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**Pretreatment of Neutralized Cladding
Removal Waste Sludge: Status Report**

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Summary

This report describes the status of process development for pretreating Hanford neutralized cladding removal waste (NCRW) sludge, of which $\sim 3.3 \times 10^6$ L is stored in Tanks 103-AW and 105-AW at the Hanford Site. The initial baseline process chosen for pretreating NCRW sludge is to dissolve the sludge in nitric acid and extract the transuranic (TRU) elements from the dissolved sludge solution with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). This process converts the NCRW sludge into a relatively large volume of low-level waste (LLW) to be disposed of as grout, leaving only a small volume of high-level waste (HLW) requiring vitrification in the Hanford Waste Vitrification Plant (HWVP).

The CMPO extraction process has been tested on actual dissolved NCRW solution; results are presented in Section 2. These test results demonstrated that, in principle, the CMPO extraction process can be used to separate the TRUs from the bulk sludge components. The decontamination factor (DF)^(a) was ~ 900 .

Subsequent to this test, a number of potential problems were identified including: 1) instability of dissolved NCRW sludge solutions, 2) formation of interfacial crud in the CMPO extraction contacts, and 3) the 0.2 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) stripping agent would result in the production of ~ 6000 canisters of glass because of the low tolerance for P in the HWVP melter. These three problems have been addressed; potential remedies are presented in Sections 3 (solution stability), 4 (interfacial crud), and 5 (solvent stripping).

Stable dissolved NCRW sludge solutions can be obtained by first washing the sludge with water or dilute NaOH, then dissolving the sludge in HNO_3/HF at a $\text{F}/(\text{Zr} + \text{Al})$ ratio equal to 2. Interfacial crud can be prevented by raising the $\text{F}/(\text{Zr} + \text{Al})$ ratio to 4 or more (for Zr concentrations less than 0.15 M in the extraction contactor). Two methods have been proposed to solve the stripping problem. First, a dilute acid solution containing an agent to reduce Pu(IV) to Pu(III) could be used to strip the TRUs from the CMPO solvent. Although this method is theoretically sound, there may be problems because of the kinetics of the reduction reaction. The second method is to separate the U from the dissolved sludge solution before extracting the TRUs with CMPO. This separation would allow the use of a dilute acid solution in tandem with a very dilute complexing agent (e.g., HEDPA or $\text{H}_2\text{C}_2\text{O}_4$) to strip the TRUs. Also, only a small amount of U would remain in the HLW stream. A third stripping method—using dilute HNO_3/HF —has also been considered, but the volume of glass produced during NCRW disposal would be driven by the fluoride added to the HLW stream by the use of HF. Use of dilute HNO_3/HF would not meet the objectives of the NCRW pretreatment process outlined in this report.

(a) The DF is defined as the quantity of a given species in solution before treatment divided by the quantity after treatment.

The proposed flowsheet to be used to pretreat NCRW sludge is presented in Section 6. This flowsheet involves the following steps: 1) washing the sludge with dilute NaOH, 2) dissolving the washed sludge in HNO₃/HF, 3) extraction of U with tri-n-butyl phosphate (TBP), and 4) extraction of TRUs with CMPO. By implementing this flowsheet, the bulk sludge components (including U) may be disposed of as grout with a TRU content of <0.1 nCi/g. The HLW portion of the waste can be vitrified in approximately 70 canisters.

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1.0 Introduction

For several years, the Pacific Northwest Laboratory (PNL)^(a) has been investigating methods to pretreat Hanford neutralized cladding removal waste (NCRW) sludge. This work has been conducted at the request of Westinghouse Hanford Company (WHC). The current status of the process development for pretreating NCRW sludge is described in this report.

In the past, Zircaloy-clad U fuel was chemically decladded using the Zirflex process (Swanson 1961); NCRW sludge was formed when the decladding solution was neutralized for storage in carbon-steel tanks. This sludge, which is currently stored in Tanks 103-AW and 105-AW on the Hanford Site, primarily consists of $\text{Zr}(\text{OH})_4$ and NaF. Sodium nitrate and nitrite are present in the sludge, along with significant quantities of Al, La, U, and minor constituents. The transuranic (TRU) content of NCRW sludge is about 2000 nCi/g of dry sludge. Because this exceeds the 100 nCi/g U.S. Nuclear Regulatory Commission (NRC) Class C limit (10 CFR 61) for TRUs, the sludge must be handled as high-level waste (HLW).

When this investigation began, a variety of NCRW sludge pretreatment options were considered: 1) separation of Pu and Am solids from the Zr solids by exploiting possible differences in settling rates, 2) selective leaching of Pu and Am from the sludge, 3) sludge dissolution followed by separation of Pu and Am from Zr by LaF_3 precipitation, and 4) sludge dissolution followed by separation of Pu and Am from Zr by extraction with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (Swanson 1991a). The initial results indicated that the most promising method of pretreating NCRW sludge was sludge dissolution followed by extraction of the TRU elements with CMPO (Swanson 1991a, 1991b, 1991c). Thus, subsequent work focused on developing this pretreatment method.

Based on the early success with the selected pretreatment method, a design basis experiment (DBE) was conducted in FY 1991 (Swanson 1991b) to demonstrate the overall process. The results from the DBE are reviewed in Section 2 and serve as a basis for further discussion.

Subsequent to the DBE, the following issues arose concerning the pretreatment of NCRW sludge:

- corrosion of stainless steel piping and equipment
- precipitation from dissolved NCRW sludge solutions
- interfacial crud formation during the CMPO extraction step

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

- excessive quantity of complexing agent 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) used to strip TRUs from the CMPO solvent.

Work in FY 1991 and 1992 focused on resolving these issues.

Regarding the corrosion problem, the TRU extraction process was originally to be implemented in an existing Hanford facility (B Plant). Corrosion tests conducted with simulated dissolved NCRW solutions indicated that the imbedded piping in B Plant might be susceptible to corrosion during the processing of NCRW sludge (Barker, Schwenk, and Divine 1990; Barker, Swanson, and Lumetta 1991). However, it has since been decided that B Plant will not be used to process Hanford tank wastes; rather, a pretreatment facility will be built. Thus, corrosion of piping in B Plant is no longer a problem. Corrosion of piping in the new facility can be minimized by choosing appropriate alloys for construction. Experimental studies will be required to determine which alloys will resist corrosion by process solutions expected to be encountered in the new facility. No further discussion of the corrosion issue will be included in this report.

The three remaining issues—dissolved NCRW solution stability, interfacial crud formation, and the stripping agent—will be addressed in Sections 3, 4, and 5, respectively.

A flowsheet for pretreating NCRW sludge will be presented in Section 6. This flowsheet is based on the current knowledge of NCRW sludge chemistry. The flowsheet is designed to achieve the following pretreatment process objectives:

- separation of Am and Pu from the major sludge constituents (Na, Zr)
- separation of Am and Pu from U (if U is not disposed of in glass)
- concentration of Am and Pu in a small volume, in a form compatible with the feed specifications for the Hanford Waste Vitrifcation Plant (HWVP).

2.0 NCRW Design Basis Experiment

By the end of FY 1990, the development of the CMPO TRU extraction process for NCRW sludge had progressed to the point that a DBE could be performed. This experiment was conducted in the first quarter of FY 1991. Detailed results of this experiment were reported by Swanson (1991b), but they are reviewed in this section as a basis for further discussion.

