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**Sludge Treatment and Extraction Technology
Development: Results of FY 1993 Studies**

G. J. Lumetta
B. M. Rapko
M. J. Wagner
C. D. Carlson
R. J. Barrington

March 1994

Work Supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

This report describes experimental results from work conducted in FY 1993 under the Sludge Treatment and Extraction Technology Development Task of the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project at Pacific Northwest Laboratory (PNL). Experiments were conducted in the following six general areas: 1) sludge washing, 2) sludge leaching, 3) sludge dissolution, 4) actinide separation by solvent extraction and extraction chromatography, 5) Sr separation by solvent extraction, and 6) extraction of Cs from acidic solution.

The major activities and results of this work were as follows:

- Sludge washing and caustic leaching tests were conducted on sludges from four different single-shell tanks (SST) (B-110, C-109, C-112, and U-110). The effects of sludge washing and caustic leaching varied among the sludges (Table S.1). The behavior of P was of major importance because 1) there is a low tolerance for P in the feed to the Hanford Waste Vitrification Plant (HWVP) (thus, P tends to be the limiting component in the volume of high-level waste [HLW] glass required for disposal), 2) P composes a significant fraction of the sludge mass in the four examined tanks, and 3) one of the planning assumptions under the new (September 1993) tank remediation strategy is that 98% of the P in the tank wastes is removed by caustic leaching (i.e., enhanced sludge washing). In the case of B-110 sludge, a significant fraction ($\geq 97\%$) of the P was removed by a combination of sludge washing and caustic leaching. For C-112 sludge, 84% of the P was removed from the sludge by a combination of sludge washing and caustic leaching. In contrast, only 42% of the P in the C-109 sludge was removed by sludge washing and caustic leaching. Likewise, for U-110 sludge, only 35% to 49% of the P was removed by caustic leaching. However, additional P was removed from the U-110 sludge by leaching with carbonate. Regarding the behavior of Al (another major SST sludge component), a combination of sludge washing and caustic leaching removed $\sim 80\%$ of the Al from C-109, C-112, and U-110 sludges.
- Sludge washing and acid dissolution tests were conducted on sludges from three SSTs (B-110, C-109, and C-112). The ability of 2 M HNO_3 (100°C) to dissolve the sludges varied (Table S.2). For example, B-110 sludge dissolved readily in 2 M HNO_3 , with nearly complete dissolution of the solids. The small amount of silicon-containing material that did not dissolve in 2 M HNO_3 dissolved in 2 M HNO_3 plus 0.9 M HF. In contrast, large fractions of the C-109 and C-112 sludges did not dissolve in 2 M HNO_3 . The undissolved residue in these cases contained primarily Al, Fe, Na, and Si (which may indicate the presence of an aluminosilicate material such as cancrinite). Further treatment of these residues with HNO_3 plus HF, and $\text{H}_2\text{C}_2\text{O}_4$ resulted in minimal dissolution of the remaining solid.

- Performing a caustic leach on SST sludges before acid dissolution can improve sludge dissolution; this was illustrated with sludge from Tank U-110. In previous studies, significant fractions of Al (~65%), Fe (~35%), and Si (~80%) remained undissolved after a portion of washed U-110 sludge was treated with 2 M HNO₃ (Lumetta, Wagner, Colton, and Jones 1993). When this sludge was leached with 5 M NaOH (100°C) before treating with 2 M HNO₃, the undissolved residue contained <10% of the Al and <15% of the Si. A significant fraction of the Fe (~25%) still remained undissolved, however.
- Complexant concentrate sludge from Tank AN-102 dissolved readily in HNO₃. Preliminary transuranic extraction (TRUEX) and Sr extraction (SREX) tests with solutions derived from dissolving this sludge indicated that the transuranics (TRUs) and Sr can be extracted using these processes.
- Although originally promising, the sulfonated catechol, Tiron®, was found to be ineffective at leaching Pu and Am from neutralized cladding removal waste (NCRW) sludge.
- A systematic study of potential agents for leaching Cr from alkaline tank sludges was performed. The removal of Cr from certain tank sludges might be beneficial for reducing the quantity of HLW glass produced during vitrification (Lumetta and Swanson 1993a). This study revealed that permanganate is the most promising reagent to achieve selective Cr leaching.
- A preliminary test of a flowsheet for pretreating NCRW sludge was conducted, and the results were promising. The pretreatment process involves washing the NCRW sludge with dilute NaOH, dissolving the sludge in HNO₃/HF, adding ascorbic acid to adjust the Pu valence to +3, extracting U with tributyl phosphate (TBP), and extracting TRUs with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). Near-complete Zr dissolution (99%) was achieved. The residue remaining after dissolution contained primarily Si. Ninety-nine percent of the U in the sludge was extracted in the TBP cycle, separating U from the TRU portion of the sludge. Good extraction of the TRUs from the dissolved sludge solution was achieved with CMPO, the TRU decontamination factor (DF) was 200.^(a) Stripping TRUs from the solvent was accomplished with 0.01 M HNO₃ followed by 0.01 M H₂C₂O₄.
- An alternative CMPO flowsheet for pretreating NCRW sludge was tested using a simulated dissolved NCRW solution. In this flowsheet, the TRUs are selectively stripped from the CMPO solvent by using a dilute HNO₃ solution containing a reducing agent. In this case, most of the U remained in the organic phase during the stripping stages and was removed from the solvent with a carbonate solution. The test results suggested that Am and Pu can be stripped using a

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(a) The DF is defined as the amount of material (e.g., TRU) entering the process divided by the amount exiting in the low-level waste (LLW) stream.

solution consisting of 0.1 M HNO_3 plus 0.1 M ascorbic acid. Approximately 10% of the U would be stripped along with the TRUs, the remaining 90% of the U would be stripped by the carbonate solvent wash solution.

- Work was begun to develop a pretreatment flowsheet for Tank B-110 sludge that would separate TRUs and ^{90}Sr from the bulk components of the sludge. A number of possible flowsheets were tested using a simulated dissolved B-110 solution, and the most promising flowsheet was tested using actual B-110 sludge. The preferred approach involved dissolving the sludge in acid, extracting the TRUs with CMPO, and extracting Sr with di-t-butylcyclohexano-18-crown-6 (SREX process). The test results indicated that U and Bi coextract with the TRUs, but the TRUs can be selectively stripped from the extract using a solution of 0.075 M HNO_3 plus 0.01 M ascorbic acid. Under these conditions, the U and Bi remain in the organic phase and are, thus, separated from the TRUs. The U and Bi can be stripped from the solvent using a complexant or a complexant-containing carbonate solution. The SREX process was shown to effectively separate Sr from the bulk sludge constituents, with a Sr DF of $\sim 9,000$.
- A study was begun of the TRU extractant dihexyl-N,N-diethylcarbamoylmethyl phosphonate (DHDECMP). DHDECMP extracts Am(III), Pu(IV), U(VI), and Bi(III) from nitrate media. Measured distribution coefficients suggested that separation of Bi from the TRUs may be difficult. Iron(III) was not extracted to any appreciable extent with DHDECMP. Zirconium(IV) was extracted by DHDECMP to some extent, but the distribution coefficient for Zr was low under conditions necessary to prevent interfacial crud formation ($F/\text{Zr} > 4.5$). The distribution behaviors of Am(III) and Pu(IV) at low acid concentrations were very sensitive to the presence of acidic impurities in the solvent. If efficient removal of such impurities from the solvent could be achieved, it may be practical to strip Pu(IV) from the solvent by using a dilute HNO_3 solution. However, if these impurities build-up during processing, then a stripping agent (reductant or complexant) must be added to strip the TRUs. Third-phase formation was also found to be a problem with this extractant at high HNO_3 concentrations. Because of this, a nitrate salt must be added to reach a nitrate concentration high enough to achieve good TRU extraction.
- A study was begun of the TRU extractant N,N'-dimethyl-N,N'-dibutyl-(2-tetradecyl)propane-1,3-diamide (DIAMIDE-14). Early results were questioned because the first batch of extractant used was not pure. A second batch of DIAMIDE-14 was prepared and purified by liquid chromatography. Preliminary Am extraction data obtained using the purified material corroborated the results reported by French researchers. Minor differences were likely due to diluent effects.
- Preliminary U/TEVA-Spec™ column loading and elution tests were performed using UO_2^{2+} solutions in 2 M HNO_3 . With an initial U feed concentration of 0.005 M and a flow rate of 20 column volumes (cv)/h, significant breakthrough did not occur until more than 20 cv of feed had passed through the column. With higher U concentrations and higher flow rates, break-

through occurred earlier, as expected. Uranium was efficiently eluted from the column using 0.02 M HNO₃. The column did not degrade during the limited testing performed here.

- Cesium was extracted from an actual Hanford sludge waste using 0.05 M di(t-butylbenzo)-21-crown-7 plus 0.05 M dinonylnaphthalenesulfonic acid in triethylbenzene.
- Cesium can be removed from acid solutions using polyoxometallates. Screening studies using phosphotungstic acid or ammonium molydophosphate indicated that >95% removal of Cs from 1 M HNO₃ can be achieved by a single contact with these materials.

Table S.1. Comparison of Sludge Washing and Caustic Leaching for Four SST Sludges

	Component Dissolved, % ^(a)			
	B-110	C-109	C-112	U-110 ^(b)
Al	≤53	81	85	79 (4)
Ca	19	1	1	52(26)
Cr	64	84↔75	88	74↔47(≤20)
Fe	0	5	5	1 (0)
P	≥97	42	84	49↔35(51↔18)
Si	74	16	11	8(≤4)

- (a) Percent of each component dissolved by a combination of sludge washing and caustic leaching. All washes were with 0.1 M NaOH, caustic leaches were with 3 M NaOH for B-110, C-109, and C-112, and 5 M NaOH for U-110 (all operations at 100°C). In each case, the sludge was subjected to two successive caustic leach treatments.
- (b) Following the caustic leach, the U-110 sludge was digested at 100°C with two successive portions of 1 M K₂CO₃. The percentage of each component dissolved in the carbonate leach is given in parentheses.

Table S.2. Comparison of Acid Dissolution for Three SST Sludges

	B-110 Sludge		C-109 Sludge		C-112 Sludge	
	<u>g/g Sludge</u>	<u>In Residue^(a), %</u>	<u>g/g Sludge</u>	<u>In Residue^(a), %</u>	<u>g/g Sludge</u>	<u>In Residue^(a), %</u>
Al	1.5E-03→1.1E-03	≤30	1.4E-1	75	1.1E-02	48
Ca	8.7E-04	3	1.2E-2	7	2.6E-02	14
Cr	8.9E-04	0	4.3E-4	7	1.4E-03→3.3E-04	84→23
Fe	2.0E-02	2	1.6E-2	36	6.8E-02	49
Na	1.1E-01	0	5.7E-2	11	1.6E-01	10
P	1.8E-02	0	9.5E-3	5	5.9E-02→5.6E-02	6→0
Pb	1.2E-03→9.9E-04	≤15	4.9E-3	11	2.6E-03→1.3E-03	50→0
Si	7.0E-03	17	4.9E-2	91	2.8E-02	91
Sr	2.4E-04	0	2.9E-042.7E-4	≤33	9.2E-04→7.6E-04	17→0

(a) Percent of each component in the undissolved solids after treating the sludge (at 100°C) with 1) 0.1 M NaOH and 2) 2 M HNO₃.

Glossary

AA	atomic absorption
CMPO	octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
cv	column volumes
DF	decontamination factor
DHDECMP	dihexyl-N,N-diethylcarbamoylmethyl phosphonate
DIAMIDE-14	N,N'-dimethyl-N,N'-dibutyl-(2-tetradecyl)propane-1,3-diamide
DOE	U.S. Department of Energy
DST	double-shell tank
DtBB21C7	di-(t-butylbenzo)-21-crown-7
EDTA	ethylenediaminetetraacetate
EF	extraction factor
FTIR	Fourier transform infrared
HDNNS	dinonylnaphthalenesulfonic acid
HEDPA	1-hydroxyethane-1,1-diphosphonate
HLW	high-level waste
HWVP	Hanford Waste Vittrification Plant
ICP	inductively coupled plasma atomic emissions spectroscopy
LANL	Los Alamos National Laboratory
LLW	low-level waste
MIX	macroreticular ion exchange
NCRW	neutralized cladding removal waste
NMR	nuclear magnetic resonance
NPH	normal paraffin hydrocarbon
NRC	U.S. Nuclear Regulatory Commission
O/A	organic-to-aqueous phase ratio
PNL	Pacific Northwest Laboratory
SEM	scanning electron microscopy
SREX	Sr extraction
SST	single-shell tank
TBP	tributyl phosphate
Tiron®	4,5-dihydroxy-1,3-benzenedisulfonate
TLC	thin layer chromatography
TPH	hydrogenated tetrapropylene
TRU	transuranic
TRUEX	transuranic extraction
TWRS	Tank Waste Remediation System
XRD	x-ray diffraction

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Acknowledgments

The authors would like to thank L. Ballou and J. L. Swanson for reviewing this document. We gratefully acknowledge I. E. Burgeson, C. O. Harvey, and S. W. Thompson for performing chemical and radiochemical analyses.

1.0 Introduction

Methods are being developed to treat and dispose of the large volumes of radioactive defense wastes currently stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site in southeastern Washington State. The current baseline scenario for the treatment and disposal of these wastes involves partitioning the wastes into a small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). The HLW will be vitrified into borosilicate glass and disposed of in a geologic repository, while the LLW will be disposed of onsite. The LLW disposal form was initially planned to be grout, but an agreement was reached in late FY 1993 that the LLW disposal form would also be glass.

Because of the relatively high cost of HLW disposal, pretreatment methods are being developed to minimize its volume. Pacific Northwest Laboratory (PNL)^(a) is investigating various methods for such pretreatment. The methods under consideration for the tank sludges range from simply washing the sludges with dilute NaOH, to dissolving the sludges in acid and extracting key radionuclides from the dissolved sludge solutions. The data collected in this effort will be used to support a planned 1998 decision on the extent of pretreatment to be performed on the Hanford tank sludges.

In FY 1993, under the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project, PNL investigated the following sludge pretreatment techniques: 1) sludge washing, 2) sludge leaching, 3) sludge dissolution, 4) solvent extraction for transuranic (TRU) removal, 5) alternative actinide removal (sorption processes), 6) solvent extraction for Sr removal, and 7) removal of Cs from acidic waste streams by both solvent extraction and ion exchange. The results of this research are reported in this document.

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

2.0 Washing, Caustic Leaching, and Dissolution of Tank B-110 Sludge

Experiments were conducted using sludge from single-shell tank (SST) 241-B-110 (hereafter referred to as B-110 sludge) to determine the quantity and composition of sludge remaining after sludge washing and caustic leaching. The efficacy of various acid solutions in dissolving this sludge was also investigated.^(a) The results of these experiments are reported in this section.

The primary waste type stored in Tank B-110 resulted from the second decontamination cycle of the bismuth phosphate process, which was performed at Hanford in the 1940s and 1950s to recover and purify Pu from irradiated fuel. The sludge formed when this waste was adjusted to high pH contains Bi, Cr, Fe, Si, phosphates, and sulfates. Other wastes added to this tank include fission product waste produced in campaigns (in the 1960s) to isolate various fission products, and ion exchange waste from the B Plant Cs recovery process.

2.1 Washing of Tank B-110 Sludge

The sample used in the washing study was a composite of the five segments obtained in the 1989 Core 1. A 5.15-g portion of this B-110 sludge (labeled B110-4) was slurried with 14.5 mL of 0.1 M NaOH, and 2.20 g (labeled B110-4-1) of the resulting slurry was used in this experiment. Assuming complete homogeneity of the slurry, portion B110-4-1 contained 0.58 g of B-110 sludge.

The sludge washing procedure is summarized in Figure 2.1. The washing procedure consisted of treating the sludge with two successive portions of 0.1 M NaOH (~3.5 mL/g sludge for each wash step) at 100°C. The sludge was then washed with water at room temperature to remove residual soluble material; the wash water was combined with the 0.1 M NaOH wash solutions for analysis. After each step, the sludge wash mixture was cooled to room temperature (if it had been heated). The mixture was then centrifuged, and the supernatant liquid was decanted. Upon completion of the sludge washing steps, the washed sludge was used in the caustic leaching experiment (Section 2.2). The sludge wash solution was analyzed by inductively coupled plasma atomic emissions spectroscopy (ICP) and radiochemical methods. Particle size analysis was performed on a portion of the washed sludge.

The percentage of each major sludge component found in the wash solutions is given in Table 2.1. The behavior of Na is not listed in Table 2.1 because the total amount of Na found in the sludge washing and caustic leaching experiments was dominated by the amount of NaOH added during the procedure (see Section 2.2). Another portion of B-110 sludge was washed with 0.1 M NaOH as part of the acid dissolution experiment (Section 2.3, Table 2.2). In that case, 93% of the Na was removed from the sludge in the washing procedure.

After Na, P was the most completely dissolved element (among those determined by ICP). The ICP analyses indicated that 84% to 87% of the P was in the sludge wash solution. The removal of

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(a) The sludge washing, caustic leaching, and acid dissolution experiments were conducted in plastic vials to avoid leaching Si from glass vials.

a significant portion of the P from the sludge by washing with dilute NaOH is important because, based on characterization data for B-110 sludge, P is the component that will likely dictate the volume of borosilicate glass produced in disposal of this waste. Preliminary estimates suggest that removing 85% of the P from the B-110 sludge would reduce the quantity of glass by approximately 50%.

Other components found in the sludge wash solution included Ca (10%), Cr (10%), and Si (25%). Dissolving these materials in the wash step is not expected to have a large impact on the disposal costs for the B-110 sludge.

The wash solutions were radiochemically analyzed for TRUs (total alpha), ^{90}Sr , and gamma emitters. The only gamma-emitting radioisotope found in the wash solutions was ^{137}Cs . The ^{137}Cs content of the sludge was $14.9 \mu\text{Ci/g}$ sludge, which was consistent with the average value of $14.7 \mu\text{Ci/g}$ sludge given in the Core 1 characterization report.^(a) The majority (82%) of the ^{137}Cs reported to the wash solution. The sludge wash solution contained $< 1.2 \times 10^{-4} \mu\text{Ci/mL}$ TRU and $1.8 \times 10^{-3} \mu\text{Ci/mL}$ ^{90}Sr , which represented $< 0.8\%$ of the TRU and 0.01% of the ^{90}Sr in the sludge, respectively.

Particle size analysis was performed on a sample of the washed B-110 sludge. The results were obtained in terms of the percentage of the total *number* of particles present in a given particle size range, and in terms of the percentage of the total particulate *volume* occupied by particles within a given particle size range (assuming the particles to be spheres). The results are presented in Figure 2.2. All the particles were less than $5 \mu\text{m}$ in diameter, and 90% were smaller than $1.5 \mu\text{m}$ in diameter. However, 70% of the volume occupied by the washed sludge particles consisted of particles greater than $2 \mu\text{m}$ in diameter.

2.2 Caustic Leaching of Tank B-110 Sludge

The washed B-110 sludge sample B110-4-1 (see Section 2.1) was digested in strong (2.3 to 3 M) NaOH solution at 100°C for a total of 10 h as summarized in Figure 2.1. Again, after each step, the sludge leach mixture was cooled to room temperature and centrifuged, then the supernatant liquid was decanted. The residual sludge was washed once with water to remove residual soluble materials; the water wash solution was combined with the caustic leach solutions for analysis. Upon completion of the sludge leaching steps, the leached sludge was sampled for particle size analysis, then was dissolved for analysis by treating with 3.2 mL of 1.9 M HNO_3 /0.6 M HF solution at 100°C for 1 h. The sludge leach solution and the dissolved sludge solution were analyzed by ICP and radiochemical methods.

The results of this caustic leaching experiment are given in Table 2.1. The most significant finding was that 13% of the P was dissolved in this step. Thus, the combination of sludge washing and caustic leaching removed $\geq 97\%$ of P from the B-110 sludge. Calcium, Cr, and Si were partially solubilized in the caustic leach step, and most of the ^{137}Cs remaining after the washing step dissolved under the caustic leach conditions. Aluminum, Fe, Mg, and Pb did not dissolve in either weak or strong NaOH solution. The caustic leach solution contained $< 1.2 \times 10^{-4} \mu\text{Ci/mL}$ TRU and $1.4 \times 10^{-2} \mu\text{Ci/mL}$ ^{90}Sr , which represented $< 0.8\%$ of the TRU and 0.09% of the ^{90}Sr in the sludge, respectively.

(a) Jones, T. E. 1990. *SST Waste Characterization Project: Core 1 Data Report*. Unpublished. Pacific Northwest Laboratory, Richland, Washington.

For most of the major sludge components, the quantities found in this experiment agreed with those given in the Core 1 characterization report.^(a) For example, 0.021 g Fe/g sludge was found here, whereas an average value of 0.017 g Fe/g sludge was reported in the Core 1 characterization document. Likewise, ~0.018 g P/g sludge was found in this work, whereas 0.016 g P/g sludge was reported in the Core 1 characterization document. The TRU content of the sludge was 0.20 $\mu\text{Ci/g}$ sludge, which agreed with the value of 0.25 $\mu\text{Ci/g}$ sludge reported earlier.^(a) The 220 μCi $^{90}\text{Sr/g}$ sludge found here agreed with the 217 $\mu\text{Ci/g}$ sludge reported earlier.

The results of the particle size analysis of the leached sludge are given in Figure 2.3. The probability number distribution graph indicates that virtually 100% of the particles were smaller than 2 μm in diameter, but the probability volume distribution graph indicates that a significant fraction (~25%) of the particulate volume was occupied by the particles larger than 2 μm in diameter. There appeared to be two general sets of particles. The first set consisted of particles in the range 0.2 to 2.4 μm in diameter and occupied ~70% of the particulate volume. The second set consisted of particles in the range 3 to 8 μm in diameter and occupied ~25% of the particulate volume. The probability number density graph for the caustic leached sludge (Figure 2.3) was similar to that for the washed sludge (Figure 2.2), but on average the particulate volume of the washed sludge was occupied by particles larger than those in the caustic-leached sludge.

Samples of the washed sludge and the caustic-leached sludge were provided to other workers for scanning electron microscopy (SEM) and x-ray diffraction (XRD) analyses. Those analytical results will be reported elsewhere.

2.3 Acid Dissolution of Tank B-110 Sludge

Another portion of the B110-4 slurry (see Section 2.1) was used for an acid dissolution test. In this experiment, the B-110 sludge was washed with 0.1 M NaOH, then was subjected to several different acid solutions to effect dissolution. The experimental procedure is summarized in Figure 2.4.

The sludge settling behavior was investigated in the first wash step. After settling for 95 h, the volume of the settled sludge was nearly constant at ~2.0 mL/g of unwashed sludge used. After performing the sludge settling test, the sludge was subjected to additional wash steps similar to those described in Section 2.1.

In the dissolution steps, the sludge was subjected to more stringent conditions with each subsequent step. The sludge was treated with, in succession, 0.1 M HNO_3 , 2 M HNO_3 , 1 M $\text{H}_2\text{C}_2\text{O}_4$, and 1.8 M HNO_3 /0.9 M HF; each treatment was for 1 h at 100°C. This series of steps completely dissolved the sludge.

The acid dissolution test results are presented in Table 2.2. The results of the sludge washing steps agree with those obtained earlier (Section 2.1). A large fraction of the sludge was dissolved by adjusting pH to 1 with HNO_3 , then heating at 100°C for 1 h. Treatment of the undissolved fraction with

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(a) Jones, T. E. 1990. *SST Waste Characterization Project: Core 1 Data Report*. Unpublished. Pacific Northwest Laboratory, Richland, Washington.

2 M HNO_3 at 100°C dissolved most of the remaining sludge. The residue remaining after dissolution in 2 M HNO_3 consisted primarily of a Si compound. Oxalic acid had little effect on dissolving this residual material, but treatment with 2 M HNO_3 plus 0.9 M HF effected complete dissolution.

In the pH 1 step, only 39% of the TRU material dissolved, thus such a treatment would not render the remaining solids non-TRU. The TRU material and ^{90}Sr were dissolved in 2 M HNO_3 . The total alpha content of the sludge was 0.20 (Table 2.1) to 0.29 (Table 2.2) $\mu\text{Ci/g}$ sludge. Gamma spectrometry revealed that ~65% of the TRU activity was due to ^{241}Am . The ^{90}Sr content was ~220 $\mu\text{Ci/g}$ sludge.

These results suggest that the B-110 sludge can be completely dissolved for advanced separation processes such as the transuranic extraction process (TRUEX) (Horwitz et al. 1985) and the Sr extraction process (SREX) (Horwitz, Dietz, and Fisher 1991). A two-step dissolution procedure is recommended (following sludge washing). First, the washed sludge should be treated with 2 M HNO_3 at 100°C. After a solid/liquid separation, the remaining solid should be digested at 100°C in 2 M HNO_3 plus 1 M HF. The two solutions can then be combined and clarified for processing.

Figure 2.1. Summary of Sludge Washing and Caustic Leaching Experiment for Tank B-110 Sludge

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Figure 2.2. Particle Size Analysis of Washed B-110 Sludge: a) Probability Number Density Graph, b) Probability Volume Denisty Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

Figure 2.3. Particle Size Analysis of Caustic-Leached B-110 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

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Figure 2.4. Summary of Sludge Washing and Acid Dissolution Experiment for Tank B-110 Sludge

Table 2.1. Washing and Caustic Leaching of Tank B-110 Sludge

<u>Component</u>	<u>g/g Sludge^(a)</u>	<u>Wash, %</u>	<u>Caustic Leach, %</u>	<u>Leached Sludge, %</u>
Al	1.5E-03⇌7.0E-04	≤27	≤26	≥47
Bi	2.5E-02⇌2.4E-02	≤2	≤1	≥97
Ca	9.0E-04	10	9	81
Cr	8.9E-04	10	54	36
Fe	2.1E-02	0	0	100
Mg	1.5E-04	0	0	100
P	1.9E-02⇌1.8E-02	87⇌84	13	≤3
Pb	1.3E-03⇌9.7E-04	≤14	≤13	≥73
Si	1.3E-02	25	49	26
Sr	2.2E-04	0	0	100

<u>Component</u>	<u>μCi/g Sludge</u>	<u>Wash, %</u>	<u>Caustic Leach, %</u>	<u>Leached Sludge, %</u>
Total Alpha	0.20	0	0	100
⁹⁰ Sr	220	0	0.1	99.9
¹³⁷ Cs	14.9	82	15	3
²⁴¹ Am(gamma)	0.13	0	0	100

(a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and leach solutions and in leached sludge, and dividing the total by the mass (in grams) of sludge used in the experiment.

Table 2.2. Washing and Acid Dissolution of Tank B-110 Sludge

Component	g/g Sludge ^(a)	Wash, %	pH=1, %	2 M HNO ₃ , %	1 M H ₂ C ₂ O ₄ , %	2 M HNO ₃ / 0.9 M HF, %
Al	1.5E-03↔1.1E-03	≤18	≥70	≤5	≤3	≤4
Bi	2.1E-02	0	14	85	1	0
Ca	8.7E-04	10	74	12	2	1
Cr	8.9E-04	10	59	31	0	0
Fe	2.0E-02	0	41	57	2	0
Mg	1.8E-04	9	84	5	1	2
Na	1.1E-01	93	7	0	0	0
P	1.8E-02	82	3	15	0	0
Pb	1.2E-03↔9.9E-04	≤11	70↔59	30↔26	≤2	≤2
Si	7.0E-03	31	49	3	1	16
Sr	2.4E-04	0	91	9	0	0

Component	μCi/g Sludge	Wash, %	pH=1, %	2 M HNO ₃ , %	1 M H ₂ C ₂ O ₄ , %	2 M HNO ₃ / 0.9 M HF, %
Total Alpha	0.29	0	39	59	1	1
⁹⁰ Sr	218	0	87	13	0	0
¹³⁷ Cs	14.6	72	27	1	0	0
²⁴¹ Am(gamma)	0.19	0	61	38	1	0

(a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and dissolved sludge solutions, and dividing the total by the mass (in grams) of sludge used in the experiment.

3.0 Washing, Caustic Leaching, and Dissolution of Tank C-109 Sludge

Experiments were conducted using sludge from SST 241-C-109 (hereafter referred to as C-109 sludge) to determine the quantity and composition of sludge remaining after sludge washing and caustic leaching. The efficacy of various acid solutions in dissolving this sludge was also investigated.^(a) The results of these experiments are reported in this section.

The primary waste type stored in Tank C-109 was that from the tributyl phosphate (TBP) uranium extraction process operated at U Plant. This waste is expected to contain various Na, Fe, and U salts. Wastes in such tanks were treated with ferrocyanide to scavenge ¹³⁷Cs from the supernatant solutions. Other wastes added to this tank include the first-cycle decontamination waste from the bismuth phosphate process, cladding (Al and/or Zr) wastes, and ion exchange waste from the B Plant Cs recovery process.

3.1 Washing of Tank C-109 Sludge

A small-scale sludge washing test was conducted using a portion of the composite sample of Core 47 taken from C-109 in 1992. The composite sludge sample had been diluted with 3 parts of water (by weight). An 8-g portion (labeled C109-1) of the diluted sludge was obtained for the sludge washing, caustic leaching, and acid dissolution experiments. Aqueous NaOH (0.06 mL of 10 M) was added to the slurry so that the wash solution was ~0.1 M NaOH. A 2.15-g portion (C109-1-1) of this slurry was taken for the sludge washing experiment. Assuming complete homogeneity of the slurry, portion C109-1-1 contained 0.53 g of the Core 47 composite sludge sample.

The sludge washing procedure is summarized in Figure 3.1. The washing procedure consisted of treating the sludge with two successive portions of 0.1 M NaOH (~3.5 mL/g sludge for each wash step) at 100°C. The sludge was then washed with water at room temperature to remove residual soluble material, and the wash water was combined with the 0.1 M NaOH wash solutions for analysis. After each step, the sludge wash mixture was cooled to room temperature (if it had been heated). The mixture was then centrifuged, and the supernatant liquid was decanted. Upon completion of the sludge washing steps, the washed sludge was dried at 50°C to a constant weight and was used in the caustic leaching experiment (Section 3.2). The sludge wash solution was analyzed by ICP and radiochemical methods. Particle size analysis was performed on a portion of the washed sludge.

The percentage of each major sludge component found in the wash solutions is given in Table 3.1. The behavior of Na is not listed in Table 3.1 because the total amount of Na found in the sludge washing and caustic leaching experiments was dominated by the amount of NaOH added during the procedure (see Section 3.2). Another portion of C-109 sludge was washed with 0.1 M NaOH as part of the

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(a) The sludge washing, caustic leaching, and acid dissolution experiments were conducted in plastic vials to avoid leaching Si from glass vials.

acid dissolution experiment (Section 3.3, Table 3.2). In that case, 76% of the Na from the sludge was dissolved in the washing procedure. It can be assumed that a comparable amount of the Na originally present in the sludge was removed during the wash step in this experiment.

Unlike B-110 sludge (see Section 2.0), the majority of the P contained in C-109 was not removed by sludge washing. The ICP analyses showed that only 33% of the P was in the sludge wash solution. Undissolved P may limit the usefulness of simple sludge washing for reducing the volume of HLW glass produced while vitrifying C-109 sludge.

Sludge washing removed only 8% of the Al from the C-109 sludge, so this pretreatment method would not be effective in removing Al from the HLW stream. Interestingly, 5% of the Fe in the sludge dissolved during washing. This may be due to solubilization of hexacyanoferrate species expected to be in this waste. A large fraction of the Cr (75% to 84%) in the sludge was removed by sludge washing. Although there is low tolerance for Cr in the Hanford Waste Vitrification Plant (HWVP) feed, further study is needed to determine if removing Cr from this sludge would significantly reduce the HLW glass volume.

The wash solutions were radiochemically analyzed for TRUs (total alpha), ^{90}Sr , ^{99}Tc , and gamma emitters (Table 3.1). The total alpha concentration in the sludge was $0.85 \mu\text{Ci/g}$ sludge, which agreed reasonably well with the value of $0.99 \mu\text{Ci/g}$ sludge reported earlier (Simpson, Borsheim, and Jensen 1993a). Very little TRU material (as indicated by the total alpha analysis) was in the wash solution. This solution contained $< 1.5 \times 10^{-4} \mu\text{Ci TRU/mL}$, which represented $< 0.3\%$ of the TRU material in the sludge.

The sludge wash solution contained an appreciable amount ($0.18 \mu\text{Ci/mL}$) of ^{90}Sr , which represented 0.5% of the total ^{90}Sr in the sludge. The measured concentration of ^{90}Sr in the sludge was $610 \mu\text{Ci } ^{90}\text{Sr/g}$. This value does not agree well with the value of $1,180 \mu\text{Ci } ^{90}\text{Sr/g}$ reported earlier (Simpson, Borsheim, and Jensen 1993a). These differences are likely due to analytical errors, because the ^{90}Sr analysis is difficult to perform.

As would be expected for pertechnetate ion, the majority of the ^{99}Tc was washed from the sludge with 0.1 M NaOH . Between 92% and 96% of the ^{99}Tc was in the wash solution.

The only gamma-emitting radioisotopes detected in the wash solutions were ^{137}Cs and ^{210}Pb . The ^{137}Cs content of the sludge was $405 \mu\text{Ci/g}$ sludge. Only 8% of the ^{137}Cs was in the wash solution. This may be due to the Cs being held by the ferrocyanide reported to be in Tank C-109. However, this is not supported by the ICP data, which indicated some solubility of Fe in the wash step, but not in the caustic leach step.

A small fraction (14%) of the ^{210}Pb dissolved in the wash step, and the remainder dissolved in the caustic leach step. This is consistent with the formation of $[\text{Pb}(\text{OH})_4]^{2-}$. The behavior of ^{210}Pb was different from that of the bulk Pb in the tank, indicating that the ^{210}Pb was present in a different chemical form than the bulk Pb. This is not surprising considering that the source of the bulk Pb (process chemicals) was different from that of the ^{210}Pb (decay of ^{238}U).

Particle size analysis was performed on a sample of the washed C-109 sludge. The results were obtained in terms of the percentage of the total *number* of particles present in a given particle size range, and in terms of the percentage of the total particulate *volume* occupied by particles within a

given particle size range (assuming the particles to be spheres). The results are presented in Figure 3.2. Virtually, all the particles were less than 8 μm in diameter, and 80% were smaller than 1.5 μm in diameter. Thus, the particles in washed C-109 sludge were on average somewhat larger than those in B-110 sludge. When considered by volume, 80% of the volume occupied by the washed sludge particles consisted of particles greater than 5 μm in diameter. The maximum particle size observed was $\sim 40 \mu\text{m}$ in diameter.

3.2 Caustic Leaching of Tank C-109 Sludge

The washed and dried C-109 sludge sample C109-1-1 (see Section 3.1) was digested in strong (3 M) NaOH solution at 100°C as summarized in Figure 3.1. Again, after each step, the sludge leach mixture was cooled to room temperature and centrifuged, and the supernatant liquid was decanted. Upon completion of the sludge leaching steps, the remaining sludge was dried to a constant weight. The sludge leach solution was analyzed by ICP and radiochemical methods. Particle size analysis was performed on a portion of the leached sludge.

The results of this caustic leaching experiment are given in Table 3.1. Only an additional 9% of the P was dissolved in this step. Thus, the combination of sludge washing and caustic leaching removed 42% of the P from the C-109 sludge. A large portion (73%) of the Al dissolved during caustic leaching; thus, the sludge washing and caustic leaching procedures removed a total 81% of the Al from the sludge. A small percentage of the Si (16%) was removed by sludge washing and caustic leaching; most of this (12%) was achieved during the caustic leaching step.

The caustic leach solution was radiochemically analyzed for TRUs (total alpha), ^{90}Sr , ^{99}Tc , and gamma emitters (Table 3.1). As was the case with the wash solution, very little TRU material (as indicated by the total alpha analysis) was in the caustic leach solution. This solution contained $< 1.5 \times 10^{-4} \mu\text{Ci TRU/mL}$, which represented $< 0.2\%$ of the TRU material in the sludge. As with the wash solution, the caustic leach solution also contained an appreciable amount ($0.072 \mu\text{Ci/mL}$) of ^{90}Sr , which represented 0.3% of the total ^{90}Sr in the sludge.

The amount of ^{99}Tc in the caustic leach solution was below the detection limit ($< 1.4 \times 10^{-4} \text{ Ci}/\mu\text{mL}$). Thus, $< 5\%$ of the ^{99}Tc was solubilized in this step. Four percent of the ^{99}Tc remained in the residual sludge, which suggested that this portion of the Tc was not present as pertechnetate ion.

As was the case with the wash solution, the only gamma-emitting radioisotopes found in the caustic leach solution were ^{137}Cs and ^{210}Pb . The behavior of these isotopes was discussed in the previous section.

The results of the particle size analysis of the leached sludge are given in Figure 3.3. The probability number distribution graph indicates that virtually 100% of the particles were smaller than 5 μm in diameter, but the probability volume distribution graph indicates that a significant fraction ($\sim 70\%$) of the particulate volume was occupied by the particles larger than 5 μm in diameter. As was observed for B-110 sludge, the particles in the caustic-leached C-109 sludge were on average smaller than those in the washed sludge. Based on the probability number distribution, the median particle size for the washed sludge was 0.95 μm in diameter, whereas that for the caustic-leached sludge was 0.76 μm in

diameter. Likewise, based on the probability volume distribution, the median particle size for the washed sludge was 13.49 μm in diameter, whereas that for the caustic-leached sludge was 9.55 μm in diameter.

Samples of the washed sludge and the caustic-leached sludge were provided to other workers for SEM and XRD analyses. Those analytical results will be reported elsewhere.

3.3 Acid Dissolution of Tank C-109 Sludge

A 4.3-g portion of the C109-1 slurry (see Section 3.1), containing 1.1 g of the Core 47 composite sample, was used for an acid dissolution test. In this experiment, the C-109 sludge was washed with 0.1 M NaOH, rinsed with water, and was subjected to several different acid solutions to effect dissolution. The experimental procedure is summarized in Figure 3.4.

