain no transuranic elements (TRU) will be processed into a cementitious grout and disposed in large underground monitored vaults. Those wastes containing TRU will be processed to remove the TRU; the TRU fraction will be sent to a vitrification plant for deep geological disposal and the remainder will be converted to a grout. Because organic complexants in the waste may cause the grout to have unacceptable properties, either from a processing or a regulatory standpoint, these organics may need to be destroyed before the waste is grouted. The work reported here was carried out at the Pacific Northwest Laboratory^(a) in direct support of a future decision concerning the need to destroy complexants in the stored waste before final disposal.

There are several important issues to be considered with regard to the presence of organics in complexant wastes and of the disposal of those wastes by conversion to a cementitious grout. The foremost of these issues concerns the potential grout processing problems that might result from the presence of organic complexants. Organic additives are routinely used in the cement industry to alter the processing properties in order to accomplish certain tasks. Therefore, uncontrolled and high concentrations of organics could adversely affect the set time, gel strength development, set strength, and amount of drainable liquid. A grout that gels quickly could lead to blockage of the pipes between the grout mixer and the disposal vault or, once the grout reaches the vault, cause a steep angle of repose such that the vault cannot be filled completely. Organics within the grout could chemically or radiolytically decompose to generate gases which could pressurize the grout pores and cause premature cracking of the grout monolith. Of equal concern are the problems that may result from the release of the organics from the grouted waste. If the presence of the organics causes enhanced radionuclide migration in the soils or if some of the organics are found to be hazardous, i.e., regulated, then the public safety would become a greater issue than if the waste could be considered strictly as a chemical waste.

All of these issues bear directly on the decision of whether or not to destroy the organic content of complexant wastes before processing these wastes to a grout. In light of the work performed this year, the processing of complexant wastes may no longer be an issue. However, the regulatory issue, while somewhat mitigated by the results from the work performed this year, still needs to be resolved.

Past efforts in this program have included grouting studies and organic analyses with both actual and synthetic complexant wastes. In FY 1983, a preliminary risk assessment showed that complexant waste in Tank 102AZ presented a low risk with respect to radiation dose-to-man, and thus was an acceptable candidate for grouting. However, the high quantities of TRU in the waste raise a regulatory issue. An extensive, statistically designed grouting study was performed in

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

FY 1984 using a synthetic waste, the composition of which was based upon analyses of the waste that was in Tank 102AZ at the time. In all, 90 grout samples were prepared, representing 30 compositional variations at three mix ratios. Data from these tests were analyzed statistically to yield empirical models that were used to determine the effects of component variability, possibly resulting from waste variability or process upsets. Several acceptable grout compositions were identified on the basis of this work with respect to the processing requirements of the Transportable Grout Facility. One grout was then prepared using actual radioactive waste from Tank 102AZ. This grout behaved somewhat differently from those prepared from synthetic wastes and the difference was attributed to the presence of unidentified organic compounds. However, differences in processing between the synthetic and the radioactive grout could not be ruled out. In FY 1985, an increased emphasis was placed on determining the organic species that were present in the complexant waste. During the last part of FY 1984, it was learned that the waste in Tank 102AZ had been moved and that the bulk of the complexant waste now resided in Tank 107AN. Samples of this waste were analyzed but less than 50% of the organic content had been determined. Scouting studies using a synthetic waste were performed. Organics tested were oxalic, gluconic, and tartaric acids, Magnifloc 835A (a flocculating agent), and residues from the sugar denitration process. Acceptable grouts were obtained for all solutions tested except gluconic and tartaric acids and the sugar denitration residues; these gave excess drainable liquids and poor compressive strengths. Pore fluid analyses indicated that the type of complexant played an important role on the chemistry of the fluids and on the rheological properties of the grouts.

During this past year, emphasis was placed on obtaining a quantitative measure of the organics present in the waste from Tank 107AN. This effort proved to be successful with 75% of the organics now identified. Several initial attempts to make grouts from synthetic TRUEX waste failed when the grouts either had extensive drainable liquids or poor setting properties. Grouts with acceptable properties were made when the carbonate that is lost in TRUEX processing was replaced. Two 20 mL and one 50 mL grout samples were made from samples of the waste from Tank 107AN. The two 20 mL grout samples are being tested using the ANS 16.1 Leach Test and the 50 mL sample was made to determine the rheological properties. Rheological properties acceptable to the Transportable Grout Facility were obtained from the 50 mL sample.

2.0 Conclusions

The following conclusions resulted from the work performed in FY 1986:

1. Chelating and complexants do not adversely affect grout processing properties, but the regulatory issues of grout leaching and pressurization still remain.
2. Loss of inorganic carbon during the TRUEX process must be replaced in order to make a grout that has acceptable properties for the Transportable Grout Facility.
3. None of the organics identified to date should cause either the waste or the resulting grout to be a listed hazardous waste. Other factors may, however, make the grout a listed waste.
4. Laboratory studies using waste samples from Tank 107AN have shown that grouts with acceptable properties for the Transportable Grout Facility can be made.
5. Processing of Tank 107AN waste using TRUEX will result in extensive foaming and release of NO_x gases when HNO_3 is added to the waste. This may cause processing problems in B-Plant.
6. Laboratory studies indicate that the organic content of the grouted waste is readily released during leaching under ANS 16.1 test conditions.
7. Organic analyses of these wastes are sufficiently complicated that several methods are needed to completely identify the organic content.