In the DBE, a series of batch contacts was performed to simulate the counter-current solvent extraction flowsheet depicted in Figure 2.1. The flowsheet experiment consisted of the following steps: 1) sludge dissolution and solution clarification by filtration, 2) adjustment of the solution so that its composition represented a blend of the feed and the three scrub streams shown in Figure 2.1, 3) extraction, 4) scrubbing (with three different streams), and 5) stripping. The functions of the three scrub streams were to 1) remove extracted Zr and fluoride with aqueous oxalic acid, 2) remove extracted oxalic acid with nitric acid, and 3) remove extracted nitric acid with water. The batch solvent extraction contacts performed to test the flowsheet depicted in Figure 2.1 are summarized in Table 2.1.

Figure 2.1. Solvent Extraction Flowsheet Simulated in the NCRW DBE

Table 2.1. Summary of Contacts Performed to Test the Solvent Extraction Flowsheet (Figure 2.1)

Contact	Step	Aqueous Phase	Organic Phase	O/A ^(a)	Organic Vol., mL
A	Extr 1	Feed ^(b)	TRUEX Solvent	0.33	8
B	Extr 2	From A	TRUEX Solvent	0.33	1
C	Extr 3	From B	TRUEX Solvent	0.33	0.67
D	Scrub 1	1.5 <u>M</u> HNO ₃ + 0.05 <u>M</u> H ₂ C ₂ O ₄ ^(c)	From A	1	7
E	Scrub 2	1.5 <u>M</u> HNO ₃ + 0.05 <u>M</u> H ₂ C ₂ O ₄	From D	1	6
F	Scrub 3	2.3 <u>M</u> HNO ₃ ^(d)	From E	1.5	5
G	Scrub 4	2.3 <u>M</u> HNO ₃	From F	1.5	4
H	Scrub 5	Water	From G	3	3.5
I	Scrub 6	Water	From H	3	3
J	Strip 1	0.21 <u>M</u> HEDPA ^(e)	From I	3	2.5
K	Strip 2	0.21 <u>M</u> HEDPA	From J	3	2
L	Strip 3	0.21 <u>M</u> HEDPA	From K	3	1.5
M	Wash	0.25 <u>M</u> Na ₂ CO ₃	From L	1	1

(a) O/A = Volume of the organic phase divided by the volume of the aqueous phase.

(b) The feed solution was a diluted dissolved NCRW sludge solution (see text).

(c) Composition represents a blend of the three scrub streams shown in Figure 2.1.

(d) Composition represents a blend of the second and third scrub streams shown in Figure 2.1.

(e) HEDPA = 1-Hydroxyethane-1,1-diphosphonic acid.

In the sludge dissolution step of the DBE, a 2.45-g portion of NCRW sludge was slurried with 19 mL of water. While the slurry was stirred, HNO₃ (3.8 mL of 15.7 M) was added dropwise, which gave a HNO₃ concentration of 1.8 M. After the final addition of HNO₃, the mixture was further stirred for 2 h at ambient temperature. The NCRW sludge dissolved readily; 98% of the Zr and virtually 100% of the Na dissolved. However, significant fractions of the Al (25%) and P (43%) did not dissolve in HNO₃. There were 0.016 g of Al/g sludge and 0.003 g of P/g sludge in the NCRW sample; thus, 0.004 g of Al and 0.001 g of P would remain undissolved for each gram of NCRW sludge dissolved in this manner.

To prepare the feed for the solvent extraction process, the dissolved NCRW sludge solution was clarified by filtration through a 0.2- μ m membrane filter, then 8.33 mL of water and 0.63 mL of 15.7 M HNO₃ were added to 15 mL of the filtrate. After 0.35 mL of this solution was removed for various analyses, 0.24 mL of 1 M H₂C₂O₄ was added to complete preparation of the aqueous phase for the first extraction contact. This solution represented a blend of the feed solution and the three scrub streams shown in Figure 2.1. The adjusted feed solution was found to contain 0.10 M Zr, 1.14 M Na, 0.049 M K, 0.045 M Al, 0.035 M Si, 0.004 M U, 0.0004 M La, 0.37 M F, 0.01 M H₂C₂O₄, and 1.7 M H⁺. The feed solution also contained 62 nCi/mL of Pu and 9.5 nCi/mL of Am.

The solvent used in this DBE consisted of 0.2 M CMPO plus 1.4 M tri-n-butyl phosphate (TBP) dissolved in a normal paraffin hydrocarbon (NPH). It was washed with aqueous carbonate solution before use. Eight milliliters of the CMPO solvent was contacted with 24 mL of the feed solution for 30 s. The mixture was centrifuged to ensure separation of the two phases. Portions of both the organic and aqueous phases were subjected to additional contacts; the aqueous phase was contacted twice with fresh solvent, and the organic phase was contacted with a series of scrub and strip solutions (summarized in Table 2.1).

The results of the three extraction contacts are shown in Figure 2.2. The TRUs were effectively extracted from the dissolved NCRW solution. The TRU distribution coefficients^(a) in the first, second, and third extractions were 69, 34, and ~6, respectively. The raffinate from the third extraction contained only 0.1% of the TRU activity originally present in the feed. Na and Al were not extracted; a small but significant fraction of Zr was extracted. As expected based on work by Horwitz et al. (1985), a large fraction of the HNO₃ was also extracted.

Figure 2.2. Results of Extraction Contacts From the NCRW DBE

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- (a) The distribution coefficient is defined as the concentration of a given element in the organic phase divided by the concentration in the aqueous phase.

The behaviors of the TRUs, Zr, F⁻, and H⁺ in the scrub contacts are shown in Figure 2.3. The small portion of the extracted Zr was removed from the solvent during the first three scrub contacts; Zr was not detected in solutions from subsequent contacts. Thus, oxalic acid is very effective at removing Zr from the extract. Of the extracted F, 99.3% had been scrubbed out after the sixth scrub contact; the data in Figure 2.3 suggest that the residual F⁻ may be difficult to remove from the extract. The TRUs remained in the organic phase throughout the six scrub contacts.

1-Hydroxyethane-1,1-diphosphonic acid efficiently stripped the TRUs from the scrubbed extract (Figure 2.4). Over 99% of the TRUs were stripped in the first strip contact. The amount of TRUs present after the third strip was below detection limits.

These DBE results served as proof-of-principle that the CMPO TRU extraction process could be used to separate TRUs from the bulk components (Zr and Na) of NCRW sludge. The extraction of the TRUs was very good; only ~0.1 nCi/mL of alpha activity remained in the aqueous phase after the third extraction, compared to 72 nCi/mL in the feed solution. Good separation of the alpha-emitting radionuclides from most nonradioactive materials was achieved. For example, the feed solution contained ~7800 nCi TRU/g of Zr, but the aqueous phase from the third extraction contained only

Figure 2.3. Results of the Scrub Contacts From the NCRW DBE

Figure 2.4. Results of the Stripping Contacts From the NCRW DBE

11 nCi/g of Zr. Likewise, the feed solution contained ~ 4400 nCi TRU/g of Na, whereas the aqueous phase from the third extraction contained only 5 nCi TRU/g of Na. The elements that were not well separated from the TRUs were U and the lanthanides (e.g., La, Ce, and Eu).

3.0 NCRW Sludge Dissolution and Dissolved NCRW Sludge Solution Stability

This section contains discussions of NCRW sludge dissolution behavior and sludge solution stability. Also presented is a method recommended for dissolving NCRW sludge.