The sludge settling behavior was investigated in the second wash step. After settling for 22 h, the volume of the settled sludge was nearly constant at ~ 2.4 mL/g of unwashed sludge used. After performing the sludge settling test, the sludge washing procedure in this experiment was similar to that described in Section 3.1.

For the first dissolution step, the washed sludge was slurried in 2 mL of water; the pH of the mixture was 11.49. The procedure called for the addition of concentrated HNO_3 to lower the pH to 1.0. However, due to a malfunction of the pH meter, too much HNO_3 was added (total of 0.489 g of conc. HNO_3 added). Titrimetric analysis indicated the HNO_3 concentration was 0.7 M. In subsequent dissolution steps, the conditions were increasingly more stringent. The sludge was successively treated with 0.7 M HNO_3 , 2 M HNO_3 , 1.8 M HNO_3 /0.9 M HF, and 1 M $\text{H}_2\text{C}_2\text{O}_4$; each treatment was for 1 h at 100°C. Finally, the residue was dried to a constant weight at 80°C. The weight of the undissolved residue was 0.35 g.

The results of the acid dissolution test are presented in Table 3.2. A large fraction of the washed sludge was dissolved in 0.7 M HNO_3 (100°C for 1 h). In particular, most of the Ca (91%), Pb (84%), and U ($\geq 54\%$) dissolved under these conditions. Treatment of the undissolved fraction with 2 M HNO_3 at 100°C resulted in further dissolution of these components. In addition, a total 64% (3% was in the wash solution) of the Fe in the sludge was solubilized at this point. Near-complete dissolution of La was achieved, and 56% of the Mn was dissolved. The combination of sludge washing and dissolution in HNO_3 (0.7 M followed by 2 M) solubilized 95% of the P contained in the sludge.

Significantly, the combination of sludge washing and dissolution in HNO_3 (0.7 M followed by 2 M) dissolved relatively little Al. Only 26% of the Al dissolved in these steps, and further treatment of the sludge with 1.8 M HNO_3 /0.9 M HF resulted in dissolution of only another 15% of the Al. After all dissolution steps, 59% of the Al remained undissolved. Because Al is a major sludge component, efforts should be made to maximize dissolution of this element. As discussed in the Section 3.2, $\sim 20\%$ of the Al in this sludge remained undissolved after a combination of sludge washing and caustic leaching. Thus, it is recommended that the C-109 sludge be subjected to sludge washing and caustic leaching before dissolving in acid. This approach would result in more complete sludge dissolution.

In addition to Al, the undissolved residue also contained a large portion of the Si (90%). This element may prove more difficult to dissolve, since only 16% dissolution of Si was achieved by washing and caustic leaching (Section 3.2). However, large loadings of Si are expected to be achievable in the HLW borosilicate glass form. The impact of the undissolved C-109 sludge on the quantity of HLW glass produced remains to be determined.

The radiochemical data are presented in Table 3.2. As was observed before (Section 3.1), the sludge wash solution contained little TRU material ($< 1.5 \times 10^{-4} \mu\text{Ci/mL}$). Nearly 90% of the TRU material dissolved in 0.7 M HNO_3 at 100°C. This was especially true for Am, 95% of which dissolved under these conditions. Most of the remaining TRU material dissolved in 2 M HNO_3 at 100°C. Similarly, 95% of the ^{90}Sr dissolved in 0.7 M HNO_3 . Treatment with 2 M HNO_3 and 1.8 M HNO_3 /0.9 M HF resulted in further dissolution of ^{90}Sr , but 2% of this radioisotope remained in the undissolved solids. Technetium-99 was detected only in the sludge wash solution; >95% of the ^{99}Tc was removed from the sludge by washing with 0.1 M NaOH.

The observed behavior of ^{137}Cs was very unexpected. The data indicate that 99% of the ^{137}Cs remained in the undissolved residue. This result must be called into question, since the quantity of ^{137}Cs in the sludge (7,170 $\mu\text{Ci/g}$) was found to be an order of magnitude higher in this experiment than in the sludge washing/caustic leaching experiment (405 $\mu\text{Ci/g}$). The latter value is more consistent with the value of 870 $\mu\text{Ci/g}$ found in the tank waste characterization program (Simpson, Borsheim, and Jensen 1993a). Thus, the ^{137}Cs data from this experiment are of questionable utility.

The results of this experiment suggest the C-109 sludge can be almost completely dissolved for advanced separation processes. A three-step dissolution procedure is recommended (following sludge washing). First, the washed sludge should be treated with 3 M NaOH at 100°C for several hours to maximize Al dissolution. Second, the caustic-leached sludge should be treated with 2 M HNO_3 at 100°C. After a solid/liquid separation, the remaining solid should be digested at 100°C in 2 M HNO_3 plus 1 M HF. The sludge wash and caustic leach solutions can be combined and processed by ion exchange to remove ^{137}Cs (and, if necessary, ^{90}Sr) before disposal as LLW. The two acidic dissolved sludge solutions can be combined and clarified for processing.

Figure 3.1. Summary of Sludge Washing and Caustic Leaching Experiment for Tank C-109 Sludge

Figure 3.2. Particle Size Analysis of Washed C-109 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

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Figure 3.3. Particle Size Analysis of Caustic-Leached C-109 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

Figure 3.4. Summary of Sludge Washing and Acid Dissolution Experiment for Tank C-109 Sludge

Table 3.1. Components Found During Washing and Caustic Leaching of Tank C-109 Sludge

Components	g/g Sludge ^(a)	Wash, %	Leach, %	Leached Sludge, %
Al	5.4E-02	8	73	19
Ba	1.7E-04 ~~1.2E-04~~	≤14	≤12	≥74
Bi	4.1E-03 ~~1.9E-03~~	≤29	≤25	≥46
Ca	8.0E-03	1	0	99
Cr	3.8E-04 ~~3.4E-04~~	84 ~~75~~	≤11	16 ~~14~~
Fe	9.1E-03	5	0	95
La	1.0E-3 ~~7.7E-04~~	≤14	≤12	≥74
Mn	8.6E-4 ~~8.1E-04~~	≤3	≤2	≥95
Nd	9.7E-04	21	12	67
P	7.4E-03	33	9	58
Pb	3.5E-3 ~~3.4E-03~~	≤4	41 ~~40~~	59 ~~56~~
Si	5.4E-03	4	12	84
Sr	1.8E-4 ~~1.4E-04~~	≤13	≤11	≥75
U	1.6E-2 ~~7.3E-03~~	≤29	≤26	≥45

Components	μCi/g Sludge	Wash, %	Leach, %	Leached Sludge, %
Total α	0.85	<0.3	<0.2	>99.5
^{239,240} Pu	0.51	0	0	100
²³⁸ Pu	0.011	0	0	100
²⁴¹ Am(α)	0.32	0	0	100
²⁴¹ Am(γ)	0.32	0	0	100
⁹⁰ Sr	610	0.5	0.3	99.3
⁹⁹ Tc	0.040	96 ~~92~~	<5	4
¹³⁷ Cs	405	8	90	2
⁶⁰ Co	0.071	0	0	100
¹⁵⁴ Eu	0.45	0	0	100
¹⁵⁵ Eu	0.50	0	0	100
²¹⁰ Pb	15	14	86	0

(a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and leach solutions and in the leached sludge, and dividing the total by the mass (in grams) of sludge used in the experiment.

Table 3.2. Components Found During Washing and Acid Dissolution of Tank C-109 Sludge

Components	g/g Sludge ^(a)	Wash, %	0.7 M HNO ₃ , %	2 M HNO ₃ , %	1.8 M HNO ₃ / 0.9 M HF, %	1 M H ₂ C ₂ O ₄ , %	Residual
Al	1.4E-01	2	17	7	15	1	59
As	2.1E-04↔3.1E-04	≤18	≤6	≤5	≤4	≤5	≥62
B	3.5E-04↔3.0E-04	≤9	≤3	≤2	83↔71	≥3	14↔12
Ba	2.5E-04↔2.4E-04	≤6	61↔57	≥11	≥3	≥4	21↔20
Bi	4.6E-03↔2.7E-03	≤17	70↔41	30↔17	≤3	≤5	≤17
Ca	1.2E-02	0	91	2	1	0	6
Cr	4.3E-04	69	22	3	0	0	7
Cu	1.5E-04↔1.3E-04	≤10	24↔22	≥5	≥4	4↔3	62↔56
Fe	1.6E-02	3	48	13	5	9	22
La	1.3E-03↔1.2E-03	≤6	49↔42	51↔43	≤1	≤2	≤6
Mg	9.7E-04↔7.3E-04	≤16	29↔22	≤4	4↔3	≤4	67↔50
Mn	1.4E-03	0	45	11	9	17	19
Na	5.7E-02	76	13	0	1	0	10
Nd	1.9E-03	7	42	4	2	3	42
P	9.5E-03	27	64	5	1	0	4
Pb	4.9E-03	0	84	5	1	1	9
Sb	3.5E-04↔1.9E-04	≤22	≤8	≤6	≤5	≤6	≥54
Si	4.9E-02	1	8	0	1	0	90
Sr	2.9E-04↔2.7E-04	≤5	65↔62	6↔5	≥1	0	28↔27
Ti	1.2E-03	0	2	1	1	1	96
U	1.9E-02↔1.0E-02	≤16	≥54	≤4	≤3	≤5	≤17
Zn	1.8E-04↔1.3E-04	≤17	78↔55	≤4	≤3	≤5	22↔15
Zr	4.0E-04↔3.8E-04	≤4	≥2	≤1	21↔20	≥1	76↔72

Table 3.2. (contd)

Components	$\mu\text{Ci/g Sludge}$	Wash, %	0.7 M HNO_3 , %	2 M HNO_3 , %	1.8 M HNO_3 / 0.9 M HF , %	1 M H $2\text{C}_2\text{O}_4$, %	Residue, %
Total α	1.17	0	88	10	0.5	0.5	1
$^{239,240}\text{Pu}$	0.49	0	82	14	3	0	1
^{238}Pu	0.012	0	69	13	0	0	18
$^{241}\text{Am}(\alpha)$	0.48	0	96	2	0	1	1
$^{241}\text{Am}(\gamma)$	0.43	0	95	5	0	0	0
^{90}Sr	1640	0	95	2	1	0	2
^{99}Tc	0.045-0.043	>94.9	<1.2	<0.9	<0.7	<0.9	<1.5
$^{137}\text{Cs}^{(b)}$	4,170	1	0	0	0	0	100
^{154}Eu	0.58	0	96	4	0	0	0
^{155}Eu	0.62	0	97	3	0	0	0
^{210}Pb	45	2	94	3	1	0	0

- (a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and leach solutions and in the leached sludge, and dividing the total found by the mass (in grams) of sludge used in the experiment.
- (b) The ^{137}Cs data may be erroneous (see text).

4.0 Washing, Caustic Leaching, and Dissolution of Tank C-112 Sludge

An experiment was conducted using sludge from SST 241-C-112 (hereafter referred to as C-112 sludge) to determine the quantity and composition of sludge remaining after sludge washing and caustic leaching. The efficacy of various acid solutions in dissolving this sludge was also investigated.^(a) The results of these experiments are reported in this section.

The primary waste type stored in Tank C-112 was from the TBP uranium extraction process operated at U Plant. This waste is expected to contain various Na, Fe, and U salts. Wastes in these tanks were treated with ferrocyanide to scavenge ^{137}Cs from the supernatant solutions. Other wastes added to this tank include the first-cycle decontamination waste from the bismuth phosphate process, cladding (Al and/or Zr) wastes, and ion exchange waste from the B Plant Cs recovery process. The waste in Tank C-112 should be similar to that in C-109.

4.1 Washing of Tank C-112 Sludge

A small-scale sludge washing test was conducted using a portion of actual C-112 sludge. The sample was a composite of the two segments obtained in the 1992 Core 36 from Tank C-112. The composite sludge sample had been diluted with 3 parts water (by weight). An 8-g portion (labeled C112-1) of the diluted sludge was obtained for the sludge washing and caustic leaching experiments. Aqueous NaOH (0.06 mL of 10 M) was added to the slurry so that the wash solution was ~ 0.1 M NaOH. A 2.30-g portion (C112-1-1) of this slurry was taken for the sludge washing experiment. Assuming complete homogeneity of the slurry, portion C112-1-1 contained 0.57 g of the Core 36 composite sludge sample.

The sludge washing procedure is summarized in Figure 4.1. The washing procedure consisted of treating the sludge with two successive portions of 0.1 M NaOH (~ 3.5 mL/g sludge for each wash step) at 100°C . The sludge was then washed with water at room temperature, and the wash water was combined with the 0.1 M NaOH wash solutions for analysis. After each step, the sludge wash mixture was cooled to room temperature (if it had been heated). The mixture was then centrifuged, and the supernatant liquid was decanted. Upon completion of the sludge washing steps, the washed sludge was dried to a constant weight at 50°C , then was used in the caustic leaching experiment (Section 4.2). The sludge wash solution was analyzed by ICP and radiochemical methods. Particle size analysis was performed on a portion of the washed sludge.

(a) The sludge washing, caustic leaching, and acid dissolution experiments were conducted in plastic vials, so that leaching of Si from glass vials would be avoided.

The percentage of each major sludge component found in the wash solutions is given in Table 4.1. The addition of Na during the wash and caustic leaching procedures made the tracking of this element difficult in this experiment. However, by accounting for the Na added in the procedure, the amount of Na originally in the sludge was estimated to be 0.10 g/g sludge. This value compared favorably to the value of 0.12 g Na/g sludge found during the characterization of Core 36 from Tank C-112 (Simpson, Borsheim, and Jensen 1993b). Of the Na originally in the sludge, ~80% was removed by sludge washing, as expected.

The extent of P dissolution in 0.1 M NaOH was intermediate between that for B-110 and C-109 sludges. The ICP analyses indicated that nearly 50% of the P was in the sludge wash solution. Because P is a major component of this sludge, removal of 50% of the P by sludge washing would likely have a favorable impact on lowering the volume of HLW glass produced in vitrification of this waste.

Sludge washing removed only 34% of the Al from the C-112 sludge, so this pretreatment method would not effectively remove Al from the HLW stream. Similar to what was observed for C-109 sludge, 3% of the Fe in the C-112 sludge dissolved during sludge washing. Again, this may be due to solubilization of hexacyanoferrate species expected to be in this waste. A significant fraction of the Cr (48%) in the sludge was removed by sludge washing. Although there is low tolerance for Cr in the HWVP feed, further study is needed to determine if removing Cr from this sludge would have much impact in reducing the HLW glass volume produced during vitrification.

The wash solutions were radiochemically analyzed for TRUs (total alpha), ^{90}Sr , ^{99}Tc , and gamma emitters (Table 4.1). The total alpha concentration in the sludge was 0.155 $\mu\text{Ci/g}$ sludge, which agreed well with the value of 0.17 $\mu\text{Ci/g}$ sludge reported earlier (Simpson, Borsheim, and Jensen 1993b). Very little TRU material (as indicated by the total alpha analysis) was in the wash solution. This solution contained $< 1.5 \times 10^{-4}$ $\mu\text{Ci TRU/mL}$, which represented $< 1.4\%$ of the TRU material in the sludge.

The sludge wash solution contained $< 1.5 \times 10^{-3}$ $\mu\text{Ci/mL}$ of ^{90}Sr . The measured concentration of ^{90}Sr in the sludge was 68 $\mu\text{Ci } ^{90}\text{Sr/g}$, which is an order of magnitude lower than the value of 510 $\mu\text{Ci } ^{90}\text{Sr/g}$ reported earlier (Simpson, Borsheim, and Jensen 1993b). These differences are likely due to analytical errors, because the ^{90}Sr analysis is difficult to perform. For the portion of sludge used in the acid dissolution test (Section 4.3), the ^{90}Sr content was 250 $\mu\text{Ci/g}$, which better agrees with the previously reported value of 510 $\mu\text{Ci/g}$.

As would be expected for pertechnetate ion, the majority of the ^{99}Tc was washed from the sludge with 0.1 M NaOH. Greater than 96.6% of the ^{99}Tc was in the wash solution.

The only gamma-emitting radioisotopes detected in the wash solutions were ^{137}Cs and ^{210}Pb . The ^{137}Cs content of the sludge was 870 $\mu\text{Ci/g}$ sludge, which agrees with the value of 800 $\mu\text{Ci/g}$ sludge reported earlier (Simpson, Borsheim, and Jensen 1993b). Only 9% of the ^{137}Cs was in the wash solution, while 89% dissolved in the caustic leach step. This behavior was similar to that observed for the

C-109 sludge (Table 3.1). Again, one possible explanation is that the Cs may be held by the ferrocyanide reported to be in Tank C-112. However, this is not supported by the ICP data, which indicated some solubility of Fe in both the wash step and the caustic leach step.

A small fraction (10%) of the ^{210}Pb dissolved in the wash step, and the remainder dissolved in the caustic leach step. This is consistent with the formation of $[\text{Pb}(\text{OH})_4]^{2-}$. The behavior of ^{210}Pb was different from that of the bulk Pb in the tank, indicating that the ^{210}Pb was present in a different chemical form than the bulk Pb. This is not surprising considering that the source of the bulk Pb (process chemicals) was different from that of the ^{210}Pb (decay of ^{238}U).

Particle size analysis was performed on a sample of the washed C-112 sludge. The results were obtained in terms of the percentage of the total *number* of particles present in a given particle size range, and in terms of the percentage of the total particulate *volume* occupied by particles within a given particle size range (assuming the particles to be spheres). The results are presented in Figure 4.2. Virtually all the particles were less than $8\text{ }\mu\text{m}$ in diameter, and 80% were smaller than $3\text{ }\mu\text{m}$ in diameter. Thus, the particles in washed C-109 sludge were on average somewhat larger than those in B-110 sludge. When considered by volume, 80% of the volume occupied by the washed sludge particles consisted of particles greater than $4\text{ }\mu\text{m}$ in diameter. The maximum particle size observed was $\sim 20\text{ }\mu\text{m}$ in diameter.

4.2 Caustic Leaching of Tank C-112 Sludge

The washed and dried C-112 sludge sample C112-1-1 (see Section 4.1) was digested in strong (3 M) NaOH solution at 100°C as summarized in Figure 4.1. Again, after each step, the sludge leach mixture was cooled to room temperature, then was centrifuged and the supernatant liquid decanted. Upon completion of the sludge leaching steps, the leached and washed sludge was dried to a constant weight at 50°C . The sludge leach solution was analyzed by ICP and radiochemical methods. Particle size analysis was performed on a portion of the leached sludge.

The results of this caustic leaching experiment are given in Table 4.1. An additional 36% of the P was dissolved in this step, bringing the total P removed from the sludge to 84%. Thus, it appears likely that simple washing and leaching steps can be employed to remove the bulk of the P from the C-112 sludge. The impact that this will have on the volume of HLW glass generated in the vitrification of this waste has not yet been assessed.

A large portion (51%) of the Al dissolved during caustic leaching. The sludge washing and caustic leaching procedure removed a total 85% of the Al from the sludge. This would likely have a favorable impact on lowering the quantity of HLW glass produced in vitrifying this waste. A small percentage of the Si (11%) was removed by sludge washing and caustic leaching; most of this (9%) was achieved during the caustic leaching step. The behavior of Si was similar to that in C-109 sludge (Section 3.2). An additional 40% of the Cr dissolved in the caustic leaching step. Thus, washing and caustic leaching resulted in the removal of 87% of the Cr from the sludge.

The caustic leach solution was radiochemically analyzed for TRUs (total alpha), ^{90}Sr , ^{99}Tc , and gamma emitters (Table 3.1). As was the case with the wash solution, very little TRU material (as indicated by the total alpha analysis) was in the caustic leach solution. This solution contained $<1.1 \times 10^{-4} \mu\text{Ci TRU/mL}$, which represented $<0.9\%$ of the TRU material in the sludge.

The caustic leach solution contained $<0.015 \mu\text{Ci/mL}$ of ^{90}Sr , and the amount of ^{99}Tc in the was below the detection limit ($<1.5 \times 10^{-4} \mu\text{Ci/mL}$). Thus, $<3\%$ of the ^{99}Tc was solubilized in this step. A small percentage ($\sim 1\%$) of the ^{99}Tc remained in the sludge.

As was the case with the wash solution, the only gamma-emitting radioisotopes found in the caustic leach solution were ^{137}Cs and ^{210}Pb . The behavior of these isotopes was discussed in the previous section.

The results of the particle size analysis of the leached sludge are given in Figure 4.3. The probability number distribution graph indicates that virtually 100% of the particles were smaller than $6 \mu\text{m}$ in diameter, and the probability volume distribution graph indicates that $\sim 80\%$ of the particulate volume was occupied by particles smaller than $6 \mu\text{m}$ in diameter. As was observed for the B-110 and C-109 sludges, the particles in the caustic-leached C-112 sludge were on average smaller than those in the washed sludge. Based on the probability number distribution, the median particle size for the washed sludge was $1.19 \mu\text{m}$ in diameter, whereas that for the caustic-leached sludge was $0.84 \mu\text{m}$ in diameter. Likewise, based on the probability volume distribution, the median particle size for the washed sludge was $6.63 \mu\text{m}$ in diameter, whereas that for the caustic-leached sludge was $4.09 \mu\text{m}$ in diameter.

Samples of the washed sludge and caustic-leached sludge were provided to other workers for SEM and XRD analyses. Those analytical results will be reported elsewhere.

4.3 Acid Dissolution of Tank C-112 Sludge

Another 1.05-g portion of composite C-112 sludge was used for an acid dissolution test. In this experiment, the C-112 sludge was washed with 0.1 M NaOH , then was subjected to several different acid solutions to effect dissolution. The experimental procedure is summarized in Figure 4.4.

The sludge settling behavior was investigated in the second wash step. After settling for 17 h, the volume of the settled sludge was nearly constant at $\sim 2 \text{ mL/g}$ of unwashed sludge. Following the sludge settling test, the sludge washing procedure in this experiment was similar to that described in Section 4.1.

In the dissolution steps, the sludge was subjected to more stringent conditions with each subsequent step. The sludge was treated with, in succession, 0.1 M HNO_3 (pH 1), 2 M HNO_3 , 1.8 M HNO_3 , 0.9 M HF , and $1 \text{ M H}_2\text{C}_2\text{O}_4$; all steps were conducted at 100°C . Finally, the residue was dried to a constant weight at 80°C . The weight of the undissolved residue was 0.43 g .

The results of the acid dissolution test are presented in Table 4.3. Ranges are given for many of the components due to the large analytical errors associated with analysis of the residual solids. Little of the washed sludge dissolved in HNO_3 at pH 1 (100°C for 1 h). Of the major sludge components, only Ca (66%) dissolved to any great extent under these conditions; modest amounts of the Al (18%) and Na (17%) dissolved at pH 1. Treatment of the undissolved fraction with 2 M HNO_3 at 100°C resulted in further dissolution of these components. In addition, a total 51% (1% was in the wash solution) of the Fe in the sludge was solubilized at this point. Most of the U dissolved in 2 M HNO_3 . The combination of sludge washing and dissolution in HNO_3 solubilized ~94% of the P contained in the sludge.

As with C-109 sludge (Section 3.3), the combination of sludge washing and dissolution in HNO_3 (0.1 M followed by 2 M) dissolved relatively little Al, only 35%. Further treatment of the sludge with 1.8 M HNO_3 /0.9 M HF dissolved only another 10% of the Al. After all dissolution steps, 37% of the Al remained undissolved. Because Al is a major sludge component, efforts should be made to maximize its dissolution. As discussed in the Section 4.2, ~15% of the Al in this sludge remained undissolved after a combination of sludge washing and caustic leaching. Thus, it is recommended that the C-112 sludge be subjected to sludge washing and caustic leaching before dissolving in acid. This approach would result in more complete sludge dissolution.

In addition to Al, the undissolved residue also contained a large portion of the Si (53%). This element may prove more difficult to dissolve, since only 11% of the Si was dissolved by washing and caustic leaching (Section 4.2). However, large loadings of Si are expected to be achievable in the HLW borosilicate glass form. The impact of the undissolved C-109 sludge on the quantity of HLW glass produced remains to be determined.

The radiochemical data are presented in Table 4.2. As was observed before (Section 4.1), the sludge wash solution contained little TRU material ($< 1.5 \times 10^{-4} \mu\text{Ci/mL}$). A relatively small percentage (~12%) of the TRU material dissolved at pH 1 (at 100°C). Of the TRU components, Am dissolved the best (56%) under these conditions. Plutonium was not detected in the pH 1 leach solution. Most of the remaining TRU material dissolved in 2 M HNO_3 at 100°C , but even after HNO_3 /HF and $\text{H}_2\text{C}_2\text{O}_4$ treatments, ~8% of the TRUs remained undissolved.

Sixty-three percent of the ^{90}Sr dissolved at pH 1, and another 36% dissolved in 2 M HNO_3 (at 100°C). Only 1% of the ^{90}Sr remained undissolved after the acid dissolution treatment.

As with C-109 sludge, the observed behavior of ^{137}Cs was very unexpected. The data indicate that 99% of the ^{137}Cs remained in the undissolved residue. Again, this result must be called into question, since the quantity of ^{137}Cs in the sludge ($27,000 \mu\text{Ci/g}$) was much greater in this experiment than in the sludge washing/caustic leaching experiment ($870 \mu\text{Ci/g}$). The latter value agrees with the value of $800 \mu\text{Ci/g}$ found in the tank waste characterization program (Simpson, Borsheim, and Jensen 1993b). Thus, the ^{137}Cs data from this experiment are of questionable use.

FY98_4-1.PPT

Figure 4.1. Summary of Sludge Washing and Caustic Leaching Experiment for Tank C-112 Sludge

39309052.2

Figure 4.2. Particle Size Analysis of Washed C-112 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

39310011.2

Figure 4.3. Particle Size Analysis of Caustic-Leached C-112 Sludge: a) Probability Number Density Graph, b) Probability Volume Density Graph, c) Probability Number Distribution Graph, and d) Probability Volume Distribution Graph

FY03_4-2.PPT

Figure 4.4. Summary of Sludge Washing and Acid Dissolution Experiment for Tank C-112 Sludge

Table 4.1. Washing and Caustic Leaching of Tank C-112 Sludge

Components	g/g Sludge ^(a)	Wash, %	Leach, %	Leached Sludge, %
Al	4.5E-03	34	51	15
B	9.2E-04↔8.4E-04	≤5	≤4	≥91
Bi	2.8E-03↔7.6E-04	≤39	≤34	≥27
Ca	1.1E-02	1	0	99
Cr	2.7E-04	48	40	13
Fe	1.8E-02	3	2	95
Mn	2.0E-04↔1.6E-04	≤11	≤10	≥79
Na	1.0E-01	81	4	15
Nd	2.8E-03	14	8	78
P	4.2E-02	48	36	16
Pb	1.0E-03↔7.7E-04	≤13	≤11	≥76
Si	9.8E-03	2	9	89
Sr	4.2E-4↔3.7E-04	≤5	≤5	≥90
U	1.1E-1↔9.9E-02	≤4	≤4	≥92
	μCi/g Sludge	Wash, %	Leach, %	Leached Sludge, %
Total α	0.155	<1.4	<0.9	>97.7
⁹⁰ Sr	68	0	<0.3	>99.7
⁹⁹ Tc	0.074↔0.072	>96.6	<2.6	>0.8
¹³⁷ Cs	870	9	89	2
¹⁵⁴ Eu	0.043	0	0	100
²¹⁰ Pb	71	10	90	0

(a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and leach solutions and in the leached sludge, and dividing the total by the mass (in grams) of sludge used in the experiment.

Table 4.2. Washing and Acid Dissolution of Tank C-112 Sludge

Components	g/g Sludge ^(a)	Wash, %	0.1 M HNO ₃ , %	2 M HNO ₃ , %	1.8 M HNO ₃ /0.9 M HF, %	1 M H ₂ C ₂ O ₄ , %	Residue, %
Al	1.1E-02	17	18	17	10	1	37
B	2.9E-03-2.8E-03	≤1	0	≤1	32-31	≤1	68-66
Bi	1.2E-02-1.3E-03	≤9	≤2	100-11	≤2	≤4	≤73
Ca	2.6E-02	0	66	20	1	0	13
Cr	1.4E-03-3.3E-04	46-10	≤3	28-6	13-3	13-3	≤74
Fe	6.8E-02	1	0	50	1	0	47
Mn	7.7E-04-3.3E-04	≤3	59-25	41-18	≤1	≤1	≤53
Na	1.6E-01	64	17	9	1	0	9
Nd	1.2E-03-9.5E-05	≤9	≤3	100-8	≤2	≤4	≤75
P	5.9E-02-5.6E-02	43-41	0	57-53	0	0	≤6
Pb	2.6E-03-1.3E-03	≤5	≤1	100-50	≤1	≤2	≤41
Si	2.8E-02	0	5	4	33	5	53
Sr	9.2E-04-7.6E-04	≤3	63-52	37-31	0	≤1	≤13
U	2.4E-01-1.9E-01	≤2	2	98-80	0	≤1	≤15
Components	μCi/g Sludge	Wash, %	0.1 M HNO ₃ , %	2 M HNO ₃ , %	1.8 M HNO ₃ /0.9 M HF, %	1 M H ₂ C ₂ O ₄ , %	Residue, %
Total α	0.19	<1.1	11.8-11.6	78.2-76.9	1.6-1.5	<0.5	8.5-8.4
^{239,240} Pu	0.084	0	0	94	2	0	5
²³⁸ Pu	0.007	0	0	61	16	2	21
²⁴¹ Am	0.031	0	56	20	0	0	24
^{243,244} Cm	0.008	0	24	19	0	0	57
²³⁷ Np	0.067	0	4	95	0	0	1
⁹⁰ Sr	250	0	63	36	0	0	1
¹³⁷ Cs ^(b)	27,000	0.1	0.0	0.3	0.1	0.0	99.5
¹⁵⁴ Eu	0.075	0	64	36	0	0	0

(a) The quantity of each component per gram of sludge was determined by summing the amounts found in the wash and leach solutions and in the leached sludge, and dividing the total found by the mass (in grams) of sludge used in the experiment.

(b) The ¹³⁷Cs data may be erroneous (see text).

5.0 Caustic and Acid Leaching of Tank U-110 Sludge

An experiment was conducted to test a caustic and acid leaching approach for pretreating sludge from SST U-110. Experiments conducted in FY 1992 suggested that this sludge can be decontaminated to a non-TRU level by leaching with 2 M HNO_3 at 100°C (Lumetta, Wagner, Colton, and Jones 1993). It was also found that a large fraction (~65%) of the Al was difficult to dissolve. In the experiment described here, a caustic leaching step was conducted on the U-110 sludge to maximize Al dissolution before leaching the sludge with acid. This was done to reduce the amount of Al in the acidic leach solution, which in turn might reduce the tendency for interfacial crud formation if the acidic leach solution is subjected to solvent extraction processes. The caustic leaching step was followed by treatment with K_2CO_3 . This treatment was an attempt to convert the Sr in the sludge to SrCO_3 so that it would be more soluble in acid. The sludge was then leached with 2 M HNO_3 and, finally, was dissolved in HCl and HF for analysis.

The experimental procedure was as follows: A 2.038-g sample of dry tank U-110 sludge was slurried with 5.306 g of 0.1 M NaOH. A 1.189-g portion (labeled U110-2B) of this slurry was taken for this leaching experiment. Assuming complete homogeneity of the slurry, portion U110-2B contained 0.33 g of dry sludge. Water (0.5 mL) and 10 M NaOH (1.5 mL) were added to U110-2B to give a mixture containing ~5 M NaOH. After stirring and heating for 1 h at 100°C, the sludge leach mixture was allowed to cool and was centrifuged. The supernatant solution was decanted and replaced with 3 mL of 5 M NaOH. This mixture was stirred and heated at 100°C for 5.5 h. After cooling, the mixture was centrifuged and the solution was decanted. The residual sludge was next washed with two 2-mL portions of 1 M K_2CO_3 . The carbonate washing was performed by mixing the sludge with the K_2CO_3 solution for 2 h at room temperature, centrifuging, and decanting. A third 2-mL portion of 1 M K_2CO_3 was added to the sludge, and the mixture was heated at 100°C for 5 h. After cooling, the mixture was centrifuged, and the solution was decanted. A fourth 2-mL portion of 1 M K_2CO_3 was added to the sludge, and the digestion at 100°C was repeated. After the last treatment with K_2CO_3 , the sludge was washed with 5 mL of water at room temperature. It was then subjected to leaching with three 2-mL portions of 2 M HNO_3 at 100°C (1 h heating time, centrifuged and decanted after each acid leach). After washing with 5 mL of water, the leached sludge was dissolved for analysis by treating with 1 mL of 12 M HCl at 100°C followed by 1 mL of 10 M HF at 100°C.

The results are summarized in Tables 5.1 and 5.2. Digestion of the Tank U-110 sludge with 5 M NaOH at 100°C resulted in better dissolution of Al (85%) than when the sludge was washed with 0.01 M NaOH before acid leaching (Lumetta, Wagner, Colton, and Jones 1993). In the latter case, 1% of the Al dissolved during sludge washing, 33% dissolved during 2 M HNO_3 leaching, and 66% remained undissolved. The other sludge components behaved in a manner similar to that seen in the previous study.

A certain fraction (35 to 49%) of P was removed from the U-110 sludge by the treatment with 5 M NaOH. An additional 18 to 51% of the P was removed by treating with K_2CO_3 . Because the recently proposed baseline for Hanford tank sludge pretreatment relies on sludge washing/leaching, it is important to achieve near-quantitative removal of P from the tank wastes. The data obtained in this work suggest that complete removal of P by leaching with NaOH is likely to be difficult. However, leaching the sludges with carbonate after the NaOH leach may improve P removal.

As was observed in the earlier work on U-110 sludge pretreatment, greater than 90% of the TRU material was found in the acid leach solution. The acid-leached sludge contained only ~4 nCi TRU/g dry sludge. The treatment with K_2CO_3 did not improve ^{90}Sr dissolution in the acid leach step; thus, there is no benefit in using the treatment (with regards to Sr dissolution). The ^{90}Sr content of the leached sludge was ~25,000 nCi/g dry sludge.^(a) The behavior of ^{137}Cs is noteworthy because a large fraction (~60%) of this radioisotope did not leach from the sludge even under strongly alkaline conditions. This behavior is consistent with results of previous studies in which only 10% of the ^{137}Cs was removed from the sludge by washing with 0.01 M NaOH (Lumetta, Wagner, Colton, and Jones 1993). In the experiment reported here, it is estimated that the leached sludge contained less than 25 nCi ^{137}Cs /g dry sludge. Thus, it is likely that the solids remaining after strong caustic leaching and acid leaching of U-110 sludge could be handled as a U.S. Nuclear Regulatory Commission (NRC) Class C LLW.

Table 5.1. Caustic and Acid Leaching of Tank U-110 Sludge: Nonradioactive Components

Component	g/g Sludge	% In Each Leach Solution			Leached Sludge, %
		NaOH	K_2CO_3	HNO_3	
Al	1.8E-01	79	4	5	12
Ba	1.8E-03↔1.7E-03	≤1	≤2	≥94	≤2
Ca	7.1E-03	52	26	20	2
Cr	3.2E-04↔2.1E-04	74↔47	≤20	26↔17	≤16
Fe	7.8E-03	1	0	72	27
Mg	5.4E-04	26	16	49	9
Mn	2.7E-03	0	0	28	72
P	1.3E-02↔7.0E-03	49↔35	51↔18	≤24	≤23
Si	7.4E-03↔7.1E-03	8	≤4	61↔59	31↔29
Sr	3.4E-04	0	0	100	0
Zn	1.2E-03	64	32	4	0

Table 5.2. Caustic and Acid Leaching of Tank U-110 Sludge: Radioactive Components

Component	nCi/g Sludge	% In Each Leach Solution			Leached Sludge, %
		NaOH, %	K_2CO_3 , %	HNO_3 , %	
^{137}Cs	18,800	31	7	62	0
^{90}Sr	300,000	0	6	87	7
Total Alpha	290	2	3	94	1

- (a) The data in Table 5.1 indicate that 100% of the Sr was found in the acid leach solution. The disagreement between the Sr data determined by ICP and that determined by radiochemical methods (Table 5.2) may be due to analytical errors at low Sr concentrations.

6.0 Dissolution of Tank AN-102 Sludge and Preliminary Solvent Extraction Tests

An experiment was conducted to determine the dissolution behavior of sludge from double-shell tank (DST) AN-102. Sludge washing and caustic leaching were not considered to be applicable pre-treatment operations for this sludge because the waste contained in this tank is complexant concentrate. The complexants present in this waste form aqueous-soluble TRU complexes, which result in a relatively high concentration (> 100 nCi/mL) of TRU in the alkaline supernatant solution. The sludge wash and caustic leach solutions would also likely contain soluble TRU, so these steps were not attempted with this sludge.

The dissolved 102-AN sludge solutions that were generated were used in preliminary TRUEX and SREX solvent extraction tests. The results from these tests are presented in Section 6.2.

6.1 Dissolution of Tank AN-102 Sludge

Samples of three sludge segments from Tank AN-102 are available. A portion of one segment (sample label 102AN-1-DISS) was used in this experiment; this portion represented the top layer of the sludge.

A 0.74-g portion of AN-102 sludge sample 102AN-1-DISS was slurried with 4 mL of water. The pH of this slurry was 12.22. Nitric acid (0.25 mL of 15.7 M) was added to lower the pH to 1.08. The mixture was stirred and heated at 100°C for 1 h and then was allowed to cool to room temperature. The supernatant solution was slightly cloudy, even after centrifuging for 2 h, but the solution cleared after standing overnight. The solution (A) was decanted and replaced with 1 mL of 0.1 M HNO_3 . After stirring at room temperature for 10 min, the mixture was centrifuged, then the supernatant solution was decanted and combined with A.

The residual sludge was treated with 2 mL of 2 M HNO_3 at 100°C for 1 h. After cooling to room temperature, the mixture was centrifuged and allowed to stand overnight. The solution (B) was decanted and replaced with 1 mL fresh 2 M HNO_3 . After stirring at room temperature for 10 min, the mixture was centrifuged, then the solution was decanted and combined with B. The remaining solid was dissolved by treating with 1 mL of 2 M HNO_3 plus 0.1 mL of 10 M HF (1.8 M HNO_3 /0.9 M HF solution) at 100°C for 1 h (solution C).