3.0 Organic Characterization of Complex Concentrate Waste

The complex concentrate waste is being characterized in support of a decision by Rockwell to destroy the organics in these wastes. The organic content of these wastes is extremely complex and difficult to analyze. To date, the low molecular weight (MW) hydrophilic organic content of the wastes from Tank 107AN has been completely characterized. Chelating agents (HEDTA, EDTA and NTA), complexing agents (e.g., citric acid) and a myriad of chelator fragments/degradation products, have been identified. Procedures for high-performance liquid chromatography (HPLC) analyses have been developed and tested for likely chemical classes of compounds present in complex concentrate waste, such as organic acids, chelating agents, and chelator fragments. Using gas chromatographic (GC)-based analytical methods in conjunction with HPLC methods, three additional classes of organics have been identified in the waste from Tank 107AN: carboxylic acids, alkanes and phthalate esters. All of the organics identified to date account for 75.1% of the total organic carbon (TOC) content from Tank 107AN waste. Finally, analyses of a synthetic complex concentrate waste indicates that extensive degradation of chelating and complexing agents occurs rapidly (85 days) under relatively mild conditions (ambient temperature and no radiation).

3.1 Introduction

This report details progress made to date on the organic characterization effort on complex concentrate waste in support of a decision to destroy organics in these wastes. The general strategy used for the organic analysis is outlined in Figure 3.1. The initial effort consisted of general chemical analyses to determine the classes of chemical compounds present in the waste. On the basis of chromatographic fractionation coupled with ultraviolet (UV) absorption detection, it appeared that polar compounds and/or relatively nonvolatile organic compounds of high-molecular weight (MW) account for much of the waste's organic content. Design of chemical separation procedures was then begun.

The organic characterization effort for complex concentrate waste began in FY 1984 with the analysis of waste in Tank 102AZ, which was then moved to Tank 107AN. Both of these wastes were initially analyzed for their low-MW hydrophilic organic content because an appropriate analytical procedure for these organics was already in place. This procedure utilizes chemical derivatization by methylation, followed by gas chromatography (GC) and GC-mass spectrometry (GC-MS) analyses; it also makes important use of GC-Fourier transform infrared spectroscopy (GC-FTIR). The methylation-GC procedure had been developed for and utilized successfully in the analyses of groundwater leachates of low-level nuclear wastes that had been shallow land buried. However, application of the procedure to the analysis of the complex concentrate wastes has required further refinement and expansion of the scope.

The methylation-GC procedure has proven to be quite valuable for the analysis of complex concentrate wastes. Many low-MW hydrophilic organics have been identified. Qualitatively, several chelating agents (NTA, HEDTA and EDTA) and a complexing agent (citric acid) were identified in Wastes 102AZ and 107AN at millimolar (mM) or parts-per-thousand (ppt)

Figure 3.1. Analysis of Organic-Rich Nuclear Wastes

concentrations. One of the chelating agents, HEDTA, proved to be quite an analytical challenge; it exhibits fairly complex chemical behavior. Quite a number of degradation products, or chelator fragments, derived from the chelating agents were also initially detected and have since been identified. In the process, much has been learned about the complex chemical behavior of the chelator fragments, e.g., lactone and lactam cyclization. Quantitatively, the methylation-GC procedure has accounted for 40.3% of the TOC content in Tank 107AN.

At the beginning of FY 1986, the unknown, or unaccounted, TOC content of the complex concentrate waste represented 59.7% of the organic content. Considerable effort has been expended in the past year trying to isolate and identify the unknown organics. To date, two general approaches have been taken to characterize the unknown organics: 1) explore other GC-based methods designed for various chemical classes; and 2) develop HPLC methods, focusing on polar and nonvolatile, or high-MU, organics.

3.2 Organics Identified in Complex Concentrate Waste

The results of the GC, GC-MS and GC-FTIR analyses for the low-MU hydrophilic organics in Waste 107AN are depicted in Figure 3.2 and Table 3.1. Six classes of organic compounds are represented: complexing agents, chelating agents, and chelator fragments, i.e., compounds derived from the degradation of chelating agents, carboxylic acids, alkanes and phthalate esters. The concentrations of the compounds identified ranged from 64.39 mM to 0.23 mM.

3.2.1 Complexing Agents

Two complexing agents were identified in the waste. Citric acid is by far the most abundant complexing agent at 64.39 mM. Citric acid was used in B-Plant in the solvent extraction of strontium. A second complexing agent, methane tricarboxylic acid, was identified recently at 17.32 mM. This compound is not available commercially and is, therefore, presumably a degradation product derived from citric acid.

3.2.2 Chelating Agents

Three chelating agents were identified in the waste: HEDTA at 37.53 mM, EDTA at 31.41 mM, and NTA at 7.33 mM. All three of these compounds are commercially available and were used in B-Plant to hold iron and other corrosion products in solution as well as for other process chemistry reasons. The detection of methylated EDTA and NTA by GC and GC-MS was relatively straight forward. The detection of HEDTA proved to be more difficult.

In past analyses of Tank 102AZ waste and the first analyses of Tank 107AN waste, a compound with a molecular weight of 288 was identified. At first, this compound did not appear to correspond to any known standard, or commercially available, chelating agent. Yet the 288 amu species clearly had an ethylenediamine core. Consequently, it was initially identified as a chelator fragment. Closer examination of this species and comparison of its structure with methylated standards of chelating agents revealed that it is, in fact, derived from the methylation of HEDTA.