3.1 Dissolution of Washed NCRW Sludge

Solutions prepared by dissolving water-washed NCRW sludge are much more stable than those prepared by dissolving unwashed sludge.^(a) However, washing adversely affects sludge solubility because the F content is decreased. To adequately dissolve the washed sludge, F must be added to yield a $F/(Zr+Al)$ ratio of ~ 2 . This ratio may be obtained by adding HF (or a fluoride salt) along with HNO_3 during dissolution. Several experiments were conducted in which washed NCRW sludge was dissolved in HNO_3/HF . The results are summarized in Table 3.1. In each case, the washed sludge^(b) was slurried with water, and concentrated HNO_3 was added to give 2 M HNO_3 ; HF was then added to reach the desired $F/(Zr+Al)$ ratio. After it was stirred for several hours at ambient temperature, the dissolved sludge solution was clarified by filtration, and the remaining solids were dissolved in HCl/HF for analysis.

The $F/(Zr+Al)$ ratios in these experiments were significantly less than those previously encountered using unwashed composite sludge from the 1986 sampling of Tank 103-AW [$F/(Zr+Al)$ ratio was 3.6], yet good dissolution of the sludge was achieved in each case. For Experiments 55B, 55C, and 67, greater than 90% of the Zr dissolved even though the $F/(Zr+Al)$ ratio was less than 2. In Experiment 69, only 75.3% of the Zr dissolved when the $F/(Zr+Al)$ ratio was 1.3; however, when a portion of NCRW sludge taken from the same segment was dissolved at a $F/(Zr+Al)$ ratio of 2.3, 91.9% of the Zr dissolved (Experiment 66). Thus, the major portion of the Zr in these NCRW sludge samples can be dissolved at $F/(Zr+Al) \sim 2$.

The sludge samples that were dissolved had been taken from different tanks and core segments. The composition of the solids remaining after sludge dissolution varied widely, indicating that the type of residue encountered in the process depends on the strata from which the NCRW sludge originated.

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- (a) Although extensive data regarding the TRU content of NCRW wash solutions are unavailable, preliminary results suggest the TRU content of such solutions will be < 0.1 nCi TRU/mL. Thus, these solutions can likely be handled as low-level waste (LLW).
 - (b) In each case the NCRW sludge was washed repeatedly (minimum of three times) with water at ambient temperature. The details of these wash procedures are given in Lumetta and Swanson (1993a).

Table 3.1. Summarized Results of Washed NCRW Sludge Dissolution

Experiment No.	Segment	Source of Components	Sludge Components									
			Al	Cr	Fe	Na	P	Si	U	Zr	F/(Zr+Al) ¹	
55B	4	% in water wash	5.7	43	0.3	90.1	100	68.5	0	0.1	1.3	
	105-AW	% in acid dissolution	94.4	57	89.8	9.9	0	27.8	100	92.9		
	1986	% in residue	0	0	9.9	0	0	3.7	0	7		
		g/g in dry sludge	0.0021	0.0001	0.0005	0.135	0.0012	0.0311	0.0047	0.113		
55C	4	% in water wash	5.9	37.3	0.2	89.8	100	75.4	0	0.1	1.5	
	105-AW	% in acid dissolution	94.1	62.7	92.2	10.1	0	14.8	100.0	94.5		
	1986	% in residue	0	0	7.7	0.1	0	9.8	0	5.4		
		g/g in dry sludge	0	0	7.7	0.1	0	9.8	0	5.4		
66	3A	% in water wash	21.5	57.7	3.7	91.5	-	59.2	0	0	2.3	
	103-AW	% in acid dissolution	64.1	42.3	83.2	8.4	-	25.7	90.3	91.9		
	1986	% in residue	14.4	0	13.3	0.1	-	15.1	19.7	8.1		
		g/g in moist sludge	0.0004	0.0001	0.0003	0.101	0	0.0114	0.0098	0.093		
67	7A	% in water wash	42.7	53.2	0.7	81.4	-	60.3	0	0	1.8	
	1030-AW	% in acid dissolution	56.3	46.8	98.3	18.6	-	34.4	100	99.5		
	1986	% in residue	1	0	1	0	-	5.3	0	0.5		
		g/g in moist sludge	0.0019	0.0003	0.0009	0.183	0	0.0078	0.0132	0.121		
69	3A	% in water wash	6.1	65.2	1.9	93.4	-	65.9	0	0.1	1.3	
	103-AW	% in acid dissolution	71	34.8	47	6.4	-	15	100	75.3		
	1986	% in residue	22.9	0	51.1	0.2	-	19.1	0	24.6		
		g/g in moist sludge	0.0003	0.0001	0.0003	0.098	0	0.0137	0.0049	0.086		

(a) F/(Zr+Al) found in the dissolved sludge solution.

Little or no NO_x formed; this determination was based on the absence of brown fumes during washed sludge dissolution. Thus, the removal of nitrite ion (during water washing) before acid dissolution could prevent the need for an NO_x abatement system on the dissolver, which is a major advantage of sludge washing. Also, because most of the carbonate ion and hydroxide ion were also removed from the sludge during water washing, no splattering occurred during the acid dissolution of washed NCRW sludges.

The following example illustrates the sludge washing and dissolution steps for pretreating NCRW sludge. The core composite sample (1.275 g of air-dried NCRW sludge) was taken from Tank 103-AW in 1986. To determine if aging of the sludge would cause the sludge to become more difficult to dissolve, the sample was wetted with 1.5 mL of water and "aged," that is, held for 2 months at 80°C and then stored for 21 months at ambient temperature. No adverse effects were observed, and complete sludge dissolution was then achieved in two steps, as described below.

After storage, the aged sludge was washed successively with 6, 5, 5, and 5 mL of 0.1 M NaOH. During each wash, the sludge was stirred with the wash solution for a minimum of 1 h at ambient temperature. After each of the first three washes, the supernatant solution was decanted from the sludge after centrifuging. Centrifuging was also performed after the final wash, but because the supernatant solution had clouded, the mixture was allowed to stand for 2 weeks, which resulted in a clear supernatant solution. The solution was then decanted; the total volume of the wash solutions decanted from the sludge was 22 mL.

Before dissolution, washed NCRW sludge was first slurried in 5 mL of water and transferred to a plastic vial. The vessel from which the slurry had been transferred was rinsed three times with 1-mL portions of water. These rinse waters were added to the slurry in the plastic vial to ensure that all the solids were transferred into the plastic vial. The dissolution was conducted in a plastic vial to avoid leaching Si from a glass vial.

Concentrated HNO_3 (1.77 mL) and 10 M HF (0.4 mL) were added to the slurry. Water was then added to bring the total volume of the mixture to about 12 mL. The mixture was stirred at ambient temperature for 2.75 h and centrifuged, then the solution was decanted. This solution will hereafter be referred to as the "primary dissolver" solution. The concentrations of the major components in this solution were 0.014 M Al, 0.003 M Cr, 0.001 M Fe, 0.003 M K, 0.0002 M La, 0.050 M Na, 0.005 M U, 0.12 M Zr, 0.29 M F, and 2 M H^+ .^(a) The F/(Zr + Al) ratio was 2.2.

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- (a) The metal ion concentrations were determined by inductively coupled plasma-atomic emission spectroscopy. The fluoride ion concentration was determined using a fluoride selective electrode. The acid concentration was determined by potentiometric titration with standard NaOH. The acid concentration was corrected for the presence of hydrolyzable ions by the following formula: $[\text{H}^+] = [\text{H}^+]_{\text{total}} - 2[\text{Zr}] - 3([\text{Al}] + [\text{Cr}] + [\text{Fe}])$, where $[\text{H}^+]_{\text{total}}$ is the total acid concentration found by titration to pH 7.