The three dissolved sludge solutions (pH 1, 2 M HNO_3 , and 1.8 M HNO_3 /0.9 M HF) were analyzed by ICP, IC, and radiochemical methods. The results are summarized in Tables 6.1 and 6.2.

A large fraction of the sludge dissolved in dilute HNO_3 at pH 1. The undissolved solids contained Al, Cr, Si, and U. The mass of the wet sludge was 0.41 g after the pH 1 treatment. Presumably, a large fraction of this mass was due to interstitial liquid. This wet sludge contained ~ 110 nCi of TRU material, thus the TRU content of the undissolved solids was > 270 nCi/g sludge. This material might require handling as HLW.

Treatment of the residual sludge with 2 M HNO_3 at 100°C resulted in additional dissolution of Cr, Si, and U, but minimal dissolution of the remaining Al. Nearly all the remaining TRU material dissolved in 2 M HNO_3 , so the residual solids might be handled as LLW. A more definitive test of this is needed.

The material that failed to dissolve in 2 M HNO_3 did dissolve in 1.8 M HNO_3 /0.9 M HF solution at 100°C. Thus, it is likely that nearly all the sludge in Tank AN-102 can be dissolved for advanced separation processing.

For the major gamma emitters in the sludge, nearly complete dissolution occurred at pH 1. The exception was for ^{40}K , of which only 57% dissolved at pH 1. The ICP data indicated 100% dissolution of K at pH 1 (Table 6.1). The discrepancy in the behavior of K has not been resolved.

6.2 Preliminary CMPO and SREX Tests

Preliminary octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (Horwitz et al. 1985) and SREX (Horwitz, Dietz, and Fisher 1991) tests were performed to determine if the 102-AN waste is amenable to pretreatment by these methods. Solutions A (4.0 mL), B (2.0 mL), C (1.5 mL), and 15.7 M HNO_3 (0.575 mL) were combined and mixed. The resulting solution was filtered (0.45- μm), then was contacted for 60 s with the CMPO process solvent (organic-to-aqueous ratio of 0.33).^(a) After mixing was stopped, two phases disengaged rapidly, with a dispersion number of 7.5×10^{-4} (Leonard et al. 1981). The aqueous solution was analyzed before and after contact with the CMPO solvent.

The results of the CMPO test are given in Table 6.3. The results indicated good extraction of both TRUs and U from the dissolved sludge solution. The behavior of HNO_3 and F ion were typical for the CMPO process. Distribution coefficients for the nonradioactive sludge components were all ~ 0.2 , indicating that the TRUs and U can be separated from the nonradioactive components using the CMPO process.

For the SREX process test, HNO_3 was added to the aqueous phase from the CMPO contact for an HNO_3 concentration of 4.17 M. The resulting solution was mixed with the SREX process solvent^(b) (organic-to-aqueous ratio of 0.33) for 60 s. As was the case with the CMPO contact, the two phases disengaged rapidly, with a dispersion number of 5.6×10^{-4} . The aqueous solution was analyzed before and after contact with the SREX solvent.

The results of the SREX test are given in Table 6.4. The results indicated good extraction of ^{90}Sr from the dissolved sludge solution. The behavior of HNO_3 was, as expected, based on the extraction of HNO_3 in the SREX process (Horwitz, Dietz, and Fisher 1991). No significant extraction of F or the nonradioactive sludge components was observed.

(a) The CMPO process solvent consisted of 0.2 M CMPO plus 1.4 M TBP in a normal paraffin hydrocarbon (NPH).

(b) The SREX process solvent consisted of 0.2 M di-t-butylcyclohexano-18-crown-6 in 1-octanol.

From these preliminary tests, it can be concluded that the CMPO and SREX processes are promising methods of removing TRUs and Sr, respectively, from dissolved AN-102 sludge.

Table 6.1. Acid Dissolution of Tank AN-102 Sludge: ICP Data

Component	g/g Sludge	pH 1, %	2 M HNO ₃ , %	1.8 M HNO ₃ / 0.9 M HF, %
Al	8.9E-03	92	1	7
Ca	6.3E-04	95	3	2
Cr	1.3E-03	72	13	15
Fe	5.0E-03	98	1	1
Mn	3.0E-04	97	2	1
Na	1.3E-01	100	0	0
P	≤ 1.6E-03, ≥ 1.0E-03	≥ 64	≤ 21	≤ 15
Si	1.7E-03	73	8	19
U	2.2E-03	59	18	22

Table 6.2. Acid Dissolution of Tank AN-102 Sludge: Radiochemical Data

Component	μCi/g Sludge	pH 1, %	2 M HNO ₃ , %	1.8 M HNO ₃ / 0.9 M HF, %
Total Alpha	5.0E-01	97	3	0
^{239,240} Pu	6.8E-02	88	10	2
²⁴¹ Am + ²³⁸ Pu	4.1E-01	98	2	0
^{243,244} Cm	2.1E-02	99	1	0
¹³⁷ Cs	2.5E+02	100	0	0
⁶⁰ Co	1.6E-01	99	1	0
¹⁵⁴ Eu	8.2E-01	99	1	0
¹⁵⁵ Eu	8.3E-01	99	1	0
²⁴¹ Am (gamma)	5.5E-01	99	1	0
⁴⁰ K	3.6E-02	57	43	0

Table 6.3. Results of the Preliminary TRUEX Test with Dissolved AN-102 Sludge

Component	Initial Aq. Conc.	Equil. Aq. Conc.	Equil. Org. Conc., ^(a)	D
TRU	3.79E-02 $\mu\text{Ci/mL}$	3.8E-03 $\mu\text{Ci/mL}$	1.02E-01 $\mu\text{Ci/mL}$	27
U	85.6 $\mu\text{g/mL}$	1.7 $\mu\text{g/mL}$	554 $\mu\text{g/mL}$	220
HNO ₃	1.99 M	1.79 M	0.60 M	0.3
Al	0.029 M	0.027 M	0.006 M	0.2
Ca	0.0013 M	0.0013 M	0 M	~0
Cr	0.0020 M	0.0019 M	0.0003 M	0.2
Fe	0.0017 M	0.0016 M	0.0003 M	0.2
Na	0.60 M	0.57 M	0.090 M	0.2
F	0.083 M	0.083 M	~0	~0

(a) Equilibrium organic concentrations were calculated by mass balance differences between the initial and equilibrium aqueous phases.

Table 6.4. Results of the Preliminary SREX Test with Dissolved AN-102 Sludge

Component	Initial Aq. Conc.	Equil. Aq. Conc.	Equil. Org. Conc., ^(a)	D
Sr-90	6.87 $\mu\text{Ci/mL}$	0.97 $\mu\text{Ci/mL}$	17.7 $\mu\text{Ci/mL}$	18
HNO ₃	4.17 M	3.72 M	1.35 M	0.36
Al	0.025 M	0.025 M	0 M	~0
Ca	0.0011 M	0.0012 M	0 M	~0
Cr	0.0017 M	0.0017 M	0 M	~0
Fe	0.0014 M	0.0014 M	0 M	~0
Na	0.514 M	0.506 M	0.024 M	0.05
F	0.0711 M	0.0705 M	0.0018 M	0.03

(a) Equilibrium organic concentrations were calculated by mass balance differences between the initial and equilibrium aqueous phases.

7.0 Selective Sludge Leaching

Two intermediate sludge processing concepts are discussed in this section: leaching TRUs from tank sludges, and leaching Cr from tank sludges. Although both approaches involve selective sludge leaching, they differ from one another in implementation. In the case of TRU leaching, the goal is to decontaminate the sludge so that it can be handled as LLW. This approach may be applicable to waste from many tanks. For the Cr leach approach, which is only applicable for wastes that are high in Cr (e.g., Plutonium Finishing Plant [PFP] sludge), the TRUs remain in the sludge, and the residual sludge is vitrified. The volume of glass is reduced because the glass volume would no longer be controlled by the amount of Cr present.

7.1 Leaching of TRUs from Alkaline Tank Sludge

In some instances, it might be useful to selectively leach TRU elements from alkaline tank sludges, without solubilizing the bulk components of the sludge. In this way, certain tank sludges might be decontaminated to the point that they could be handled as LLW. An experiment was conducted to test the feasibility of using complexants to leach TRUs from alkaline tank sludges. In this experiment, a Pu(IV)-traced $\text{Fe}(\text{OH})_3$ sludge was treated with three complexing agents at pH ~ 12 . The complexants were ethylenediaminetetraacetate (EDTA), 4,5-dihydroxy-1,3-benzenedisulfonate (Tiron®), and 1-hydroxyethane-1,1-diphosphonate (HEDPA). Approximately 0.1 g of the $\text{Fe}(\text{OH})_3$ sludge was treated with ~ 2.5 mL of 0.02 M complexant solution in each test.

The Pu(IV)-traced $\text{Fe}(\text{OH})_3$ sludge was formed by adjusting a Pu(IV)-traced $\text{Fe}(\text{NO}_3)_3$ solution to pH 13 with NaOH. After standing overnight at room temperature, the mixture was centrifuged, and the supernatant solution was decanted. The Pu-traced $\text{Fe}(\text{OH})_3$ sludge was slurred with 10 mL of water, then four 1-mL portions (Pu/Fe 1, Pu/Fe 2, Pu/Fe 3, and Pu/Fe 4) of the slurry were taken for the leaching tests. The leaching experiment was set up as described in Table 7.1. Pu/Fe 1 served as a blank to determine what happened in the absence of a complexant. The other three portions of $\text{Fe}(\text{OH})_3$ sludge were treated with ~ 0.02 M solutions of the complexants at pH 12 to 13. The sludge/complexant mixtures were stirred at room temperature for 22.5 h, then samples of the solution phase were taken for alpha counting. The mixtures were then stirred at 80°C for 1.75 h. After cooling, samples of the liquid phase were again drawn for alpha counting by liquid scintillation techniques.

The relative total alpha concentrations found in each leaching solution are presented in Table 7.1. For all three complexants tested, the supernatant solution had elevated alpha concentrations compared to the blank (Pu/Fe 1). However, Tiron® was the most effective at solubilizing the Pu.

To determine the percentage of Pu and Fe dissolved in the Tiron® leaching procedure, the leach solution from Pu/Fe 3 was separated, and the leached sludge was washed three times with 5 mL of water. The water wash solutions were combined with the Tiron® leach solution for analysis. The remaining sludge was then dissolved in 2.4 M HCl for analysis. Samples of the sludge leach solution and the dissolved sludge solution were analyzed by alpha counting and by ICP. The results are presented in Table 7.2. Greater than 70% of the Pu dissolved in the Tiron® solution, while only 2% of

the Fe dissolved; thus, Tiron® has a higher affinity for Pu(IV) than for Fe(III). These results suggest that Tiron® might be used to selectively remove Pu from alkaline tank sludges.

Based on the initial promising results, another set of leaching tests was conducted using Tiron® and the Pu(IV)-traced Fe(OH)₃ sludge. In this case, a 0.5-mL portion of the sludge/water slurry was transferred to each of 12 vials. Water was added to each vial in the quantities shown in Table 7.3. Tiron® was added either as a 0.1 M solution or as a solid as indicated in Table 7.3, to give final Tiron® concentrations of 0.01 or 0.1 M. For vials TIRON-1 and -2, 1 M HNO₃ (0.01 and 0.03 mL, respectively) was added to give pH ~ 11. For vials TIRON-7 and -8, the initial pH was 6.8; 10 M NaOH (0.05 mL) was added to give pH ~ 11. For vials TIRON-3, -4, -9, and -10, 10 M NaOH (0.1, 0.1, 0.18, and 0.18 mL, respectively) was added to give pH ~ 13. Finally, for vials TIRON-5, -6, -11, and -12, 10 M NaOH (0.5 mL each) was added to give pH ~ 13.5. The leach mixtures were stirred at room temperature or 100°C as indicated in Table 7.3. Those samples that were heated were held at 100°C for ~ 7 h, then were allowed to cool overnight. Total stirring time was ~ 24 h. Each sample was centrifuged, then the leach liquor was decanted. The sludge was washed with 5 mL of water, and the wash solution was combined with the leach liquor for analysis. The leached sludge was dissolved in 6 M HCl at 100°C for analysis. Both the leach and the dissolved sludge solutions were analyzed by ICP and by total alpha counting.

The results of this series of leaching tests are shown in Table 7.4. In general, heating the sludge leach mixture had little effect. However, in those cases where [Tiron®] was 0.1 M, and the pH was ≥ 13, there were some temperature effects. For example, in comparing TIRON-9 with TIRON-10, and TIRON-11 with TIRON-12, it appeared that increasing temperature increased dissolution of both Pu and Fe.

Increasing pH had a significant effect only when the Tiron® concentration was 0.1 M and the temperature was 100°C. This effect is seen in Figure 7.1, where the percentage of Pu leached is plotted as a function of pH. In the case of 0.1 M Tiron® at 100°C, the percentage of Pu leached increased with increasing pH. Likewise, the percentage of Fe found in the leach solution also increased with increasing pH in the 0.1 M Tiron®/100°C series of experiments. In all other cases, no significant effect of pH was observed.

Significant Tiron® concentration effects were observed only in those experiments where the pH was ≥ 13 and the mixtures were heated at 100°C. For example, in comparing TIRON-4 with TIRON-10, and TIRON-6 with TIRON-12, it appeared that increasing the Tiron® concentration increased dissolution of Pu (and Fe).

Overall, the results of these leaching tests were disappointing. The conditions that yielded the best leaching of Pu (high pH, high temperature), also resulted in significant dissolution of Fe. However, this approach was thought to still have merit, especially for wastes that are low in Fe, such as NCRW sludge.

A series of leaching tests was performed with actual NCRW sludge. A 0.9-g portion of NCRW sludge^(a) was mixed in ~ 10 mL of water for 1 h. After centrifuging, the supernatant solution was

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(a) The portion of NCRW sludge used in this experiment was derived from a composite sample of segments 3 to 6 from the May 1990 core sampling of Tank AW-105.

decanted. Ten milliliters of fresh water was added to the washed sludge, and the mixture was stirred. The resulting slurry was divided into six approximately equal portions. Water was added to each portion of slurry so that the total volume of each portion was 5 mL. Leaching tests were performed with four of these samples. One (portion 76F) was leached with silver persulfate in dilute HNO_3 (pH 1), one (portion 76H) was leached with Tiron® at pH 13, and the other two (portions 76E and 76G) served as blanks.

Nitric acid (0.07 mL of 12 M) was added to two portions (76E and 76F) of the NCRW slurry to adjust the pH to 1.07. Potassium persulfate and AgNO_3 were added to portion 76F to give concentrations of 0.5 M and 0.2 M, respectively. Both 76E and 76F were stirred overnight at room temperature. After centrifuging, two 0.1-mL aliquots of the supernatant solutions in 76E and 76F were taken for analysis. The mixtures were then stirred again and were heated at 50°C for 1 h. Again, the mixtures were centrifuged, and the supernatant solutions were sampled. The concentration of $\text{K}_2\text{S}_2\text{O}_8$ in 76F was then increased to 1.0 M, and 76E and 76F were stirred for 1 h at 60°C. After cooling, the supernatant leach liquors were decanted. The remaining sludge was first washed with 0.1 M HNO_3 , then was dissolved in 6 M HCl /1 M HF for analysis.

For the Tiron® leaching test, one portion (76H) of the NCRW slurry was made 0.1 M in Tiron®. The pH of portions 76G and 76H were adjusted to 13 with 10 M NaOH . The mixtures were stirred at room temperature for ~16 h. Aliquots of the supernatant solution were drawn for analysis. The mixtures were then stirred at 100°C for 5 h. After cooling, the mixtures were centrifuged and the leach liquor was decanted. The remaining sludge was first washed with water, then was dissolved in 6 M HCl /1 M HF for analysis.

The results from the NCRW sludge leaching tests are presented in Table 7.5. Clearly, leaching with silver persulfate was much more successful than leaching with Tiron®. Over 90% of the TRU activity was found in the silver persulfate leach solution. The fact that only 42% of the TRU activity was found in the corresponding blank (76E) indicates that the presence of an oxidant (e.g., silver persulfate) is essential to successfully leach TRUs in dilute acid solution. These results were consistent with those found earlier (Swanson 1991). More definitive tests of the silver persulfate leaching method are needed to determine if sufficient TRU can be leached from the NCRW sludge so that the leached sludge can be handled as LLW. However, the silver persulfate leaching method might not be very useful because ~50% of the Zr dissolved under the leaching conditions.

7.2 Leaching of Cr from Tank Sludges

One approach under consideration for minimizing the volume of borosilicate glass produced in vitrifying Hanford tank sludges involves selectively solubilizing (leaching) glass-limiting components of the sludges while leaving the TRU elements undissolved. The leached sludge could then be vitrified into a smaller volume of glass than if leaching had not been performed. For example, Cr is the limiting component in PFP sludge. It has been estimated that ~2,500 canisters of glass would be produced during vitrification of washed PFP sludge; removal of Cr would reduce the number of glass canisters to ~500 (Lumetta, Swanson, and Barker 1993).

Previous work has shown that Cr can be leached from PFP sludge by treatment with alkaline solutions of KMnO_4 (Lumetta and Swanson 1993a). The mechanism of Cr dissolution was determined to

involve formation of soluble Cr(VI) (as CrO_4^{2-}) from insoluble Cr(III). This approach suffers from the precipitation of one atom-equivalent of reduced Mn (as MnO_2) for each atom-equivalent of Cr dissolved; however, since the vitrification process is much more tolerant of Mn than Cr, this drawback is not severe. Still, an alternative that would not add to the mass of the sludge might be even more useful since this could even further decrease the number of glass canisters produced in the disposal of PFP sludge. Therefore, an examination of alternatives to permanganate for the selective dissolution of Cr was conducted.

A variety of potential methods to leach Cr(III) were tested using either $\text{Cr}(\text{OH})_3$ or Cr_2O_3 as the source of Cr(III). Several potential leaching agents were surveyed. Two classes of leaching agents were considered: oxidants and complexants. Oxidants work by changing the oxidation state of the insoluble Cr(III) to water soluble Cr(VI). For the purposes of this study, the oxidants had to meet two criteria. First, the redox potential of the reagent must be such that Cr(III) can be oxidized to Cr(VI):

Second, the oxidant itself and its reduced form must be soluble under the leaching conditions. Several potential oxidants were selected that satisfy these criteria: persulfate ($\text{S}_2\text{O}_8^{2-}$), potassium peroxymonosulfate (Oxone®, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), and perborate (BO_3^-). Oxidation with MnO_4^- was also investigated for comparison.

The second class of reagents was complexants, materials with large binding constants for Cr and that form water soluble complexes. Using these criteria, a sulfonated catechol, Tiron®, acetohydroxamic acid [$\text{CH}_3\text{C}(\text{O})\text{NH}(\text{OH})$], picolinic acid (pyridine-2-carboxylic acid), and ammonia were selected for investigation.

The effects of mixing and temperature on Cr(III) dissolution were investigated. The baseline condition involved vigorous stirring at room temperature for 1 h. In addition, the effect of heat (90°C with vigorous stirring for 1 h) and mixing (ultrasound sonication for 1 h at room temperature) were examined.

Another evaluated parameter was the effect of the initial form of the "insoluble" Cr(III) on Cr dissolution. For this reason, the potential leaching agents were tested on both Cr(III) oxide and on Cr(III) hydroxide. Chromium oxide, Cr_2O_3 , was reagent grade and was used as received. Chromium hydroxide, " $\text{Cr}(\text{OH})_3$," was provided by others at PNL. Analysis of the dried solid indicated the material was about 15% by weight Na and 26% by weight Cr. If the remainder of the material's weight was due to O (with a minor contribution from H), the empirical formula for the chromium hydroxide was more accurately represented by " $(\text{NaOH})_{1.3}\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$," with an equivalent weight of 209. Comparison of the infrared (IR) spectrum of the chromium hydroxide material to that of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ indicated there was no nitrate in the product.

In a typical experiment, three portions of either Cr_2O_3 [$\sim 20 \text{ mg}$, $\sim 0.263 \text{ meq Cr(III)}$] or $(\text{NaOH})_{1.3}\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ [$\sim 20 \text{ mg}$, $\sim 0.096 \text{ meq Cr(III)}$] and the leaching agent (in the proportions indicated in Table 7.2) were placed in each of three 150-mL beakers. One hundred milliliters of either 0.1 M NaOH or 0.01 M acid was added to each portion as indicated in Table 7.6. One of the mixtures

was stirred at room temperature (condition A), the second was placed in a sonicating bath (condition B), and the third was heated at 90°C (condition C). After 1 h, the amount of water that had evaporated from the third mixture was replenished. Forty-milliliter samples of each mixture were transferred to 50-mL centrifuge tubes and were centrifuged for at least 5 min at 3,000 rpm. Aliquots of the clarified solutions were analyzed spectrophotometrically for the presence of soluble chromium species. Both 1-cm and 0.1-cm pathlength cells were used as needed. Blank backgrounds were employed using solutions of the same composition as those of the experiment except for the presence of Cr.

Several control experiments were performed. First, conversion from $\text{Cr}_2\text{O}_7^{2-}$ to CrO_4^{2-} was verified to be rapid as the solution changed from acidic to alkaline, with the Cr(VI) in the form of CrO_4^{2-} in 0.1 M NaOH and in the form of $\text{Cr}_2\text{O}_7^{2-}$ in 0.1 M HNO_3 . Second, all the examined oxidants were shown to convert a soluble Cr(III) source, $\text{Cr}(\text{NO}_3)_3$, to Cr(VI) when the solution was heated to 90°C for 1 h with the ratio of Cr to oxidant being that used in the leaching tests. Finally, the UV-visible spectrum of $\text{Cr}(\text{NO}_3)_3$ was shown to be identical in either 0.01 M formic acid or 0.01 M HNO_3 .

The results of the Cr leaching experiments are summarized in Table 7.6. To establish a baseline, the extent of dissolution of the Cr(III) compounds in 0.01 M HNO_3 and 0.1 M NaOH was studied under conditions similar to those used in the tests with the leaching agents (Table 7.6, Experiments 1 to 12). Chromium(III) did not dissolve appreciably; under all three experimental conditions, less than 1 % of the Cr dissolved.

Permanganate was by far the most successful of the leaching agents examined. Of the three test conditions used (A, B, and C), those at 90°C were most effective, followed by sonication and room temperature stirring, respectively—a finding generally held for all the systems that were examined. The order of effectiveness is best explained as simply a temperature effect, since the sonicated solutions warmed slightly by the end of the contact time. Permanganate was effective under both basic and acidic conditions, with the heated solutions dissolving greater than 97% of the Cr in all cases. For these systems, the amount of Cr that dissolved was verified not only by measuring the amount of Cr(VI) formed, but by measuring the decrease in the amount of MnO_4^- present. Good agreement between these two indicators of Cr dissolution was obtained.

The other oxidants that were examined, persulfate, Oxone® (SO_5^{2-}) or perborate, were much less effective than MnO_4^- for Cr dissolution. Like MnO_4^- , the Cr(III) source had a marked influence on the effectiveness of the oxidant: all these oxidants were much more effective at oxidizing $\text{Cr}(\text{OH})_3$ than Cr_2O_3 .

The complexing agents were the least effective of all the reagents in dissolving insoluble Cr(III), whatever the source. These experiments were hampered by the fact the UV-visible spectra were much less sensitive to the presence of Cr than in the experiments with oxidants, due to the much smaller molar extinction coefficients for Cr(III) species compared to Cr(VI) species. Still, in no instance did the Cr(III) solids visibly dissolve and, even with the decreased sensitivity, if more than 10% of insoluble Cr(III) present had dissolved, its presence would have been readily detectable. Note that the complexing agents were tested only under basic conditions since competing protonation reactions would reduce their effectiveness under acidic conditions.

The poor results found with these complexing agents did not appear to result from the instability of the Cr compounds to hydrolysis in 0.1 M NaOH, which would cause any dissolved Cr(III) to reprecipitate. Two pieces of evidence were obtained to refute such an explanation. First, the solids found at the

conclusion of the reaction of Cr_2O_3 with complexants were the green color of Cr_2O_3 and not the black of $\text{Cr}(\text{OH})_3$. Second, a control experiment was conducted in which base was added to solutions of $\text{Cr}(\text{III})$ nitrate and complexing agent in the proportions used for the leaching experiments until the solutions were 0.1 M in hydroxide. In all cases, the solutions remained homogeneous, and UV-visible spectra (with their characteristic ~ 590 nm absorbance) were consistent with a $\text{Cr}(\text{III})$ species.

Chromium(III) is known to form the water soluble ammonia complex, $[\text{Cr}(\text{NH}_3)_6]^{3+}$. Indeed, adding $\text{Cr}(\text{NO}_3)_3$ to 2 M NH_4OH yielded a colored solution with a spectrum fairly similar to $\text{Cr}(\text{NO}_3)_3$ in 0.01 M HNO_3 . Thus, under these strong alkaline conditions, $\text{Cr}(\text{III})$ can be kept in solution by complexation with ammonia, which suggests that $\text{Cr}(\text{III})$ might be leached from alkaline tank sludges with ammonia. A series of experiments (Table 7.6, Experiments 19 to 24) was conducted to test this hypothesis. In all cases, less than 5% of the Cr was dissolved by treatment with 2 M NH_4OH . It appears that, even though the formation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is thermodynamically favored, the kinetics of its formation from solid $\text{Cr}(\text{OH})_3$ or Cr_2O_3 are such that a practical leaching procedure cannot likely be developed based on this chemistry.

Thus, based on results to date, the only generally effective method for leaching Cr from alkaline sludges involves treating the sludge with MnO_4^- at 90°C for at least 1 h. This treatment dissolves essentially all the $\text{Cr}(\text{III})$, but also results in the deposition of a stoichiometric equivalent of MnO_2 over conditions ranging from 0.1 M H^+ to 0.1 M OH^- . The reason for the unique effectiveness of permanganate versus other oxidants remains unclear.

Figure 7.1. Effect of pH on the Leaching of Pu with Tiron®

Table 7.1. Summary of Pu Leaching Experiment

	Slurry Samples			
	Pu/Fe 1	Pu/Fe 2	Pu/Fe 3	Pu/Fe 4
Complexant	None	0.5 mL 0.1 M EDTA	0.5 mL 0.1 M Tiron®	0.25 mL 0.2 M HEDPA
mL Water	2.5	2.0	2.0	2.25
mL 1 M NaOH	0	0	0	0.125
pH, initial	12.5	12.6	12.3	12.2
pH, final	12.4	12.5	11.8	12.0
Total alpha, RT ^(a)	0.0	62	1450	100
Total alpha, 80°C ^(b)	1	4	1550	42

(a) Total alpha activity (from Pu) in cpm/mL in the solution after the treatment at room temperature.

(b) Total alpha activity (from Pu) in cpm/mL in the solution after the treatment at 80°C.

Table 7.2. Leaching of Pu with Tiron®

	Pu	Fe
% in Leach Solution	72	2
% in Leached Sludge	28	98

Table 7.3. Experiment to Determine the Effects of pH, Temperature, and Tiron® Concentration on the Leaching of Pu(IV) from Fe(OH)₃ Sludge

Vial	Water, mL	0.1 M Tiron®, mL	Tiron®, g	[Tiron®] ^(a) , M	Temperature	pH
TIRON-1	4.0	0.5	0	0.01	R.T. ^(b)	10.6
TIRON-2	4.0	0.5	0	0.01	100°C	11.0
TIRON-3	4.0	0.5	0	0.01	R.T. ^(b)	13.0
TIRON-4	4.0	0.5	0	0.01	100°C	13.1
TIRON-5	3.5	0.5	0	0.01	R.T. ^(b)	13.6
TIRON-6	3.5	0.5	0	0.01	100°C	13.6
TIRON-7	4.5	0	0.166	0.1	R.T. ^(b)	11.7
TIRON-8	4.5	0	0.166	0.1	100°C	11.5
TIRON-9	4.5	0	0.166	0.1	R.T. ^(b)	13.0
TIRON-10	4.5	0	0.167	0.1	100°C	13.0
TIRON-11	4.0	0	0.166	0.1	R.T. ^(b)	13.6
TIRON-12	4.0	0	0.167	0.1	100°C	13.5

(a) Concentration of Tiron® in the leach solution.

(b) R.T. is room temperature.

Table 7.4. Results of Experiment to Determine the Effects of pH, Temperature, and Tiron® Concentration on the Leaching of Pu(IV) from Fe(OH)₃ Sludge

Vial	[Tiron®] ^(a) , M	Temperature	pH	In Leach Solution		In Leached Sludge	
				Fe, %	Pu, %	Fe, %	Pu, %
TIRON-1	0.01	R.T. ^(b)	10.6	2	24	98	76
TIRON-2	0.01	100°C	11.0	3	21	97	79
TIRON-3	0.01	R.T. ^(b)	13.0	2	21	98	79
TIRON-4	0.01	100°C	13.1	1	11	99	89
TIRON-5	0.01	R.T. ^(b)	13.6	1	23	99	77
TIRON-6	0.01	100°C	13.6	0	18	100	82
TIRON-7	0.1	R.T. ^(b)	11.7	21	21	79	79
TIRON-8	0.1	100°C	11.5	5	25	95	75
TIRON-9	0.1	R.T. ^(b)	13.0	3	22	97	78
TIRON-10	0.1	100°C	13.0	14	51	86	49
TIRON-11	0.1	R.T. ^(b)	13.6	4	28	96	72
TIRON-12	0.1	100°C	13.5	40	76	60	24

(a) Concentration of Tiron® in the leach solution.

(b) R.T. is room temperature.

Table 7.5. Results of NCRW Sludge Leaching Tests

Test	Description	TRU	Zr Leached, %
		Leached, %	
76E	Blank for silver persulfate	42	12
76F	Silver persulfate	91	49
76G	Blank for Tiron [●]	2	2
76H	Tiron [●]	9	7

Table 7.6. Summary of Cr Leaching Experiments

Experiment	Experimental Conditions	Cr(III) Source	Leachant	Eq. Cr(III), mmol	Eq. Leachant, mmol	Leachant/Cr(III)	Cr Dissolved, %
1	0.1M NaOH, A ^(a)	Cr ₂ O ₃	None	1.32	NA ^(b)	NA	< 1
2	0.1M NaOH, B ^(c)	Cr ₂ O ₃	None	1.32	NA	NA	< 1
3	0.1M NaOH, C ^(d)	Cr ₂ O ₃	None	1.32	NA	NA	< 1
4	0.1M NaOH, A	Cr(OH) ₃	None	0.096	NA	NA	< 1
5	0.1M NaOH, B	Cr(OH) ₃	None	0.096	NA	NA	< 1
6	0.1M NaOH, C	Cr(OH) ₃	None	0.096	NA	NA	< 1
7	0.01M HNO ₃ , A	Cr ₂ O ₃	None	0.263	NA	NA	< 1
8	0.01M HNO ₃ , B	Cr ₂ O ₃	None	0.263	NA	NA	< 1
9	0.01M HNO ₃ , C	Cr ₂ O ₃	None	0.263	NA	NA	< 1
10	0.01M HNO ₃ , A	Cr(OH) ₃	None	0.096	NA	NA	< 1
11	0.01M HNO ₃ , B	Cr(OH) ₃	None	0.096	NA	NA	< 1
12	0.01M HNO ₃ , C	Cr(OH) ₃	None	0.096	NA	NA	< 1
13	0.01M HCO ₂ H, A	Cr ₂ O ₃	None	0.263	NA	NA	< 1
14	0.01M HCO ₂ H, B	Cr ₂ O ₃	None	0.263	NA	NA	< 1
15	0.01M HCO ₂ H, C	Cr ₂ O ₃	None	0.263	NA	NA	< 1
16	0.01M HCO ₂ H, A	Cr(OH) ₃	None	0.096	NA	NA	< 1
17	0.01M HCO ₂ H, B	Cr(OH) ₃	None	0.096	NA	NA	< 1
18	0.01M HCO ₂ H, C	Cr(OH) ₃	None	0.096	NA	NA	< 1
19	2M NH ₄ OH, A	Cr ₂ O ₃	None	0.263	NA	NA	< 5
20	2M NH ₄ OH, B	Cr ₂ O ₃	None	0.263	NA	NA	< 5
21	2M NH ₄ OH, C	Cr ₂ O ₃	None	0.263	NA	NA	< 5
22	2M NH ₄ OH, A	Cr(OH) ₃	None	0.096	NA	NA	< 5
23	2M NH ₄ OH, B	Cr(OH) ₃	None	0.096	NA	NA	< 5
24	2M NH ₄ OH, C	Cr(OH) ₃	None	0.096	NA	NA	< 5
25	0.1M NaOH, A	Cr ₂ O ₃	KMnO ₄	0.263	0.4	1.52 to 1	ca. 16
26	0.1M NaOH, B	Cr ₂ O ₃	KMnO ₄	0.263	0.4	1.52 to 1	ca. 36
27	0.1M NaOH, C	Cr ₂ O ₃	KMnO ₄	0.263	0.4	1.52 to 1	ca. 97
28	0.1M NaOH, A	Cr(OH) ₃	KMnO ₄	0.096	0.096	1 to 1	ca. 13
29	0.1M NaOH, B	Cr(OH) ₃	KMnO ₄	0.096	0.096	1 to 1	ca. 17

Table 7.6. (contd)

Experiment	Experimental Conditions	Cr(III) Source	Leachant	Eq. Cr(III), mmol	Eq. Leachant, mmol	Leachant/Cr(III)	Cr Dissolved, %
30	0.1M NaOH, C	Cr(OH) ₃	KMnO ₄	0.096	0.096	1 to 1	ca. 60
31	0.01M HNO ₃ , A	Cr ₂ O ₃	KMnO ₄	0.263	0.264	1 to 1	ca. 22
32	0.01M HNO ₃ , B	Cr ₂ O ₃	KMnO ₄	0.263	0.264	1 to 1	ca. 68
33	0.01M HNO ₃ , C	Cr ₂ O ₃	KMnO ₄	0.263	0.264	1 to 1	ca. 98
34	0.01M HNO ₃ , A	Cr(OH) ₃	KMnO ₄	0.096	0.200	1 to 1	ca. 14
35	0.01M HNO ₃ , B	Cr(OH) ₃	KMnO ₄	0.096	0.200	1 to 1	ca. 14
36	0.01M HNO ₃ , C	Cr(OH) ₃	KMnO ₄	0.096	0.200	1 to 1	ca. 0
37	0.1M HNO ₃ , C	Cr ₂ O ₃	KMnO ₄	0.263	0.264	1 to 1	ca. 100
38	0.1M NaOH, A	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	0.525	2 to 1	ca. 0
39	0.1M NaOH, B	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	0.525	2 to 1	ca. 0
40	0.1M NaOH, C	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	0.525	2 to 1	ca. 1
41	0.1M NaOH, A	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	0.407	2 to 1	ca. 0
42	0.1M NaOH, B	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	0.407	2 to 1	ca. 0
43	0.1M NaOH, C	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	0.407	2 to 1	ca. 0
44	0.01M HNO ₃ , A	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	1.3	5 to 1	ca. 0
45	0.01M HNO ₃ , B	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	1.3	5 to 1	ca. 0
46	0.01M HNO ₃ , C	Cr ₂ O ₃	K ₂ S ₂ O ₈	0.263	1.3	5 to 1	ca. 2
47	0.01M HNO ₃ , A	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	1.3	7 to 1	ca. 0
48	0.01M HNO ₃ , B	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	1.3	7 to 1	ca. 3
49	0.01M HNO ₃ , C	Cr(OH) ₃	K ₂ S ₂ O ₈	0.096	1.3	7 to 1	ca. 37
50	0.01M HNO ₃ , A	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 3
51	0.01M HNO ₃ , B	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 13
52	0.01M HNO ₃ , C	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 3
53	0.01M HNO ₃ , A	Cr(OH) ₃	K ₂ S ₂ O ₈ + Ag(I)	0.096	1.3	7 to 1	ca. 4
54	0.01M HNO ₃ , B	Cr(OH) ₃	K ₂ S ₂ O ₈ + Ag(I)	0.096	1.3	7 to 1	not measured
55	0.01M HNO ₃ , C	Cr(OH) ₃	K ₂ S ₂ O ₈ + Ag(I)	0.096	1.3	7 to 1	ca. 18
56	0.1M HNO ₃ , C	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 5
57	0.01M HNO ₃ , A	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 2
58	0.01M HNO ₃ , B	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 13
59	0.01M HNO ₃ , C	Cr ₂ O ₃	K ₂ S ₂ O ₈ + Ag(I)	0.263	1.3	5 to 1	ca. 6.5
60	0.1M NaOH, A	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 0
61	0.1M NaOH, B	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 0

Table 7.6. (contd)

Experiment	Experimental Conditions	Cr(III) Source	Leachant	Eq. Cr(III), mmol	Eq. Leachant, mmol	Leachant/Cr(III)	Cr Dissolved, %
62	0.1M NaOH, C	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 3
63	0.1M NaOH, A	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 0
64	0.1M NaOH, B	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 0
65	0.1M NaOH, C	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 1
66	0.01M HNO ₃ , A	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 0
67	0.01M HNO ₃ , B	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 0
68	0.01M HNO ₃ , C	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 1
69	0.01M HNO ₃ , A	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 0
70	0.01M HNO ₃ , B	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 0
71	0.01M HNO ₃ , C	Cr(OH) ₃	Oxone®	0.096	0.400	2 to 1	ca. 20
72	0.1M HNO ₃ , C	Cr ₂ O ₃	Oxone®	0.263	0.529	2 to 1	ca. 18
73	0.1M NaOH, A	Cr ₂ O ₃	NaBO ₃	0.263	1.27	4.8 to 1	ca. 0
74	0.1M NaOH, B	Cr ₂ O ₃	NaBO ₃	0.263	1.27	4.8 to 1	ca. 0
75	0.1M NaOH, C	Cr ₂ O ₃	NaBO ₃	0.263	1.27	4.8 to 1	ca. 0
76	0.01M HNO ₃ , A	Cr ₂ O ₃	NaBO ₃	0.263	1.53	5.8 to 1	ca. 1
77	0.01M HNO ₃ , B	Cr ₂ O ₃	NaBO ₃	0.263	1.53	5.8 to 1	ca. 2
78	0.01M HNO ₃ , C	Cr ₂ O ₃	NaBO ₃	0.263	1.53	5.8 to 1	ca. 3
79	0.01M HNO ₃ , A	Cr(OH) ₃	NaBO ₃	0.096	1.27	6.5 to 1	ca. 3
80	0.01M HNO ₃ , B	Cr(OH) ₃	NaBO ₃	0.096	1.27	6.5 to 1	ca. 23
81	0.01M HNO ₃ , C	Cr(OH) ₃	NaBO ₃	0.096	1.27	6.5 to 1	ca. 39
82	0.1M HNO ₃ , C	Cr ₂ O ₃	NaBO ₃	0.263	1.53	5.8 to 1	ca. 0
83	0.1M NaOH, A	Cr ₂ O ₃	CH ₃ C(O)N(OH)H	0.263	1.33	5.1 to 1	< ca. 1
84	0.1M NaOH, B	Cr ₂ O ₃	CH ₃ C(O)N(OH)H	0.263	1.33	5.1 to 1	< ca. 3
85	0.1M NaOH, C	Cr ₂ O ₃	CH ₃ C(O)N(OH)H	0.263	1.33	5.1 to 1	< ca. 7
86	0.1M NaOH, A	Cr(OH) ₃	CH ₃ C(O)N(OH)H	0.096	1.00	5.1 to 1	ca. 0
87	0.1M NaOH, B	Cr(OH) ₃	CH ₃ C(O)N(OH)H	0.096	1.00	5.1 to 1	ca. 0
88	0.1M NaOH, C	Cr(OH) ₃	CH ₃ C(O)N(OH)H	0.096	1.00	5.1 to 1	ca. 0
89	0.1M NaOH, A	Cr ₂ O ₃	Tiron®	0.263	1.32	5 to 1	ca. 0
90	0.1M NaOH, B	Cr ₂ O ₃	Tiron®	0.263	1.32	5 to 1	ca. 0
91	0.1M NaOH, C	Cr ₂ O ₃	Tiron®	0.263	1.32	5 to 1	ca. 0
92	0.1M NaOH, A	Cr(OH) ₃	Tiron®	0.096	0.972	5 to 1	ca. 0
93	0.1M NaOH, B	Cr(OH) ₃	Tiron®	0.096	0.972	5 to 1	ca. 0
94	0.1M NaOH, C	Cr(OH) ₃	Tiron®	0.096	0.972	5 to 1	ca. 0
95	0.1M NaOH, A	Cr ₂ O ₃	PA ^(e)	0.263	1.32	5 to 1	ca. 0
96	0.1M NaOH, B	Cr ₂ O ₃	PA	0.263	1.32	5 to 1	ca. 0
97	0.1M NaOH, C	Cr ₂ O ₃	PA	0.263	1.32	5 to 1	ca. 0

Table 7.6. (contd)

Experiment	Experimental Conditions	Cr(III) Source	Leachant	Eq. Cr(III), mmol	Eq. Leachant, mmol	Leachant/ Cr(III)	Cr Dissolved, %
98	0.1M NaOH, A	Cr(OH) ₃	PA	0.096	0.972	5 to 1	ca. 0
99	0.1M NaOH, B	Cr(OH) ₃	PA	0.096	0.972	5 to 1	ca. 0
100	0.1M NaOH, C	Cr(OH) ₃	PA	0.096	0.972	5 to 1	ca. 0

(a) For condition A, the mixtures were stirred at room temperature.