Figure 3.2. GC Analysis of Hydrophilic Organics[†] in Organic Complexant Waste from Tank 107AN

The identification of the 288 amu species is outlined in Figure 3.3. Analysis of methylated HEDTA by GC and GC-MS yielded the same molecular weight species (288 amu) identified in complexant wastes. This was initially surprising because the expected molecular weight of methylated HEDTA ($\text{Me}_3\text{-HEDTA}$) should be 320. Analysis of the MU 288 species using GC-FTIR revealed the presence of a strong lactone absorbance. Consequently, the methylated lactone structure depicted in Figure 3.3 was derived. The hydroxyethyl group of HEDTA resists methylation by BF_3 /methanol and, instead, forms a cyclic, or intramolecular, lactone with one of the HEDTA's acetate ligands.

The identification of the MU 288 species as HEDTA was a major breakthrough, but the sensitivity, or response factor, of methylated HEDTA to GC analysis was substantially lower than that of EDTA or NTA, 30% less on a molar basis. This apparent discrepancy was resolved when the methylated HEDTA was analyzed by direct probe - MS (DP-MS). The MU 288 lactone accounted for 30% of the species detected. Trimethylated HEDTA with an unreacted, or free,

Table 3.1. Organics^(a) Identified in Organic Complexant Waste from Tank 107AN

	Concentration ^(b)	
	mM	g/L
<u>Chelating/Complexing Agents</u>		
Citric Acid	64.39	4.61
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA) ^(c)	37.53	4.53
Ethylenediaminetetraacetic Acid (EDTA)	31.41	3.77
Methane Tricarboxylic Acid	17.32	1.45
Nitritotriacetic Acid (NTA)	7.33	0.53
<u>Chelator Fragments</u>		
Ethylenediaminetriacetic Acid (ED3A) ^(d)	17.91	1.72
N-(2-Hydroxyethyl)ethylenediamine-N,N'-diacetic Acid (HED0A) ^(e)	2.39	0.26
N-(ethylene)ethylenediaminetriacetic Acid (E ₂ DTA)	2.28	0.23
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA) ^(h)	2.14	0.18
N-(2-Hydroxyethyl)-N'-(methyl)ethylenediamine-N,N'-diacetic Acid (MeHEDD'A) ^(f)	1.83	0.20
N-(methyl)ethylenediamine-N,N'-diacetic Acid (MeEDDA) ^(g)	1.02	0.08
Iminodiacetic Acid (IDA)	187.9	10.92
<u>Molecular Weight (MW) Species⁽ⁱ⁾</u>		
A: MW 122	0.90	0.04
F: MW 173	0.23	0.02
J: MW 247	0.90	0.08
<u>Carboxylic Acids</u>		
Docos-13en-oic Acid	2.50	0.67
Hexanedioic Acid	2.04	0.15
Hexadecanoic Acid	2.04	0.39
Phthalic Acid	1.10	0.10
Nonanedioic Acid	0.83	0.07
Tetradecanoic Acid	0.68	0.12
Pentanedioic Acid	0.60	0.04
Octadecanoic Acid	0.54	0.11
Hydroxybutanedioic Acid	0.33	0.01
Butanedioic Acid	0.10	0.01
<u>Alkanes</u>		
nC ₂₃ —nC ₃₅	7.77	2.50
<u>Phthalate Esters</u>		
Dibutylphthalate	1.24	0.23
Diethylphthalate	0.05	0.01
Total Organic Carbon (TOC)	3670	44.00
% TOC Identified - 75.1%		

(a) Identified as methyl esters (BF₃/methanol)

(b) Quantitation based on six CC analyses with FID detection; the standard deviations are: citric acid, $\pm 5.7\%$; EDTA, $\pm 7.0\%$; HEDTA, $\pm 12.2\%$; NTA, $\pm 3.1\%$; ED3A, $\pm 2.6\%$; MeEDD'A, $\pm 9.1\%$; Methane Tricarboxylic Acid, HEDDA and MeHEDDA, $\pm 7.0\%$ each; and MW species, $\pm 7.0\%$ each.

(c-h) Identified by GC-MS and FT-IR as: (c) MW 288 lactone; (d) MW 244 lactam; (e) MW 230 dehydrated dimethylester; (f) MW 230 lactone; (g) MW 186 lactam; (h) and MW 773 lactone.

(i) MWs assigned to unknown chelator fragments on the basis of electron impact (70 eV) GC-MS.

Figure 3.3. Source of the MW 288 Chelator Fragment (HEDTA)

hydroxyethyl group accounted for the remaining 70% of the HEDTA. It is speculated that this species is simply too polar to migrate through the GC columns.

To test whether the trimethylated HEDTA was sorbed onto the GC column, two experiments were performed. First, HEDTA was silylated and the product analyzed by MS and GC-MS. A single species, the tetratrimethylsilyl ether of HEDTA - was obtained, which chromatographed nicely as a single GC peak. As a second test, methylated HEDTA was silylated using the silylation reagents N,-bis (trimethylsilyl)acetamide (BSA) and Trimethylchlorosilane (TMCS). The reaction product was then analyzed by MS and GC-MS. Two species were identified as two distinct GC peaks: first, the MU 288 lactone and, second, the mixed derivative of HEDTA, the trimethyl ester, mono(trimethylsilyl)ether of HEDTA. This confirmed that the underivatized hydroxyethyl group of HEDTA rendered any such derivative too polar to migrate through the GC column. Such chemical complexities are often encountered when analyzing chelating agents or their degradation products.