The residual solid was treated with 2.2 mL of 1.9 M HNO₃/0.7 M HF at 100°C for 1 h, resulting in complete dissolution of the solid. The concentrations of the major components in this "secondary dissolver" solution were 0.091 M Al, 0.002 M Cr, 0.001 M Fe, 0.014 M P, 0.001 M U, and 0.083 M Zr.

The total quantities and the percentages of each major sludge component found in the sludge wash solution, primary dissolver solution, and secondary dissolver solution are given in Table 3.2. The most abundant element in the sludge was Na, and 95% of this was found in the sludge wash solution. The behavior of K was identical to that of Na. Greater than 80% of the Zr was found in the primary dissolver, while the remainder was in the secondary dissolver solution. Interestingly, almost all of the Si dissolved in the sludge wash step, while only 16% of the Al dissolved in the alkaline wash. Greater than 50% of the Al remained after the primary dissolution step, but this dissolved completely in the secondary dissolution step. No P was found in either the sludge wash solution or the primary dissolver solution. The secondary dissolution step was needed to achieve dissolution of P. Given the low tolerance for P in the feed to the HWVP, *a secondary dissolver is recommended for use in processing NCRW sludge to minimize the quantity of P-containing TRU solids requiring vitrification.*

The feed for the CMPO TRU extraction process may contain a combination of the primary and secondary dissolver solutions; such a combination is not expected to adversely affect the process. The primary and secondary dissolver solutions (12 mL and 4 mL, respectively) from the experiment described above were mixed, and the resulting solution was itself combined with 14 mL of a solution obtained by dissolving (primary dissolution only) a washed portion of Segment 7A from the 1986 core sampling of Tank 103-AW. The resulting solution was adjusted with HF to produce a F/(Zr + Al) ratio of 4.6, and oxalic acid was added to yield [H₂C₂O₄] concentration of 0.012 M. This feed solution contained 0.013 M Al, 0.11 M Na, 0.005 M U, 0.13 M Zr, 1.8 M H⁺, and 86 nCi/mL of TRU. After three successive contacts with the 0.2 M CMPO solvent, the aqueous solution contained less than 0.14 nCi/mL of TRU. Thus, the decontamination factor (DF) achieved was greater than 620. Virtually no extraction of Al or Na was observed, and less than 10% of the Zr was extracted. As discussed in Section 2, the Zr can be scrubbed from the CMPO solvent with H₂C₂O₄. Thus, complete dissolution of NCRW sludge, followed by extraction of the TRUs with CMPO is a feasible pretreatment approach.

3.2 Dissolved NCRW Sludge Solution Stability

The stability of washed NCRW sludge solutions was compared to unwashed NCRW sludge solutions. Based on the results presented in Table 3.3, solutions obtained from washed NCRW sludge are stable for much longer periods of time than those obtained from unwashed sludge. Solutions prepared by dissolving washed NCRW sludge in HNO₃/HF [with F/(Zr + Al) ~ 2] are sufficiently stable that a plant equipment cleanout capability may not be necessary.

Table 3.2. Results of Sludge Washing and Dissolution Experiment Using Composite Core Sample From Tank 103-AW (1986)

Source of Components	Quantities of Components											
	Na	Zr	K	Si	U	Al	Cr	P	Fe	La	Ni	Ba
In Sludge, g/g	2.0E-01	1.3E-01	1.8E-02	1.6E-02	1.5E-02	1.3E-02	3.3E-03	1.3E-03	7.2E-04	3.3E-04	2.1E-04	1.3E-04
In Wash, %	95	0	95	97	10	16	46	0	0	0	29	0
In Primary Dissolver, %	5	82	5	2	83	27	44	0	77	93	58	82
In Secondary Dissolver, %	0	18	0	1	7	57	10	100	23	7	13	18

Table 3.3. Stability of Dissolved Sludge Solutions Toward Precipitation

	Components, <u>M</u>				F/(Zr + Al) Ratio	Stability, days
	<u>Zr</u>	<u>Al</u>	<u>Na</u>	<u>H⁺</u>		
<u>Unwashed Sludge:</u>						
	0.24	0.053	1.78	0.6	2.9	> 1, < 2
	0.10	0.023	0.76	1.4	2.9	> 1, < 2
	0.13	0.015	1.75	1.2	2	> 20
<u>Washed Sludge:</u>						
	0.18	0.006	0.20	1.7	1.8	> 170
	0.16	0.002	0.07	1.7	2.3	> 5, < 34
	0.13	0.011	0.06	1.8	2.5	> 225
	0.12	0.001	0.05	1.5	1.3	> 150

A systematic study was undertaken to identify the variables that affect the solution stability of washed NCRW sludge. This study focused on the five major sludge components: Zr, Al, F, Na, and K. A series of solutions was prepared with constant concentrations of Zr and Al, but varying concentrations of F, Na, and K. These solutions were monitored over several months for precipitate formation. The results are summarized in Table 3.4. The following conclusions can be drawn:

- for the given concentrations of Zr, Al, Na, and K, increasing the F concentration to a $F/(Zr + Al) > 3.7$ produces less stable solutions
- for the given concentrations of Zr, Al, F, and K, increasing the Na concentration produces less stable solutions
- for the given concentrations of Zr, Al, F, and Na, increasing the K concentration produces less stable solutions.

Thus, the most stable solutions examined here were obtained when $[Na] = [Zr]$ and the $F/(Zr + Al) < 4$. In the parametric study described in Table 3.4, the Al concentration was maintained constant. Because Al is complexed by F⁻, its role in dissolved NCRW sludge solution stability is likely to be significant. Further parametric studies should be performed to address the effects of Al on solution stability.

Table 3.4. Components That Affect NCRW Sludge Solution Stability

Concentrations of Components				F/(Zr + Al) Ratio	[HNO ₃]	Minimum Stability, days	Maximum Stability, days
[Zr]	[Al]	[Na]	[K]				
0.14	0.0104	0.14	0.0077	0.27	1	65	n.d.
0.14	0.0104	0.14	0.0077	0.42	1	65	n.d.
0.14	0.0104	0.14	0.0077	0.57	1	65	n.d.
0.14	0.0104	0.14	0.0077	0.72	1	1	2
0.14	0.0104	0.14	0.0077	0.87	1	0	0
0.14	0.0104	0.24	0.0077	0.57	1	37	43
0.14	0.0104	0.39	0.0077	0.57	1	1	2
0.14	0.0104	0.64	0.0077	0.57	1	0	0
0.14	0.0104	0.89	0.0077	0.57	1	0	0
0.14	0.0104	1.14	0.0077	0.57	1	0	0
0.14	0.0104	0.14	0.108	0.57	1	2	8
0.14	0.0104	0.14	0.258	0.57	1	2	8
0.14	0.0104	0.14	0.408	0.57	1	**	1

n.d. = not determined.

3.3 Recommended NCRW Sludge Wash and Dissolution Procedure

Given current knowledge, the following primary dissolution procedure is recommended to dissolve NCRW sludge for the CMPO TRU extraction process: 1) wash the sludge with water (or dilute NaOH) to remove the bulk of the Na, K, NO_3^- , NO_2^- , and F^- ; 2) add water and HNO_3 to the sludge to reach the expected concentrations of 0.2 M Zr and 2 M HNO_3 ; 3) add HF until the $\text{F}/(\text{Zr} + \text{Al})$ ratio equals 2; 4) mix at ambient temperature for 1 to 2 h, then filter. This method should result in good dissolution of the sludge, creating solutions that are very stable. The wash step will reduce gas (NO_x and CO_2) generation during the acidification step.