(b) Not applicable.

(c) For condition B, the mixtures were sonicated.

(d) For condition C, the mixtures were stirred at 90°C.

(e) PA = picolinic acid.

8.0 Test of the TRUEX Flowsheet for NCRW Sludge

An experiment was conducted to test a flowsheet for pretreating NCRW sludge. The flowsheet was described in a recent report (Lumetta and Swanson 1993b) and is illustrated here in Figures 8.1 and 8.2. This experiment served primarily as a "dry run" for the design basis experiment (DBE), which was performed later in FY 1993.^(a) Because this experiment was a dry run for the DBE, a detailed set of analyses was not performed for the various process solutions. Rather, selected solutions were analyzed to show that the process was performing as expected. The experimental procedure tested all aspects of the flowsheet including sludge washing, sludge dissolution, extraction of U with TBP, and extraction of TRUs with CMPO.

The sample of NCRW sludge used in this experiment was a composite of several different NCRW sludge samples. These individual sludge samples and the amount of each sample used are listed in Table 8.1. The total weight of the moist composite sample was 10.3 g, and its volume was 6.2 mL.

8.1 NCRW Sludge Washing

Twenty milliliters of 0.1 M NaOH was added to the composite NCRW sludge sample, and the mixture was agitated for 35 min using a mechanical shaker. The sludge wash mixture was centrifuged for 5 min, then the supernatant solution was decanted. This procedure was repeated three times, so that the sludge was washed with a total of 80 mL of 0.1 M NaOH. The wash solution was filtered through a 0.45- μ m membrane filter. The solid material that filtered from the wash solution was combined with the washed sludge for dissolution (see Section 8.2).

The percentages of each major sludge component found in the sludge wash solution are given in Table 8.2. Much of the Cr (23%), Na (85%), Ni (39%), P (74%), and Si (45%) were removed from the sludge during the washing procedure; only 7% of the Al was removed. The partial removal of Cr and P might be significant because of the impact these elements have on the planned glass melter for HWVP. The solubilization of a significant portion of the Ni was unexpected; the reason for this is not clear. The Zr, lanthanides, and actinides were insoluble in 0.1 M NaOH, as expected. The sludge wash solution contained less than 0.15 nCi TRU/mL and thus, could likely be handled as LLW.

8.2 NCRW Sludge Dissolution

Water, HNO₃, and HF were added to the washed NCRW sludge to give a composition of ~2 M HNO₃ and 0.47 M HF. After these additions, the total volume of the mixture was 34 mL. The mixture was agitated for 2 h at room temperature using a mechanical shaker. There was considerable solid remaining after this treatment, so additional HNO₃ and HF were added to increase their concentrations to ~2.2 M, and 0.67 M, respectively (and the volume by 2 mL). The mixture was shaken overnight. After centrifuging for 5 min, the solution was decanted from the undissolved portion of the

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(a) The NCRW design basis experiment will be described in a separate report.

sludge. The dissolved sludge solution (solution A) was filtered through a 0.45- μm membrane filter. Solution A contained 2.4 M HNO_3 , 0.25 M Zr, 0.042 M Al, and 1.0 M F; thus, the $\text{F}/(\text{Zr} + \text{Al})$ ratio was 3.4.

The filtered solids were combined with the undissolved portion of the sludge, and 13 mL of 2 M HNO_3 /0.8 M HF was added; the total volume was 20 mL. After heating at 100°C for 1 h, the mixture was cooled to room temperature and was filtered through a 0.45- μm membrane filter to yield solution B. Solution B contained 2.3 M HNO_3 , 0.12 M Zr, 0.071 M Al, and 1.2 M F; thus, the $\text{F}/(\text{Zr} + \text{Al})$ ratio was 6.3. The undissolved residue was dissolved for analysis by two successive treatments with 12 M HCl (each for 1 h at 100°C), and finally by KOH fusion.

The percentages of each major sludge component found in the dissolved sludge solutions (A and B) and in the residue are given in Table 8.2. Virtually complete dissolution of most of the sludge components was achieved. Most notably, Al, Cr, Fe, La, P, U, and Zr were completely dissolved. Silicon appeared to be the dominant element in the undissolved residue.^(a) The relatively large amount of solid that did not dissolve in the two-step HNO_3 /HF treatment should have little impact on the volume of glass resulting from vitrification of the residue if it is predominantly a Si mineral. The relatively large amount of undissolved solids was unexpected. Apparently, the NCRW sludge sample used in this experiment contained a disproportionate amount of other material that had been left in the tank as a heel before NCRW was added.

8.3 Preparation of the Solvent Extraction Feed

Dissolved NCRW solutions A and B were filtered (0.45- μm) and combined to give a solution containing ~ 2.5 M HNO_3 and ~ 1 M HF as well as 0.2 M Zr. To avoid interfacial crud formation in the CMPO extraction cycle (Lumetta and Swanson 1993b), HF was added to yield a $\text{F}/(\text{Zr} + \text{Al})$ ratio of 4.7. To prevent Pu extraction by TBP, the Pu valence was adjusted to +3 by adding ascorbic acid to a concentration of 0.01 M. The solution was clear after standing at room temperature for 23 h. As a precaution, the solution was filtered before performing the solvent extraction contacts. The concentrations of the important sludge components in the feed solution are given in Table 8.3; this solution also contained 2.5 M HNO_3 and 1.2 M F.

8.4 TBP Extraction of U

Thirty-six milliliters of the feed solution was combined with 4.0 mL of 0.2 M HNO_3 and the resulting solution was shaken for 30 s with 8.0 mL of 30% TBP (in NPH). The phases were allowed to separate by gravity, and the time required for the phases to separate was measured along with the total height of the two-phase mixture, so that dispersion numbers could be calculated. The mixture was centrifuged for 1 min to ensure complete phase separation, then portions of the aqueous and organic phases were subjected to further contacts as indicated in Table 8.4. Selected samples were taken for ICP, radiochemical, and titrimetric analyses. Note that several errors were made in the volumes of the

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(a) Ni was also found in the undissolved solid. It is not clear whether this Ni originated in the NCRW sludge or was derived from the Ni crucible used in the KOH fusion procedure.

scrub and strip solutions used. Based on the flowsheet illustrated in Figure 8.2, the organic-to-aqueous phase ratio should have been 2.0 in the three scrub contacts and 3.33 in the first two strip contacts. These errors do not affect the validity of the conclusions drawn from this experiment.

The results of the TBP extraction steps are summarized in Table 8.3. Based on published data (HAPO 1955), the three TBP extraction contacts were expected to remove greater than 95% of the U from the dissolved sludge solution. This was indeed the case, as 99% of the U was extracted. Extraction of the other major sludge components was not observed. TRU material was not found in the carbonate strip solution from the TBP cycle, indicating that if any TRU extracted, it was successfully scrubbed from the TBP solvent.

8.5 Extraction of TRUs with CMPO

To more closely simulate the conditions of the CMPO extraction section resulting from the flowsheet in Figure 8.2, the aqueous phase from the third TBP extraction (TBP3) was diluted by a factor of 1.56 to give a composition of 1.74 M HNO_3 , 0.015 M $\text{H}_2\text{C}_2\text{O}_4$, ~0.6 M F, and 0.11 M Zr. The solution was mixed for 30 s with 0.2 M CMPO/1.4 M TBP in NPH (hereafter referred to as the CMPO solvent) at an organic-to-aqueous phase ratio of 0.29. Again, the phases were allowed to separate by gravity, and the required separation time was measured along with the total height of the two-phase mixture, so that dispersion numbers could be calculated. The mixture was centrifuged for 1 min to ensure complete phase separation, then portions of the aqueous and organic phases were subjected to further contacts as indicated in Table 8.5. Selected samples were taken for ICP, radiochemical, and titrimetric analyses.

The results of the CMPO extraction steps are summarized in Table 8.3. Near complete (99.5%) extraction of the TRUs was achieved in three extraction contacts [organic-to-aqueous (O/A) 0.29]. The overall decontamination factor (DF)^(a) achieved was 200. This DF is an order of magnitude less than that predicted by the Generic TRUEX Model (Lumetta and Swanson 1993b), but it is certainly adequate to meet the objectives of the NCRW pretreatment process. The reason for the lower than expected DF is unknown. As expected, La and U were extracted with CMPO. Also, a small, but significant, fraction of the Zr was extracted. Analysis of the organic phase from the first CMPO scrub contact (contact CSCRUB1A) indicated that 99% of the Zr that was extracted was removed from the solvent in this first scrub contact. The other major sludge components were not extracted.

One of the major issues concerning the application of the CMPO extraction process in pretreating Hanford tank wastes is the stripping agent to be used. Early work focused on using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) to strip the TRUs. Although this reagent was very effective as a

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(a) The decontamination factor is defined as the quantity of TRU in the solution before treatment, divided by the quantity after treatment.

stripping agent, it was unacceptable because of the excessive amount of P that would be introduced into the HLW stream (which would adversely affect the vitrification process).^(a)

In the experiment performed here, 0.01 M HNO₃ + 0.0015 M H₂C₂O₄ was used to strip the TRUs. A dilute HNO₃ strip alone might have been effective because the Pu had been reduced to Pu(III) before the solvent extraction steps. The trivalent actinides [e.g., Am(III) and Pu(III)] can be stripped from the CMPO solvent with dilute acid. However, a polishing strip step using a small volume of 0.01 M H₂C₂O₄ was also included to strip any Pu that was reoxidized to Pu(IV) during the scrub and strip steps. The results of this experiment indicate that this is a viable approach to stripping the TRUs from the CMPO solvent. The TRU content of the organic phase from strip contact CSTRIP1B was below detection limit (< 0.1 nCi/mL). No alpha activity was detected in either the organic or aqueous phases from the final contact with HEDPA (contact CSTRIP3), which was employed after the carbonate wash step as a polishing step for analytical purposes.

8.6 Other Results from the NCRW Pretreatment Test

Other data collected during the NCRW pretreatment experiment included dispersion numbers and the distribution behavior of HNO₃. The dispersion number (N_{Di}) is defined by the following equation:

$$N_{Di} = \frac{1}{t} \sqrt{\frac{h}{g}} \quad (8.1)$$

where t is the time for the two phases to separate in seconds, h is the total height of the two phases in meters, and g is the acceleration due to gravity = 9.81 m/s² (Leonard et al. 1981). The dispersion number for each solvent extraction contact is listed in Table 8.6. The phase disengagement behavior was favorable in all the solvent extraction contacts performed. Viable processes using centrifugal contactors can be designed for systems where the dispersion number is as low as 3×10^{-4} (R. Leonard, Argonne National Laboratory, personal communication). The dispersion numbers observed in this experiment were well above this limit.

The behavior of HNO₃ in the TBP and CMPO solvent extraction cycles is summarized in Table 8.7. The measured distribution coefficients for the TBP portion of the flowsheet are consistent with published data (HAPO 1955). The distribution behavior of HNO₃ in the CMPO contacts is also consistent with published data (Horwitz et al. 1985). However, the aqueous phase HNO₃ concentration in the last scrub contact (CSCRUB3C) was lower than expected from the Generic TRUEX Model

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(a) This conclusion was reached based on early flowsheets that did not consider separation of U from the TRUs. Under those conditions, the amount of HEDPA needed was determined by the amount of U present, because HEDPA complexes U (Lumetta and Swanson 1993c). Much less HEDPA would be required if U is removed by extraction with TBP, making this stripping agent much more attractive.

(GTM) predictions (Lumetta and Swanson 1993b). At this low acid concentration, the trivalent actinides would strip. Thus, the flowsheet will be modified for the actual DBE so that the acid concentration in the scrub steps is high enough to avoid stripping the TRUs.

Figure 8.1. Washing and Dissolution Flowsheet for Pretreating NCRW Sludge

Figure 8.2. Solvent Extraction Flowsheet for Pretreating NCRW Sludge

Table 8.1. Makeup of NCRW Composite Sample

<u>Tank</u>	<u>Core Date</u>	<u>Segments</u>	<u>Sample Label</u>	<u>Weight, g</u>
103-AW	1989	6 to 10	103AW-COMP	5.152
105-AW	1990	3	SOL# 3	1.126
105-AW	1990	4	SOL# 4	1.006
105-AW	1990	5	SOL# 5	1.005
105-AW	1990	6	SOL# 1	1.017
105-AW	1990	7	SEG# 7	1.025
			SOLIDS	

Table 8.2. Summary of the NCRW Washing and Dissolution Steps

	<u>g/g Sludge</u>	<u>Wash, %</u>	<u>Solution A, %</u>	<u>Solution B, %</u>	<u>Residue, %</u>
Al	7.2E-03	7	44	46	3
Ca	1.4E-03	5	75	18	2
Cr	2.6E-03	23	44	31	2
Fe	2.8E-03	0	66	31	3
La	4.0E-04	0	81	19	0
Mg	1.2E-04	0	73	23	4
Mn	7.7E-04	0	75	24	1
Na	1.6E-01	85	12	3	0
Ni	1.8E-04	39	37	11	13
P	1.8E-03 ↔ 1.1E-03	68 ↔ 46	≤ 15	32 ↔ 22	≤ 17
Si	1.2E-02	45	1	26	28
U	1.2E-02	≤ 5	81 ↔ 75	19 ↔ 18	≤ 2
Zr	8.3E-02	0	77	22	1

Table 8.3. Result of the NCRW Solvent Extraction Contacts

	Concentrations						
	Al, M	La, M	Na, M	Si, M	U, M	Zr, M	TRU,
SX Feed ^(a)	0.052	0.00064	0.24	0.024	0.0098	0.20	-- ^(b)
Aq. TBP1, Initial ^(c)	0.047	0.00058	0.22	0.021	0.0088	0.18	-- ^(b)
Aq. TBP1, Final	0.050	0.00060	0.23	0.023	0.0023	0.19	300
Org. TBP, Final ^(d)	0	0	0	0	0.0325	0	--
D ^(e)	~0	~0	~0	~0	14	~0	
Aq TBP3, Final	0.049	0.00058	0.22	0.022	8.7E-05	0.19	285
% Extracted by TBP	0.0	0.0	0.0	0.0	99.0	0.0	--
Aq. CMPO1, Initial	0.029	0.00036	0.13	0.013	5.1E-05	0.11	183
Aq. CMPO1, Final	0.029	0.00013	0.13	0.013	1.9E-06	0.11	23.8
Org. CMPO1, Final ^(c)	0	0.000792	0	0	1.7E-04	0	548
D ^(e)	~0	6.092633	~0	~0	89	~0	23
Aq. CMPO3, Final	0.029	<1.4E-5	0.13	0.013	1.1E-07	0.097	0.9
% Extracted by CMPO	0.0	>96	0.0	0.0	99.8	11.8	99.5

(a) The [F] in the feed solution was 1.2 M.

(b) TRU concentration could not be determined accurately due to U interference in the alpha spectrum.

(c) Calculated using the concentrations found in the feed solution.

(d) Calculated by mass balance from that found in the aqueous phase.

(e) The distribution coefficient, D, equals the concentration in the organic phase divided by the concentration in the aqueous phase.

Table 8.4. Solvent Extraction Contacts Performed to Simulate the TBP Extraction Cycle

Contact	O/A ^(a)	Aqueous Phase	Organic Phase
TBP1	0.20	See note (b)	8.0 mL 30% TBP
TBP2	0.20	37.5 mL aq from TBP1	7.5 mL 30% TBP
TBP3	0.20	35 mL aq from TBP2	7.0 mL 30% TBP
TSCRUB1	1.6	3.75 mL 0.2 M HNO ₃	6.0 mL org from TBP1
TSCRUB2	1.7	3.0 mL 0.2 M HNO ₃	5.0 mL org from TSCRUB1
TSCRUB3	1.6	2.5 mL 0.2 M HNO ₃	4.0 mL org from TSCRUB2
TSTRIP1	2.5	1.2 mL 0.25 M Na ₂ CO ₃	3.0 mL org from TSCRUB3
TSTRIP2	2.2	0.9 mL 0.25 M Na ₂ CO ₃	2.0 mL org from TSTRIP1
TSTRIP3	0.33	1.5 mL 0.2 M HEDPA	0.5 mL org from TSTRIP2

(a) O/A = organic-to-aqueous phase ratio.

(b) The aqueous phase for contact TBP1 consisted of 36 mL of adjusted feed solution plus 4 mL 0.2 M HNO₃.

Table 8.5. Solvent Extraction Contacts Performed to Simulate the CMPO Extraction Cycle

Contact	O/A ^(a)	Aqueous Phase	Organic Phase
CMPO1	0.29	— ^(b)	14.2 mL CMPO
CMPO2	0.29	5.0 mL aq from CMPO1	1.45 mL CMPO
CMPO3	0.29	2.5 mL aq from CMPO2	0.725 mL CMPO
CSCRUB1AA	0.75	16 mL Scrub Solution 1 ^(c)	12 mL org from CMPO1
CSCRUB1BB	0.75	14.7 mL Scrub Solution 1	11 mL org from CSCRUB1A
CSCRUB2AA	1.00	10 mL Scrub Solution 2 ^(d)	10 mL org from CSCRUB1B
CSCRUB2BB	1.00	9 mL Scrub Solution 2	9.0 mL org from CSCRUB2A
CSCRUB2CC	1.00	8 mL Scrub Solution 2	8.0 mL org from CSCRUB2B
CSCRUB2DD	1.00	7 mL Scrub Solution 2	7.0 mL org from CSCRUB2C
CSCRUB3AA	1.50	4 mL 0.01 M HNO ₃	6.0 mL org from CSCRUB2D
CSCRUB3BB	1.50	3.67 mL 0.01 M HNO ₃	5.5 mL org from CSCRUB3A
CSCRUB3CC	1.50	3.33 mL 0.01 M HNO ₃	5.0 mL org from CSCRUB3B
CSTRIP1A	0.43	10.5 mL Strip Solution 1 ^(e)	4.5 mL org from CSCRUB3C
CSTRIP1B	0.43	9.3 mL Strip Solution 1	4.0 mL org from CSTRIP1A
CSTRIP2A	3.00	1.17 mL 0.01 M H ₂ C ₂ O ₄	3.5 mL org from CSTRIP1B
CSTRIP2B	3.00	1.0 mL 0.01 M H ₂ C ₂ O ₄	3.0 mL org from CSTRIP2A
CSTRIP2C	3.00	0.83 mL 0.01 M H ₂ C ₂ O ₄	2.5 mL org from CSTRIP2B
CSTRIP2D	3.00	0.67 mL 0.01 M H ₂ C ₂ O ₄	2.0 mL org from CSTRIP2C
CWASH	9.60	0.16 mL 0.25 M Na ₂ CO ₃	1.5 mL org from CSTRIP2D
CSTRIP3	0.33	1.5 mL 0.2 M HEDPA	0.5 mL org from CWASH

(a) O/A = organic-to-aqueous phase ratio.

(b) The aqueous phase for contact CMPO1 consists of 30 mL of the aqueous phase from contact TBP3 plus 4.8 mL 0.15 M H₂C₂O₄ plus 4.8 mL 5.0 M HNO₃ plus 9.6 mL 0.01 M HNO₃.

(c) Scrub solution 1 consists of 0.04 M H₂C₂O₄ in 1.3 M HNO₃.

(d) Scrub solution 2 consists of 1.67 M HNO₃.

(e) Strip solution 1 consists of 0.0015 M H₂C₂O₄ in 0.01 M HNO₃.

Table 8.6. Dispersion Numbers from the NCRW Solvent Extraction Contacts

<u>Contact</u>	<u>Height, mm</u>	<u>Time, s</u>	<u>N_{Di}</u>
TBP1	99	160	6.3E-04
TBP2	94	170	5.8E-04
TBP3	89	169	5.6E-04
TSCRUB1	36	44	1.4E-03
TSCRUB2	47	66	1.0E-03
TSCRUB3	39	52	1.2E-03
TSTRIP1	25	55	9.2E-04
TSTRIP2	18	50	8.6E-04
CMPO1	42	72	9.1E-04
CMPO2	40	85	7.5E-04
CMPO3	26	80	6.4E-04
CSCRUB1A	63	80	1.0E-03
CSCRUB1B	59	32	2.4E-03
CSCRUB2A	46	28	2.4E-03
CSCRUB2B	41	64	1.0E-03
CSCRUB2C	37	64	9.6E-04
CSCRUB2D	53	64	1.1E-03
CSCRUB3A	37	72	8.5E-04
CSCRUB3B	33	75	7.7E-04
CSCRUB3C	30	76	7.3E-04
CSTRIP1A	30	52	1.1E-03
CSTRIP1B	42	24	2.7E-03
CSTRIP2A	29	64	8.5E-04
CSTRIP2B	24	57	8.7E-04
CSTRIP2C	25	56	9.0E-04
CSTRIP2D	21	49	9.4E-04

Table 8.7. Behavior of HNO₃ in the TBP and CMPO Extraction Cycles

<u>Contact</u>	<u>[HNO₃], aq.</u>	<u>[HNO₃], org.</u>	<u>D, HNO₃</u>
Initial Aq. TBP1	2.24		
TBP1	2.16	0.42	0.19
TBP2	2.08	0.41	0.20
TBP3	2.01	0.41	0.20
TSCRUB1	0.69	0.12	0.17
TSCRUB2	0.51	0.05	0.10
TSCRUB3	0.41	0.01	0.02
CMPO1	1.52	0.49	0.32
CMPO2	1.41	0.47	0.33
CMPO3	1.26	0.4	0.32
CSCRUB1A	1.33	0.32	0.24
CSCRUB1B	1.31	0.37	0.28
CSCRUB2A	1.57	0.64	0.41
CSCRUB2B	1.65	0.69	0.42
CSCRUB2C	1.62	0.64	0.40
CSCRUB2D	1.64	0.41	0.25
CSCRUB3A	0.58	0.3	0.52
CSCRUB3B	0.23	0.13	0.57
CSCRUB3C	0.09	0.05	0.56
CSTRIP1A	0.01		

9.0 Alternative NCRW CMPO Flowsheet

As an alternative to the TRU extraction flowsheet shown in Figure 8.2, the separation of TRUs from the main components of NCRW sludge (including U) might be achieved without using a TBP cycle or a complexant (e.g., $\text{H}_2\text{C}_2\text{O}_4$) stripping agent. In this alternative approach, the solution used to strip the CMPO extract consists of dilute HNO_3 plus a reducing agent to adjust the Pu valence to +3. The trivalent actinides, Am(III) and Pu(III), would be stripped by the dilute acid solution, while most of the U would remain in the solvent. This approach was studied using a simulated dissolved NCRW solution. The goal of the study was to demonstrate 1) efficient extraction of TRUs from the dissolved sludge solution, 2) selective stripping of Am and Pu, and 3) removal of the U left in the organic phase after the selective TRU strip.

This study consisted of three tasks. First, an appropriate Pu reductant was selected. Ascorbic acid was chosen because of its mild reducing power ($E_0 = 0.127 \text{ V}$ at pH 5.0) and the innocuous nature of the reducing agent and its reaction products. Experiments designed to verify the speed and efficacy of an ascorbic acid reduction of Pu(IV) were undertaken. Second, the GTM (Vandegrift et al. 1992) was used to predict TRU distribution behavior for a given flowsheet. Third, a series of batch contacts designed to simulate the chosen flowsheet was performed to measure the actual Pu and U distribution values.

9.1 Ascorbic Acid Reduction of Pu(IV)

The ability of ascorbic acid to lower the Pu distribution coefficients in the CMPO process (by reducing Pu to the +3 oxidation state) was tested. Previously published research (Mincher 1989) indicated the distribution coefficients of Pu(III) and Am(III) are nearly identical for given extraction conditions. Thus, it was expected that, like Am(III), Pu(III) would be stripped from the CMPO solvent with dilute HNO_3 . A comparison was undertaken of the distribution coefficients of Am and Pu in the presence of ascorbic acid. Reduction of Pu(IV) by ascorbic acid under the conditions of the experiment would result in Pu distribution coefficients the same as those for Am.

Nitric acid solutions containing 0.1 M ascorbic acid were traced with Pu(IV) or Am(III) and then were immediately mixed with an equal volume of the CMPO solvent at room temperature for 60 s. After centrifuging to ensure phase separation, the alpha activity of each phase was determined by liquid scintillation counting. The results are given in Table 9.1

The distribution coefficients for Am and Pu were remarkably close--within 10% at the high acid end--indicating that effective Pu reduction occurred in the time of a normal distribution measurement, i.e., 60 s of vortex mixing. Ascorbic acid should thus be a suitable reagent for reductively stripping Pu from the CMPO process solvent.

9.2 Use of the GTM to Model the Alternative CMPO Flowsheet

The GTM was used to model the 17-stage countercurrent extraction system illustrated in Figure 9.1. Two different scenarios were modeled. In the first scenario, the HNO_3 concentration in the

strip solution (entering at stage 15) was set at 0.01 M, while in the second scenario, the HNO₃ concentration in the strip solution was set at 0.1 M.

The compositions of the various entering and exiting streams predicted by the GTM are given in Tables 9.2 and 9.3 for the 0.01 M HNO₃ case and the 0.1 M HNO₃ case, respectively. The GTM results indicated that the strip solution must be around 0.1 M in HNO₃ if the U is to be significantly retained in the organic stream; that is, if *selective* stripping of TRUs is to be achieved.

9.3 Test of the Alternative CMPO Flowsheet with Simulated NCRW

Based on the GTM results, a series of batch contacts was performed to simulate the scrubbing and stripping portions of the CMPO flowsheet with the reductive strip option; Table 9.4 summarizes the batch contacts. The simulated dissolved NCRW feed solution for the flowsheet test was composed of the following: 1.5 M HNO₃, 0.8 M HF, 0.16 M Zr(IV), 0.16 M Na⁺, 0.0007 M La(III), 0.0036 M U(VI).^(a) The distribution coefficients for U(VI) and Pu(IV) were measured by liquid scintillation counting techniques. The behaviors of U(VI) and Pu(IV) were determined separately. That is, contacts were performed for a feed solution containing U, then an identical set of contacts was performed with a Pu-traced feed solution that did not contain U. This procedure was necessary for the counting method used here because the alpha activity from U is not distinguishable from that due to Pu. The results are given in Table 9.5.

The results of the experiment indicate that 7% of the U would end up in the HLW stream and 93% in the LLW stream. Only qualitative comparison of the experimental results to the GTM predictions can be made because 1) the feed solution in this experiment was not diluted to account for the scrub streams, and 2) the GTM assumes countercurrent process conditions. Nevertheless, the results are reasonably close to the GTM prediction of 12% of the U in the HLW stream and 88% of the U in the LLW stream. For Pu, the results indicate that 99% would end up in the HLW stream and 1% in the LLW stream. The GTM predictions are 98% and 2%, respectively.

The test results revealed that the flowsheet is not fully optimized. The Pu began to strip earlier than expected. The Pu distribution coefficient was less than 1 in the final scrub step (contact 9). This was likely due to the presence of residual oxalic acid, which would lower the Pu(IV) distribution coefficient. This also raised the question of whether oxalate carryover to the stripping section could have been responsible for the observed Pu stripping behavior.

To test this, an experiment was conducted in the absence of oxalate. The CMPO solvent containing HNO₃ at the concentration expected in the final scrub step was contacted with the 0.1 M HNO₃/0.1 M ascorbic acid stripping solution. To perform this experiment without repeating the entire set of batch contacts, the aqueous and organic nitrate concentrations were calculated for the final scrub step using the GTM. The HNO₃ calculated concentrations were 0.26 M for the aqueous phase and 0.064 M for the organic phase. Based on the known D values for HNO₃ (Lumetta and Swanson 1993c), a contact was performed that resulted in these HNO₃ concentrations. The system was then spiked with Pu,

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(a) Zirconium(IV) was added as ZrO(NO₃)₂ and U(VI) was added as UO₂(NO₃)₂; all other metal ions were added as the nitrate salts.

and the organic phase was subjected to the strip contacts analogous to those described in Table 9.4. The conditions for these contacts are summarized in Table 9.6.

The calculated and experimental distribution coefficients for Pu are given in Table 9.6 and Figure 9.2. In general, the agreement was good, especially in the strip stages, which indicated that Pu reduction occurred as expected. The measured values also agreed quite well with those measured in the primary experiment (Table 9.5). Although the Pu distribution coefficient in the first strip contact was relatively high (~ 1), the low organic-to-aqueous ratio in this contact gave an extraction factor of ~ 0.5 , so that the Pu (and Am) was stripped.

The results from this study were very encouraging and suggest that the reductive stripping approach to removing TRUs from the loaded CMPO solvent should be further considered.

Figure 9.1. CMPO Flowsheet for Pretreating NCRW Sludge Using a Reductive Stripping Solution

Figure 9.2. Results of the Reductive Pu Stripping Test

Table 9.1. Extraction of Am and Pu with CMPO in the Presence of 0.1 M Ascorbic Acid

<u>[HNO₃], M</u>	<u>D, Am</u>	<u>D, Pu</u>
1.0	11.8	13.3
0.1	0.45	0.64
0.01	0.014	0.008

Table 9.2. GTM Results for Flowsheet Simulation (Figure 9.1), with 0.01 M HNO₃ Concentration in the Strip Solution

<u>Description</u>	<u>Component Concentration, M</u>							
	<u>H</u>	<u>Na</u>	<u>La</u>	<u>Zr</u>	<u>U</u>	<u>Am</u>	<u>F</u>	<u>C₂O₄</u>
Feed	2.3E+00	1.6E-01	7.0E-04	1.6E-01	3.6E-03	1.0E-05	8.0E-01	0.0E+00
Raffinate	1.9E+00	9.8E-02	1.6E-06	9.8E-02	2.9E-08	5.8E-09	4.9E-01	1.5E-02
TRU Product	4.2E-02	1.0E-21	7.3E-04	1.0E-21	3.4E-03	1.0E-05	3.1E-03	2.6E-04
Carb. Wash	—	0.5	1.3E-11	1.7E-31	7.0E-04	7.6E-13	1.5E-07	1.3E-11

Table 9.3. GTM Results for Flowsheet Simulation (Figure 9.1), with 0.1 M HNO₃ Concentration in the Strip Solution

Description	Component Concentration, M							
	H	Na	La	Zr	U	Am	F	C ₂ O ₄
Feed	2.3E+00	1.6E-01	7.0E-04	1.6E-01	3.6E-03	1.0E-05	8.0E-01	0.0E+00
Raffinate	1.9E+00	9.8E-02	1.6E-06	9.8E-02	2.9E-08	5.8E-09	4.9E-01	1.5E-02
TRU Product	1.3E-01	1.0E-21	7.2E-04	1.0E-21	4.4E-04	1.0E-05	3.0E-03	2.3E-04
Carb. Wash	--	0.5	5.0E-06	1.7E-31	6.6E-03	4.3E-07	1.0E-04	6.8E-05

Table 9.4. Solvent Extraction Contacts Performed to Test Portions of the Flowsheet in Figure 9.1

Contact	Description	Aqueous Phase	mL Aq.	Organic Phase	mL Org.
1	Extraction	Feed ^(a)	34.4	CMPO Solvent	10
2	Scrub 1A	Scrub 1 ^(b)	11.3	From 1	8.5
3	Scrub 1B	Scrub 1	10.7	From 2	8
4	Scrub 2A	Scrub 2 ^(c)	7.5	From 3	7.5
5	Scrub 2B	Scrub 2	7	From 4	7
6	Scrub 2C	Scrub 2	6.5	From 5	6.5
7	Scrub 3A	0.01 M HNO ₃	4	From 6	6
8	Scrub 3B	0.01 M HNO ₃	3.67	From 7	5.5
9	Scrub 3C	0.01 M HNO ₃	3.33	From 8	5
10	Strip 1A	0.1 M AA ^(d) /0.1 M HNO ₃	8	From 9	4
11	Strip 1B	0.1 M AA/0.1 M HNO ₃	7	From 10	3.5
12	Strip 1C	0.1 M AA/0.1 M HNO ₃	6	From 11	3
13	Strip 1D	0.1 M AA/0.1 M HNO ₃	5	From 12	2.5
14	Carb. Wash	0.25 M Na ₂ CO ₃	2	From 13	2

- (a) The feed solution consisted of 1.5 M HNO₃, 0.8 M HF, 0.16 M Zr(IV), 0.16 M Na, 0.0007 M La(III), 0.0036 M U(VI).
- (b) Scrub 1 consisted of 0.04 M H₂C₂O₄ plus 1.13 M HNO₃, which represented a blend of the three scrub streams indicated in Figure 9.1.
- (c) Scrub 2 consisted of 1.51 M HNO₃, which represented a blend of the second two scrub streams indicated in Figure 9.1.
- (d) AA = ascorbic acid.

Table 9.5. Results of Solvent Extraction Contacts Performed to Test Portions of the Flowsheet in Figure 9.1

<u>Contact</u>	<u>Description</u>	<u>D, Uranium</u>	<u>D, Plutonium</u>
1	Extraction	82	12.2
2	Scrub 1A	88	26.5
3	Scrub 1B	199	10.6
4	Scrub 2A	136	38.1
5	Scrub 2B	60	32.5
6	Scrub 2C	76	216
7	Scrub 3A	265	67.4
8	Scrub 3B	78	5.65
9	Scrub 3C	16	0.22
10	Strip 1A	30	0.75
11	Strip 1B	30	0.71
12	Strip 1C	28	0.65
13	Strip 1D	35	1.04
14	Carb. Wash	0.00	0.00

Table 9.6. Reductive CMPO Stripping Test

Contact	Description	Aqueous Phase	mL Aq.	Organic Phase	mL Org.	D, Pu Found	D, Pu ³⁺ Calc. (GTM)
A	Last Scrub	0.36 <u>M</u> HNO ₃	3.33	CMPO Solvent	5.0	7.46	456
B	Strip 1A	0.1 <u>M</u> AA ^(a) /0.1 <u>M</u> HNO ₃	8.0	From A	4.0	1.05	1.53
C	Strip 1B	0.1 <u>M</u> AA/0.1 <u>M</u> HNO ₃	7.0	From B	3.5	0.70	1.03
D	Strip 1C	0.1 <u>M</u> AA/0.1 <u>M</u> HNO ₃	6.0	From C	3.0	0.70	0.98
E	Strip 1D	0.1 <u>M</u> AA/0.1 <u>M</u> HNO ₃	5.0	From D	2.5	0.66	0.97
F	Carb. Wash	0.25 <u>M</u> Na ₂ CO ₃	2.0	From E	2.0	5.6E-05	7.0E-05

(a) AA = ascorbic acid.