3.2.3 Chelator Fragments

The third class of hydrophilic organics identified in the waste from Tank 107AN are the chelator fragments, presumably derived from the chemical, thermal, and/or radiolytic degradation of the chelating agents. Ten chelator fragments were detected in the waste solution (Table 3.1). Seven of the chelator fragments have been completely identified. Three have been only partially identified on a molecular weight basis as MU 122, MU 173, and MU 247 species. By far the most abundant chelator fragment or organic is IDA at 187.9 mM. The other identified chelator fragments include HEDDA, MeHEDD'A, MeEDD'A, ED3A, E₂DTA, and HEIDA at concentrations ranging from 0.23 to 17.91 mM. The structures of these compounds, depicted in Figure 3.4, clearly point to varying degrees of degradation of NTA, EDTA, and/or HEDTA.

Identification of the lactone formation in methylated HEDTA greatly facilitated the identification of several chelator fragments, but the effort was far from routine. With the information on lactone formation, two chelator fragments, MeHEDD'A and HEIDA, were identified as intramolecular lactones. The identification of HEIDA proved to be puzzling in that both the lactone and dimethyl ester were detected by GC, GC-MS, and GC-FTIR analyses. For reasons not completely understood, the unmasked hydroxyethyl group of HEIDA does not prevent it from being chromatographed, unlike HEDTA. The identification of HEDDA showed that the hydroxyethyl group is capable of several reactions. In this case, an ethylenediaminediacetic acid was identified as the dimethyl ester with an ethylene attached to one of the nitrogens, presumably derived from the dehydration of the hydroxyethyl group.

The identification of three other chelator fragments, ED3A, MeEDD'A, and MeEDDA, was also made possible by GC-FTIR analyses. It was discovered that these compounds exist as intramolecular lactams. Presumably because an acetate ligand is missing, one of the acetates can react with the unmasked nitrogen to form the lactam. The lactam breakthrough on ED3A's structure was made because it is quite abundant and had been detected previously in waste from Tank 102AZ. Initially, ED3A was reported as a MU 244 chelator fragment. There is ample evidence in the literature (Means and Alexander 1981) and from work at Rockwell (Delegard 1980) and at PNL (Toste, Kirby and Pahl 1984) that HEDTA undergoes chemical and/or biological degradation to form ED3A. The mechanism for formation of ED3A is depicted in Figure 3.5.

Chelating/Complexing Agents:

Chemical Form Detected by GC and GC-MS:

a) Identified as methyl esters:

b) Identified as Intramolecular lactone:

c) Identified as Intramolecular lactam:

d) Identified as dehydrated dimethyl ester

e) Identified as lactone and dimethyl ester

Degradation Products:

R9105012.9

Figure 3.4. Chelating/Complexing Agents^(a) and Their Degradation Products Wastes

Figure 3.5. Probable Source of ED3A

3.2.4 Other Organics

Using other GC-based procedures in conjunction with HPLC techniques, three other classes of organics were identified in the waste from Tank 107AN. A number of monocarboxylic and dicarboxylic acids were identified ranging in concentration from 0.1 to 2.5 mM. These compounds complex with metal ions but the association is much weaker than metal chelates. A number of alkanes ranging from nC_{23} to nC_{35} were also identified in the waste, accounting for 5.7% of the TOC content. These compounds are undoubtedly derived from oils or solvents. Finally, two phthalate esters commonly used as plasticizers were identified in the waste.

As indicated in Table 3.1, all of the organics identified to date account for 75.1% of the TOC content of Tank 107AN waste. This leaves 24.9% of the waste's organic content unknown.

3.3 Development of HPLC-based Procedures

Considerable effort has been spent in developing analytical procedures for isolating and identifying the organics in Tank 107AN waste, i.e., the organics not detected and identified by GC and GC-MS analyses. Because of the tremendous power of GC-MS analyses, GC-based methods were explored first, but with only marginal success. Therefore, HPLC procedures were investigated. Several HPLC procedures have been developed for separating organic acids, chelating agents, chelator fragments, and high-MU organics. To date, these procedures have been developed using mixtures of standard compounds. Until recently, lack of an HPLC system for radioactive work has prevented testing of the HPLC procedures with actual waste. However, several of the procedures have tested well with a synthetic complex concentrate waste prepared in the laboratory for testing grouts. An HPLC system for radioactive analyses was purchased recently, but both facilities and organizational problems have postponed the installation and analysis of Tank 107AN waste until next fiscal year.