A secondary dissolver may be used to dissolve the solids remaining after the primary dissolution procedure. The secondary dissolver is recommended to minimize the amount of P-containing TRU solids requiring vitrification, which in turn would minimize the number of glass canisters needed to dispose of the waste. In the secondary dissolution procedure, the remaining solids would be treated with 2 M HNO_3 /1 M HF at 100°C. The resulting solution could be added to the solution from the primary dissolution procedure and adjusted as feed to the CMPO TRU extraction process (or other separation process that might be implemented).

4.0 Interfacial Crud

Early investigations of the CMPO extraction of TRUs from dissolved NCRW solution indicated that the process may be hindered by the formation of interfacial crud (Swanson 1991a, 1991c). The factors that affect interfacial crud formation have since been investigated in detail. The critical factor appears to be the $F/(Zr+Al)$ ratio, which governs the distribution behavior of Zr; i.e., the higher the $F/(Zr+Al)$ ratio, the less Zr is extracted. Variations of this ratio were investigated for their effects on interfacial crud formation; the ratio was adjusted by adding HF to the dissolved sludge solution. The study results are summarized in Table 4.1 and Figure 4.1.

The data in Table 4.1 indicate that for a given concentration of Zr in the dissolved sludge solution, the tendency to form interfacial crud decreases with increasing $F/(Zr+Al)$ ratios. For example, in the series of contacts 66-SX8 to -SX15 and 66-SX17 to -SX21, the Zr concentration was maintained at 0.082 M , while the $F/(Zr+Al)$ ratio was varied between 2.2 and 4.6. The amount of crud present decreased visibly as the $F/(Zr+Al)$ ratio was increased. When $F/(Zr+Al)$ was equal to or greater than 4.1, crud did not form. Similar tendencies were observed in the series of contacts 602A-3 to -12, 602A-13A to -13F, 67-SX2 to -SX9, 69-SX1 to -SX4, and 75-SX1 to -SX19.

These results imply that the formation of interfacial crud is linked to the concentration of Zr in the organic phase. When the $F/(Zr+Al)$ ratio is high, Zr forms a hydrophilic complex with F^- , and the extraction of Zr is suppressed. The data presented in Figure 4.2 support this hypothesis. As the $F/(Zr+Al)$ ratio is increased, the distribution coefficient for Zr tends to decrease. Further data on the distribution of Zr as a function of the $F/(Zr+Al)$ ratio are needed to confirm this hypothesis, but it appears that at a low $F/(Zr+Al)$ ratio, the concentration of a certain Zr species in the organic phase exceeds its solubility in that phase, leading to interfacial crud formation.

Data also indicate that time is an important variable in preventing interfacial crud formation. After the aqueous feed solution is adjusted with F^- , some period of time must be allowed before the solvent extraction contact is performed, presumably due to slow equilibration of Zr-F species. For example, in contact 602A-8 (Table 4.1) interfacial crud was observed initially, but the crud had disappeared after the mixture was allowed to stand overnight. In solvent extraction contact 602A-12, the feed solution was adjusted to a $F/(Zr+Al)$ ratio of 4 and was contacted immediately with the CMPO solvent; interfacial crud formed. But after the mixture was stirred at ambient temperature for 30 min, the crud had dissolved. The time required to ensure that adequate Zr-F equilibration has occurred has not yet been rigorously defined, but a minimum of 1 h is recommended.

The interfacial crud observations made to date are summarized in Figure 4.1. The operating range for the CMPO TRU extraction process can be tentatively defined based on the data in Figure 4.1. The Zr concentration in the aqueous phase of the extraction contactors should be maintained below 0.15 M , while the $F/(Zr+Al)$ ratio is kept above 4.5. Based on results obtained to date, interfacial crud should not form under these conditions. However, further testing is needed to definitively determine the operating range of the process.

Table 4.1. Summary of Interfacial Crud Observations for TRUEX Solvent Extraction Contacts for Dissolved NCRW Solutions

Contacts	Organic Aqueous	Initial Aqueous Concentration, M						F/(Zr + Al)	Crud Formation
		[Al]	[Na]	[Zr]	[F]	[H ⁺]	Time, h ^(a)		
602A-3	0.33	0.11	0.7	0.12	0.28	1.1	—	1.2	Yes
602A-4	0.33	0.014	0.7	0.12	0.28	1.1	—	2.1	Yes
602A-5	0.33	0.11	0.7	0.12	0.28	1.1	—	1.2	Yes
602A-6	0.33	0.014	0.7	0.12	0.28	1.1	—	2.1	Yes
602A-8	0.33	0.014	0.71	0.12	0.53	1.1	0	4	Yes ^(b)
602A-9 ^(c)	0.33	0.014	0.71	0.12	0.53	1.1	~24	4	No
602A-11	0.33	0.014	0.71	0.12	0.53	1.1	3	4	No
602A-12A	0.28	0.014	0.71	0.12	0.53	1.1	0	4	Yes
602A-12B	0.28	0.014	0.71	0.12	0.53	1.1	0.5	4	No
602A-13A	0.33	0.015	0.75	0.13	0.30	1.2	0.1	2.1	Yes
602A-13B	0.33	0.015	0.74	0.13	0.35	1.2	1	2.4	Yes
602A-13C	0.33	0.014	0.73	0.13	0.39	1.2	1	2.7	Yes
602A-13D	0.32	0.014	0.73	0.13	0.44	1.2	1	3	Yes
602A-13E	0.32	0.014	0.72	0.12	0.48	1.2	1	3.6	Yes
602A-13F	0.32	0.014	0.71	0.12	0.52	1.1	0.5	3.9	No
66-SX8	0.33	0.001	0.034	0.082	0.18	2.2	0.8	2.2	Yes
66-SX9	0.33	0.001	0.034	0.082	0.21	2.1	0.8	2.5	Yes
66-SX10	0.33	0.001	0.034	0.082	0.24	2.1	0.8	2.9	Yes
66-SX11	0.33	0.001	0.034	0.082	0.26	2.1	0.8	3.1	Yes
66-SX12	0.33	0.001	0.034	0.082	0.28	2	1.3	3.4	Yes
66-SX13	0.33	0.001	0.034	0.082	0.31	2	1.3	3.7	Yes
66-SX14	0.33	0.001	0.034	0.082	0.34	2	1.3	4.1	No
66-SX15	0.33	0.001	0.034	0.082	0.36	2	1.3	4.3	No
66-SX17	0.33	0.001	0.034	0.082	0.38	2	0.7	4.6	No
66-SX18	0.33	0.001	0.034	0.082	0.41	1.9	0.7	4.9	No
66-SX21	0.33	0.001	0.034	0.082	0.38	0.9	2.2	4.6	No
67-SX2	0.33	0.052	0.107	0.087	0.08	0.8	—	0.6	Yes
67-SX3	0.33	0.103	0.107	0.087	0.08	0.8	—	0.4	Yes
67-SX4	0.33	0.003	0.107	0.087	0.08	0.8	—	0.9	Yes
67-SX6	0.33	0.003	0.107	0.087	0.08	1.2	1.3	0.9	Yes
67-SX7	0.33	0.003	0.107	0.087	0.23	1.2	1.3	2.6	Yes
67-SX8	0.33	0.003	0.107	0.087	0.28	1.1	16.7	3.1	No
67-SX9	0.33	0.003	0.107	0.087	0.33	1.1	16.7	3.7	No
69-SX1	0.33	0.001	0.023	0.061	0.18	1.2	1.5	2.9	Yes
69-SX2	0.33	0.001	0.023	0.061	0.28	1.1	1.5	4.5	No
69-SX3	0.33	0.001	0.023	0.061	0.33	1	1.5	5.3	No
69-SX4	0.33	0.001	0.023	0.061	0.38	1	1.5	6.1	No
75-SX1	0.33	0.014	0.19	0.19	0.56	1.0	24	2.7	Yes
75-SX2	0.33	0.014	0.19	0.19	0.66	1.0	24	3.2	Yes
75-SX3	0.33	0.014	0.19	0.19	0.76	1.0	24	3.7	Yes
75-SX4	0.33	0.014	0.19	0.19	0.86	1.0	24	4.2	Yes
75-SX5	0.33	0.014	0.19	0.19	0.96	1.0	24	4.7	No
75-SX6	0.33	0.017	0.24	0.24	0.70	1.2	24	2.7	Yes
75-SX7	0.33	0.017	0.24	0.24	0.82	1.2	24	3.2	Yes