10.0 CMPO and SREX Flowsheet for Pretreating B-110 Sludge

A flowsheet for separating TRUs and ^{90}Sr from dissolved Tank B-110 sludge is being developed. Originally, the process was envisioned to involve three solvent extraction cycles: 1) TBP extraction of U, 2) CMPO extraction of TRUs, and 3) DtBC18C6 (SREX) extraction of ^{90}Sr .^(a) Two proposed flowsheets containing these three solvent extraction cycles were tested using a simulated dissolved B-110 sludge solution. Subsequently, a third flowsheet was tested that contained only the CMPO and SREX cycles. In the latter case, most of the U was separated from the TRUs by selective stripping of the CMPO solvent.

Because the pretreatment flowsheet for B-110 sludge continues to evolve, the results of the flowsheet tests are presented in the order they were performed. This organization allows the reader to understand the flowsheet modification made after the completion of each test.

10.1 Preparation of Simulated Dissolved B-110 Sludge Solution

The preparation of the simulated dissolved B-110 sludge solution used in these experiments is summarized in Table 10.1. The various components were added in the order shown in the table. The intended concentrations of the various components are given in Table 10.1, along with the values determined experimentally.

10.2 First Proposed Flowsheet for Pretreating B-110 Sludge

The first flowsheet proposed for pretreating B-110 sludge is shown in Figure 10.1. This flowsheet was a modified version of that proposed for pretreating NCRW sludge (Lumetta and Swanson 1993b). A series of batch contacts was performed to test this flowsheet using the simulated dissolved B-110 solution. Contacts were performed to test the TBP, CMPO, and SREX solvent extraction cycles.

10.2.1 Test of the First Proposed TBP Cycle for Pretreating B-110 Sludge

The batch contacts performed to test the TBP cycle of the flowsheet depicted in Figure 10.1 are summarized in Table 10.2. Ascorbic acid (0.1 g) was added to 50 mL of the simulated dissolved B-110 sludge solution, so that the ascorbic acid concentration was $\sim 0.01 \text{ M}$. The ascorbic acid functioned to adjust the Pu valence to +3, so that Pu would not be extracted by TBP. To represent the contribution of the scrub stream in the TBP extraction section, 10.6 mL of 0.2 M HNO_3 was added. Finally, the solution was spiked with Pu(IV). The resulting solution contained 2.09 M HNO_3 and

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(a) TBP = tri-n-butyl phosphate, CMPO = octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, and DtBC18C6 = di(t-butylcyclohexano)-18-crown-6.

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0.14 M HF. This solution was contacted for 60 s with 30% TBP (in NPH) at an organic-to-aqueous phase ratio of 0.2. The aqueous phase from this extraction was subjected to two subsequent extractions with 30% TBP, and the organic phase was subjected to scrub and strip steps as indicated in Table 10.2.

Interfacial crud was observed in all three TBP extraction contacts. Although the chemical nature of this crud was not determined, adding HF to the aqueous feed solution reduced the propensity to form crud. Indeed, with [HF] at 0.4 M in the aqueous phase, interfacial crud did not form. Thus, feed adjustment with HF was incorporated into subsequent flowsheets (see Section 10.3).

Because interfacial crud formed in the TBP extractions and precipitates formed in the CMPO extraction cycle (see Section 10.2.2), detailed analyses of the process solutions from this experiment were not performed. However, total alpha analyses were performed for aqueous and organic phases using liquid scintillation methods. The results are given in Table 10.3. Most of the alpha activity in these solutions was attributed to Pu; ~0.01% of the alpha activity in the initial aqueous solution was due to U. The results indicate that ascorbic acid effectively suppressed Pu extraction under these conditions. Furthermore, at least 99.7% of the extracted Pu was removed from the extract during the scrub steps, so that only ~0.01% of the Pu in the feed reported to the TBP strip solution. The mass balance calculations for this set of data revealed good recovery.

10.2.2 Test of the First Proposed CMPO Cycle for Pretreating B-110 Sludge

The aqueous phase from the third TBP extraction described in Table 10.2 was used to test the CMPO solvent extraction cycle shown in Figure 10.1. As indicated in the flowsheet, the aqueous phase exiting the third TBP extraction stage has a relative flow of 100, while the scrub streams from the CMPO cycle have a combined flow of 64. In order for the aqueous phase in the CMPO extractions to represent a blend of the aqueous raffinate from the TBP cycle and the three scrub streams for the CMPO cycle, 48.1 mL of the aqueous phase from the third TBP extraction was mixed with 7.69 mL of 0.15 M $\text{H}_2\text{C}_2\text{O}_4$, 1.23 mL of 5 M HNO_3 , and 0.20 mL of 0.01 M HNO_3 .^(a) A precipitate immediately formed when $\text{H}_2\text{C}_2\text{O}_4$ was added, which was likely because an insoluble Bi oxalate complex formed. The solution was clarified by filtration, and a series of batch solvent extraction contacts was performed as described in Table 10.4. The results are presented in Table 10.5.

Plutonium was extracted effectively; a DF^(b) of nearly 12,000 was achieved. However, precipitation problems were encountered in the scrub (contacts 11 and 12) and strip steps (contact 21). Low mass balances were obtained for Pu in these steps, indicating that some Pu was carried down with the precipitate.

(a) An error was made in the procedure. To properly represent the flowsheet shown in Figure 4.1, 7.69 mL of 5 M HNO_3 , and 15.38 mL of 0.01 M HNO_3 should have been added.

(b) The DF is defined as the quantity of Pu in the feed solution divided by the quantity in the raffinate.

Because the precipitations indicated that this version of the flowsheet was not likely to succeed, detailed analyses of the process solutions were not performed. Rather, the flowsheet was modified to try to eliminate the precipitation and interfacial crud problems (see Section 10.3).

10.2.3 Test of the First Proposed SREX Cycle for Pretreating B-110 Sludge

An initial test of the SREX process for separating Sr from dissolved B-110 sludge was conducted in FY 1992 (Lumetta, Wagner, Colton, and Jones 1993). The SREX flowsheet tested in that experiment was similar to that shown in Figure 10.1, except that the scrub solution consisted of 0.5 M HNO_3 as was suggested by Horwitz, Dietz, and Fisher (1991). In that initial experiment, a significant fraction of the extracted Sr was lost from the organic phase during the scrub steps. Thus, a higher concentration (1.0 M) of HNO_3 was used in the scrub step in the experiment described in this section.

Ten milliliters of the aqueous phase from the third CMPO extraction (contact 10) was taken for tests of the SREX cycle shown in Figure 10.1. Two milliliters of a ^{85}Sr tracer solution was added so the behavior of Sr could be followed by gamma counting techniques. Nitric acid (2.31 mL of 15.7 M) was added to adjust the HNO_3 concentration in the SREX feed solution to 4 M (as indicated in Figure 10.1). Then, 1.22 mL of 1.0 M HNO_3 was added to represent the SREX scrub solution that flows into the SREX extraction stages. The resulting solution was contacted for 60 s with the SREX process solvent.^(a) After separation of the two phases by centrifugation, the aqueous phase was subjected to additional extraction contacts, and the organic phase was subjected to a series of scrub and strip contacts as indicated in Table 10.6. The results are summarized in Table 10.7.

As found previously (Lumetta, Wagner, Colton, and Jones 1993), good Sr extraction was achieved using the SREX process. The DF for Sr was 1,200. Note that the mass balance recoveries for the second, third, and fourth extraction contacts (contacts 27, 28, and 29) were low; the reason for this is unknown. Good retention of Sr in the organic phase during the scrubbing steps was achieved, but the Sr did not begin to strip in the first strip contact (contact 32), as expected. This behavior can be attributed to the relatively high distribution coefficient for Sr at the acidity present in that particular contact. The subsequent strip contact (contact 33) indicated that Sr can indeed be stripped from the solvent using dilute HNO_3 .

10.2.4 Conclusions from Tests of the First Proposed Flowsheet for Pretreating B-110 Sludge

The following conclusions were drawn from the experiments performed to test the flowsheet depicted in Figure 10.1.

(a) The SREX process solvent consisted of 0.2 M di-*t*-butylcyclohexano-18-crown-6 (DtBC18C6) in 1-octanol. The DtBC18C6 used in this study was supplied by Parish Chemical Company (Orem, Utah) and was derived from Parish Lot Number 3ISQ. The DtBC18C6 was used as received.

- Interfacial crud formed in the TBP extraction contacts. The process chemistry must be modified to prevent crud formation.
- Precipitates formed from the simulated dissolved B-110 sludge solution when oxalic acid was present. Elimination of oxalic acid from the flowsheet is desirable.
- Reduction with ascorbic acid was effective in minimizing Pu extraction in the TBP cycle.
- Plutonium was effectively removed from the simulated dissolved sludge solution by extraction with CMPO.
- The HNO_3 concentration in the last CMPO scrub stage was so low (0.07 M) that Am(III) would be expected to strip in that stage. The process flowsheet must be adjusted to prevent TRUs from refluxing in the CMPO scrub section.
- Strontium did not strip at the expected stage in the flowsheet. The process flowsheet must be adjusted so that Sr strips correctly.

The flowsheet was modified in an attempt to eliminate these problems. These modifications are discussed in the next section.

10.3 Second Proposed Flowsheet for Pretreating B-110 Sludge

The second flowsheet proposed for pretreating B-110 sludge is shown in Figure 10.2. This flowsheet includes the following modifications: 1) oxalic acid was eliminated as a scrub solution, 2) HF was added to the solvent extraction feed to give $[\text{HF}] \sim 0.4 \text{ M}$ in the TBP extraction stages, and 3) the relative flow rates were changed in the SREX cycle. Each of these three modifications will be discussed separately.

10.3.1 Modification 1: Elimination of Oxalic Acid Scrub

The presence of oxalic acid was hypothesized to cause certain metals (e.g., Bi) to precipitate in the aqueous CMPO process solutions. Oxalic acid was originally used in the proposed flowsheet (Figure 10.1) to scrub extracted Fe(III) from the solvent; however, the need for this is questionable. The GTM (Vandegrift et al. 1992) was used to calculate the distribution coefficient for Fe(III) under several different conditions. The results are given in the following table:

GTM Run	Initial Aqueous Concentrations				D, Fe Predicted
	H^+ , <u>M</u>	Fe^{3+} , <u>M</u>	F^- , <u>M</u>	$C_2O_4^{2-}$, <u>M</u>	
1	1.7	0.08	0	0	0.064
2	1.7	0.08	0.14	0	0.0068
3	1.7	0.08	0.14	0.001	0.0066

The Fe distribution coefficients predicted by the GTM suggest that oxalic acid is unnecessary to suppress the extraction of Fe. Even in the absence of F^- or $C_2O_4^{2-}$, the distribution coefficient for Fe is sufficiently low that separation of the TRUs from Fe should be easily achieved. Furthermore, the presence of 0.14 M F^- (as would be expected with dissolved B-110 sludge) reduced the Fe distribution coefficient by an order of magnitude.

Thus, the flowsheet was changed to remove oxalic acid, which allowed a decrease to just two CMPO scrub sections. The first of these comprises three stages, and the scrub solution introduced there is 2.0 M HNO_3 . The second scrub section consists of two stages in which the extract is scrubbed with 0.01 M HNO_3 to reduce the HNO_3 concentration. In addition, the $H_2C_2O_4$ solution used in the second strip section was replaced with 0.001 M HEDPA. The phosphorus introduced into the HLW stream by use of this dilute HEDPA solution would not likely have a large impact on the volume of HLW glass produced (Lumetta and Swanson 1993b).

10.3.2 Modification 2: Addition of HF to the Solvent Extraction Feed

Raising the HF concentration in the TBP extraction stages to ~ 0.4 M prevented the formation of interfacial crud. The GTM was used to predict the effect of such an elevated F^- level on the distribution coefficient of key metal ions in the CMPO cycle. The results were as follows:

Component	Concentration in Aqueous Feed, $\underline{M}^{(a)}$	D
H ⁺	1.7	0.40
Fe ³⁺	0.08	4.8E-4
Cr ³⁺	0.003	0.001
Bi ³⁺	0.022	195
Al ³⁺	0.009	1.5E-7
Na ⁺	0.11	0.001
Ca ²⁺	0.004	0.001
Mg ²⁺	0.002	0.001
La ³⁺	0.001	35.2
UO ₂ ²⁺	6E-6	80.8
Am ³⁺	1E-6	58.7
F ⁻	0.4	0.56
PO ₄ ³⁻	0.065	0.047

(a) These concentrations were used as input parameters to the GTM.

The GTM predicted that, as illustrated by the Am(III) distribution coefficients, the trivalent actinides^(a) should be extracted under the high fluoride conditions. Thus, this modification to the flowsheet was not expected to diminish the effectiveness of the CMPO extraction process in separating the TRUs from the nonradioactive bulk sludge components (other than the trivalent lanthanides).

10.3.3 Modification 3: Change of Relative Flow Rates for the SREX Cycle

The test of the flowsheet depicted in Figure 10.1 revealed that the Sr distribution coefficient was 2.0 in the first SREX strip stage. The flowsheet must be adjusted to lower the Sr distribution coefficient so that Sr strips at the desired part of the process. To make this adjustment, it is necessary to know the distribution coefficient for Sr (D_{Sr}) as a function of aqueous HNO₃ concentration. D_{Sr} versus

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(a) Plutonium should be present as Pu(III) in the CMPO extraction stages due to the presence of ascorbic acid.

aqueous $[\text{HNO}_3]$ was plotted using the data collected in the test described in Section 10.2.3 (Figure 10.3). These D_{Sr} data agree well with those reported in the literature (Dietz and Horwitz 1993), which are also plotted in Figure 10.3 for comparison. This plot shows that the aqueous $[\text{HNO}_3]$ must be less than 0.35 M for D_{Sr} to be less than 1.

Using the data plotted in Figure 10.3, and the published distribution data for the extraction of HNO_3 in the SREX process (Horwitz, Dietz, and Fisher 1991), the alternative SREX flowsheet depicted in Figure 10.2 was proposed. The expected distribution coefficients and extraction factors for Sr at each stage of this modified SREX cycle are given in Table 10.8. Data from the testing of the Figure 10.2 flowsheet using simulated dissolved sludge solution (see Section 10.3.6) support the predictions listed in Table 10.8.

10.3.4 Test of the Second Proposed TBP Cycle for Pretreating B-110 Sludge

Except for the feed solution composition, the TBP cycle in the flowsheet shown in Figure 10.2 is identical to that in Figure 10.1, thus the test of this part of the modified flowsheet was very similar to the test described in Section 10.2.1. In this case, ascorbic acid (0.06 g) was added to 30 mL of the simulated dissolved B-110 sludge solution, so that the concentration of ascorbic acid was $\sim 0.01 \text{ M}$. To represent the contribution of the scrub stream in the TBP extraction section, 3.3 mL of 0.2 M HNO_3 was added, and 1.0 mL of 10 M HF was added to prevent interfacial crud formation. Finally, the solution was spiked with Pu(IV). The resulting solution was found to contain 2.46 M H^+ and 0.38 M F^- . This solution was contacted for 60 s with 30% TBP (in NPH) at an organic-to-aqueous phase ratio of 0.2. The aqueous phase from this extraction was subjected to two subsequent extractions with 30% TBP as described in Table 10.9. Because satisfactory results were obtained with the earlier TBP scrub and strip contacts (Section 10.2.1), these flowsheet steps were not tested here.

No interfacial crud was observed in the TBP extraction contacts, indicating that the addition of HF to the feed successfully prevented crud formation. The Pu distribution coefficients (Table 10.10) were $\sim 20\%$ lower than those observed in the first flowsheet test (Table 10.3), which might be due to complexation of Pu by fluoride ion.

Inductively coupled plasma atomic emission spectroscopic analyses of the initial aqueous solution and the aqueous phase from contact 3A (TBP raffinate) revealed that most of the bulk constituents of the B-110 sludge were not extracted by TBP. The exceptions were Ca and Bi, for which 12% and 50% were extracted, respectively. The Bi result is especially surprising, because trivalent ions in general have low distribution coefficients for extraction with TBP. Although the scrub portion of the TBP cycle was not examined in this experiment, it is likely that the Ca and Bi can be scrubbed from the loaded solvent.

10.3.5 Test of the Second Proposed CMPO Cycle for Pretreating B-110 Sludge

The aqueous phase from the third TBP extraction described in Table 10.9 (contact 3A) was used to test the CMPO solvent extraction cycle shown in Figure 10.2. As indicated in the flowsheet, the aqueous phase exiting the third TBP extraction stage has a relative flow of 100, while the scrub streams from the CMPO cycle have a combined flow of 32. For the aqueous phase in the CMPO extractions to represent a blend of the aqueous raffinate from the TBP cycle and the two scrub streams for the CMPO cycle, 25.8 mL of the aqueous phase from the third TBP extraction was mixed with 4.1 mL of 2.0 M HNO_3 and 4.1 mL of 0.01 M HNO_3 . The resulting solution was used to perform the series of batch solvent extraction contacts described in Table 10.11. The results are presented in Table 10.12.

There are several points that must be noted here. First, Pu extraction with CMPO was not very effective; Pu distribution coefficients were only ~ 2 . Thus, with the flow rates employed, a DF of only 5 was achieved in the three extractions performed. The low extraction of Pu likely resulted from complexation of Pu by fluoride ion. Fluoride ion would be expected to complex to Pu(IV), but would not be expected to strongly complex Pu(III). In the preparation of the aqueous feed solution used in this experiment, the Pu(IV) spike was added after ascorbic acid and HF. It appeared that the high fluoride concentration hindered the reduction of Pu(IV) by the ascorbic acid. Complexation of Pu(IV) by fluoride would lower the Pu distribution coefficient.

The second point of interest is that the Pu did not strip in contacts 13A and 14A. The relatively high Pu distribution coefficients observed for the scrub contacts suggest that some Pu(IV) was present in the extract, which is in accord with the indication from the extraction contacts. Plutonium(IV) would not be stripped by dilute acid. However, the Pu was effectively stripped by the 0.001 M HEDPA solution, as would be expected for either Pu(III) or Pu(IV) (Lumetta and Swanson 1993c).

The third important observation from this experiment was that precipitation occurred in the strip contacts (contacts 13A, 14A, and 15A). Some tests were conducted to determine the likely source of this precipitation; these are discussed in the following paragraphs.

The precipitate was first hypothesized to be a La(III)-HEDPA complex. HEDPA has been reported to form complexes with Nd(III), which have limited solubility (Leonard et al. 1992). Based on a La distribution coefficient of 15 for the CMPO extraction and scrub steps, the La concentration in the aqueous phase from the first strip contact was expected to be 0.0012 M. A solution was prepared that consisted of 0.001 M $\text{La}(\text{NO}_3)_3$, 0.06 M HNO_3 , and 0.00025 M HEDPA, which were the concentrations of these components expected in the aqueous phase from the first strip contact (contact 13A). No precipitate formed in this solution. Thus, it is unlikely that La was the source of the precipitate.

Bismuth was another sludge component that was hypothesized to be the source of the precipitate. To test this hypothesis, a solution was prepared that consisted of 0.035 M $\text{Bi}(\text{NO}_3)_3$, 0.06 M HNO_3 , and 0.00025 M HEDPA, which were the concentrations of these components expected in the aqueous phase from the first strip contact (contact 13A). In this case, the Bi(III) did not dissolve completely. Thus, it is likely that the source of the precipitation in the strip contacts was Bi(III).

Of the bulk sludge constituents, only Bi and La were extracted to any extent by CMPO. Both of these elements were quantitatively extracted in the three CMPO extraction steps.

10.3.6 Test of the Second Proposed SREX Cycle for Pretreating B-110 Sludge

Twelve milliliters of the aqueous phase from the third CMPO extraction (contact 6A) was taken for tests of the SREX cycle shown in Figure 10.2. Two milliliters of a ^{85}Sr tracer solution was added so the behavior of Sr could be followed by gamma counting techniques. Nitric acid (2.8 mL of 15.7 M) was added to adjust the HNO_3 concentration in the SREX feed solution to 4 M (as indicated in Figure 10.2). Then, 2.2 mL of 1.0 M HNO_3 was added to represent the SREX scrub solution that carries over into the SREX extraction stages. The resulting solution was contacted for 60 s with the SREX process solvent. After separating the two phases by centrifugation, the aqueous phase was subjected to additional extraction contacts, and the organic phase was subjected to a series of scrub and strip contacts as indicated in Table 10.13. The results are summarized in Table 10.14.

As was found previously (Section 10.2.3), good extraction of Sr was achieved using the SREX process. The DF for Sr was 1,100. Note that the mass balance recoveries for the second, third, and fourth extraction contacts (contacts 18A, 19A, and 20A) were low; this was also observed in the previous test (Section 10.2.3). Thus, the data reported here should be used with caution. Good retention of Sr in the organic phase during the scrubbing steps was achieved, and the Sr stripped in contact 23A as expected. The results from this SREX test compare favorably with those predicted in Table 10.8.

Inductively coupled plasma atomic emission spectroscopic analyses of the adjusted feed solution from contact 17A and the aqueous phase from contact 20A (SREX raffinate) revealed quantitative extraction of Ba, Pb, and Sr. The coextraction of Ba was expected based on published Ba distribution coefficients (Horwitz, Dietz, and Fisher 1991). Studies conducted at Argonne National Laboratory on an extraction chromatographic material, based on the SREX chemistry, revealed that this material has a high affinity for Pb (Horwitz, Chiarizia, and Dietz 1992). The results obtained here show that the affinity of DtBC18C6 for Pb is retained in the solvent extraction system.

The behavior of Ba and Pb will have to be accounted for in SREX flowsheet designs. Distribution coefficients suggest that improved Sr/Ba separation can be achieved by running the extraction at higher HNO_3 concentration, and that Sr/Pb separation can be achieved by selectively stripping Sr from the solvent. No Pb was found in the aqueous phase from the first SREX strip step (contact 23A), while the Sr concentration in that solution was $5.2 \times 10^{-4} \text{ M}$. This observation suggests that indeed Pb can be separated from Sr in the SREX process. A second strip section would be needed to remove the Pb from the solvent before recycling the solvent to the extraction stages.

10.3.7 Conclusions from Tests of the Second Proposed Flowsheet for Pretreating B-110 Sludge

The following conclusions were drawn from the experiments performed to test the flowsheet depicted in Figure 10.2.

- Addition of HF to the solvent extraction feed solution eliminated interfacial crud formation, but adversely affected Pu extraction by CMPO.
- A precipitate (most likely a Bi salt) formed in the CMPO strip steps.
- The TBP and SREX cycles of the flowsheet appeared to be viable, but further work is needed on the CMPO cycle.

To design a viable process for pretreating B-110 sludge (and other SST sludges), data are needed concerning the solubility of Bi(III) under various process conditions. Preliminary data on the solubility of Bi in HNO_3 solutions were collected and are presented in Appendix A. Based on these data, a third flowsheet for pretreating B-110 sludge was developed and tested.

10.4 Third Proposed Flowsheet for Pretreating B-110 Sludge

The third flowsheet proposed for pretreating B-110 sludge is shown in Figure 10.4. The major points of interest in this flowsheet are 1) an increase in the acidity of the 0.01 M ascorbic acid solution used as the CMPO stripping solution; and 2) elimination of the TBP extraction cycle, and 3) lower $[\text{F}]$ in the feed.

Preliminary Bi solubility measurements (Appendix A) indicated that the solubility of Bi increases with increasing HNO_3 concentration. As discussed in Section 10.3, the use of a 0.01 M HNO_3 solution to strip the trivalent TRUs from the CMPO solvent resulted in the formation of a precipitate, which likely contained Bi. Thus, to prevent precipitation of Bi, 0.1 M HNO_3 is called for as the CMPO strip solution in the current flowsheet.

Work with simulated NCRW solutions indicated that the use of 0.1 M HNO_3 as the CMPO strip solution would yield selective stripping of TRUs over U (see Section 9.0); this allows the TBP extraction cycle to be eliminated. Thus, the current flowsheet contains only the CMPO and SREX extraction cycles, which greatly decreases the complexity of the process. Without the TBP cycle, ascorbic acid is unnecessary in the feed solution. To achieve adequate stripping of Pu, ascorbic acid is added in both the last scrub stage and in the strip solution. The primary disadvantage of this approach is that a large relative flow rate is required for the CMPO strip stream. Extensive evaporation will be required to reduce the volume of the TRU waste stream.

In the second proposed flowsheet, HF was added to the feed to prevent interfacial crud formation in the TBP extraction steps (see Section 10.3.2). Addition of HF was not necessary to prevent interfacial crud in the CMPO extraction, so the HF addition was eliminated.

The CMPO portion of the flowsheet was tested using the simulated dissolved B-110 sludge solution. The SREX cycle was not tested because this portion of the flowsheet was identical to that in the second proposed flowsheet (Figure 10.2). The test of the SREX portion of that flowsheet was successful (Section 10.3.6). The batch solvent extraction contacts that were performed to test the third proposed CMPO cycle are summarized in Table 10.15. The adjusted feed solution was prepared by adding 2.20 mL of 0.67 M HNO_3 /0.0067 M ascorbic acid solution and 4.41 mL of 0.01 M HNO_3 /0.01 M ascorbic acid solution to 13.78 mL of the simulated B-110 solution. This solution represented a blend of the feed and scrub streams. The solution was spiked with Pu before the solvent extraction contacts were performed. The Pu content of this solution is given in Table 10.16, and the bulk composition is given in Table 10.17. After withdrawing 0.4 mL for analysis, the solution was contacted for 60 s with 10 mL of the CMPO solvent. After separating the phases by centrifugation, the aqueous phase was subjected to two additional extraction contacts, and the organic phase was subjected to a series of scrub and strip steps, as described in Table 10.15.

The extraction, scrub, and strip contacts proceeded smoothly. Neither interfacial crud nor precipitates were observed in these contacts. This observation indicated that the higher HNO_3 concentration in the strip solution (compared to the second proposed flowsheet) prevented Bi precipitation. A precipitate did form in the carbonate wash step. As will be discussed below, this was likely Bi carbonate.

The Pu contents of the various process solutions are given in Table 10.16. The concentration profile for Pu as a function of stage number is shown in Figure 10.5. Plutonium was extracted very efficiently, with a measured DF of 80,000. The exact value of this DF should be viewed with caution since a low percent recovery was obtained in the analysis of the solutions from the second and third extraction contacts (2B and 3B); however, it is clear that Pu was extracted very effectively. The lower F content of the feed in this test might have also contributed to the higher DF compared to the previous test because F is known to suppress Pu extraction. Good retention of Pu in the organic phase was observed during the scrub steps, and Pu stripping occurred at stage 8 (contact 8B) as expected. A residual amount of Pu remained in the organic phase after the third strip contact, but this represented only 0.1 % of the Pu introduced in the feed solution. The low Pu mass balance observed for contact 12B (i.e., the carbonate wash) was likely related to the precipitation that occurred in that contact.

The behavior of Bi is summarized in Figure 10.6. As expected from known Bi distribution data (Lumetta, Wagner, Colton, and Jones 1993), Bi was extracted by CMPO. The Bi remained in the organic phase during the scrub steps and was not stripped by 0.1 M HNO_3 /0.01 M ascorbic acid solution. This behavior suggests that the TRUs (Pu and Am) can be separated from Bi by selective stripping with dilute acid, as has recently been suggested (Swanson 1993). Because most of the Bi remained in the organic phase after the stripping contacts, the precipitate that formed in the carbonate wash step was likely Bi carbonate. A second strip step might be needed to remove Bi (and possibly U) from the solvent before the carbonate wash step. This strip stream would be segregated from the TRU

strip stream. A complexing agent such as HEDPA might be used to strip Bi. Alternatively, the complexing agent could be added directly to the carbonate solution to prevent Bi precipitation.

The behavior of U(VI) is summarized in Figure 10.7. As expected, U(VI) was effectively extracted by CMPO. The U concentration in the aqueous phase in the second extraction contact was below the detection limit ($< 4 \times 10^{-7}$ M) for the laser fluorimetry technique used here. The U remained in the organic phase during the scrub steps. As was the case with Bi, U was not stripped by the 0.1 M HNO_3 /0.01 M ascorbic acid solution. Thus, the trivalent TRUs can be separated from both Bi and U by selective stripping with dilute acid. The U was quantitatively stripped from the solvent in the carbonate wash.

The distribution coefficients for the various sludge components in the first extraction contact are given in Table 10.17. Of particular interest is the behavior of Fe. The distribution coefficient for Fe(III) in the extraction was only 0.09. This value confirms that oxalic acid is not required to suppress Fe extraction in the CMPO extraction cycle (see Section 10.3.1).

Based on these results, the flowsheet shown in Figure 10.4 is considered a viable method for separating TRUs and Sr from the bulk nonradioactive constituents of Tank B-110 sludge. A second strip step should be added to remove Bi from the solvent before the carbonate wash step, or a complexant should be added to the carbonate wash solution to prevent Bi precipitation. A test of this method with actual B-110 sludge will be described in the next section.

10.5 Pretreatment Test Using Actual B-110 Sludge

A pretreatment flowsheet test was conducted using actual sludge from Tank B-110. The sludge was first washed with dilute NaOH, then dissolved in HNO_3 . The dissolved sludge solution was subjected to a series of batch contacts to simulate the flowsheet illustrated in Figure 10.8. The results of this test are presented in this section.

10.5.1 Washing and Dissolution of B-110 Sludge

A 3.43-g portion of a composite sample (Sample 90-4316) from Core 1 of Tank B-110 was used in this experiment. Previous tests with this material indicated that it was readily soluble in HNO_3 media (Lumetta, Wagner, Colton, and Jones 1993). The sludge was slurried in ~ 15 mL of 0.1 M NaOH and was heated at 100°C for 1 h. After cooling to room temperature, the mixture was centrifuged and the clear supernatant solution was decanted. The sludge was washed in a similar manner with another 10-mL portion of 0.1 M NaOH, then the sludge was dissolved in acid as follows.

The washed sludge was mixed with 10 mL of water, giving a slurry with pH 11.9. Nitric acid (0.27 mL of 15.7 M) was added to lower the pH to 1.0. An additional 1.8 mL of 15.7 M HNO_3 was added to yield an effective HNO_3 concentration of 2 M. The dissolution mixture was heated at 100°C for 1 h, then was allowed to cool to room temperature. This treatment dissolved nearly all the solids.

The dissolution mixture was centrifuged, and the dissolved sludge solution (A) was decanted from the small amount of residual solids. The residual solids were treated with 5.3 mL of 1.9 M HNO_3 /0.6 M HF at 100°C for 1 h. This treatment completely dissolved the remaining solids (solution B). The two dissolved sludge solutions (A and B) were combined for use in the solvent extraction test (solution C).

10.5.2 CMPO and SREX Test with Actual Dissolved B-110 Sludge Solution

Solution C represented the feed solution in Figure 10.8. For the batch contact representing stage 2 in the flowsheet,^(a) the feed solution was adjusted to account for the two CMPO scrub sections. Adjustment was accomplished by mixing 13.8 mL of solution C with 2.2 mL of 2.0 M HNO_3 and 4.4 mL of 0.01 M HNO_3 /0.01 M ascorbic acid. The adjusted feed solution was sampled for analysis (total of 0.3 mL removed), then the solution was contacted with the CMPO solvent (organic-to-aqueous ratio of 0.5) for 60 s. The extraction mixture was centrifuged to ensure complete phase separation. Portions of the aqueous and organic phases were subjected to various additional extraction, scrub, and strip contacts as summarized in Table 10.18.^(b) Aliquots of the aqueous phase from each contact were taken for ICP, radiochemical,^(c) and titrimetric analyses.

The results of total alpha analyses are summarized in Table 10.19. The CMPO extraction cycle performed as expected. The TRU content of the aqueous raffinate after the second CMPO extraction was 2.43×10^{-4} $\mu\text{Ci/mL}$; thus, the TRU DF achieved in the two extraction contacts was 150. The distribution coefficients for the TRUs remained well above 1 throughout the scrub stages, and the TRUs were effectively stripped with the 0.075 M HNO_3 /0.01 M ascorbic acid solution.

The U concentration in each aqueous phase from the CMPO cycle test was determined by laser fluorimetry, with the results being summarized in Table 10.20. Again, these data showed that the CMPO extraction cycle performed as expected. The U content of the aqueous raffinate after the second CMPO extraction was less than 3.17×10^{-7} M; thus, the U DF achieved in the two extraction contacts was >490. The U distribution coefficients remained well above 1 throughout the scrub and strip stages. Thus, by employing a stripping solution consisting of 0.075 M HNO_3 /0.01 M ascorbic acid, a U/TRU separation can be achieved. The U was stripped in the second strip step with HEDPA.

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- (a) Originally, the flowsheet had three CMPO extraction stages (as in Figure 10.4). However, due to the limited quantity of dissolved B-110 sludge available, only two CMPO extraction stages were employed in this test, so that enough solution was available to test the SREX cycle.
  - (b) A precipitate formed in the first CMPO extraction contact. Most of this precipitate was located at the interface between the two phases, but some settled to the bottom of the aqueous phase. Subsequent tests with solution C indicated this problem could be alleviated by diluting the feed with water by a factor of ~ 1.5 .
  - (c) The aqueous phase from the second CMPO extraction was traced with ^{85}Sr before using this solution to test the SREX cycle. This was done so that the behavior of Sr could be followed by gamma counting techniques, which is much less costly than performing analyses for ^{90}Sr .

The behavior of Bi (Table 10.21) was similar to that of U. The Bi content of the aqueous raffinate after the second CMPO extraction was less than 3.59×10^{-4} M. Like U, the Bi distribution coefficients remained well above 1 throughout the scrub and strip stages. Thus, by employing a stripping solution consisting of 0.075 M HNO_3 /0.01 M ascorbic acid, a Bi/TRU separation can be achieved. The Bi was stripped in the second strip step with HEDPA.

Other major sludge components were not extracted by CMPO. Small amounts of Al (1.2%), Fe (1.1%), Na (8.9%), Pb (10.5%), and Si (9.5%) were extracted, but these elements were not detected in the strip solutions, indicating that they were successfully scrubbed from the solvent. Calcium, Cr, or Sr were not appreciably extracted.

The behavior of Sr in the SREX solvent extraction test is summarized in Figure 10.9. The SREX process performed as expected based on the previous test with simulated dissolved B-110 sludge solution (see Section 10.3.6). A very high DF ($\sim 9,000$) for ^{85}Sr was achieved in four extraction contacts. Strontium was retained in the extract during the scrubbing contacts and was stripped with 0.01 M HNO_3 . The distribution coefficient for Sr in the first strip contact (stage 20) was 0.8, which is somewhat high for efficient stripping. In retrospect, it would be best to scrub the solvent with 0.5 M HNO_3 as originally proposed by Horwitz, Dietz, and Fisher (1991). In a previous SREX test with dissolved B-110 sludge solution, the Sr distribution coefficient was ~ 4 in the last scrub step when 0.5 M HNO_3 was used as the scrub solution (Lumetta, Wagner, Colton, and Jones 1993). Although this led to loss of Sr from the extract under batch conditions, this Sr distribution coefficient would be acceptable under countercurrent process conditions. More efficient stripping was observed in that earlier test; D_{Sr} was 0.2 in the first strip stage.

The Sr distribution coefficients measured during this experiment are compared to those reported in the literature (Dietz and Horwitz 1993) in Figure 10.10. The results obtained here agree very well with the literature values.

Lead was extracted along with Sr; however, the extracted Pb was not stripped from the solvent, which agreed with the earlier test performed with simulated dissolved B-110 sludge solution (Section 10.3.6). The Pb distribution coefficient in the first strip contact was > 11 . This implies that Pb can be separated from the Sr, but a second strip section must be added to the process flowsheet to strip Pb from the solvent.

10.5.3 Conclusion

The results of the CMPO and SREX test with actual B-110 sludge indicated that the flowsheet depicted in Figure 10.8, though not optimized, is a viable approach to pretreating the sludge stored in Tank B-110. The TRUs and ^{90}Sr can be separated from the bulk sludge components and disposed of as HLW. The other sludge constituents (Al, Bi, Fe, Na, etc.) could be disposed of as LLW.

Figure 10.1. First Proposed Solvent Extraction Flowsheet for Pretreating Tank B-110 Sludge

Figure 10.2. Second Proposed Solvent Extraction Flowsheet for Pretreating Tank B-110 Sludge

Figure 10.3. Extraction of Sr with 0.2 M DtBC18C6 in 1-Octanol: Distribution Coefficient for Sr Versus Aqueous HNO_3 Concentration. Linear regression was performed for those points depicted as open circles.

PVE_04.PPT

Figure 10.4. Third Proposed Solvent Extraction Flowsheet for Pretreating Tank B-110 Sludge

Figure 10.5. Concentration Profile for Pu in the Test of the Flowsheet Shown in Figure 10.4 Using Simulated Dissolved B-110 Solution

Figure 10.6. Concentration Profile for Bi in the Test of the Flowsheet Shown in Figure 10.4 Using Simulated Dissolved B-110 Solution

Figure 10.7. Concentration Profile for U in the Test of the Flowsheet Shown in Figure 10.4 Using Simulated Dissolved B-110 Solution

Figure 10.8. Flowsheet Tested with Actual Dissolved B-110 Sludge Solution

Figure 10.9. Concentration Profile for Sr in the Test of the SREX Portion of the Flowsheet Shown in Figure 10.8. The Sr concentrations are relative to that initially in the aqueous phase for the first SREX contact; the relative Sr concentration in that solution was 100.

Figure 10.10. Comparison of the Sr Distribution Coefficients Measured with Actual B-110 Sludge to Those Reported in the Literature. The line shown represents a third-order polynomial fit of the literature data.