3.3.1 Chelating Agents

A number of observations made with the methylation-GC procedure prompted work on developing an HPLC procedure for analyzing chelating agents. First, the complex chemistry displayed by HEDTA and ED3A suggests that certain chelating agents and chelator fragments may be difficult or impossible to analyze by GC procedures. When ethylenediaminediacetic acid (EDDA), a commercially available chelator fragment, was analyzed using the methylation-GC procedure, methylated-EDDA did not chromatograph at all. Thus, an HPLC procedure may complement the methylation-GC procedure by uncovering chelator fragments that cannot be analyzed using a GC-based procedure. If nothing else, such a procedure should be an excellent check on the reliability of the methylation-GC procedure. To date, a reverse-phase HPLC procedure has been developed and tested on a mixture of chelating agent standards. The procedure uses a C_8 -reverse phase column with a methanol/acetic acid (pH 4.2) mobile phase. The chelating agents are detected as copper chelates at 280 nm by adding $Cu(NO_3)_2$ to the mobile phase. It was necessary to use an ion-pairing agent to minimize the chelating agents polarity; cetyltrimethylammonium bromide (CTAB) was selected as the ion-pairing reagent. As Figure 3.6 illustrates, the procedure works well for a variety of standards. The procedure is currently being tested using

Figure 3.6. HPLC of Chelating Agents

the synthetic waste sample. The preliminary results are very encouraging. HEDTA, NTA and EDTA have been detected in the synthetic waste. Moreover, the spectral peaks are split perhaps because different metal chelates are slightly resolved.

3.3.2 Chelator Fragments

The reverse-phase HPLC procedure developed for the chelating agents did not work well for the chelator fragments. The procedure was tested on three commercially available chelator fragments, HEIDA, EDDA and IDA, and it was found that the compounds are not retained on the C₈ column at all, presumably because they are too polar. Therefore, an anion exchange column

was used with the conditions shown in Figure 3.7. A reasonable separation of HEIDA, EDDA and IDA was achieved. This procedure will be tested on the synthetic waste.

3.3.3 Organic Acids

An HPLC procedure has also been developed for organic acids. A number of acids, notably glycolic acid, proved to be difficult or impossible to analyze by GC procedures. The HPLC procedure that has been developed separates at least nine organic acids: oxalic acid, citric acid, D-tartaric acid, D-gluconic acid, glyoxylic acid, glycolic acid, formic acid, acetic acid and hexanoic acid. Three criteria were used to select the standard compounds: 1) discussions with Rockwell personnel on the history of the waste in Tank 107AN, 2) speculation about likely decomposition products of the source-term organics, and 3) chromatographic considerations. For example, hexanoic acid was included to test whether aliphatic acids would chromatograph well. As Figure 3.8 illustrates, the HPLC procedure works well for all of the organic acids tested. Hexanoic acid elutes much later, indicating that the conditions are optimal for more polar acids. To date, the procedure has been tested on synthetic sucrose denitration solutions. A number of resolvable species were isolated and are currently being examined.

3.4 Organic Diagenesis in Nuclear Wastes

Preparation of the synthetic complex concentrate waste for grouting experiments provided an opportunity to study the degradation of organics in a complex concentrate waste, at least in the absence of radiation. The composition of the waste is shown in Table 4.1 (see Section 4.2). An aliquot of the waste was taken 85 days after preparation and storage at ambient temperature and analyzed using the methylation-GC procedure. The results were quite surprising. Extensive organic diagenesis, or degradation, of the organics had occurred rapidly (85 days) under relatively mild conditions, i.e., no radiation and ambient temperatures. The results of the analyses are tabulated in Table 3.2. The organic content is quite similar to that of the actual waste. In addition to the organics that were present in the solution at make-up, quite a number of chelator fragments were identified, and are clearly derived from the degradation of the chelating and complexing agents. Contrary to what one might have predicted, NTA did not undergo any degradation. Only 18% of the citric acid was degraded, presumably, to methane tricarboxylic acid. Both HEDTA and EDTA underwent extensive degradation, 71% and 72%, respectively. If one looks for mass balance, methane tricarboxylic acid accounts for 91% of the citric acid degradation. The chelator fragments account for only 41% of chelator degradation, suggesting that the chelator fragments have further degraded to species not amenable to GC analyses, perhaps to amines, which may be determined by HPLC.

Figure 3.7. HPLC of Chelator Fragments

Figure 3.8. HPLC of Organic Acids

Table 3.2. Hydrophilic Organics^(a) Identified in Synthetic Organic Complexant Waste

<u>Chelating/Complexing Agents</u>	<u>Concentration^(b)</u>	
	<u>mM</u>	<u>gC/L</u>
Citric Acid	61.81	4.45
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA) ^(c)	10.76	1.29
Ethylenediaminetetraacetic Acid (EDTA)	8.65	1.04
Nitrilotriacetic Acid (NTA)	6.90	0.50
Methane Tricarboxylic Acid	7.34	0.48
<u>Chelator Fragments</u>		
N(ethylene)ethylenediaminetriacetic Acid (E ₂ DTA)	3.43	0.35
Ethylenediaminetriacetic Acid (ED3A) ^(d)	2.03	0.19
Iminodiacetic Acid (IDA)	100.89	4.97
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA) ^(e)	0.51	0.04
N-(2-Hydroxyethyl)-N'(methyl)ethylenediamine-N,N'-diacetic Acid (MeHEDD'A) ^(f)	0.17	0.02
N-(2-Hydroxyethyl)ethylenediamine-N,N'-diacetic Acid (HEDDA) ^(g)	0.13	0.01
Molecular Weight (MW) Species ^(h)		
D: MW 247	0.84	0.08
<u>Carboxylic Acids</u>		
Docos-13en-oic Acid	2.50	0.67
Hexanedioic Acid	1.36	0.10
Hexadecanoic Acid	1.24	0.24
Octadecanoic Acid	0.84	0.18
Docos-13en-oic Acid	0.77	0.27
Tetradecanoic Acid	0.43	0.07
Phthalic Acid	0.18	0.02
<u>Phthalate Esters</u>		
Diethylphthalate	6.53	1.89
Dibutylphthalate	0.08	0.01
Total Organic Carbon (TOC)	1572	18.86
% TOC Identified - 89.5%		

(a) Identified as methyl esters (BF₃/methanol).