Table 4.1. (contd)

Contacts	Organic Aqueous	Initial Aqueous Concentration, M					Time, h ^(a)	F/(Zr + Al)	Crud Formation
		[Al]	[Na]	[Zr]	[F]	[H ⁺]			
75-SX8	0.33	0.017	0.24	0.24	0.95	1.2	24	3.7	Yes
75-SX9	0.33	0.017	0.24	0.24	1.1	1.2	24	4.2	Yes
75-SX10	0.33	0.017	0.24	0.24	1.2	1.2	24	4.7	Yes
75-SX12	0.33	0.010	0.13	0.13	0.58	0.6	24	4.2	No
75-SX13	0.33	0.010	0.13	0.13	0.71	0.6	24	5.2	No
75-SX14	0.33	0.012	0.15	0.15	0.70	0.8	24	4.2	No
75-SX15	0.33	0.012	0.15	0.15	0.86	0.8	24	5.2	No
75-SX16	0.33	0.008	0.10	0.10	0.41	0.5	3	3.7	No
75-SX17	0.33	0.008	0.10	0.10	0.46	0.5	3	4.2	No
75-SX18	0.33	0.008	0.10	0.10	0.57	0.5	3	5.2	No
75-SX19	0.33	0.005	0.06	0.06	0.25	0.3	3	3.7	No

(a) Time lapse between adjustment of the feed with F and contact with the TRUEX solvent.

(b) Crud disappeared upon standing overnight.

(c) Aqueous solution was heated at 100°C for 40 min before contact. This induced a small amount of precipitation. The solution was clarified by centrifuging and decanting from the solid before the contact.

Figure 4.1. Interfacial Crud Formation in TRUEX Contacts With Dissolved NCRW Sludge. The F/(Zr + Al) ratio was adjusted as appropriate by addition of HF to the aqueous solutions. A minimum of 1 h was allowed before contacting with the TRUEX process solvent.

Figure 4.2. Distribution of Zr as a Function of $F/(Zr + Al)$ in TRUEX Contacts With Dissolved NCRW Sludge

5.0 Solvent Stripping

Stripping extracted TRUs from the CMPO solvent has become a critical issue in the extraction of TRUs from dissolved NCRW sludge solutions. The initial studies of the CMPO extraction process used a solution consisting of 0.2 M HEDPA to strip the TRUs from the solvent (Swanson 1991a, 1991b, 1991c). However, the use of 0.2 M HEDPA as the stripping agent was recently ruled out for two reasons. First, using 0.2 M HEDPA would lead to an excessive amount of P in the HWVP feed, which would result in production of a large amount of glass (~6000 canisters) in disposal of the TRUs. Second, HEDPA strips U as well as the TRUs. The separation of U from the TRUs could minimize the number of glass canisters, especially in the event that the TRUEX process is applied to the single-shell tank (SST) wastes, which contain a large inventory of U.

When the excess P problem was first identified, a study was initiated to determine if lower concentrations of HEDPA could be used to strip the TRUs. Lower HEDPA concentrations would result in a decreased amount of P in the feed to HWVP. The major findings of this study (Lumetta and Swanson 1993a, 1993b) were as follows:

- The distribution coefficient (D_{Am}) for Am extraction by CMPO is proportional to the fourth order of the HNO_3 concentration and inversely proportional to the square of the HEDPA concentration.
- The minimum concentration of HEDPA that can be used to strip the TRUs is dictated by the amount of U present in the extract.
- A solution consisting of 0.25 M Na_2CO_3 plus 0.002 M HEDPA can be used to strip TRUs from the CMPO solvent.

The fourth-order dependence of D_{Am} on the HNO_3 concentration, and the inverse dependence of D_{Am} on the square of the HEDPA concentration, dictate that adequate scrubbing of HNO_3 must be achieved for dilute solutions of HEDPA to effectively strip the TRUs. These relationships are illustrated in Figure 5.1, which shows the stripping efficiency (for batch contacts) of aqueous HEDPA solutions at three concentrations (0.05, 0.025, and 0.002 M) that would be expected if the scrubbed extract contained 0.1 or 0.2 M HNO_3 . Based on the data in Figure 5.1, efficient stripping of Am can obviously be achieved at HEDPA concentrations much below the 0.2 M concentration used in the initial studies. For example, at the initial concentration of 0.2 M HNO_3 in the organic phase, two contacts with 0.05 M HEDPA result in the removal of 99% of the Am. However, with an additional stage, this level of stripping can be exceeded with 0.025 M HEDPA. The importance of scrubbing HNO_3 from the extract before the strip step is clearly illustrated in Figure 5.1. For all HEDPA concentrations, markedly better stripping efficiencies are achieved when the initial organic HNO_3 concentration is 0.1 M rather than 0.2 M. This is a result of the fourth-order dependence of D_{Am} on the HNO_3 concentration.

Figure 5.1. Calculated Stripping of Am From the CMPO Solvent With Aqueous HEDPA Solutions, Based on Batch Contacts (Organic-to-Aqueous Phase Ratio = 3)

The predicted stripping efficiencies depicted in Figure 5.1 apply only if U is not present in the scrubbed extract. Because HEDPA forms a water-soluble complex with U, the presence of U decreases the TRU stripping efficiency of HEDPA. In fact, the U concentration in the scrubbed extract will dictate the minimum amount of HEDPA needed to strip the TRUs. For example, in the DBE (Section 2) the U concentration in the aqueous phase in the first strip contact was 0.034 M. If each U binds two HEDPA ligands, a minimum of 0.07 M HEDPA would be needed to efficiently strip the TRUs.

The use of Na_2CO_3 to strip TRUs was investigated as an alternative to the HEDPA stripping agent. A 0.25 M Na_2CO_3 solution stripped the TRUs and U from the solvent, but La (another component of NCRW sludge) precipitated in the carbonate solution. Further work indicated that a small addition of HEDPA (0.002 M) to the Na_2CO_3 solution might prevent the La from precipitating. This method appeared very promising for stripping TRUs from the CMPO solvent and offered the advantage of simplifying the process flowsheet by combining the strip and solvent wash steps.