Table 10.1. Recipe for Simulated Dissolved B-110 Sludge Solution

Addition	Description	Amount Added	Concentration	
			Desired	Found
1	SiO ₂	0.523 g	0.044 <u>M</u> Si	0.029 <u>M</u> Si
2	Water	25 mL		
3	10 <u>M</u> HF	3.4 mL	0.17 <u>M</u> F	0.15 <u>M</u> F
4	Stirred and heated (100°C) for 1 h, then allowed to cool.			
5	Water	75 mL		
6	12.1 <u>M</u> HNO ₃	33 mL	2.0 <u>M</u> HNO ₃	2.3 <u>M</u> HNO ₃
7	1.6 <u>M</u> Al(NO ₃) ₃	1.3 mL	0.01 <u>M</u> Al	0.013 <u>M</u> Al
8	0.1 <u>M</u> Ba(NO ₃) ₂	0.06 mL	3 x 10 ⁻⁵ <u>M</u> Ba	3.3 x 10 ⁻⁵ <u>M</u> Ba
9	Bi(NO ₃) ₃ · 5H ₂ O	2.321 g	0.024 <u>M</u> Bi	0.024 <u>M</u> Bi
10	Ca(NO ₃) ₂ · 4H ₂ O	0.231 g	4.9 x 10 ⁻³ <u>M</u> Ca	5.3 x 10 ⁻³ <u>M</u> Ca
11	Cr(NO ₃) ₃ · 9H ₂ O	0.308 g	3.8 x 10 ⁻³ <u>M</u> Cr	4.0 x 10 ⁻³ <u>M</u> Cr
12	Fe(NO ₃) ₃ · 9H ₂ O	7.324 g	0.089 <u>M</u> Fe	0.092 <u>M</u> Fe
13	La(NO ₃) ₃ · 6H ₂ O	0.09 g	0.001 <u>M</u> La	0.001 <u>M</u> La
14	Mg(NO ₃) ₂ · 6H ₂ O	0.09 g	1.7 x 10 ⁻³ <u>M</u> Mg	1.8 x 10 ⁻³ <u>M</u> Mg
15	NaNO ₃	2.03 g	0.19 <u>M</u> Na ^(a)	0.19 <u>M</u> Na
16	NaH ₂ PO ₄ · H ₂ O	2.03 g ^(a)	0.074 <u>M</u> P ^(b)	0.072 <u>M</u> P
17	Pb(NO ₃) ₂	0.08 g	1.2 x 10 ⁻³ <u>M</u> Pb	1.3 x 10 ⁻³ <u>M</u> Pb
18	0.1 <u>M</u> Sr(NO ₃) ₂	1.4 mL	6.8 x 10 ⁻⁴ <u>M</u> Sr	7.9 x 10 ⁻⁴ <u>M</u> Sr
19	UO ₂ (NO ₃) ₂ · 6H ₂ O	0.07 g	6.4 x 10 ⁻⁴ <u>M</u> U	6.6 x 10 ⁻⁴ <u>M</u> U
20	Water	60 mL		
21	Stirred overnight at room temperature, then filtered.			

(a) Includes Na added as NaH₂PO₄ · H₂O.

(b) Too much NaH₂PO₄ · H₂O was inadvertently added; ideally, the P concentration should be 0.029 M.

Table 10.2. Batch Contacts Performed to Test the First Proposed TBP Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
1	TBP Extraction 1	Adjusted Feed ^(b)	30% TBP ^(c)	0.2	55.6
2	TBP Extraction 2	From 1	30% TBP	0.2	53.1
3	TBP Extraction 3	From 2	30% TBP	0.2	50.6
4	TBP Scrub 1	0.2 <u>M</u> HNO ₃	From 1	2	4.52
5	TBP Scrub 2	0.2 <u>M</u> HNO ₃	From 4	2	3.52
6	TBP Scrub 3	0.2 <u>M</u> HNO ₃	From 5	2	2.52
7	TBP Strip/Wash	0.25 <u>M</u> Na ₂ CO ₃	From 6	3.33	0.91

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 50 mL of the simulated dissolved B-110 sludge solution (Table 10.1) plus 0.1 g of ascorbic acid plus 5.6 mL of 0.2 M HNO₃. This solution was spiked with Pu(IV).

(c) The diluent for the TBP extractant was normal paraffin hydrocarbon (NPH).

Table 10.3. Results from the Batch Contacts Performed to Test the First Proposed TBP Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Total Alpha, cpm/mL		Recovery, %	D, Pu	Aq. [HNO ₃], <u>M</u>
			Aqueous	Organic			
	Initial Aqueous		6.56E5				2.09
1	TBP Extraction 1	0.2	6.33E5	7.70E4	99	0.12	1.98
2	TBP Extraction 2	0.2	6.40E5	7.31E4	103	0.11	1.90
3	TBP Extraction 3	0.2	6.31E5	6.46E4	101	0.10	2.06 ^(b)
4	TBP Scrub 1	2	1.31E5	1.02E4	98	0.08	0.77
5	TBP Scrub 2	2	1.84E4	9.03E2	99	0.05	0.39
6	TBP Scrub 3	2	1.27E3	2.17E2	94	0.17	0.25
7	TBP Strip/Wash	3.33	7.04E2	0	98	~0	

(a) O/A = organic-to-aqueous phase ratio.

(b) Based on the quality of the titration curve obtained for this solution, this value is likely erroneous.

Table 10.4. Batch Contacts Performed to Test the First Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
8	CMPO Extraction 1	Adjusted Feed ^(b)	CMPO ^(c)	0.29	57.2
9	CMPO Extraction 2	From 8	CMPO	0.29	53.9
10	CMPO Extraction 3	From 9	CMPO	0.29	51.4
11	CMPO Scrub 1A	Solution 1 ^(d)	From 8	0.75	20.7
12	CMPO Scrub 1B	Solution 1	From 11	0.75	19.3
13	CMPO Scrub 1C	Solution 1	From 12	0.75	18.0
14	CMPO Scrub 2A	Solution 2 ^(e)	From 13	1.0	12.5
15	CMPO Scrub 2B	Solution 2	From 14	1.0	11.5
16	CMPO Scrub 2C	Solution 2	From 15	1.0	10.5
17	CMPO Scrub 2D	Solution 2	From 16	1.0	9.5
18	CMPO Scrub 3A	0.01 M HNO ₃	From 17	1.5	5.66
19	CMPO Scrub 3B	0.01 M HNO ₃	From 18	1.5	5.00
20	CMPO Scrub 3C	0.01 M HNO ₃	From 19	1.5	4.33
21	CMPO Strip 1A	Solution 3 ^(f)	From 20	0.75	7.33
22	CMPO Strip 1B	Solution 3	From 21	0.75	5.99
23	CMPO Strip 2A	0.01 M H ₂ C ₂ O ₄	From 22	3.0	1.33
24	CMPO Strip 2B	0.01 M H ₂ C ₂ O ₄	From 23	3.0	1.16
25	CMPO Wash	0.25 M Na ₂ CO ₃	From 24	8.0	0.37

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 48.1 mL of the aqueous phase from the third TBP extraction (contact 3, Table 10.2) plus 7.7 mL of 0.15 M H₂C₂O₄, plus 1.23 mL of 5 M HNO₃, plus 0.2 mL of 0.01 M HNO₃.

(c) The CMPO solvent consisted of 0.2 M CMPO plus 1.4 M TBP in NPH. The solvent was washed with 0.25 M Na₂CO₃ prior to use.

(d) Solution 1 = 0.038 M H₂C₂O₄ plus 1.25 M HNO₃, which represents a blend of the three scrub solutions in the CMPO cycle.

(e) Solution 2 = 1.67 M HNO₃, which represents a blend of the second and third scrub solutions in the CMPO cycle.

(f) Solution 3 = 0.008 M HNO₃ plus 0.003 M H₂C₂O₄, which represents a blend of the two strip solutions.

Table 10.5. Results from the Batch Contacts Performed to Test the First Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Pu cpm/mL		Recovery, %	D, Pu	Aq. [HNO ₃], M
			Aqueous	Organic			
	Initial Aqueous		4.61E5				1.69
8	CMPO Extraction 1	0.29	1.91E4	1.39E6	92	73	1.52
9	CMPO Extraction 2	0.29	7.64E2	6.07E4	96	79	1.37
10	CMPO Extraction 3	0.29	3.9E1	2.03E3	82	52	1.33
11	CMPO Scrub 1A	0.75	3.32E3	1.14E6	82	345	1.36
12	CMPO Scrub 1B	0.75	2.90E4	1.02E6	93	35	1.31
13	CMPO Scrub 1C	0.75	6.68E4	8.92E5	96	13	1.31
14	CMPO Scrub 2A	1.0	8.03E3	9.03E5	102	110	1.58
15	CMPO Scrub 2B	1.0	1.79E3	9.08E5	101	505	1.65
16	CMPO Scrub 2C	1.0	1.26E3	9.06E5	100	720	1.65
17	CMPO Scrub 2D	1.0	1.89E3	9.05E5	100	480	1.65
18	CMPO Scrub 3A	1.5	2.47E3	9.16E5	101	371	0.73
19	CMPO Scrub 3B	1.5	1.65E4	9.14E5	101	55	0.22
20	CMPO Scrub 3C	1.5	5.99E4	8.64E5	99	14	0.07
21	CMPO Strip 1A	0.75	2.05E5	6.37E3	32	0.03	0.02
22	CMPO Strip 1B	0.75	4.38E3	2.83E2	95	0.05	
23	CMPO Strip 2A	3.0	5.47E2	4.85E0	99	0.09	
24	CMPO Strip 2B	3.0	7.25E0	3.75E0	130	0.5	
25	CMPO Wash	8.0	1.87E2	1E0	89	0.05	

(a) O/A = organic-to-aqueous phase ratio.

Table 10.6. Batch Contacts Performed to Test the First Proposed SREX Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
26	SREX Extraction 1	Adjusted Feed ^(b)	SREX ^(c)	0.37	13.0
27	SREX Extraction 2	From 26	SREX	0.37	10.5
28	SREX Extraction 3	From 27	SREX	0.37	8.03
29	SREX Extraction 4	From 28	SREX	0.37	5.53
30	SREX Scrub 1	1.0 M HNO ₃	From 26	3.0	1.24
31	SREX Scrub 2	1.0 M HNO ₃	From 30	3.0	0.97
32	SREX Strip 1	0.01 M HNO ₃	From 31	3.0	0.66
33	SREX Strip 2	0.01 M HNO ₃	From 32	3.0	0.35

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 10 mL of the aqueous phase from the third CMPO extraction (contact 10, Table 10.4) plus 2.0 mL of ⁸⁵Sr tracer solution, plus 2.31 mL of 15.7 M HNO₃, plus 1.22 mL of 1.0 M HNO₃.

(c) The SREX solvent consisted of 0.2 M di-t-butylcyclohexano-18-crown-6 in 1-octanol.

Table 10.7. Results from the Batch Contacts Performed to Test the First Proposed SREX Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Strontium-85, cpm/mL		Recovery, %	D, Sr	Aq. [HNO ₃], M
			Aqueous	Organic			
	Initial Aqueous		3.82E5				3.36
26	SREX Extraction 1	0.37	5.66E4	7.97E5	92	14	2.90
27	SREX Extraction 2	0.37	6.92E3	9.79E4	76	14	2.69
28	SREX Extraction 3	0.37	1.23E3	1.33E4	80	11	2.86 ^(b)
29	SREX Extraction 4	0.37	3.22E2	1.88E3	83	5.8	2.27
30	SREX Scrub 1	3.0	6.77E4	7.73E5	100	11	2.03
31	SREX Scrub 2	3.0	9.96E4	7.48E5	101	7.5	1.48
32	SREX Strip 1	3.0	3.34E5	6.63E5	104	2.0	0.65
33	SREX Strip 2	3.0	1.14E6	3.00E5	102	0.3	

(a) O/A = organic-to-aqueous phase ratio.

(b) Based on the quality of the titration curve obtained for this solution, this value is likely erroneous.

Table 10.8. Predicted Sr Distribution Coefficients and Extraction Factors for the SREX Cycle Depicted in Figure 10.3^(a)

Process Step	O/A ^(b)	Aq. [HNO ₃], M	Org. [HNO ₃], M	D _{Sr}	EF ^(c)
SREX Feed		4.00			
SREX Extr. 1	0.33	3.15	0.77	15	5
SREX Extr. 2	0.33	2.93	0.67	15	5
SREX Extr. 3	0.33	2.73	0.60	15	5
SREX Extr. 4	0.33	2.55	0.53	15	5
SREX Scrub 1A	2.5	2.02	0.36	10	25
SREX Scrub 1B	2.5	1.41	0.19	7	17
SREX Strip 1A	1.0	0.19	0.006	0.4	0.4
SREX Strip 1B	1.0	0.02	~0	0.01	0.01

(a) Predictions are based on batch contacts.

(b) O/A = organic-to-aqueous phase ratio.

(c) The extraction factor (EF) is equal to the distribution coefficient for Sr times the O/A.

Table 10.9. Batch Contacts Performed to Test the Second Proposed TBP Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
1A	TBP Extraction 1	Adjusted Feed ^(b)	30% TBP ^(c)	0.2	33.9
2A	TBP Extraction 2	From 1	30% TBP	0.2	30.8
3A	TBP Extraction 3	From 2	30% TBP	0.2	28.3

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 30 mL of the simulated dissolved B-110 sludge solution (Table 10.1) plus 0.06 g of ascorbic acid plus 3.3 mL of 0.2 M HNO₃ plus 1.0 mL 10 M HF. This solution was spiked with Pu(IV).

(c) The diluent for the TBP extractant was normal paraffin hydrocarbon (NPH).

Table 10.10. Results from the Batch Contacts Performed to Test the Second Proposed TBP Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Total Alpha, cpm/mL		Recovery, %	D, Pu	Aq. HNO ₃ , M
			Aqueous	Organic			
	Initial Aqueous		7.19E5				2.46
1A	TBP Extraction 1	0.2	5.93E5	5.67E3	83 ^(b)	0.008 ^(b)	2.27
2A	TBP Extraction 2	0.2	6.93E5	5.28E3	97	0.008	2.18
3A	TBP Extraction 3	0.2	6.92E5	5.18E3	100	0.008	2.08

(a) O/A = organic-to-aqueous phase ratio.

(b) Because the aqueous alpha concentrations found for contacts 2A and 3A were higher than that found for 1A, it can be assumed that the low mass balance for contact 1A was the result of an erroneously low measured aqueous alpha concentration. Assuming the measured organic alpha concentration is correct, then the aqueous alpha concentration for contact 1A should have been 7.18E5. This latter value was used to calculate the mass balance for contact 2A and to calculate the Pu distribution coefficient for contact 1A.

Table 10.11. Batch Contacts Performed to Test the Second Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
4A	CMPO Extraction 1	Adjusted Feed ^(b)	CMPO ^(c)	0.36	34.0
5A	CMPO Extraction 2	From 4A	CMPO	0.36	31.6
6A	CMPO Extraction 3	From 5A	CMPO	0.36	29.1
7A	CMPO Scrub 1A	2.0 M HNO ₃	From 4A	1.5	7.4
8A	CMPO Scrub 1B	2.0 M HNO ₃	From 7A	1.5	6.8
9A	CMPO Scrub 1C	2.0 M HNO ₃	From 8A	1.5	6.1
10A	CMPO Scrub 2A	0.01 M HNO ₃	From 9A	3.0	2.7
12A	CMPO Scrub 2B	0.01 M HNO ₃	From 10A	3.0	2.4
13A	CMPO Strip 1A	Solution 1 ^(d)	From 12A	0.75	8.2
14A	CMPO Strip 1B	Solution 1	From 13A	0.75	6.9
15A	CMPO Strip 2A	0.01 M HEDPA	From 14A	3.0	1.4
16A	CMPO Strip 2B	0.01 M HEDPA	From 15A	3.0	1.1

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 25.8 mL of the aqueous phase from the third TBP extraction (contact 3a, Table 10.9), plus 4.1 mL 2.0 M HNO₃, plus 4.1 mL of 0.01 M HNO₃.

(c) The CMPO solvent consisted of 0.2 M CMPO plus 1.4 M TBP in NPH. The solvent was washed with 0.25 M Na₂CO₃ before use.

(d) Solution 1 = 0.0075 M HNO₃ plus 0.00025 M HEDPA, which represents a blend of the two strip solutions.

Table 10.12. Results from the Batch Contacts Performed to Test the Second Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Pu, cpm/mL		Recovery, %	D, Pu	Aq. HNO ₃ , M
			Aqueous	Organic			
	Initial Aqueous		5.25E5				1.62
4A	CMPO Extraction 1	0.36	2.98E5	7.61E5	109	2.6	1.61
5A	CMPO Extraction 2	0.36	1.52E5	3.93E5	98	2.6	1.45
6A	CMPO Extraction 3	0.36	1.09E5	1.44E5	106	1.3	1.33
7A	CMPO Scrub 1A	1.5	3.71E4	7.16E5	97	19	1.13
8A	CMPO Scrub 1B	1.5	1.39E4	7.30E5	103	53	1.01
9A	CMPO Scrub 1C	1.5	1.35E4	7.26E5	101	54	0.97
10A	CMPO Scrub 2A	3.0	1.51E4	7.27E5	101	48	0.48
12A	CMPO Scrub 2B	3.0	3.24E4	7.18E5	100	22	0.29
13A	CMPO Strip 1A	0.75	1.09E5	5.20E5	93	4.8	0.07
14A	CMPO Strip 1B	0.75	8.14E4	2.53E5	70	3.1	Not determined
15A	CMPO Strip 2A	3.0	1.83E5	1.05E4	28	0.06	Not determined
16A	CMPO Strip 2B	3.0	1.92E4	8.95E0	61	0.005	Not determined

(a) O/A = organic-to-aqueous phase ratio.

Table 10.13. Batch Contacts Performed to Test the Second Proposed SREX Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	O/A ^(a)	Aqueous Volume, mL
17A	SREX Extraction 1	Adjusted Feed ^(b)	SREX ^(c)	0.33	18.7
18A	SREX Extraction 2	From 26	SREX	0.33	16.2
19A	SREX Extraction 3	From 27	SREX	0.33	13.7
20A	SREX Extraction 4	From 28	SREX	0.33	11.2
21A	SREX Scrub 1	1.0 M HNO ₃	From 17A	2.5	2.0
22A	SREX Scrub 2	1.0 M HNO ₃	From 21A	2.5	1.6
23A	SREX Strip 1	0.01 M HNO ₃	From 22	1.0	3.1
24A	SREX Strip 2	0.01 M HNO ₃	From 23A	1.0	2.1
25A	SREX Strip 3	0.01 M HNO ₃	From 24A	1.0	1.1

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 12 mL of the aqueous phase from the third CMPO extraction (contact 6A, Table 10.11) plus 2.0 mL of ⁸⁵Sr tracer solution, plus 2.8 mL of 15.7 M HNO₃, plus 2.2 mL of 1.0 M HNO₃.

(c) The SREX solvent consisted of 0.2 M di-t-butylcyclohexano-18-crown-6 in 1-octanol.

Table 10.14. Results from the Batch Contacts Performed to Test the Second Proposed SREX Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Strontium-85, cpm/mL		Recovery, %	D, Sr	Aq. [HNO ₃], M
			Aqueous	Organic			
	Initial Aqueous		1.69E5				3.37
17A	SREX Extraction 1	0.33	3.12E4	3.93E5	95	13	3.09
18A	SREX Extraction 2	0.33	3.92E3	4.95E4	65	13	2.86
19A	SREX Extraction 3	0.33	7.15E2	6.33E3	72	8.9	2.75
20A	SREX Extraction 4	0.33	1.60E2	9.17E2	65	5.7	2.56
21A	SREX Scrub 1	2.5	2.78E4	3.90E5	102	14	1.95
22A	SREX Scrub 2	2.5	4.72E4	3.90E5	105	8.3	1.42
23A	SREX Strip 1	1.0	2.37E5	1.43E5	97	0.6	0.23
24A	SREX Strip 2	1.0	1.23E5	1.35E3	87	0.01	Not measured
25A	SREX Strip 3	1.0	1.38E3	5.5E1	106	0.04	Not measured

(a) O/A = organic-to-aqueous phase ratio.

Table 10.15. Batch Contacts Performed to Test the Third Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	Aqueous Phase	Organic Phase	Q/A ^(a)	Aqueous Volume, mL
1B	CMPO Extraction 1	Adjusted Feed ^(b)	CMPO ^(c)	0.5	20.0
2B	CMPO Extraction 2	From 1B	CMPO	0.5	10.0
3B	CMPO Extraction 3	From 2B	CMPO	0.5	5.00
4B	CMPO Scrub 1A	Solution 1 ^(d)	From 1B	1.54	4.55
5B	CMPO Scrub 1B	Solution 1	From 4B	1.54	3.90
6B	CMPO Scrub 1C	Solution 1	From 5B	1.54	3.25
7B	CMPO Scrub 2	Solution 2 ^(d)	From 6B	2.31	1.73
8B	CMPO Strip A	Solution 3 ^(d)	From 7B	0.33	9.00
9B	CMPO Strip B	Solution 3	From 8B	0.33	6.00
10B	CMPO Strip C	Solution 3	From 9B	0.33	4.50
11B	CMPO Strip D	Solution 3	From 10B	0.33	3.00
12B	Carb. Wash	0.25 M NaCO ₃	From 11B	1.0	0.50

(a) O/A = organic-to-aqueous phase ratio.

(b) The adjusted feed solution consisted of 13.78 mL of the simulated dissolved B-110 sludge solution, plus 2.2 mL of 0.67 M HNO₃/0.0067 M ascorbic acid, plus 4.41 mL of 0.1 M HNO₃/0.01 M ascorbic acid.

(c) The CMPO solvent consisted of 0.2 M CMPO plus 1.4 M TBP in NPH. The solvent was washed with 0.25 M Na₂CO₃ prior to use.

(d) Solution 1 = 0.67 M HNO₃ plus 0.01 M ascorbic acid, which is the second scrub solution. Solution 3 = 0.1 M ascorbic acid, which is the strip solution.

Table 10.16. Results from the Batch Contacts Performed to Test the Third Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

Contact	Description	O/A ^(a)	Pu, cpm/mL		Recovery, %	D, Pu	Aq. HNO ₃ , M
			Aqueous	Organic			
	Initial Aqueous		5.58E5			84	1.79
1B	CMPO Extraction 1	0.5	1.36E4	1.14E6	104	66	1.52
2B	CMPO Extraction 2	0.5	3.47E2	2.30E4	87	62	1.27
3B	CMPO Extraction 3	0.5	7EO	4.32E2	64	62	1.10
4B	CMPO Scrub 1A	1.54	1.78E4	1.11E6	98	33	0.96
5B	CMPO Scrub 1B	1.54	3.33E4	1.09E6	100	25	0.79
6B	CMPO Scrub 1C	1.54	4.38E4	1.07E6	101	3.9	0.72
7B	CMPO Scrub 2	2.31	2.50E5	9.71E5	100	0.8	0.35
8B	CMPO Strip A	0.33	2.61E5	1.98E5	101	0.6	0.13
9B	CMPO Strip B	0.33	5.68E4	3.36E4	103	0.6	0.11
10B	CMPO Strip C	0.33	9.27E3	5.51E3	99	0.7	0.11
11B	CMPO Strip D	0.33	1.48E3	1.06E3	100		0.11
12B	Carb. Wash	1.0	1.8E2	2EO	17		Not determined

(a) O/A = organic-to-aqueous phase ratio.

Table 10.17. Results of the First Extraction Contact to Test the Third Proposed CMPO Solvent Extraction Cycle for Pretreating B-110 Sludge

<u>Components</u>	<u>Initial Aq., M</u>	<u>Extraction 1, Aq., M</u>	<u>Extraction 1, Org., M</u>	<u>D</u>
Al	8.95E-03	8.39E-03	1.12E-03	0.13
- Ba	2.20E-05	2.20E-05	0.00E+00	0.00
Bi	1.59E-02	1.16E-03	2.95E-02	25.50
Ca	3.58E-03	3.35E-03	4.52E-04	0.13
Cr	2.70E-03	2.58E-03	2.23E-04	0.09
Fe	6.22E-02	5.95E-02	5.41E-03	0.09
La	7.39E-04	2.17E-04	1.04E-03	4.80
Mg	1.24E-03	1.24E-03	0.00E+00	0.00
Na	1.31E-01	1.25E-01	1.31E-02	0.11
Pb	8.75E-04	8.02E-04	1.46E-04	0.18
Si	1.94E-02	1.77E-02	3.23E-03	0.18
Sr	5.34E-04	5.00E-04	6.89E-05	0.14
HNO ₃	1.79E+00	1.52E+00	5.40E-01	0.36
F	1.05E-01	1.01E-01	8.00E-03	0.08

Table 10.18. Batch Contacts Performed to Test the B-110 Sludge Pretreatment Flowsheet

Stage ^(a)	Description	O/A ^(b)	Aqueous Phase	Aq. Vol, mL	Organic Phase
2	CMPO Extraction 1	0.5	Adjusted Feed	20.10	CMPO Solvent
3	CMPO Scrub 1A	1.54	Scrub Solution 1 ^(c)	5.84	From Stage 2
4	CMPO Scrub 1B	1.54	Scrub Solution 1	5.19	From Stage 3
5	CMPO Scrub 1C	1.54	Scrub Solution 1	4.55	From Stage 4
6	CMPO Scrub 2	2.31	Scrub Solution 2 ^(d)	2.60	From Stage 5
7	CMPO Strip 1A	0.33	Strip Solution 1	15.15	From Stage 6
8	CMPO Strip 1B	0.33	Strip Solution 1	12.12	From Stage 7
9	CMPO Strip 1C	0.33	Strip Solution 1	9.09	From Stage 8
10	CMPO Strip 1D	0.33	Strip Solution 1	6.06	From Stage 9
11	CMPO Strip 2	2	0.2 M HEDPA	0.75	From Stage 10
12	Carb Wash	7	0.25 M Na ₂ CO ₃	0.07	From Stage 11
11	CMPO Extraction 2	0.5	From Stage 2	16.00	CMPO Solvent
17	SREX Extr 1	0.33	— ^(e)	19.8	SREX Solvent
18	SREX Scrub 1A	2.54	1.0 M HNO ₃	2.17	From Stage 17
19	SREX Scrub 1B	2.54	1.0 M HNO ₃	1.77	From Stage 18
20	SREX Strip 1A	1.00	0.01 M HNO ₃	3.50	From Stage 19
21	SREX Strip 1B	1.00	0.01 M HNO ₃	2.50	From Stage 20
22	SREX Strip 1C	1.00	0.01 M HNO ₃	1.50	From Stage 21
16	SREX Extr 2	0.33	From Stage 17	5.00	SREX Solvent
15	SREX Extr 3	0.33	From Stage 16	3.00	SREX Solvent
14	SREX Extr 4	0.33	From Stage 15	1.50	SREX Solvent

(a) Represents the stage numbers in Figure 10.8

(b) O/A - organic-to-aqueous phase ratio.

(c) Scrub solution 1 = 0.67 M HNO₃ plus 0.003 M ascorbic acid.

(d) Scrub solution 2 = 0.01 M HNO₃ plus 0.01 M ascorbic acid.

(e) The initial aqueous phase for the first SREX extraction was prepared by mixing 14.0 mL of the aqueous phase from CMPO extraction 2 with 3.3 mL 15.7 M HNO₃, 2.6 mL of 1.0 M HNO₃, and 0.2 mL of ⁸⁵Sr tracer solution.

Table 10.19. Behavior of Alpha Emitters in the CMPO Flowsheet Test with Actual Dissolved B-110 Sludge

Description	O/A ^(a)	Total Alpha $\mu\text{Ci/mL}$		D, α	Aq. HNO_3 , <u>M</u>
		Aqueous	Organic ^(b)		
Initial Aqueous		3.59E-2			1.68
CMPO Extraction 1	0.5	1.63E-3	6.49E-2	40	1.46
CMPO Extraction 2	0.5	2.43E-4	2.77E-3	11	1.22
CMPO Scrub 1A	1.54	3.26E-3	6.28E-2	19	0.97
CMPO Scrub 1B	1.54	3.41E-3	6.06E-2	18	0.82
CMPO Scrub 1C	1.54	3.76E-3	5.81E-2	15	0.75
CMPO Scrub 2	2.31	1.11E-2	5.34E-2	4.9	0.38
CMPO Strip 1A	0.33	1.49E-2	8.23E-3	0.6	0.13
CMPO Strip 1B	0.33	2.54E-3	5.36E-4	0.2	0.10
CMPO Strip 1C	0.33	1.77E-4	--	--	0.09
CMPO Strip 1D	0.33	<1.4E-4	--	--	0.09
CMPO Strip 2	2.0	<1.5E-4	--	--	Not determined
Carb. Wash	1.0	<1.5E-4	--	--	Not determined

(a) O/A = organic-to-aqueous phase ratio.

(b) Organic phase concentrations were calculated by mass balance; the total recovery for U was 81%.

Table 10.20. Behavior of U in the CMPO Flowsheet Test with Actual Dissolved B-110 Sludge

Description	O/A ^(a)	Uranium, M		D, U	Aq. HNO ₃ , M
		Aqueous	Organic ^(b)		
Initial Aqueous		1.55E-4			1.68
CMPO Extraction 1	0.5	9.96E-7	2.50E-4	250	1.46
CMPO Extraction 2	0.5	≤3.17E-7	--	--	1.22
CMPO Scrub 1A	1.54	1.48E-6	2.49E-4	170	0.97
CMPO Scrub 1B	1.54	1.48E-6	2.48E-4	170	0.82
CMPO Scrub 1C	1.54	2.47E-6	2.46E-4	100	0.75
CMPO Scrub 2	2.31	2.50E-6	2.45E-4	98	0.38
CMPO Strip 1A	0.33	9.08E-6	2.18E-4	24	0.13
CMPO Strip 1B	0.33	9.71E-6	1.88E-4	19	0.10
CMPO Strip 1C	0.33	9.37E-6	1.60E-4	17	0.09
CMPO Strip 1D	0.33	8.74E-6	1.34E-4	15	0.09
CMPO Strip 2	2.0	2.67E-4	--	--	Not determined
Carb. Wash	1.0	≤3.2E-7	--	--	Not determined

(a) O/A = organic-to-aqueous phase ratio.

(b) Organic phase concentrations were calculated by mass balance; the total recovery for U was 81%.

Table 10.21. Behavior of Bi in the CMPO Flowsheet Test with Actual Dissolved B-110Sludge

Description	O/A ^(a)	Aqueous	Organic ^(b)	D, Bi	Aq. HNO ₃ , M
Initial Aqueous		1.28E-2			1.68
CMPO Extraction 1	0.5	5.07E-4	2.17E-2	43	1.46
CMPO Extraction 2	0.5	≤3.59E-4	--	--	1.22
CMPO Scrub 1A	1.54	≤3.59E-4	2.17E-2	≥60	0.97
CMPO Scrub 1B	1.54	≤3.59E-4	2.17E-2	≥60	0.82
CMPO Scrub 1C	1.54	≤3.59E-4	2.17E-3	≥60	0.75
CMPO Scrub 2	2.31	4.35E-4	2.15E-2	49	0.38
CMPO Strip 1A	0.33	1.73E-3	1.63E-2	9.5	0.13
CMPO Strip 1B	0.33	1.81E-3	1.08E-2	6.0	0.10
CMPO Strip 1C	0.33	1.16E-3	7.29E-3	6.3	0.09
CMPO Strip 1D	0.33	8.18E-4	4.81E-3	5.9	0.09
CMPO Strip 2	2.0	9.62E-3	--	--	Not determined
Carb. Wash	1.0	≤3.59E-4	--	--	Not determined

(a) O/A = organic-to-aqueous phase ratio.

(b) Organic phase concentrations were calculated by mass balance; the total recovery for Bi was 84%.

11.0 TRU Extraction Using Dihexyldiethylcarbamoymethyl Phosphonate

Dihexyldiethylcarbamoymethyl phosphonate (DHDECMP) has been extensively investigated as a potential extractant for selectively removing TRU elements from acidic waste streams. First proposed in the 1960s (Siddall 1963, 1964), its properties were explored in the 1970s by Schulz et. al. (Schulz and McIsaac 1975; Schulz and Navratil 1982), and in the 1980s by several research groups in the U.S., including Argonne National Laboratory (Horwitz, Kalina, and Muscatello 1981; Horwitz, Muscatello, Kalina, and Kaplan 1981), Idaho National Engineering Laboratory (McIsaac 1982; McIsaac and Baker 1983), and Los Alamos National Laboratory (LANL) (Marsh and Yarbrow 1988). Before 1980, evaluations of DHDECMP were complicated by the poor quality of the extractant, particularly with respect to the presence of acidic organophosphorus impurities, which can greatly alter the material's TRU extraction characteristics. In the late 1970s, however, methods for preparing fairly pure DHDECMP became available (Schroeder, McIsaac, and Krupa 1980; Bowen and Paine 1986; Saran 1989), and new investigations were begun. One result of these new investigations was the development of the transuranium extraction (TRUEX) process, which uses an extractant of related structure, octyl(phenyl)-N,N-diisobutylcarbamoymethylphosphine oxide (CMPO).

The chemistry of the CMPO extractant and that of DHDECMP are, in essence, different only in degree. The more basic phosphoryl group in CMPO makes it a more powerful extractant of TRUs than DHDECMP. Conversely, the ability of CMPO to strongly bind tetravalent and hexavalent TRUs even in weak HNO_3 media dictates that a stripping agent (e.g., a complexing or reducing agent) be introduced to efficiently remove Pu(IV) and U(VI) from the process solvent. Recently, it has been suggested that a TRU extraction flowsheet based on DHDECMP may be superior to one based on CMPO. The weaker binding of TRUs by DHDECMP, while making the initial extraction of TRUs to the organic phase more difficult, might allow TRUs to be stripped back to the aqueous phase simply by decreasing the HNO_3 concentration. Under this proposed scheme, use of a special stripping agent would be unnecessary.

A study was initiated in FY 1993 to determine if pretreatment flowsheets based on DHDECMP would be superior to those based on CMPO. Such an evaluation requires basic extraction data for DHDECMP. Work in FY 1993 focused on collecting extraction data for HNO_3 , Am(III), Pu(IV), U(VI), Bi(III), Fe(III), and Zr(IV), which are important Hanford tank sludge constituents. In addition, the effects of solvent purification methods on Am and Pu distribution were determined. These methods were aimed at removing trace acidic organophosphorus impurities that could inhibit stripping of the TRUs.

11.1 Extraction of HNO_3 with DHDECMP

The DHDECMP used in this study was provided by Dr. Barbara Smith of LANL. Normal paraffin hydrocarbon and TBP were obtained from in-house stocks. Isopar M, a mixture of aliphatic branched hydrocarbons, was obtained from Exxon Chemical Corporation (Houston, Texas). All other bulk chemicals were of reagent grade and were used as received.

The DHDECMP extractant solution was prepared as follows: 27.3 g (0.075 mole) of DHDECMP and 28.0 g (0.105 mole) of TBP were placed in a 100-mL volumetric flask. Diluent (either NPH or Isopar M) was added to the 100-mL mark. The resulting solution was then contacted three times with 50-mL portions of 0.25 M Na_2CO_3 , followed by two or three 50-mL portions of deionized water. Separation of the layers was aided by centrifugation (5 min at 2000 rpm) as needed. The extractant solutions consisted of 0.75 M DHDECMP plus 1.05 M TBP.

To obtain the HNO_3 distribution measurements, the aqueous HNO_3 solutions were analyzed before and after contact with equal volumes of the DHDECMP extractant. Nitric acid concentrations were determined by potentiometric titration with standard NaOH. Aliquots (ranging from 0.02 to 1 mL) of the solution to be analyzed were added to 10 mL of deionized water. The resulting solutions were titrated with 0.05 M NaOH using a Mettler DL21 automatic titrator. The organic phase HNO_3 concentration was determined by the difference between the initial and equilibrium aqueous HNO_3 concentrations. As a control for some of the extractant contacts, aliquots (ranging from 0.01 to 1 mL) of the organic phase also were added to 10 mL of deionized water and titrated. In those cases, the material balance between the initial aqueous HNO_3 concentration and the sum of the equilibrated organic and aqueous phase HNO_3 concentrations was excellent, with typically >98% and often >99% of the initial HNO_3 accounted for.

Figure 11.1 and Table 11.1 summarize HNO_3 extraction by 0.75 M DHDECMP/1.05 M TBP in either NPH or Isopar M. The distribution coefficients are independent of the nature of the diluent or the solvent purification method [Na_2CO_3 wash versus macroreticular ion exchange (MIX) (see Section 11.2) treatment].

Nitric acid distribution measurements with an initial aqueous HNO_3 concentration > 2 M were not meaningful due to third-phase formation, regardless of whether Isopar M or NPH was used as the diluent. Higher aqueous $[\text{NO}_3]$ can be obtained without leading to third-phase formation, however, if NaNO_3 is used rather than HNO_3 to increase the total $[\text{NO}_3]$ beyond 2 M, as illustrated in Figure 11.2 [some $\text{UO}_2(\text{NO}_3)_2$ was added for color contrast]. A third liquid phase was clearly evident when 7.5 M HNO_3 was contacted with 0.75 M DHDECMP/1.05 M TBP in Isopar M, but no third phase was evident for the contact with a 2.0 M HNO_3 /5.5 M NaNO_3 solution. For comparison, a contact of 7.5 M HNO_3 with the CMPO solvent is also shown in Figure 11.2. No third phase was evident in this case.

The tendency for third-phase formation for DHDECMP solutions at high HNO_3 with aliphatic hydrocarbons diluents has been recognized in the literature (Schulz and Navratil 1982), although one recent study (Marsh and Yarbrow 1988) examined HNO_3 solutions up to 7.5 M with no report of third-phase formation. Because of the tendency toward third-phase formation, aromatic hydrocarbons or chlorinated hydrocarbons are used as diluents for most distribution measurements involving DHDECMP; with these diluents, third-phase formation is less likely to occur.

11.2 The Effect of DHDECMP Solvent Purification Method

During the course of this project, the CMPO solvent used for TRU extraction studies had sufficient acidic impurities to significantly alter the TRU distribution coefficients at low $[\text{HNO}_3]$. Furthermore, it has been noted that neutral, carbamoylmethylphosphine oxide extractants such as CMPO, used in the TRUEX extraction process, can contain, or develop as a result of radiolysis or hydrolysis, acidic

organophosphorus impurities at low HNO_3 concentrations. Analogous acidic organophosphorus impurities can develop in DHDECMP. Because the history of the DHDECMP used in this study was not known in detail, the effects of solvent purification treatments on metal distribution coefficients were examined.