(b) Quantitation based on three GC analyses with FID detection; the standard deviations are: citric acid, $\pm 10.3\%$; EDTA, $\pm 13.3\%$; HEDTA, $\pm 6.6\%$; NTA, $\pm 10.9\%$; ED3A, $\pm 11.0\%$; MeDD'A, $\pm 10.9\%$; Methane Tricarboxylic Acid, HEDDA and MeHEDD'A, $\pm 10.8\%$ each; and MW species D, $\pm 14.1\%$ each.

(c-g) Identified by GC-MS and FT-IR as: (c) MW 288 lactone; (d) MW 244 lactam; (e) MW 173 lactone; (f) MW 230 lactone; and (g) MW 230 dehydrated dimethylester.

(h) MWs assigned to unknown chelator fragments on the basis of electron impact (70 eV) GC-MS.

4.0 Preparation of Radioactive Grouts

Prior to preparation of radioactive grouts, procedures were developed and verified using nonradioactive materials and simulated TRUEX waste. In the past, grouts had been made using simulated complexant waste. These earlier studies indicated that the organics present in the waste should not hinder the production of acceptable grouts. Addition of the TRUEX organics to the simulated waste also did not cause any problems for the formation of acceptable grouts. However, problems were encountered when trying to make grouts from nonradioactive waste after the TRUEX process was performed on the simulated waste. The first subsection of this section details the studies using nonradioactive materials that led to the successful production of radioactive grouts, and the second subsection details the studies done with the radioactive materials.

4.1 Studies with Nonradioactive Materials

4.1.1 Simulated Tank 107AN Waste Makeup

Simulated waste was prepared according to the composition listed in Table 4.1. The compounds were added in the order listed in the table to a volume of deionized water that was half of the desired final volume of simulated waste. The four organics were added in the proportions that they were identified in Tank 107AN waste; however, the TOC content contributed by these compounds accounts for only 30% of the total found in the actual waste. The Na_2CO_3 and NaOH additions were staggered to increase the Na content and achieve a final carbonate concentration of 1.22 M. Specifically, 108 g/L Na_2CO_3 were added while the solution was still acidic, which caused CO_2 to be liberated. The pH was increased by adding for each liter of solution 55 mL of 19 M NaOH and then 129 g of Na_2CO_3 . Finally, the pH was increased to 12.6 using 19 M NaOH, and then the NaNO_2 was added. The final product contained a dark brown precipitate and an amber-colored supernate. The precipitate accounted for 1.6% of the total solution mass.

4.1.2 Simulated TRUEX Process Procedure

The simulated waste described above was treated by a simulated TRUEX process (Leonard et al. 1985) to produce the final waste for grouting. The flow sheet (Figure 4.1) shows the procedure for treating 100 mL of simulated waste (precipitate + supernate). During the addition of concentrated nitric acid to the waste, the evolution of gases caused foaming. After the foaming had ceased and the solution was clear, sodium oxalate was added and the solution stirred to dissolve all the material. Next, a solution of 0.5 M HNO_3 + 0.01 M Fe was added, followed by 0.5 mL of CMPO/TPB per liter of original waste. This quantity of CMPO/TPB represents the amount that may find its way into the waste due to carry over and is well in excess of the solubility limit (Vandegrift et al. 1984). The pH of this TRUEX solution was then increased using 19 M NaOH. During this step of the procedure, precipitates reformed, and the solution gelled. The addition of more 19 M NaOH caused the gel to dissipate, and when the pH was approximately 12, the waste was a two-phase slurry. The solids were allowed to settle, the supernate was

Table 4.1. Composition of Simulated Tank 107AN Complexant Concentrate Waste Used for FY 1986 Laboratory Activities

Compound	g/L	M
Concentrated Nitric Acid	164.44 mL	2.61
Al(NO ₃) ₃ •9H ₂ O	78.78	0.21
Fe(NO ₃) ₃ •9H ₂ O	15.35	0.038
Ca(NO ₃) ₂ •4H ₂ O	5.90	0.025
Cr(NO ₃) ₃ •9H ₂ O	1.80	0.0045
KNO ₃	4.65	0.046
La(NO ₃) ₃ •6H ₂ O	0.12	0.00028
Nd(NO ₃) ₃ •5H ₂ O	0.40	0.00098
Mg(NO ₃) ₂ •6H ₂ O	2.82	0.011
Mn(SO ₄)H ₂ O	1.22	0.0072
Ni(NO ₃) ₂ •6H ₂ O	2.33	0.008
Zn(NO ₃) ₂ •8H ₂ O	0.22	0.0073
Na ₂ HPO ₄	3.12	0.022
NaCl	2.40	0.041
Na ₂ B ₄ O ₇	4.23	0.021
Cu(NO ₃) ₂ •3H ₂ O	0.10	0.00042
Pb(NO ₃) ₂	0.60	0.0018
(NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	0.79	0.00064
Cd(NO ₃) ₂ •4H ₂ O	0.17	0.00055
Na ₄ EDTA•2H ₂ O*	13.08	0.031
NaCitrate•2H ₂ O*	18.81	0.064
Na ₃ HEDTA•2H ₂ O*	14.36	0.038
Na ₂ NTA*	1.73	0.073
Na ₂ CO ₃	237.00	2.24
	108	
	129 after pH > 7	
NaOH (19 M)	55 mL	
	16 mL after last sodium carbonate addition	
NaHO ₂	55.20	0.80