Based on previous work, by the end of FY 1991, it was thought that a solution consisting of 0.25 M Na_2CO_3 plus 0.002 M HEDPA would be used to strip the CMPO solvent. However, two issues arose that necessitated a re-evaluation of this stripping agent. First, the potential need to separate the TRUs from U became apparent because of the likely retrieval and pretreatment of the SST wastes, which contain a large U inventory. Although TRU/U separation is not necessarily a critical

issue in pretreating NCRW sludge, it is important if the SSTs are included in the overall tank pretreatment effort. Routing the U to HWVP may not be desirable because of the large volume of glass that would be produced in disposing of all the U. To render the TRU extraction process applicable to all the various wastes, the process should be designed so that the TRUs can be separated from the U.

The second issue that prompted a re-evaluation of the stripping agent was the effects of added Na. The introduction of Na into the TRU strip was postulated as undesirable because added Na (from the Na_2CO_3) would increase the number of glass canisters needed to dispose of the TRU portion of the waste.^(a) Given this information, the use of a Na_2CO_3 /HEDPA strip solution was abandoned. Sodium citrate, which had been under investigation, was also ruled out as a stripping agent.^(b)

A number of processing schemes are currently under investigation to resolve these two issues. The two most promising are 1) reducing Pu to Pu(III) in the strip stages, so that both Am and Pu can be stripped with dilute HNO_3 , and 2) removing U from the dissolved sludge solution by extraction with TBP before extracting TRUs with CMPO.

In FY 1992, an experiment was conducted to test the feasibility of stripping the TRUs with a solution of 0.01 M ferrous sulfamate (FS) in 0.01 M HNO_3 . In this experiment, a dissolved NCRW sludge solution (0.13 M Zr, 0.61 M F⁻, and 1.8 M HNO_3) was contacted with the CMPO solvent at an organic-to-aqueous phase ratio of 0.35. The organic phase from this extraction was scrubbed twice with 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ in 1.5 M HNO_3 (organic-to-aqueous phase ratio of 3), then was scrubbed three times with water (organic-to-aqueous phase ratio of 3). To strip the TRUs, the scrubbed extract was contacted three successive times with a solution consisting of 0.01 M FS in 0.01 M HNO_3 . In the FS strip contacts, the organic and aqueous phases were mixed for only 10 s to simulate the short residence times that might be expected in centrifugal contactors. If centrifugal contactors were used, rapid reduction of Pu(IV) to Pu(III) would be essential. Finally, residual TRU material in the solvent was stripped with 0.2 M HEDPA.

In the three FS strip contacts, the distribution coefficients for the alpha-emitting TRU radio-nuclides were 2, 0.3, and 0.1, respectively. Although 98.3% of the TRUs was stripped in the FS strip contacts, the high distribution coefficient in the first contact would not be acceptable under processing conditions, because the TRUs would reflux in the first strip stage. The HNO_3 concentration in the scrubbed extract was 0.07 M, which should have resulted in distribution coefficients of 0.5 for both Am(III) and Pu(III), as calculated by the Generic TRUEX Model (Vandegrift et al. 1990). Thus, the

-
- (a) The TRU stream generated from the TRU extraction process will possibly be stored as an acidic solution in a stainless steel tank before it is fed to HWVP. If this stream is stored in a carbon steel tank, neutralization will be required. In this case, the argument against using Na_2CO_3 as the stripping agent is not as important.
 - (b) Ammonium citrate could be used as a stripping agent, but the effect of ammonium ion in the overall processing scheme is uncertain. Historically, ammonium ion has been avoided in nuclear processing schemes, but ammonium citrate as a stripping agent should not be ruled out.

high distribution coefficient in the first FS strip contact likely resulted from the presence of some unreduced Pu(IV). Therefore, if this method is to be employed, the conditions for reducing Pu(IV) to Pu(III) must be better defined.

Significantly, only 12% of the U in the scrubbed extract was stripped in the FS contacts; the remainder was found in the 0.2 M HEDPA strip. Thus, if perfected, this method would allow some degree of U separation from the TRUs. The inclusion of a solvent scrub stream in the stripping stage would enhance separation of U from TRU.

Recently, a screening study was conducted to test the approach in which U is removed from the dissolved NCRW sludge solution before extracting the TRUs with CMPO. A simulated dissolved NCRW solution^(a) was contacted three successive times with 30% TBP in NPH at an organic-to-aqueous phase ratio of 0.2. Ascorbic acid was added to the feed solution to adjust the Pu valence to the +3 oxidation state to prevent Pu extraction; this valence adjustment is key to the success of this approach. The organic phase in the first contact was yellow, indicating the U had been extracted. The aqueous and organic phases in the subsequent TBP contacts were colorless, suggesting that near complete extraction of U had been achieved in the first contact. The concentration of U decreased from 0.0023 M in the feed solution to less than 3.4×10^{-4} M in the aqueous phase from the third TBP extraction contact, indicating that >85% of the U was extracted. The exact percentage of U extracted could not be determined because the U concentration in the aqueous phase from the third TBP extraction contact was below the analytical detection limit. The total alpha^(b) distribution coefficient in the first extraction contact with TBP was 0.1; this measurement included the alpha activity from U, so the distribution coefficient for Pu was actually <0.1.

The aqueous phase from the third TBP extraction was contacted with the CMPO solvent, and the extract was scrubbed and stripped according to the scheme outlined in Table 5.1. The distribution coefficients for the total alpha activity for each contact are listed in Table 5.1, and the concentration profile for the alpha activity is presented in Figure 5.2. The results indicate that the Pu began to strip in the last scrub step, and virtually complete stripping had been achieved after the first contact with 0.001 M HEDPA. The scrub and strip steps must be balanced properly to prevent the TRUs from beginning to strip in the final scrub stage. These results serve as a proof-of-principle for this NCRW sludge pretreatment method. A flowsheet for pretreating the dissolved NCRW sludge by such a procedure is presented in Section 6. This method would achieve the following: 1) separation of U from the TRUs, 2) separation of the TRUs from the other bulk sludge constituents (i.e., Na, Zr, Al), and 3) stripping of the TRUs without adding an excessive amount of P to the TRU waste stream.

-
- (a) This solution consisted of 0.11 M $\text{ZrO}(\text{NO}_3)_2$, 0.14 M NaNO_3 , 0.001 M $\text{La}(\text{NO}_3)_3$, 0.0023 M $\text{UO}_2(\text{NO}_3)_2$, 0.54 M HF , and 1.9 M HNO_3 . The solution was spiked with Pu (10,700 dpm/mL), and ascorbic acid was added to a concentration of 0.01 M.
- (b) The total alpha concentrations of the aqueous and organic phases were determined by liquid scintillation counting.

Table 5.1. Solvent Extraction Contacts Performed to Test Uranium Extraction From Simulated Dissolved NCRW Solution