Many methods have been reported for purifying DHDECMP (Schulz and Navratil 1982). Unfortunately, most of them address purification of highly impure (i.e., 65%) DHDECMP samples rather than removal of trace amounts of deleterious impurities. However, removal of small amounts of acidic impurities from CMPO has recently been studied (Chiarizia and Horwitz 1990; Tse, Reichley-Yinger, and Vandegrift 1992). Based on the results of these studies, two potential methods for purifying DHDECMP were chosen: 1) treatment with alumina, and 2) treatment with a macroreticular anion exchange resin in its hydroxide form (referred to as the MIX treatment).

For the alumina treatments, a given amount of alumina containing 3% Na_2O (LaRoche Chemicals Inc., Baton Rouge, Louisiana) was mixed with the carbonate-washed DHDECMP solution for 2 h at room temperature. The mixture was centrifuged, and the extractant solution was decanted from the alumina.

For the MIX treatment, a column of Amberlyst® A-27 was prepared by washing with aqueous 1 M NaOH until the eluant tested negative for Cl^- (i.e., addition of silver nitrate to an acidified aliquot of the eluent did not cause AgCl to precipitate). The resin was then washed with water until the eluant tested neutral with pH paper. The resin was removed from the column and washed with three equal portions of ethanol and two equal portions of hexane, with the resin separated each time by filtration through a 2- μm membrane. The resin was finally dried overnight under vacuum at room temperature. About 25 mg of this resin per mL of DHDECMP solution was mixed with the DHDECMP solution for 2 h at room temperature. The organic solution was filtered through a medium sintered-glass frit, and the filtrate was contacted with 2:1 (volume:volume) 0.25 M Na_2CO_3 , then 0.1 M HNO_3 , and finally three times with water. The overall volume losses for the DHDECMP solution from the MIX treatment were <10%.

The results of the various purification methods on the distribution coefficients are presented for Am(III) in Figure 11.3, and for Pu(IV) in Figure 11.4. While negligible effects were observed on the distribution coefficients at 0.5 M HNO_3 for any of the purification methods, at lower acid concentrations (e.g., 0.01 M HNO_3), decreases in D of greater than an order of magnitude were found for both Pu(IV) and Am(III) for the alumina and MIX treated solvent (compared to only Na_2CO_3 wash).

The presence of acidic organophosphorus impurities was manifested at low acidities by an increase in D_{Pu} and D_{Am} values as the aqueous HNO_3 concentrations decreased. In their absence, D_{Pu} and D_{Am} values decreased as the aqueous HNO_3 concentrations decreased.

The contact method used in the purification step appeared to have some small influence on the efficiency of the solvent purification step. In one case, a DHDECMP solution was contacted with alumina via the batch method as described above. In another instance, the DHDECMP solution was passed through a column of alumina. Contact with the alumina via the column method with an alumina/DHDECMP ratio of 250 mg/mL gave higher Pu(IV) distribution coefficients, values very similar to those that resulted from a batch contact at a ratio of 125 mg/mL. The relatively quick column contact seemed somewhat less effective at removing acidic impurities than the more prolonged batch contact.

Finally, the HNO_3 distribution coefficients were unaffected by purifying the extractant solution. This, and the lack of change in D_{Am} and D_{Pu} at 0.5 M initial aqueous HNO_3 , indicates that the solvent purification did not alter the gross composition of the DHDECMP solution.

Deciding which method of DHDECMP purification is optimal requires balancing two opposing parameters. On the one hand, the TRU distribution coefficients decrease at low acid. Here, the trend is clear; the greater the amount of material used in the treatment, the lower the distribution coefficients at low acid. Indeed, the lowest values observed for this study ($D_{\text{Am}} = 0.0015$ at 0.01 M HNO_3) were equal to or better than literature values ($D = \text{ca. } 0.002$ at 0.01 M HNO_3 , Mathur, Murali, and Natarajan 1991) obtained using a highly pure DHDECMP (0.4 M) in benzene.

On the other hand, using large amounts of sorbent in the purification step leads to increased losses of the extractant. With alumina, the losses could be considerable, about 40% of the extractant remained with the alumina after phase separation by centrifugation at a ratio of 0.5 g alumina/mL extractant.

In this study, the purification method chosen for further investigations of the DHDECMP extractant was the MIX treatment. This sorbent represents a compromise between efficacy at removing acidic impurities and extractant loss (< 10%).

11.3 Distribution Measurements

The extraction of important Hanford sludge waste constituents by DHDECMP was studied as a function of nitrate ion concentration. The investigated waste constituents were Am(III), Pu(IV), U(VI), Bi(III), Fe(III), and Zr(IV). The effects of oxalate and fluoride ions on the distribution behavior of these waste constituents were also investigated. Oxalate and fluoride ions will likely be present in process solutions because 1) they are present in the wastes, or 2) they might be added to assist in tank sludge dissolution.

11.3.1 Methods

Unless otherwise noted, the solvent used was 0.75 M DHDECMP plus 1.05 M TBP in NPH, and the solvent had been purified using the MIX procedure described in Section 11.2. The organic to aqueous phase ratio was one to one. In most instances, the metal distribution measurements were performed with the same initial aqueous HNO_3 concentrations as the HNO_3 distribution measurements (Section 11.1). In these cases, the equilibrium aqueous $[\text{HNO}_3]$ was assumed to be the same as that found in the HNO_3 distribution measurements. However, in a few cases, the equilibrium aqueous HNO_3 concentrations were determined by extrapolation or interpolation from a plot of initial aqueous $[\text{HNO}_3]$ versus equilibrium aqueous $[\text{HNO}_3]$ (Figure 11.5).

Plutonium(IV) was added as a stock solution in either 6 or 7 M HNO_3 . The +4 oxidation state was verified by adding 1 μL of the Pu solution to 1 mL of 0.3 M HNO_3 , followed by contact with 1 mL of 0.5 M thenoyltrifluoroacetone in xylene. A D_{Pu} of greater than 200 was found. Americium(III) was added as a stock solution in 0.3 M HNO_3 .

Metal distribution coefficients were determined by mixing 1 mL of the DHDECMP solvent with 1 mL of the appropriate aqueous phase for 60 s. After centrifuging, aliquots of the aqueous phase were taken for analysis. In the case of the Am and Pu measurements, aliquots of the organic phase were also taken.

Americium and Pu concentrations in each phase at equilibrium were determined by liquid scintillation counting. The counting was performed by mixing a 0.1-mL aliquot of the appropriate phase with 5 mL of either OPTI-FLUOR® or ULTIMA GOLD® liquid scintillation cocktail (Packard Instrument Co., Downers Grove, Illinois). To compensate for possible quenching effects, 0.1 mL of the tracer-free other phase was added. The relative alpha activity of each phase was determined using a Packard TRI-CARB 2500 Liquid Scintillation Analyzer.

The distribution of U(VI) was determined in a manner similar to that used for Am and Pu, except that enough solid uranyl nitrate hexahydrate was added directly to the aqueous phase to make it 0.05 M before DHDECMP contact. The U concentration for each phase was determined by alpha-counting with a liquid scintillation counter as described above.

Bismuth nitrate distribution measurements were performed by adding 12 μ L of a 0.1 M Bi(III) stock solution in 1 M HNO_3 to 1.19 mL of the appropriate aqueous solution to give a solution 0.001 M in Bi before contacting with the DHDECMP solvent. A 0.2-mL aliquot of the aqueous phase was placed in 9.8 mL of 0.01 M HNO_3 and was analyzed by atomic absorption (AA) spectroscopy. The remaining 1 mL of Bi solution was mixed with 1 mL of the DHDECMP extractant for 60 s. After centrifugation, another aliquot was taken from the aqueous phase for Bi analysis by AA spectroscopy. The organic phase Bi concentration was determined by the difference between the initial and equilibrium aqueous phase Bi concentrations.

Iron(III) distribution coefficients were measured by adding 11.5 μ L of a stock solution (0.1 M in Fe^{3+} and 0.001 M in HNO_3) to 1.19 mL of the appropriate aqueous nitrate solution. A 0.15-mL aliquot was removed and diluted to a total volume of 10 mL with 0.01 M in HNO_3 . The remaining approximately 1 mL of Fe solution was mixed with 1 mL of the DHDECMP extractant for 60 s. After centrifugation, a 0.15-mL aliquot was removed from the aqueous phase and diluted to 10 mL with 0.01 M in HNO_3 . The Fe concentrations of the aqueous solution before and after the extraction were determined by AA spectroscopy. The organic phase concentration was determined by difference.

For both the Bi(III) and the Fe(III) analyses, the AA spectrometer was calibrated with standard solutions of known concentration immediately before the analyses. The standard solutions were periodically remeasured during the analyses to ensure a constant instrument response. The calibration curves for these elements were linear, typical correlation coefficients of >0.9999 were obtained.

11.3.2 Extraction of Am(III) with DHDECMP

The distribution coefficients for Am(III) were examined as a function of nitrate concentration. The effects of 0.1 M HF or 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ on the Am extraction were also determined. The examined nitrate concentrations ranged from an initial aqueous concentration of 7.5 M nitrate (2 M HNO_3 and

5.5 M NaNO₃), to 0.05 M nitrate (0.05 M HNO₃). The results are shown in Figure 11.6, where D_{Am} is plotted against the equilibrium aqueous nitrate concentration.

A log-log plot of D_{Am} versus [NO₃] shows good linearity (Figure 11.6), with only a slight curvature toward higher acid concentrations—a curvature that is reduced as NaNO₃ replaces HNO₃ in supplying the total nitrate concentration. In addition, the use of NaNO₃ allows access to very high D_{Am} values should they be required. Even without recourse to NaNO₃, the D_{Am} value ~ 3 with an initial aqueous [HNO₃] of 2 M should allow >99% of the Am(III) to be removed in no more than four (1:1) contacts.

The data also indicate that stripping should be readily achieved by decreasing the aqueous nitrate concentration. Since D_{Am} was less than 0.01 at 0.05 M HNO₃, the limiting factor in Am stripping will be the number of steps required to remove the HNO₃ from the organic phase.

The presence of 0.1 M HF had essentially no effect on the distribution coefficients for Am(III), consistent with a previously published report (Marsh and Yarbrow 1988). However, oxalic acid markedly suppressed the extraction of Am(III), decreasing the distribution coefficient by a factor of 4 at the highest nitrate concentration examined and by greater than an order of magnitude at the lowest nitrate concentrations.

The decrease in the distribution coefficients for Am(III) in the presence of oxalic acid has important ramifications for any TRU-separations flowsheet based on the DHDECMP extractant. Use of oxalic acid to inhibit extraction of unwanted elements such as Zr⁴⁺ and Fe³⁺ is frequently specified for CMPO-based flowsheets. If required for the DHDECMP-based pretreatment of NCRW sludge, using oxalic acid would necessitate a very high aqueous nitrate concentration to maintain the distribution coefficient for Am(III) above 1. Because of the enhanced tendency for third-phase formation with the DHDECMP extractant compared to CMPO, such high nitrate concentrations would require metal nitrates rather than HNO₃ as a nitrate source (above 2 M HNO₃).

The effect of diluent on Am(III) extraction was investigated; data obtained with DHDECMP in NPH and in Isopar M are compared in Figure 11.7. No significant differences were observed between the two diluents.

Several research groups have recently measured Am distribution coefficients using DHDECMP as the extractant (Table 11.2). Although in many instances direct comparison was difficult because of differing extractant concentrations, the magnitude of the Am distribution coefficients measured here was consistent with those previously reported.

11.3.3 Extraction of Pu(IV) with DHDECMP

The distribution coefficients for Pu(IV) were also examined as a function of nitrate concentration, both in the absence of complexants and in the presence of 0.1 M HF or 0.05 M H₂C₂O₄. The nitrate concentrations that were examined ranged from an initial aqueous concentration of 7.5 M nitrate (2 M HNO₃ and 5.5 M NaNO₃), to 0.05 M nitrate (0.05 M HNO₃). The results are shown in Figure 11.8.

The extraction of Pu(IV) with DHDECMP was roughly an order of magnitude greater than the extraction of Am(III), with favorable extraction achieved at nitrate concentrations greater than 1 M. Both oxalic acid and fluoride affected the distribution coefficients for Pu(IV). The presence of 0.1 M HF dramatically decreased the distribution coefficients, ranging from a factor of 26 at the highest nitrate concentration to a factor of >4,000 at the lowest nitrate concentrations. Such behavior agrees with that reported in earlier published work (Marsh and Yarbrow 1988). Oxalic acid also decreased Pu(IV) distribution coefficients, but to a lesser extent than fluoride; the presence of 0.05 M oxalic acid decreased the Pu(IV) distribution coefficients a factor of 4 at high nitrate concentrations, and by factor of >300 at low nitrate concentrations.

An explanation of the larger decreases in Pu(IV) distribution coefficients at low nitrate concentrations may be that the added complexants competed favorably with trace amounts of the acidic organophosphorus impurities present in the extractant. The presence of the acidic organophosphorus impurities normally results in higher distribution coefficients at low aqueous nitrate concentrations. Negation of these impurities' influence would, therefore, enhance the relative differences in distribution coefficients at low nitrate as compared to high nitrate.

The Pu distribution data corroborate the suggestion of Marsh and Yarbrow (1988) that Pu could be stripped from the solvent without addition of complexing or reducing agents. However, the stripping ability of dilute HNO_3 is marginal and is very sensitive to the presence of acidic organophosphorus impurities in the solvent (Section 11.2). Extremely aggressive solvent cleanup would be required during processing to strip with dilute HNO_3 alone. It may be difficult to achieve adequate solvent cleanup under processing conditions. Even with such solvent cleanup, enough solvent degradation may occur during the extraction and scrubbing steps of a DHDECMP-based process to prevent Pu stripping by dilute HNO_3 alone.

The effect of diluent on the Pu(IV) extraction is given in Figure 11.9. No significant differences were observed between the NPH and Isopar M.

There are few values available in the literature for comparison with this work. Marsh and Yarbrow (1988) report a $D(\text{Pu(IV)})$ of ~ 2.8 for contact with initially 0.45 M $[\text{HNO}_3]$, and $D(\text{Pu(IV)})$ of ~ 8 with initially 1.5 M $[\text{HNO}_3]$, which compare to values of 2 and 10, respectively, for the MIX-treated DHDECMP extractant.

11.3.4 Extraction of U(VI) with DHDECMP

The measured distribution coefficients for U(VI) as a function of equilibrium aqueous nitrate concentration are presented in Figure 11.10. In most cases, uranyl nitrate was added to an aqueous nitrate solution to give 0.05 M U(VI). The data presented in Figure 11.10 are corrected for the additional 0.1 M nitrate ion added to the initial aqueous concentration caused by adding uranyl nitrate as well as for the loss of nitrate that is associated with uranyl ion extraction into the organic phase, which is a significant correction under high $D_{\text{U(VI)}}$ conditions. Three measurements were made at lower U(VI) concentrations, with the aqueous solution analyzed for U by laser fluorimetry instead of scintillation counting, before and after contact with the DHDECMP extractant. The general agreement between the two methods indicates both methods are acceptable.

The presence of fluoride ion decreased the distribution coefficients of U(VI) at all but the highest aqueous nitrate concentrations measured. Decreases in the distribution coefficients ranged from a factor of 2 for an initial aqueous nitrate concentration of 2 M to about a factor of 7 at the lowest initial aqueous nitrate concentrations measured. Although no decrease was observed at the highest nitrate concentration, the distribution coefficients were sufficiently large that a greater uncertainty is associated with these numbers. Such a decrease in distribution coefficients in the presence of fluoride was consistent with previous literature conclusions (Marsh and Yarbrow 1988). In contrast, oxalic acid had a minimal effect on the U(VI) distribution coefficients at all aqueous nitrate concentrations measured.

Diluent (NPH versus Isopar M) had little effect on U(VI) extraction, as can be seen in Figure 11.11. The U(VI) distribution coefficients measured in NPH and Isopar M were almost identical.

Comparisons of these results with other recent results are few and complicated by differing diluents and concentrations. Table 11.3 summarizes the relevant data that are available. Where close comparisons are possible, the agreement is good between the values reported in the literature and those measured here.

11.3.5 Extraction of Bismuth(III) with DHDECMP

The distribution behavior of Bi(III) in the TRU extraction process is of interest because a relatively large inventory of Bi is in the SSTs at the Hanford Site. This Bi originated during the purification of Pu by coprecipitation with BiPO_4 . The distribution coefficients for Bi(III) were measured as a function of aqueous nitrate concentration alone or in the presence of either 0.1 M HF or 0.05 M $\text{H}_2\text{C}_2\text{O}_4$.

The extraction of Bi(III) with DHDECMP is summarized in Figure 11.12. The magnitude of the Bi distribution coefficients is roughly between that of U(VI) and Am(III), indicating that Bi(III) will be coextracted with the TRUs. Because Bi is a major constituent of many of the SSTs, separation of this element from the TRUs may be needed to reduce the HLW volume. The distribution data suggest that separation might be achieved by stripping with 0.3 M HNO_3 . At 0.3 M NO_3^- , the distribution coefficient for Bi(III) is ~ 2 , whereas that for trivalent actinides (e.g., Am) is ~ 0.2 . A reducing agent, such as ascorbic acid, would be required to adjust the Pu valence to the +3 state so that its distribution coefficient would be near that of Am(III) and so allow it also to be stripped. A similar approach is being considered for the CMPO process (see Section 10.4).

Both fluoride and oxalic acid inhibited extraction of Bi(III) by DHDECMP. The presence of 0.1 M fluoride decreased Bi(III) extraction by a factor of 4 at the highest aqueous nitrate concentration examined, and no extraction at all was observed for initial aqueous nitrate concentrations below 0.1 M. Oxalic acid may have a greater effect, but efforts to measure the distribution coefficients for the initially 0.001 M $\text{Bi}(\text{NO}_3)_3$ solutions were inhibited for all but the 7.5 M initial aqueous nitrate concentration measurement because of precipitate formation in the aqueous phase, presumably bismuth oxalate. For the single measurement obtained, the presence of oxalic acid decreased the distribution coefficient by a factor of 20.

Few quantitative reports of Bi(III) extraction are available, so a comparison with values obtained by other research groups is not possible.

11.3.6 Extraction of Fe(III) with DHDECMP

The distribution coefficients for Fe(III) were measured as a function of aqueous nitrate concentration alone or in the presence of either 0.1 M HF or 0.05 M $\text{H}_2\text{C}_2\text{O}_4$. The results are shown in Table 11.4. Contact of any Fe(III) solution with the DHDECMP extractant did not appreciably decrease the aqueous Fe(III) concentration, indicating that Fe(III) was not extracted to any significant extent by DHDECMP under the conditions examined.

11.3.7 Extraction of Zr(IV) with DHDECMP

The distribution of Zr in the TRU extraction process is of interest because of the high amounts of Zr in NCRW sludge. With the lower TRU distribution coefficients for the DHDECMP extractant versus the CMPO extractant, the complication of potential Zr extraction becomes even more important. With the CMPO process, complexants such as oxalic acid and fluoride can be added to complex the Zr and inhibit its extraction into the organic phase. However, with the DHDECMP extractant, such complexants may reduce the TRU distribution coefficients to the point where the process is ineffectual. Therefore, the question must be addressed whether Zr is significantly extracted by DHDECMP.

Two sets of experiments were undertaken to evaluate Zr extraction. First, Zr distribution coefficients were measured by contacting 0.05 M zirconyl nitrate solutions with the DHDECMP extractant at an organic-to-aqueous phase ratio of 1. The initial aqueous solutions were prepared by dissolving zirconyl nitrate into a given concentration of HNO_3 , and then by adjusting the $[\text{F}]/[\text{Zr}]$ ratio with 10 M HF. A $[\text{F}]/[\text{Zr}]$ ratio of at least 4 was required to prevent interfacial crud from forming on contact with the extractant. With a $[\text{F}]/[\text{Zr}]$ ratio of 4, Zr distribution was measured as a function of nitrate concentration.

The second experiment compared Zr extraction with DHDECMP to that with CMPO. In this set of measurements, a synthetic dissolved NCRW sludge solution was used. The synthetic NCRW solution was prepared by adding NaOH to a Zr solution. The Zr solution was prepared by dissolving Zircaloy in ammonium fluoride/ammonium nitrate solution (the Zirflex Process, Swanson 1961)--a procedure analogous to that which formed the actual NCRW sludge. The feed solution was calculated to have the following concentrations: $[\text{Zr}] = 0.12 \text{ M}$, $[\text{F}] = 0.25 \text{ M}$, $[\text{Na}] = 0.02 \text{ M}$, $[\text{NO}_3] = 2.5 \text{ M}$, $[\text{HNO}_3] = 2 \text{ M}$. This solution was adjusted with 10 M HF to the desired $[\text{F}]/[\text{Zr}]$ ratio and was then mixed with the DHDECMP extractant. The distribution coefficients for Zr were determined by ICP, and a tendency to form interfacial crud was noted.

The extraction results are summarized Table 11.5 and Figure 11.13. In general, under conditions where interfacial crud does not form, the Zr extraction by DHDECMP was low but appreciable, with a distribution coefficient for Zr of 0.27 at the highest nitrate concentrations (7.5 M) measured. Indeed, even at high Zr concentrations (0.12 M), the distribution coefficient for Zr at 2 M HNO_3 was only 0.12 when the F/Zr ratio was 4.5. Therefore, any partitioning of Zr to a HLW stream seems unlikely with DHDECMP as the TRU extractant. To the extent zirconium is extracted, a nitrate scrub solution can be employed to remove the extracted zirconium from the loaded solvent.

These experiments also compared the relative tendencies of DHDECMP and CMPO to form interfacial crud using a synthetic NCRW feed. The results are shown in Table 11.5. Two points are apparent. First, with respect to the CMPO system, a $[\text{F}]/[\text{Zr}]$ ratio of 3 to 4 is required to prevent

interfacial crud formation. This agrees well with the results obtained using actual dissolved NCRW sludge (Lumetta and Swanson 1993b). Second, the DHDECMP extractant required higher $[F]/[Zr]$ ratios to prevent interfacial crud formation, with a $[F]/[Zr]$ ratio of 4 to 4.5 required. This most likely correlates with the relative extractant concentrations required for the respective systems (0.75 M DHDECMP for the DHDECMP/TBP system versus 0.2 M CMPO for the CMPO-based system).

In summary, higher $[F]/[Zr]$ ratios are required for practical processing with a DHDECMP-based versus a CMPO-based extractant. However, under conditions necessary to avoid interfacial crud formation, the Zr distribution coefficients for the DHDECMP-based extractant are low, so adding complexants may not be required to scrub Zr from the extract.

11.3.8 Summary and Conclusions from DHDECMP Study

To date, the several aspects of the DHDECMP evaluation have been accomplished. Distribution measurements as a function of nitrate concentration were completed for the TRUs, U, and other significant elements. Where comparison is possible, the results generally agree well with other work reported in the literature. In addition, third-phase formation at high HNO_3 concentrations was observed, and the HNO_3 concentrations at which a third phase forms were quantified. Methods were evaluated for the removing trace amounts of acidic organophosphorus impurities.

Most of the information necessary to develop a preliminary DHDECMP-based flowsheet for processing Hanford tank wastes is available. This information is based on the distribution coefficient measurements for HNO_3 , Am(III), Pu(IV), U(VI), Bi(III), Fe(III), and Zr(IV) as a function of nitrate concentration alone and in the presence of complexants (e.g., fluoride or oxalate). Because more data are available for the CMPO processing of NCRW sludge than any other Hanford tank waste (Lumetta and Swanson 1993b), efforts will be focused on pretreating this waste type with a DHDECMP-based extractant. In this way, the performance of DHDECMP can be compared directly with CMPO. Batch testing of a DHDECMP flowsheet for pretreating NCRW sludge is scheduled for FY 1994.

Following are general conclusions about the usefulness of DHDECMP as an extractant:

- Extraction of TRUs is possible, although, unless a metal nitrate such as sodium nitrate is added to the feed, a large number of stages may be required to achieve adequate TRU removal.
- The probable presence of fluoride in the feed solution will greatly exacerbate the Pu(IV) extraction.
- Uranium and Bi will be coextracted with the TRUs.
- Stripping of TRUs may be possible by simply decreasing the HNO_3 concentration. However, unless acidic impurities are efficiently removed from the solvent, Pu(IV) will not be effectively stripped with dilute HNO_3 , and, even if effective removal is possible, the stripping of Pu(IV) is problematic. Effective separation of Pu(IV) from Bi(III) and U(VI) appears unlikely. At HNO_3 concentrations (less than 0.2 M HNO_3) where the distribution coefficient for Pu(IV) is

less than 1, the distribution coefficients for U(VI) are < 3 and those for Bi(III) are ~ 1 or lower, indicating a substantial portion of the U and Bi would end up in the HLW stream through use of a simple dilute HNO_3 strip.

- Adding a reducing agent to the stripping solution should more effectively separate U and Bi from Pu. For example, at 0.3 M HNO_3 , the distribution coefficients for the trivalent actinides [e.g., Am(III) and Pu(III)] would be expected to be ~ 0.2 (Figure 11.6), whereas that for U(VI) would be ~ 7 (Figure 11.10), and that for Bi(III) would be ~ 2 (Figure 11.12). Thus, a flowsheet can be designed in which TRUs are separated from the majority of the U and Bi. Except for the trivalent lanthanides, other sludge components are not expected to extract to any great extent.

Figure 11.1. Extraction of HNO_3 Using 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.2. Illustration of Third-Phase Formation with DHDECMP: left) 7.5 M HNO₃ Contacted with 0.2 M CMPO/1.4 M TBP in NPH; center) 7.5 M HNO₃ Contacted with 0.75 M DHDECMP/1.05 M TBP in Isopar M; right) 2.0 M HNO₃/5.5 M NaNO₃ Contacted with 0.75 M DHDECMP/1.05 M TBP in Isopar M. A small amount of U was added to each contact to help visualize the demarkation of the third phase.

Figure 11.3. Effect of Solvent Purification Method on Am Extraction with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.4. Effect of Solvent Purification Method on Pu(IV) Extraction with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.5. Equilibrium Aqueous HNO₃ Concentration as a Function of Initial Aqueous HNO₃ Concentration in HNO₃ Extraction with 0.75 M DHDECMP Plus 1.05 M TBP in NPH, O/A = 1.0

Figure 11.6. Extraction of Am(III) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.7. Extraction of Am(III) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH and Isopar M

Figure 11.8. Extraction of Pu(IV) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.9. Extraction of Pu(IV) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH and Isopar M

Figure 11.10. Extraction of U(VI) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.11. Extraction of U(VI) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH and Isopar M

Figure 11.12. Extraction of Bi(III) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH

Figure 11.13. Extraction of Zr(IV) with 0.75 M DHDECMP Plus 1.05 M TBP in NPH. The initial aqueous Zr concentration was 0.12 M and the initial nitrate concentration was 2 M.

Table 11.1. Extraction of HNO₃ By DHDECMP

<u>Initial Aq. [NO₃], M</u>	<u>Final Aq. [NO₃], M</u>	<u>D, HNO₃</u>	<u>Diluent</u>
0.0098	0.0066	0.48	NPH
0.30	0.22	0.36	NPH
1.00	0.68	0.47	NPH
1.99	1.29	0.54	NPH
0.051	0.045	0.13	NPH ^(a)
0.10	0.085	0.18	NPH ^(a)
0.20	0.16	0.25	NPH ^(a)
0.50	0.36	0.39	NPH ^(a)
1.01	0.69	0.46	NPH ^(a)
1.49	1.00	0.49	NPH ^(a)
2.01	1.33	0.51	NPH ^(a)
7.5 ^(b)	6.30	0.19	NPH ^(a)
0.20	0.16	0.25	Isopar M
0.45	0.33	0.36	Isopar M
1.00	0.67	0.49	Isopar M
1.50	0.95	0.58	Isopar M
2.00	1.27	0.57	Isopar M
7.5 ^(b)	6.31	0.19	Isopar M

(a) Solvent was pretreated using the MIX treatment, see Section 11.2.

(b) Initial aqueous phase consisted of 2 M HNO₃ + 5.5 M NaNO₃.

Table 11.2. Extraction of Am(III) With DHDECMP: Data Reported in the Literature

<u>[DHDECMP]</u>	<u>[HNO₃]</u>	<u>D, Am(III)</u>	<u>Diluent</u>	<u>Reference</u>
0.4 M	0.01 M	0.002	Benzene	Methur, Murali, Natarajan 1991
0.4 M	0.3 M	0.02	Benzene	Methur, Murali, Natarajan 1991
0.4 M	0.7 M	0.07	Benzene	Methur, Murali, Natarajan 1991
0.4 M	0.9 M	0.1	Benzene	Methur, Murali, Natarajan 1991
0.4 M	1.1 M	0.12	Benzene	Methur, Murali, Natarajan 1991
0.4 M	2 M	0.37	Benzene	Methur, Murali, Natarajan 1991
30%	0.1 M	0.07	Cyclohexane	Akatsu and Kimura 1990
30%	0.2 M	0.2	Cyclohexane	Akatsu and Kimura 1990
30%	0.4 M	0.7	Cyclohexane	Akatsu and Kimura 1990
30%	1 M	2	Cyclohexane	Akatsu and Kimura 1990
0.75 M/1 M TBP	0.45 M	0.4	Isopar H	Marsh and Yarbrow 1988
0.75 M/1 M TBP	1.5 M	2	Isopar H	Marsh and Yarbrow 1988

Table 11.3. Extraction of U(VI) with DHDECMP: Data Reported in the Literature

<u>[DHDECMP]</u>	<u>[HNO₃]</u>	<u>D, U(VI)</u>	<u>Diluent</u>	<u>Reference</u>
0.4 M	0.1 M	2.00	Benzene	Mathur, Murali, Natarajan 1991
0.4 M	0.5 M	3.55	Benzene	Mathur, Murali, Natarajan 1991
0.4 M	1 M	7.94	Benzene	Mathur, Murali, Natarajan 1991
0.4 M	2 M	22.39	Benzene	Mathur, Murali, Natarajan 1991
0.75 M/1 M TBP	0.45 M	7.94	Isopar H	Marsh and Yarbrow 1988
0.75 M/1 M TBP	1.5 M	25.12	Isopar H	Marsh and Yarbrow 1988

Table 11.4. Extraction of Fe(III) with DHDECMP

<u>[NO₃], M</u>	<u>[HF], M</u>	<u>[H₂C₂O₄], M</u>	<u>Initial Aqueous [Fe], µg/mL</u>	<u>Final Aqueous [Fe], µg/mL</u>
0.05	0	0	0.96	0.95
0.09	0	0	0.97	0.97
0.16	0	0	0.96	0.96
0.36	0	0	0.98	0.90
0.69	0	0	0.99	1.03
1	0	0	0.96	0.99
1.33	0	0	1.00	1.01
6.3	0	0	0.98	0.96
0.05	0.1	0	0.95	1.01
0.09	0.1	0	0.95	1.03
0.16	0.1	0	0.95	1.01
0.36	0.1	0	0.94	1.02
0.69	0.1	0	0.90	0.98
1	0.1	0	0.95	1.01
1.33	0.1	0	0.91	1.03
6.3	0.1	0	0.95	1.02
0.05	0	0.05	0.71	0.74
0.09	0	0.05	0.71	0.76
0.16	0	0.05	0.67	0.69
0.36	0	0.05	0.66	0.72
0.69	0	0.05	0.60	0.71
1	0	0.05	0.66	0.71
1.33	0	0.05	0.47	0.74
6.3	0	0.05	0.76	0.82

Table 11.5. Extraction of Zr with DHDECMP and CMPO

<u>Extractant</u>	<u>Initial [Zr], M</u>	<u>[NO₃], M</u>	<u>[F]/[Zr]</u>	<u>D[Zr(4+)]</u>	<u>Crud</u>
DHDECMP	0.05	7.5	0	NA ^(a)	Yes
DHDECMP	0.05	2	0	NA	Yes
DHDECMP	0.05	1	0	NA	Yes
DHDECMP	0.05	0.5	0	NA	Yes
DHDECMP	0.05	7.5	0.44	NA	Yes
DHDECMP	0.05	2	0.44	NA	Yes
DHDECMP	0.05	1	0.44	NA	Yes
DHDECMP	0.05	0.5	0.44	NA	Yes
DHDECMP	0.05	7.5	0.88	NA	Yes
DHDECMP	0.05	2	0.88	NA	Yes
DHDECMP	0.05	1	0.88	NA	Yes
DHDECMP	0.05	0.5	0.88	NA	Yes
DHDECMP	0.05	7.5	2	NA	Yes
DHDECMP	0.05	2	2	NA	Yes
DHDECMP	0.05	1	2	0.089	
DHDECMP	0.05	0.5	2	NA	Yes
DHDECMP	0.05	7.5	4	0.274	No
DHDECMP	0.05	2	4	0.020	No
DHDECMP	0.05	1	4	0.024	No
DHDECMP	0.05	0.5	4	0.053	No
DHDECMP	0.12	2	2	NA	Yes
DHDECMP	0.12	2	3	NA	Yes
DHDECMP	0.12	2	4	NA	Yes
DHDECMP	0.12	2	4.5	0.12	No
DHDECMP	0.12	2	5	0.010	No
CMPO	0.12	2	2	NA	Yes
CMPO	0.12	2	3	0.63	No
CMPO	0.12	2	4	0.37	No
CMPO	0.12	2	4.5	0.16	No
CMPO	0.12	2	5	0.047	No

(a) NA = Not applicable; i.e., Zr distribution not measured when interfacial crud was present.

12.0 Extraction of TRUs with Tetraalkylmalonamides

In recent years, researchers in France have been investigating N,N'-tetraalkylmalonamides for extracting TRUs from acidic media (Cuillerdier et al. 1991; Cuillerdier, Musikas, and Nigond 1993). The general structure of these extractants is shown in Figure 12.1. Because these extractants represent a possible alternative to the CMPO extractant, PNL initiated a study to assess the utility of these extractants in pretreating Hanford tank sludges.

The potential advantages of using tetraalkylmalonamide extractants, according to French researchers, are 1) they are relatively easy to synthesize, 2) they are expected to be less expensive than CMPO, 3) the hydrolysis and radiolysis products do not seriously affect the extraction efficiency so that solvent wash solutions are not needed, and 4) the materials can be completely converted to gaseous products by incineration, which would minimize secondary waste volume. Some of the disadvantages of these extractants are 1) it is currently unclear which tetraalkylmalonamide extractant performs best with aliphatic hydrocarbon diluents, which are preferred in the U.S., 2) separation of Am from Fe may be more difficult than in the analogous CMPO process, and 3) the reported hydrolysis rate for these extractants is rather high.

The tetraalkylmalonamide extractants initially used in this study were supplied by Dr. Barbara Smith of LANL. These materials contained a small amount of chloroform, which proved difficult to remove under vacuum. A second batch of one of the tetraalkylmalonamide extractants was then prepared and purified at PNL (Section 12.2). The extraction behavior of this second batch was similar to that reported by the French; these results will be discussed in Section 12.3.

12.1 Initial Studies with Tetraalkylmalonamides Prepared at Los Alamos National Laboratory

Two tetraalkylmalonamide extractants, with the general structure indicated in Figure 12.1, were supplied to PNL by LANL.^(a) For one of these, $R = n\text{-C}_{12}\text{H}_{25}$ (referred to as DIAMIDE-12); for the other, $R = n\text{-C}_{14}\text{H}_{29}$ (referred to as DIAMIDE-14). The tetraalkylmalonamide extractants were dissolved in either NPH or Isopar M at a concentration of 0.5 M. NPH is a mixture of straight-chain hydrocarbons, whereas Isopar M is a mixture of branched-chain hydrocarbons.

The propensity of these extractants toward third-phase formation was evaluated (Table 12.1). In general, increasing the HNO_3 concentration increased the probability of forming a third phase. The results suggest that DIAMIDE-14 is superior to DIAMIDE-12 in resisting third-phase formation. For example, when these two extractants were contacted with 3 M HNO_3 , no third phase was observed for DIAMIDE-14, but a scum formed at the aqueous-organic interface with DIAMIDE-12. No major differences were observed between the use of NPH or Isopar M as diluent. French researchers have reported that for a 0.5 M solution of DIAMIDE-14 in hydrogenated tetrapropylene (TPH), third-phase formation does not occur at $[\text{HNO}_3]$ less than 4.7 M (Cuillerdier, Musikas, and Nigond 1993). The

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(a) Before use, the tetraalkylmalonamide extractants supplied by LANL were placed under vacuum for several days at room temperature to remove volatile impurities.

differences observed here may have resulted from impurities in the DIAMIDE-14 used in this work compared to that used by the French. The Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectra of the extractants used here suggest the extractants may contain some residual CHCl_3 from the synthetic procedure. Alternatively, the differences may have been caused by a diluent effect.

Based on the third-phase observations summarized in Table 12.1, a maximum HNO_3 concentration of 1 M was chosen for Am and Pu distribution measurements. Higher nitrate concentrations were achieved by adding NaNO_3 . For each distribution measurement, the tetraalkylmalonamide solvent was pre-equilibrated with the aqueous phase by three contacts with an equal volume of the appropriate aqueous solution (minus the Am or Pu spike). The Am- or Pu-spiked aqueous phase was then contacted with the pre-equilibrated organic phase for 60 s using a vortex mixer. After centrifuging, the alpha activity in both phases was determined by liquid scintillation counting.

The results of the Am(III) and Pu(IV) distribution measurements are illustrated in Figures 12.2 and 12.3, respectively. The distribution coefficients for Am measured here were lower than those reported in the literature (Nigond 1992). Likewise, the Pu(IV) distribution coefficients measured here for nitrate concentrations greater than 1 M were generally lower than those reported by the French. An impurity in the extractants used here, or a diluent effect, were originally believed to have caused the lower values. However, subsequent study revealed that the substitution of NaNO_3 for HNO_3 was the cause of the lower TRU distribution coefficients (see Section 12.3).

Because the tetraalkylmalonamide extractants used in the initial study were of questionable purity, a second batch of DIAMIDE-14 was prepared at PNL. The synthesis of this material will be discussed in the next section. DIAMIDE-14 was chosen for subsequent study because this particular tetraalkylmalonamide is currently the extractant of choice in France.