* EDTA - ethylenediaminetetraacetic acid
HEDTA - hydroxyethylenediaminetriacetic acid
NTA - nitrilotriacetic acid

decanted, and additional NaOH was added to increase the hydroxide content to 0.1 M. This was the waste solution that was used in the grout studies.

4.1.3 Grout Preparation

Several grouts were prepared with the simulated TRUEX waste solution using two dry blends that have been identified for grouting Hanford Facilities Waste (HFW) and Neutralized Cladding Removal Waste (NCRW). The compositions of these blends are shown in Table 4.2. These blends have been shown to result in grouts with rheological properties compatible with the specifications of the Transportable Grout Facility. The solids were blended for 23 h in a twin-shell V-blender before use.

Figure 4.1. Flow Chart for the Preparation of TRUEX Waste from 100 mL of 107AN Waste

Table 4.2. Compositions of Dry Blends Used in Grout Studies

<u>Component</u>	<u>29D</u>	<u>C1</u>
Type I-II Portland Cement	41	
Type III Portland Cement		42
Class F Fly Ash	40	40
Attapulgitite Drilling Clay	11	
Hydrated Lime		10
Indian Red Pottery Clay	8	8

A small-scale grout mixer was constructed that allowed the production of small quantities of grout having shear rates and fluid properties similar to those for grouts made with the laboratory mixer. The small mixer was designed specifically for producing 20 to 50 mL of radioactive grout and was used for all grouts produced with the simulated waste. The mixer is shown in Figure 4.2. The mixer consists of a syringe tube with heat-sealed tip, a perforated teflon plunger, a stainless steel shaft, a rubber seal, and a teflon guide plug. The waste solution is placed in the syringe tube and the dry blend is added. The plunger, seal, and guide plug are inserted and the plunger reciprocated slowly until it reaches the bottom of the tube. Final mixing is accomplished in approximately 30 s at about one cycle per second. During this operation, the grout is mixed as it flows through the holes in the plunger and between the plunger and the syringe wall. Conventional laboratory-produced grouts are prepared in 1-L quantities using a Hobart mixer. Since the rheological properties of grouts containing attapulgitite are sensitive to the shear imparted during mixing, the properties of HFW grouts produced with the syringe mixer were compared with those produced with the Hobart mixer, and the two methods were found to yield comparable grouts.

4.1.4 Results

A total of 25 grouts were prepared with simulated TRUEX waste to determine whether acceptable properties would result. Because the grout volumes produced were small, rheological properties could not be measured, and acceptability was based on the amount of drainable liquids that resulted, and on the setting rates. The main variables that were assessed included various dry solids and mix ratios (solids to liquid ratio) and the use of additives. The first two grouts were produced with blend 29C listed in Table 4.2 at a mix ratio of 7.5 lb/gal. After 24 h, the grouts had set but there was approximately 30 vol% drainable liquid on the grouts. The next grouts were made at a mix ratio of 8.5 lb/gal which reduced the drainable liquid content. However, these grouts did not set. Dry blend C1 was used in the next series of grouts with basically the same results -- acceptable drainable liquids but poor setting rates. Various additives were then added to the waste before producing grouts in an attempt to increase the hydration reactions. The additives included either calcium chloride, sodium silicate, or copper nitrate. The calcium chloride and sodium silicate were used because they are known set accelerators in conventional portland cement products. These additives did not have any noticeable effect on the drainable liquids or the setting rates when compared with no additives. The copper nitrate was included to serve a dual purpose. First, nitrate salts are known set accelerators in conventional cements. Second, since EDTA has been shown to form complexes with calcium ions, adding copper ions to solution to compete with the calcium ions should allow more calcium to react to form hydration products. The copper nitrate resulted in increased drainable liquids and had no effect on the setting rate.

Figure 4.2. Photograph of the Small Hand Mixer Developed to Prepare Small Volumes of Grouts

In the past, grouts produced with simulated complexant concentrate waste did not exhibit the slow setting rates experienced with the simulated TRUEX waste even though the bulk composition of the two wastes were similar. The major differences between the simulated TRUEX waste and the starting waste were the addition of sodium oxalate and a depletion of the carbonate during the TRUEX process. Therefore, the last series of grouts were produced with dry blend 29D at a mix ratio of 8.5 lb/gal with simulated TRUEX waste containing sodium carbonate added at 0.25, 0.5, and 0.75 M. All of these grouts had developed acceptable strength after 48 h, and had approximately 1 to 2 vol% drainable liquids. Additional grouts produced with simulated TRUEX waste containing 0.5 M sodium carbonate confirmed the acceptable setting properties.