12.2 Synthesis of DIAMIDE-14

The synthesis of the DIAMIDE-14 follows the reaction scheme shown in Figure 12.4. A detailed description of the synthetic procedure is given in Appendix B. Initial synthetic attempts were frustrated by the poor quality of the purchased malonyl dichloride. Appreciable decomposition was apparent (as indicated by the dark brown suspension that occurred when the amine and acid halide were mixed), even after the reagents were purified and the reaction was operated at considerably lower temperature and with somewhat more dilute solutions than those reported in the literature. For this reason, the malonyl dichloride was purified by distillation before use. Using the purified malonyl dichloride, the unsubstituted tetraalkylmalonamide (Figure 12.1, $\text{R} = \text{H}$; which is termed DIAMIDE-0) was prepared in 32% yield. DIAMIDE-0 was easily deprotonated using KH , and the resulting carbanion was reacted with 1-bromotetradecane to give DIAMIDE-14.

The DIAMIDE-0 and DIAMIDE-14 samples provided by LANL were examined by thin layer chromatography (TLC) on silica gel with a variety of eluants. The results are presented in Table 12.2. From this information, a chromatographic purification method for crude DIAMIDE-14 was conceived. The crude material was dissolved in heptane and eluted with an aliphatic hydrocarbon to remove any

residual chloroform or unreacted 1-bromotetradecane. Switching to ethyl acetate or ethyl acetate/methanol then allowed elution of the DIAMIDE-14 and separation from any unreacted DIAMIDE-0.

The actual purification procedure required at least 6 g of silica gel per gram of crude DIAMIDE-14 because with less silica gel, the column appeared to become overloaded. Thin layer chromatography of the heptane fraction revealed the presence of a material with R_f 1 in ethyl acetate. Removal of the solvent revealed a small amount of pale yellow crystalline solid with a melting point close to room temperature. Although little effort has been expended toward characterizing this material, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy indicated that the product is some type of long-chained alkene and not an amide.

Following elution of this impurity with heptane, the DIAMIDE-14 was conveniently eluted by switching the eluant to a more polar solvent, such as ethyl acetate or ethyl acetate/methanol. After the product was eluted from the column, evaporation of the solvent completed the DIAMIDE-14 purification.

To date, the PNL-prepared material has been characterized by IR spectroscopy, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and TLC. Although characterization has occurred only to this limited extent, the close comparison in all respects with the LANL-supplied material, as well as good agreement with the available literature, leaves no doubt about the compound's identity.

The IR spectrum (neat, NaCl plates) is shown in Figure 12.5. The broad $\nu(\text{C}=\text{O})$ band at $1650 (\pm 2) \text{ cm}^{-1}$ agrees well with the reported carbonyl vibration at 1652 cm^{-1} for the DIAMIDE-14 (Nigond 1992) and is essentially identical to a neat spectrum of the LANL-prepared material. In addition, the $\nu(\text{C}=\text{O})$ band is well separated from the ethyl acetate $\nu(\text{C}=\text{O})$ band at 1743 cm^{-1} , which provides a sensitive indicator as to the presence or absence of any residual solvent.

The ^1H NMR spectrum is given in Figure 12.6. The spectrum is rather complex, but it is essentially identical to the LANL-prepared material, possesses relative intensities consistent with the proposed structure, and agrees well with the literature reports for DIAMIDE-14 (Nigond 1992). Although unambiguous assignments of the individual resonances have not been made, the presence of two sets of signals at about 0.75 to 0.95 ppm is consistent with the two types of aliphatic methyl resonances in DIAMIDE-14, one set for the two butyl groups and one set for the methyl of the 14-carbon chain. The resonances for the methyl groups attached to the amide nitrogen are seen from about 2.65 to 2.75 ppm. Of some interest is the large number of overlapping resonances that were observed, explained in part by the isomers present due to restricted rotation around the carbon-nitrogen bond typically observed with amides.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (Figure 12.7) supports this conclusion with the presence of at least three overlapping carbonyl resonances centered at 169.2 ppm. Again, the NMR spectra of the PNL- and LANL-prepared materials are the same, and the carbonyl chemical shifts are consistent with the multiple resonances around 169 ppm reported in the original synthesis, although the latter used a different solvent for this measurement.

With excellent agreement in the IR spectroscopy, ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and identical TLC behavior using six different eluants, one can be fairly confident that the PNL- and LANL-prepared materials are identical. This equivalence established, there was an additional piece of characterization relating to the product composition; the mass spectrum of the LANL material was recorded. A parent ion $[\text{DIAMIDE} + \text{H}]^+$ ($m/e = 439$) was observed with such major fragments as

$[(\text{CH}_3)(\text{C}_4\text{H}_9)\text{NC}(\text{O})]^+$ ($m/e = 114$; Fragment A) and $[\text{DIAMIDE minus Fragment A}]^+$ ($m/e = 324$). Other major signals corresponded to $[(\text{CH}_3)(\text{C}_4\text{H}_9)\text{N}]^+$ ($m/e = 86$; Fragment B) and $[\text{DIAMIDE minus Fragment B}]^+$ ($m/e = 252$). Taken with the characterization described above, these results demonstrate the high purity of the PNL-prepared DIAMIDE-14.

12.3 Studies with Purified DIAMIDE-14 Prepared at PNL

Third-phase formation tests and Am extraction measurements were also conducted with the purified form of DIAMIDE-14. The results of these tests were different from those obtained with the material provided by LANL (Section 12.1), and more closely agreed with the results reported by French researchers.

12.3.1 Third-Phase Behavior

Solutions of the purified DIAMIDE-14 in NPH or Isopar M were mixed for 60 s with equal volumes of HNO_3 solutions of varying concentrations. After centrifuging, the mixtures were checked for the presence of a third phase. Aliquots from the aqueous phase were titrated with standard NaOH to determine the equilibrium aqueous HNO_3 concentrations. The results are summarized in Table 12.3.

With NPH as diluent, the tendency to form a third phase was not markedly different than that observed with the initial batch of DIAMIDE-14 (compare Tables 12.1 and 12.3). When Isopar M was used as diluent, the third-phase behavior was actually worse with the pure DIAMIDE-14. Clearly, Isopar M can be ruled out as a diluent for this system.

The dramatic differences in the behavior of pure DIAMIDE-14 in NPH versus that in Isopar M indicate that diluent plays a significant role in governing third-phase formation, even for aliphatic diluents. Thus, the observation by the French researchers that HNO_3 concentrations up to 4.7 M can be tolerated with DIAMIDE-14 could very well be due to a diluent effect. The French diluent TPH is a branched-chain aliphatic diluent, as is Isopar M. It was expected that the behavior of Isopar M would more resemble that of TPH than would NPH. However, the reverse was observed. The reason for this behavior is unknown at present.

During the Am distribution measurements (*vide infra*) using 0.5 M DIAMIDE-14 in NPH, evidence of a third phase was observed when the equilibrium HNO_3 concentration was 3.52 M. In this particular Am distribution test, the organic and aqueous phases were clear after centrifuging, and no third phase was observed. However, when the vial was disturbed, the organic phase became cloudy, suggesting that a small amount of third phase was present. Thus, the equilibrium HNO_3 concentration is recommended to be kept below 3.5 M in this extraction system.

12.3.2 Extraction of Am

A solution of the purified DIAMIDE-14 in NPH was mixed for 60 s with equal volumes of HNO_3 solutions of varying concentrations that had been traced with Am(III). After centrifuging, aliquots of

the organic and aqueous phases were taken for liquid scintillation counting. Aliquots from the aqueous phase were also titrated with standard NaOH to determine the equilibrium aqueous HNO_3 concentrations. The results are summarized in Figure 12.8.

The measured Am(III) distribution coefficients were of the same magnitude as those reported by the French (Cuillerdier, Musikas, and Nigond 1993). Indeed, the Am(III) distribution coefficients measured for DIAMIDE-14 in NPH were slightly greater than those reported for DIAMIDE-14 in TPH.

The anomalously low Am and Pu distribution coefficients initially measured with the tetraalkylmalonamide extractants prepared at LANL (Section 12.1) are now believed to have been caused by substituting NaNO_3 for HNO_3 to obtain nitrate concentrations greater than 1 M in the initial work. This hypothesis was tested in two additional Am distribution measurements performed using the DIAMIDE-14 prepared at LANL, this time using only HNO_3 as the nitrate source. The results, shown in Figure 12.8 as filled circles, were very similar to those measured with the purified DIAMIDE-14 prepared at PNL. The Am distribution coefficients for the LANL DIAMIDE-14 were slightly less than those for the PNL DIAMIDE-14, but this can be attributed to the effective concentration of DIAMIDE-14 being ~ 15 mole percent less than 0.5 M due to the presence of CHCl_3 in that material.

12.4 Summary and Conclusions

The initial discrepancies in the TRU distribution coefficients measured here, when compared to those reported by researchers in France, have been resolved. Americium is effectively extracted at HNO_3 concentrations greater than 2 M. However, with NPH as the diluent, the HNO_3 concentration should not exceed ~ 3.5 M due to the formation of a third phase.

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Figure 12.1. General Structure of Tetraalkylmalonamide Extractants

Figure 12.2. Extraction of Am from Nitrate Media with DIAMIDE-12 and DIAMIDE-14. For the data collected here, the aqueous solutions consisted of 1.0 M HNO_3 plus enough $NaNO_3$ to give the desired total nitrate concentration. The data for DIAMIDE-14 in TPH were obtained using HNO_3 solutions (no $NaNO_3$).

Figure 12.3. Extraction of Pu(IV) from Nitrate Media with DIAMIDE-12 and DIAMIDE-14. For the data collected here, the aqueous solutions consisted of 1.0 M HNO_3 plus enough $NaNO_3$ to give the desired total nitrate concentration. The data for DIAMIDE-14 in TPH were obtained using HNO_3 solutions (no $NaNO_3$).

Figure 12.4. Synthetic Scheme for the Preparation of DIAMIDE-14

Figure 12.5. IR Spectrum of DIAMIDE-14 (neat)

Figure 12.6. ^1H NMR Spectrum of DIAMIDE-14 in Benzene-d_6

Figure 12.7. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of DIAMIDE-14 in Benzene-d_6

Figure 12.8. Extraction of Am(III) from HNO_3 with DIAMIDE-14

Table 12.1. Observations of Third-Phase Formation with the Tetraalkylmalonamide Extractants Prepared at LANL

[NO ₃], M	[HNO ₃], M ^(b)	[NaNO ₃], M	DIAMIDE-12 ^(a)		DIAMIDE-14	
			NPH	Isopar M	NPH	Isopar M
2	2	0	N	N	n.d. ^(c)	n.d.
3	3	0	Y ^(d)	Y ^(d)	N	N
4	4	0	Y	Y	Y	Y ^(d)
5	5	0	Y	Y	Y	Y
2.5	2	0.5	Y	n.d.	n.d.	n.d.
5	2	3	Y	n.d.	n.d.	n.d.
5	1	4	N	n.d.	n.d.	n.d.

(a) Y = third liquid phase observed; N = no third phase observed.

(b) Initial HNO_3 concentration.

(c) n.d. = not determined.

(d) In these cases, a separate liquid phase was not observed, but scum formed at the interface.

Table 12.2. Thin Layer Chromatography Data for Tetraalkylmalonamides

Eluant	Sample	R _f
Ethyl acetate	DIAMIDE-0	0.27
Ethyl acetate	DIAMIDE-14	0.7
Heptane	DIAMIDE-0	0
Heptane	DIAMIDE-14	0
Chloroform	DIAMIDE-0	0.04
Chloroform	DIAMIDE-14	0.14
50:50 Chloroform/heptane	DIAMIDE-0	0
50:50 Chloroform/heptane	DIAMIDE-14	0.003
80:20 Ethyl acetate/heptane	DIAMIDE-0	0.2
80:20 Ethyl acetate/heptane	DIAMIDE-14	0.67
95:5 Ethyl acetate/methanol	DIAMIDE-0	0.45
95:5 Ethyl acetate/methanol	DIAMIDE-14	0.82

Table 12.3. Observations of Third-Phase Formation with the DIAMIDE-14 Prepared at PNL

Initial [HNO ₃], M	Equilibrium [HNO ₃], M	DIAMIDE-14 ^(a)	
		NPH	Isopar M
2.44	2.23	N	n.d. ^(b)
3.18	2.76	N	n.d.
4.13	3.55	N	Y
4.7	3.90	Y	Y
5.0	4.20	Y	n.d.

(a) Y = third liquid phase observed; N = no third phase observed.

(b) n.d. = not determined.

13.0 Separation of Actinides by Extraction Chromatography

Extraction chromatography has been suggested as a possible alternative to solvent extraction for selectively removing TRU components from dissolved Hanford tank wastes (Barney and Cowan 1992; Lumetta, Wester, Morrey, and Wagner 1993). Preliminary tests of the commercially available TRU · Spec™ extraction chromatography medium (EiChroM Industries, Inc., Darien, Illinois)^(a) indicated that its usefulness in removing TRUs from dissolved Hanford tank sludges may be limited by the amount of U present in these wastes. That is, the column tended to load quickly with U, resulting in early Am breakthrough (Lumetta, Wester, Morrey, and Wagner 1993).

To alleviate this problem, a scheme (Figure 13.1) is proposed in which the dissolved sludge solution (containing the TRUs and U) is passed through a different extraction chromatographic material, U/TEVA · Spec™ (EiChroM Industries, Inc., Darien, Illinois),^(b) to first remove the U (and any tetravalent actinides present, e.g., Th). This method requires that the feed solution be treated with ascorbic acid or another reducing agent to convert Pu(IV) to Pu(III) so that Pu (and Am) will not load onto the U/TEVA · Spec™ column. After removing the U, the dissolved sludge solution is passed through a TRU · Spec™ column to separate the TRUs from the bulk sludge components.

To determine the suitability of this pretreatment approach, the effect of certain process parameters on the breakthrough characteristics of the chosen chromatographic materials must be investigated. Work in FY 1993 focused on determining the U breakthrough characteristics for a U/TEVA · Spec™ column. The effect of U breakthrough as a function of flow rate (column volumes/h) at 25°C is presented in this section. In addition to the loading tests, the elution of the columns with 0.02 M HNO₃ will also be discussed.

13.1 Experimental

The experimental system employed in this study consisted of a chromatography column, feed storage bottles, a peristaltic pump, and a fraction collector. The chromatography column was jacketed to maintain a constant temperature by using a circulating water bath. The column was 1 cm in diameter and held 10 mL of chromatographic material. The column could be loaded or eluted in either direction. The samples were collected in 4-mL increments.

Two solutions were used to determine the breakthrough characteristics of U/TEVA · Spec™. Both solutions were 2 M HNO₃ with different concentrations of UO₂(NO₃)₂. The first solution tested was 0.05 M UO₂(NO₃)₂. This concentration was selected so that the U in the samples could be analyzed by liquid scintillation counting. The first column test showed an initial breakthrough at 4.4 column volumes (cv) with 50% breakthrough at 5.4 cv. Because of this early breakthrough, the information obtained was not useful for determining the breakthrough characteristics of the material. In subsequent

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(a) The TRU · Spec™ material consists of CMPO and TBP sorbed onto Amberchrom™ CG-71. The material contains 13% CMPO and 27% TBP by weight.

(b) The U/TEVA · Spec™ material consists of diamylamyl phosphonate sorbed onto Amberchrom™ CG-71.

runs, a more dilute $\text{UO}_2(\text{NO}_3)_2$ (0.005 M) feed was used, and the $\text{UO}_2(\text{NO}_3)_2$ concentration in the effluents was determined by UV-visible spectroscopy. The samples from the first test were reanalyzed using UV-visible spectroscopy; and the results were the same as those determined by liquid scintillation counting. The detection limit for $\text{UO}_2(\text{NO}_3)_2$ using UV-visible spectroscopy was 2×10^{-5} M.

The U/TEVA · Spec™ column was washed with two column volumes of 2 M HNO_3 , then the U solution was passed through the column. The process was continued until the U concentration in the effluent was the same as that in the feed. At this point, two column volumes of 2 M HNO_3 were passed through the column to wash out any residual feed solution. The same column was used for all the tests performed, without changing the U/TEVA · Spec™ material between runs. Elution testing was performed in the upflow mode with 0.02 M HNO_3 .

13.2 Results

13.2.1 Loading

Four column loading tests have been performed to date; Table 13.1 lists the conditions used in each experiment. As stated previously, the first test was performed with 0.05 M $\text{UO}_2(\text{NO}_3)_2$, and the U concentration in the effluent was determined by liquid scintillation counting and UV-visible spectroscopy. Figure 13.2 shows the breakthrough curve for the first test. The initial breakthrough for this run occurred at 4.4 cv (one column volume equals 10 mL). The 50% breakthrough point was at 5.4 cv. This corresponded to a capacity of 64 mg U/mL, which was higher than the value of 37 mg/mL indicated by the manufacturer.

The second test was performed with 0.005 M $\text{UO}_2(\text{NO}_3)_2$ at 20 cv/h, and the effluent was analyzed by UV-visible spectroscopy. Figure 13.3 shows the breakthrough curve for this experiment. The spike occurred when the solution was allowed to remain in contact with the column for 4 h; the reason for this is unknown. The initial breakthrough for this column occurred at 23 cv with the 50% breakthrough occurring at 28.5 cv. This 50% breakthrough gives a capacity of 34 mg U/mL of column. This capacity is much closer to the results reported by the manufacturer. The third test was conducted under the same conditions as the second test. The results from the third run were similar to the second, with a 50% breakthrough at 28.5 cv.

The fourth test was run at a flow rate twice that of the second and third tests. The breakthrough curve is shown in Figure 13.4. As expected, the initial breakthrough occurred earlier for the higher flow rate, but the 50% breakthrough was in roughly the same location (29 cv). The capacity in this case was 34.5 mg U/mL of column. The results of the loading tests are very promising, showing a high capacity with no detectable bleed of the U into the effluent until after 23 cv.

13.2.2 Elution

The loaded U/TEVA · Spec™ column was eluted 0.02 M HNO_3 . All the elutions were run at 25°C with a flow rate of 20 cv/h. The elution curve from Test 2 is given in Figure 13.5. This figure shows the initial washing of the loaded column with 2 M HNO_3 followed by the elution with the 0.02 M HNO_3 . The U began eluting from the column after ~3 cv of 0.02 M HNO_3 had been passed through the column. Once elution began, nearly all of the U eluted within 2 cv of 0.02 M HNO_3 .

13.3 Summary and Conclusion

Preliminary U(VI) loading and elution tests using a U/TEVA · Spec™ column yielded promising results. With an initial U feed concentration of 0.005 M, and a flow rate of 20 cv/h, significant breakthrough did not occur until more than 20 cv of feed had passed through the column. With higher U concentrations and higher flow rates, breakthrough occurred earlier, as would be expected. Uranium was eluted from the column using 0.02 M HNO₃. Degradation of the column was not observed during the limited testing performed here.

Based on the results of this study, the actinide separation scheme outlined in Figure 13.1 is considered a promising method for pretreating Hanford tank wastes. Further testing should examine the effects of potentially interfering ions on the performance of the U/TEVA · Spec™ column and on the performance of TRU · Spec™ columns in the absence of U.

Figure 13.1. General Scheme for Separating Actinides from Dissolved Hanford Tank Sludges Using Extraction Chromatography

Figure 13.2. Breakthrough Curve for U/TEVA · Spec™ Test 1. The U concentration in the feed solution was 0.05 M, and the flow rate was 10 cv/h.

Figure 13.3. Breakthrough Curve for U/TEVA · Spec™ Test 2. The U concentration in the feed solution was 0.005 M, and the flow rate was 20 cv/h.

Figure 13.4. Breakthrough Curve for U/TEVA · Spec™ Test 4. The U concentration in the feed solution was 0.005 M, and the flow rate was 40 cv/h.

Figure 13.5. Typical U/TEVA · Spec™ Elution Curve

Table 13.1. Column Loading Conditions for U/TEVA · Spec™ Tests

<u>Test</u>	<u>[UO₂²⁺], M</u>	<u>Flow Rate, cv/h</u>	<u>Temperature, °C</u>
1	0.05	10	25
2	0.005	20	25
3	0.005	20	25
4	0.005	40	25

14.0 Separation of Cs from Acidic Media

The removal of ^{137}Cs from dissolved sludge solutions may be required if stringent limits are imposed on the ^{137}Cs content of the LLW form. This section describes the work undertaken to develop methods for removing Cs from highly acidic solutions.

A literature review of the potential methods to remove Cs from acid media was conducted at PNL as part of the TWRS Pretreatment Project. Based on the results of that study, the following areas were chosen for experimental study:

- Cs extraction with di-(t-butylbenzo)-21-crown-7 (DtBB21C7) plus dinonylnaphthalenesulfonic acid (HDNNS)
- Cs removal by ion exchange using ammonium molybdophosphate or related material
- Cs removal by precipitation with phosphotungstic acid, phosphomolybdic acid, or ammonium alum.

Experimental results of extraction with DtBB21C7 plus HDNNS are discussed in Section 14.1. Results of the initial evaluation of precipitating agents and ion exchangers for removal of Cs are presented in Section 14.2.

14.1 Extraction of Cs with DtBB21C7 Plus HDNNS

Previous work on Cs extraction with DtBB21C7 plus a lipophilic sulfonic acid used toluene as the diluent (McDowell et al. 1992). Because of the hazards associated with toluene (mainly its low flash point), its use in large-scale nuclear applications is deemed unacceptable. In this work, 1,3,5-triethylbenzene was chosen as an alternative diluent for this extraction system. 1,3,5-Triethylbenzene is not known to be a hazardous material.

The extractant solution was prepared by dissolving 0.257 g of DtBB21C7 and 0.23 g of HDNNS in 9.5 mL of 1,3,5-triethylbenzene.^(a) The extractant solution consisted of 0.05 M DtBB21C7 plus 0.05 M HDNNS and contained ~3% kerosene.

Cesium distribution coefficients were measured by mixing the 0.05 M DtBB21C7 and 0.05 M HDNNS extractant solution with an appropriate aqueous solution containing 0.0001 M Cs (traced with ^{137}Cs). The organic-to-aqueous phase ratio was 1 for each measurement. After mixing on a vortex mixer for 2 min, the phases were separated by centrifuging. Aliquots of the aqueous and organic

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(a) The DtBB21C7 used in this work was donated by Dr. Richard Bartsch of Texas Tech University. The HDNNS was obtained as a 50% solution in kerosene from Alfa Johnson Matthey, Ward Hill, Massachusetts, and was used as received. The 1,3,5-triethylbenzene was purchased from Aldrich chemical company (Milwaukee, Wisconsin).

phases were counted for ^{137}Cs using a NaI(Tl) detector. The Cs distribution coefficient was calculated as the activity in the organic phase divided by the activity in the aqueous phase.

The extraction of Cs by 0.05 M DtBB21C7/0.05 M HDNNS in 1,3,5-triethylbenzene is summarized in Figures 14.1 and 14.2. The results indicated that Cs can be extracted from a 1 M HNO_3 solution even in the presence of a 1,000-fold excess of Na. The extraction of Cs decreased with increasing concentration of HNO_3 or NaNO_3 . The data suggest that Cs can be stripped from the solvent with a solution of higher acidity (~ 5 M HNO_3).

These preliminary results were promising and suggest that further work should be conducted on this system. An experiment was conducted to determine if Cs could be extracted from an actual Hanford tank waste. A solution obtained by leaching sludge from SST U-110 with 2 M HNO_3 at 100°C was available for this test. It has been shown that washing this sludge with dilute NaOH solution followed by leaching with 2 M HNO_3 at 100°C results in $>95\%$ of the TRU activity and 90% of the ^{137}Cs activity reporting to the acid leach liquor (Lumetta, Wagner, Colton, and Jones 1993).

The 2 M HNO_3 U-110 leach solution was diluted with an equal volume of water to give a solution containing 0.12 M Al, 0.001 M Ca, 0.01 M Fe, 0.06 M Na, and 0.43 M HNO_3 . The solution was contacted three successive times with the 0.05 M DtBB21C7/0.05 M HDNNS extractant solution at an organic-to-aqueous phase ratio of 0.5. In each extraction, the two phases separated within 45 s. The Cs extraction results are presented in Figure 14.3. Greater than 99% of the Cs was extracted, and the overall DF for Cs was 140. The Cs distribution coefficients in the successive contacts were 6.4, 6.5 and 11; these are somewhat lower than would be expected based on the tracer studies, but direct comparisons cannot be made due to the more complicated matrix in the U-110 acid leach solution.

Although these initial results are very promising, additional work must be conducted to perfect the process. This work should include measuring the distribution coefficients for nonradioactive sludge components, measuring dispersion numbers, investigating other diluents, and radiolytic/hydrolytic stability of the extractant solution.

14.2 Separation of Cs from Acidic Solution by Precipitation or Ion Exchange

As separation methods, precipitation and ion exchange often offer the advantage of simplicity over other methods such as solvent extraction. Indeed, removal of Cs from acidic high-level radioactive waste by precipitation with phosphotungstic acid has been demonstrated on a large scale at Hanford (Beard and Schmidt 1964). Because of this advantage, screening tests have been performed on potential Cs precipitants and ion exchangers. Two precipitating agents were considered: phosphotungstic acid ($\text{HPT} = [\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}]$), and ammonium alum (ammonium aluminum sulfate = $[(\text{NH}_4)\text{Al}(\text{SO}_4)_2]$). Two inorganic ion exchange materials were considered: ammonium molybdophosphate (AMP = $[(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}]$), and a material purported to be a porous glass impregnated with phosphomolybdic acid (HPM-glass). The latter material was investigated because its properties (e.g., particle size, porosity) are amenable for use in column operations.

14.2.1 Materials and Methods

All chemicals were of reagent grade and were used as received. The HPM-glass was prepared as described in the literature (Moller, Bein, and Brinker 1990). This material was prepared by controlled hydrolysis of tetraethylorthosilicate, $\text{Si}(\text{OEt})_4$, in the presence of phosphomolybdic acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The isolated solid was blue, which indicated the phosphomolybdic anion was substantially reduced. The amount of glass chosen for the Cs test was based on the assumption that the final product consisted of the phosphomolybdate compound and SiO_2 being present according to the reaction stoichiometry ($\text{H}_3\text{PMo}_{12}\text{O}_{40}:\text{SiO}_2 = 1:20$).

A Cs stock solution was obtained by spiking a solution of 0.0001 M Cs in 1 M HNO_3 with a small amount of $^{137}\text{CsNO}_3$ solution. The Cs removal tests were performed by adding a weighed amount of the precipitation agent^(a) or ion exchanger to a known volume of the Cs stock solution and allowing the mixture to stir at room temperature for 1 h. The mixture was then centrifuged and aliquots were taken for analysis by gamma-counting. The concentrations of ^{137}Cs before and after treatment were determined.

14.2.2 Results and Discussion

Table 14.1 shows the results of the Cs removal tests with the two precipitating agents and the two ion exchange materials that were investigated. The use of ammonium alum as a precipitation agent was ineffective under the conditions used here. Although precipitation with ammonium alum has been used to isolate and purify radiocesium from other elements (Rupp 1956), this approach was used for macro-amounts of Cs and not for removing the trace amounts as needed here. Ammonium alum is appreciably soluble in aqueous solution,^(b) thus, a large quantity of this material would be required to design an effective process. More extensive data on the solubility of this material in HNO_3 solutions would be needed to estimate the necessary amount of aluminum alum.

The polyoxometallates as a group effectively removed Cs from acid solution, >90% of the Cs was removed with a single contact. The source of the anion did not appear to matter, since both AMP and HPT yielded comparable results, especially after taking into account the greater amount of AMP used compared to HPT. The number of waters of hydration in phosphotungstic acid is unknown but probably large. The charge ratio value given in Table 14.1 is an upper limit, because waters of hydration were not assumed to be present for calculating formula weight.

The initial attempt at preparing a more desirable form of a polyoxometallate Cs ion exchanger by incorporating it into a porous glass was unsuccessful. When contacted with the HPM-glass, the test solution turned a deep blue, then gradually lightened, and finally became colorless. Such behaviour was consistent with the dissolution of phosphomolybdate, either because the phosphomolybdate was never inside the pores of the glass in the first place, or because the glass rapidly dissolved, freeing the polyoxometallate. Only a small fraction of the expected amount of Cs removal was achieved.

(a) Although the precipitating agents were added as solid in these tests, it was assumed that they dissolved in the aqueous solution, then the corresponding Cs salt precipitated.

(b) The solubility of $\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in water is 140 g/L at 25°C and 2,000 g/L at 100°C.

Given that polyoxometallates as a class so successfully remove Cs, research on precipitation agents will focus on materials with differing charges and morphologies. The objective will be to locate a candidate with suitable physical properties to act either as a precipitation agent or as an ion exchange material.

Figure 14.1. Extraction of Cs with 0.05 M DtBB21C7/0.05 M HDNNS in 1,3,5-Triethylbenzene. Cesium distribution coefficient versus equilibrium HNO_3 concentration at a constant Na concentration (0.1 M).

Figure 14.2. Extraction of Cs with 0.05 M DtBB21C7/0.05 M HDNNS in 1,3,5-Triethylbenzene. Cesium distribution coefficient versus $NaNO_3$ concentration at a constant HNO_3 concentration (1 M).

Figure 14.3. Extraction of Cs from U-110 Sludge Acid Leach Solution with 0.05 M DtBB21C7/0.05 M HDNNS in 1,3,5-Triethylbenzene

Table 14.1. Removal of Cs by Precipitation and Ion Exchange

Precipitant/ Exchanger	Charge Ratio^(a)	Removed from Solution, %
AMP	33	90.1
HPM-glass	33	12.4
Blank 1	Not applicable	~0
AMP	10.9	99.4
HPT	≤ 10.2	97.3
Ammonium alum	13.2	1.1
Blank 2	Not applicable	~0

(a) The charge ratio = (equivalents of the polymetallate anion) x (charge of the polymetallate anion) + (equivalents of Cs) x (charge of the Cs ion).

15.0 Future Work

The following is a brief list of work proposed for FY 1994:

- Sludge washing and caustic leaching tests will be conducted on sludges from several Hanford tanks.
- Sludge washing and acid dissolution tests will be conducted on sludges from several Hanford tanks.
- Other TRU leaching approaches will be investigated.
- Additional tests will be conducted of TRU and Sr extraction flowsheets for pretreating Hanford tank sludge.
- The use of DIAMIDE-14 to extract TRUs from dissolved Hanford tank sludges will be further studied.
- A TRU extraction flowsheet using DHDECMP to pretreat NCRW sludge will be designed and tested.
- DtBB21C7 will be further studied as a Cs extractant.

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Appendix A

Solubility of Bismuth in Nitric Acid

Appendix A

Solubility of Bismuth in Nitric Acid

As was discussed in Section 10.0, the formation of Bi-containing solids hampered the CMPO solvent extraction tests for pretreating B-110 sludge. The solubility of Bi(III) in nitrate media was investigated so that a viable pretreatment flowsheet could be designed.

Bismuth nitrate pentahydrate was added to solutions containing varying concentrations of HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ until the solutions were saturated. The excess solids were mixed with the saturated solutions at $25 \pm 0.1^\circ\text{C}$ for ~ 2 weeks. After this time, aliquots of the solutions were collected, filtered, and analyzed for Bi by atomic absorption spectroscopy. The results are summarized in Figure A.1.

In general, the solubility of Bi increased with increasing $[\text{HNO}_3]$. The presence of oxalic acid lowered the Bi solubility at the higher HNO_3 concentrations, but had little effect at the lower HNO_3 concentrations.

No attempt was made to ensure that the solution/solid mixtures were at equilibrium. The data presented here may not represent the true thermodynamic solubility of Bi under these conditions. Therefore, caution should be exercised when using these data.

Figure A.1. Solubility of Bi(III) as a Function of HNO₃ Concentration

Appendix B

Synthesis of DIAMIDE-14

Appendix B

Synthesis of DIAMIDE-14

The details of the DIAMIDE-14 synthesis are described in this appendix. The synthesis was performed in two steps. First N,N'-dimethyl-N,N'-dibutylpropane-1,3-diamide (Figure 12.1, R = H) was prepared; this compound is referred to as DIAMIDE-0. This compound was then converted to DIAMIDE-14. The overall synthetic scheme is presented in Figure 12.4.

The procedure for synthesizing DIAMIDE-0 closely followed that reported in the literature (Thiollet and Musikas 1989). An addition funnel was attached to a 500-mL Schlenk flask containing a Teflon-coated magnetic stirring bar. The system was evacuated and backfilled with nitrogen three times. Dry methylene chloride (100 mL) was transferred via cannulae to the addition funnel and from there into the reaction vessel. Similarly, 43 mL (0.36 mol) of dry N,N-methylbutylamine and 50 mL (0.36 mol) of dry triethylamine were added to the reaction vessel. The reaction flask was cooled with a dry ice and isopropanol slush bath, and the addition funnel was charged with 100 mL dry methylene chloride and 17.5 mL (0.18 mol) of malonyl dichloride.^(a) The malonyl dichloride solution was added dropwise to the amine solution over approximately 2 h. Following completion of the addition, the cold bath was replaced with a heating mantle. The addition funnel was replaced with a condenser, and the system heated to reflux under nitrogen for 4 h.

The resulting suspension was extracted with an equal volume of water (the pH of the aqueous phase was basic) followed by two portions of a 1% HCl solution (the aqueous phase was acidic) and two portions of water (aqueous phase neutral). The organic layer was dried over 4-Å molecular sieves, filtered, and volatile components were removed by evaporation under vacuum at room temperature.

The residue was distilled at 1-mm Hg pressure; the distillate fraction at 145 to 150°C was collected in a container cooled with a liquid nitrogen bath. The distillate was a colorless oil which contained a small amount of a separate red liquid phase. The oil solidified to a yellow solid upon cooling. The solid was stirred overnight with about 50 mL of pentane in a septa-capped flask. The solid was filtered and then placed in about 75 mL of iso-octane. When the solvent was heated to its boiling point, the contents separated into two phases--a yellow upper phase and a small amount of red oil in the lower phase. The yellow phase was decanted and concentrated to a total volume of ~50 mL. Upon cooling in the freezer for several days, DIAMIDE-0 precipitated as a pale yellow solid. The solid was filtered and dried under vacuum to give 13.2 g (32% yield) of DIAMIDE-0. The DIAMIDE-0, although colored, possessed identical IR, ¹H, and ¹³C NMR spectra to the sample prepared at LANL, which was a white solid.

(a) The malonyl dichloride was purified by distillation under nitrogen before use.

The melting point (uncorrected) for the LANL-prepared material was 52° to 53°C, compared to a value of 51°C reported in the literature. Likewise, the melting point (uncorrected) for the PNL-prepared material was 52° to 53°C. Both preparations possessed identical TLC R_f 's with ethyl acetate as the eluant.

To prepare the DIAMIDE-14, 6 g (0.15 mol) of KH was placed in a 500-mL Schlenk flask containing a Teflon-coated magnetic stirring bar.^(a) An addition funnel was attached, and the system was transferred to a Schlenk line. Fifty milliliters of dry THF was added to the addition funnel via cannulae and from there to the Schlenk flask. The Schlenk flask was then cooled in an ice bath. Thirty grams (0.125 mol) of DIAMIDE-0 (supplied by LANL) was placed in a 250-mL Schlenk flask. The Schlenk flask was evacuated and backfilled with nitrogen three times. Dry THF (100 mL) was added to the flask containing the DIAMIDE-0, and the resulting solution was transferred via cannulae to the addition funnel. The Schlenk flask that contained the DIAMIDE-0 was rinsed three times with small portions of dry THF, and these washings were also added to the addition funnel. The DIAMIDE-0 solution was added dropwise to the KH suspension over a 3-h period. Much gas evolution (H_2) occurred on contact of the DIAMIDE-0 solution with the KH suspension. Upon completion of the addition, the ice bath was removed, and the reaction mixture was stirred at room temperature overnight.

The suspension was filtered under nitrogen, leaving a lemon yellow filtrate. 1-Bromotetradecane (34.3 g, 0.124 mol) was placed in a 250-mL Schlenk flask, which was then evacuated and backfilled with nitrogen three times; 100 mL of dry THF was added via cannulae. An addition funnel was attached to the malonamide-containing Schlenk flask, and the alkyl halide solution was transferred via cannulae to the funnel. Similarly, THF washings of the Schlenk flask containing the alkyl halide solution were transferred to the addition funnel.

The alkyl halide solution was added dropwise to the malonamide solution over about 1/2 h. The system turned brown during the addition and a precipitate formed. The mixture was stirred overnight under nitrogen at room temperature. Volatiles were removed by evaporation under vacuum at room temperature. Water (150 mL) was added to the residue followed by 200 mL of chloroform. The organic phase was extracted with two equal volumes of 1% HCl, then with two equal volumes of a saturated NaCl solution. The organic phase was dried over 4-Å molecular sieves and filtered, and the chloroform was removed under vacuum at room temperature, leaving 45.72 g (84.2% yield) of DIAMIDE-14 as a yellow oil.

The crude DIAMIDE-14 was purified by column chromatography as follows: 150 g of silica gel (Aldrich Chemical, 70-270 mesh, 60-Å) was slurred with ~500 mL of heptane and loaded onto a column. Between 15 and 25 g of crude DIAMIDE-14 was dissolved in 75 to 150 mL of heptane and loaded onto the silica gel. The column was then eluted with ~400 mL of heptane, at which time the eluant became yellow because of an as yet uncharacterized material, with a TLC R_f of 1 (using ethyl acetate as the eluant). An additional 250 to 300 mL of heptane was required to completely remove this impurity. The eluant was then changed to 95:5 (v:v) ethyl acetate:methanol, and after an additional

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(a) This operation was conducted in a dry box.

250 mL of eluant was passed through the column, a yellow eluant containing the DIAMIDE-14 (as indicated by TLC) began to elute. This band was monitored by TLC until all the DIAMIDE-14 was eluted from the column (a total volume of ~600 mL was required). The solvent was removed by rotary evaporation under vacuum, followed by overnight drying under high (<0.1 torr) vacuum. After treating all the crude DIAMIDE-14 by this method, 35.5 g of purified DIAMIDE-14 was isolated (65.4% overall yield).

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