4.2 Radioactive Grout Studies

During FY 1986 grouts were prepared from waste from Tank 107AN and grout blend 29D (Table 4.2). Two 20 mL grout samples were made for use in a Leaching test and one sample was made for viscosity measurements on freshly made grout. Prior to making these grout samples, the waste was pretreated to produce a waste with a composition similar to the alkaline waste after treatment using the TRUEX process. In support of the leach tests, the composition of Tank 107AN waste was measured by inductively coupled argon plasma (ICP) emission spectroscopy and by radiochemical methods. The results of these analyses are presented in Figures 4.3 and 4.4, respectively.

4.2.1 Preparation of Radioactive Grout Samples

To produce a waste similar to the waste that will actually be grouted, Tank 107AN waste was acidified to about 0.5 M HNO_3 using 0.33 mL of concentrated nitric acid per mL of waste. During the nitric acid addition, NO_x gases were generated and a brownish, waxy foam was noted. Sodium oxalate was then added to make the waste 0.2 M in oxalate; the sodium oxalate only partially dissolved. A small amount (0.5 $\mu\text{L/mL}$ waste) of TRUEX extractant/solvent (2.03 g CMPO in 9.6 mL TBP) was added to mimic the carry over of the TRUEX process solvent. Ferric nitrate was then added (0.04 mL of 0.5 M HNO_3 + 0.01 M $\text{Fe}(\text{NO}_3)_3/\text{mL}$ waste). To return the waste to a pH of 12, 0.12 mL of 19 M NaOH was added per mL of original waste. The final volume resulting from this treatment of the waste was 1.5 mL/mL of original waste.

To prepare the 20 mL grout samples for the leach tests, two 7 mL samples of Tank 107AN waste were pretreated as described above to produce two 10.5 mL samples of waste for grout. To allow preparation of an acceptable grout, as discussed in Section 4.1, 0.61 g of Na_2CO_3 was added to each sample. The resulting mixtures were each mixed with 11.7 g of blend 29D using the small hand mixer shown in Figure 4.2, poured into plastic vials, and cured for about one month to produce right cylindrical monoliths nominally 2.5 cm in diameter by 4.3 cm high. The cylinders weighed about 18 g and 19 g and had nominal volumes of 21 mL each.

4.2.2 Leach Tests

The leach tests are being performed in accordance with ANS 16.1 (ANS 1984). The grout samples are being exposed to Hanford groundwater. The radionuclide, TOC, and elemental contents of the leachate are being monitored. At the date of this report only the TOC analyses

Figure 4.3. Leaching Behavior for TOC from Two Grout Samples Prepared Using Radioactive Tank 107AN/TRUEX Waste

for the leachates up to 120 h have been received. Using the measured TOC for Tank 107AN waste, 30% (accumulative) of the TOC in the grout samples has been leached from the two samples. The leaching curves for the two samples, the amount of TOC leached with time, are presented in Figure 4.3. The shape of the curves is nearly what is expected for leaching controlled by diffusion. However, the increased curvature may indicate another controlling mechanism.

4.2.3 Viscosity of Grout from Tank 107AN Waste

The other activity that was done in FY 1986 was to measure the viscosity of a radioactive grout prepared using the procedure given in Section 4.1.3. To measure the viscosity, a 50 mL batch of grout was made from about 15 mL of Tank 107AN waste. The waste was first treated using the TRUEX process and then mixed with grout additives, blend 29D, in a shielded syringe mixer similar to that shown in Figure 4.2. The rheological properties of the radioactive grout were determined using a Haake Rotovisco RV-100 (Haake Buchler Instruments, Inc., Saddle Brook, New Jersey). This instrument allows the apparent viscosity to be measured at various shear rates. Since grouts are non-newtonian fluids, viscosity generally decreases with increasing shear rate. A plot of shear stress versus shear rate is shown in Figure 4.4. The data were evaluated using the power law rheological model and the flow equations (Smith 1976). The

Figure 4.4. Viscosity Curve for the 50 mL Grout Sample Prepared from Tank 107AN/TRUEX Waste

Reynolds number calculated from the power law parameters for a flow rate of 50 gpm through a 2-in.-diameter pipe was 2055, and the calculated critical flow rate was 50.7 gpm. The critical flow rate is the flow rate that results in a Reynolds number of 2100, the assumed transition point from laminar to turbulent flow (Smith 1976). Current grout formulation criteria requires a critical flow rate of <65 gpm; therefore, this grout would be compatible with the flow specifications for the Transportable Grout Facility.

5.0 Recommendations for Further Research

Although outside of the general needs of this program, extensive laboratory work is needed before a grout formulation is finally recommended for use in the Transportable Grout Facility. Most work to date has been on small-sized samples. Larger samples using synthetic waste containing all of the identified organic compounds need to be made to verify the findings that have been observed to date.

To provide direct support to the decision on whether or not to destroy organics, research is needed to address regulatory concerns. The leach tests started during this fiscal year need to be continued and the number of tests expanded. Leachates from these tests need to be chemically characterized, including the organic content. The long-term behavior of grouts made with organic complexant wastes needs to be examined using techniques in use or under development by the Grout Program. Such long-term issues should include organic/grout interactions, pressurization of the grout, mechanical strength, and chemical durability of aged grouts. Using the results from these tests, a performance assessment study is needed to ensure that there is sufficient information to address the regulatory issues. Perceived or real failure of these grouts to meet the regulatory guidelines may trigger a decision to destroy the complexants prior to making a grout from these wastes.

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