Contact	Aqueous Phase	Organic Phase	O/A ^(a)	D, alpha
TBP 1	Feed Solution	30% TBP	0.2	0.1
TBP 2	Aqueous from TBP 1	30% TBP	0.2	0.06
TBP 3	Aqueous from TBP 2	30% TBP	0.2	0.05
CMPO 1	Aqueous from TBP 3	0.2 <u>M</u> CMPO/1.4 <u>M</u> TBP	0.29	23
Scrub 1A	0.0375 <u>M</u> H ₂ C ₂ O ₄ /1.125 <u>M</u> HNO ₃	Organic from CMPO 1	0.75	20
Scrub 1B	0.0375 <u>M</u> H ₂ C ₂ O ₄ /1.125 <u>M</u> HNO ₃	Organic from Scrub 1A	0.75	15
Scrub 2A	1.5 <u>M</u> HNO ₃	Organic from Scrub 1B	1	46
Scrub 2B	1.5 <u>M</u> HNO ₃	Organic from Scrub 2A	1	68
Scrub 2C	1.5 <u>M</u> HNO ₃	Organic from Scrub 2B	1	44
Scrub 3A	0.01 <u>M</u> HNO ₃	Organic from Scrub 2C	1.5	27
Scrub 3B	0.01 <u>M</u> HNO ₃	Organic from Scrub 3A	1.5	4.3
Scrub 3C	0.01 <u>M</u> HNO ₃	Organic from Scrub 3B	1.5	0.5
Strip 1A	0.01 <u>M</u> HNO ₃	Organic from Scrub 3C	0.5	0.05
Strip 1B	0.01 <u>M</u> HNO ₃	Organic from Strip 1A	0.5	0.7
Strip 2A	0.001 <u>M</u> HEDPA	Organic from Strip 1B	3	0.008
Strip 2B	0.001 <u>M</u> HEDPA	Organic from Strip 2A	3	--
Strip 2C	0.001 <u>M</u> HEDPA	Organic from Strip 2B	3	--
Strip 2D	0.001 <u>M</u> HEDPA	Organic from Strip 2C	3	--
Wash 1	0.25 <u>M</u> Na ₂ CO ₃	Organic from Strip 2D	1	--

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

Figure 5.2. Concentration of Alpha Emitters (mainly Pu) in the CMPO Solvent Extraction Contacts Described in Table 5.1

6.0 Flowsheet for Pretreating NCRW Sludge

A sludge pretreatment flowsheet was developed based on the experimental results described in the preceding sections. The flowsheet is described in this section. The discussion of the flowsheet is divided into five parts: 1) process objectives, 2) sludge washing and dissolution, 3) TBP extraction of U, 4) CMPO extraction of the TRUs, and 5) modeling of the CMPO cycle of the flowsheet with the Generic TRUEX Model (GTM) (Vandegrift et al. 1990). This section also includes a discussion of process disadvantages and alternative flowsheets.

6.1 Process Objectives

In broad terms, the objective of the NCRW pretreatment process is to minimize the cost of waste disposal. Although the flowsheet described here is not optimized, it is expected to achieve the three following objectives:

- separate the TRU components from the waste so that the bulk of the nonradioactive components may be disposed of as low-level waste (LLW) (< 100 nCi TRU/g waste)
- route $\geq 95\%$ of the U to the LLW stream^(a)
- produce less than 100 canisters of glass for disposal of the TRU portion of the NCRW sludge.

The first objective assumes that the LLW disposal form at Hanford (i.e., grout) must meet the NRC Class C LLW criterion of < 100 nCi/g of TRU (10 CFR 61). However, for the purposes of process development, an LLW form was targeted that contains < 10 nCi/g of TRU material. The target is well below the Class C LLW criterion for two reasons: 1) achieving the needed DFs will be more difficult when the process is implemented at plant scale, and 2) there is a possibility that the LLW form must meet NRC Class A (< 10 nCi/g of TRU, 10 CFR 61) limits rather than Class C limits.

Accomplishing the second objective is essential to reduce the volume of borosilicate glass needed to dispose of the TRU portion of the NCRW sludge. If the HLW stream from the pretreatment process contained all of the U, TRUs, and La, the volume of borosilicate glass needed for TRU disposal would be driven by the amount of U present. The NCRW sludge contains approximately 2.3×10^4 kg of U

(a) For the purposes of this discussion, it is assumed that the U will be disposed of in grout. Other options for the disposition of U are 1) disposal in glass, and 2) further purification and storage for future use. Further studies are needed to determine the best option for the disposition of U.

(according to data provided by WHC), and HWVP feed specifications allow a maximum of 32 g U_3O_8 /100 g of nonvolatile oxide. With a waste loading of 25% in the HLW glass, the maximum wt% U allowable in the final glass waste form is 6.8%. Given this maximum percentage for U, and a mass of 1650 kg of glass per canister, 210 canisters of glass would be required to dispose of the U. Thus, to meet the third objective, 55% of the U must be separated from the TRUs and routed to the LLW stream. To ensure the treatment process is applicable to wastes containing higher concentrations of U (such as those in certain SSTs), a more stringent target was adopted to route 95% of the U to the LLW.

Engineers at WHC have defined a baseline pretreatment process that would result in the production of 150 canisters of glass.^(a) This baseline case assumed one dissolution step, which alone would not completely dissolve the sludge. The TRU-contaminated undissolved solids would be included in the HLW stream to be vitrified. Earlier, the pretreatment process was constrained to one dissolver by the proposed use of B Plant as the pretreatment facility. This constraint has since been lifted because a new facility will likely replace B Plant. This new facility can be designed to include a secondary dissolver; limited test results suggest that virtually complete dissolution of the NCRW sludge can be achieved with a secondary dissolution step (see Section 3). Aggressive sludge dissolution coupled with an effective TRU separation process would result in less than 150 glass canisters needed for TRU disposal; therefore, 100 canisters is a reasonable target for process development.

6.2 Sludge Washing and Dissolution

The sludge washing and dissolution portions of the flowsheet are illustrated in Figure 6.1. The sludge is washed four times with 3 volumes of 0.1 M NaOH at ambient temperature.^(b) Efficient solid/liquid separation is assumed to be achieved after each wash, so that the interstitial liquid occupies 30% of the washed sludge volume. The wash solution will contain approximately 98% of the ^{137}Cs from NCRW sludge (Lumetta and Swanson 1993a), but the amount of this radioisotope is expected to be low enough that the wash solution can be handled as LLW.

The washed sludge is dissolved in two steps. In the primary dissolution step, water is added to yield a final volume of primary dissolved sludge solution 5 times greater than the volume of the sludge being processed. Then, 10 M HF (0.23 L/L of sludge) is added to reach a F/(Zr+Al) ratio of 2,

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- (a) This baseline assumed that most of the U was routed to the LLW stream. However, the early CMPO TRU extraction flowsheets, such as that shown in Figure 2.1, would not achieve this goal because HEDPA strips U along with the TRUs (see Section 5).
 - (b) For the purpose of this discussion, the sludge wash step will be performed at ambient temperature, because experimental data are available on sludge washing at $\sim 25^\circ C$. However, washing with 0.1 M NaOH at elevated temperature could be beneficial because increased dissolution of Al in the wash step might be achieved. Increased Al dissolution would likely result in better dissolution efficiency in the primary dissolver, since a large fraction of the solids that do not dissolve in the first dissolution step contain Al (see Tables 3.2 and 6.1).

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Figure 6.1. Sludge Washing and Dissolution Portion of the NCRW Pretreatment Flowsheet

assuming all fluoride ion is removed from the sludge in the wash step. Finally, 12 M HNO₃ is added to form a solution that is 2 M HNO₃; 1.04 L of 12 M HNO₃ is needed for every liter of sludge. This amount assumes that 30% of the washed sludge volume is occupied by the 0.1 M NaOH wash solution, that each mole of Zr will consume 2 moles of H⁺, and that Al, Cr, and Fe will each consume 3 moles of acid/mole of metal. After several hours at ambient temperature, a solid/liquid separation is performed (not shown in Figure 6.1), and the solids are subjected to a secondary dissolution step.

In the secondary dissolution step, the sludge is treated at 100°C with a small volume (0.09 L/L of sludge processed) of a solution consisting of 2 M HNO₃ and 1 M HF. According to laboratory results to date, this treatment should result in complete dissolution of the remaining NCRW solids. Any undissolved solids will be routed to the vitrification facility. The quantity of undissolved solids is assumed negligible for the following discussion, and these solids will not contribute greatly to the volume of HLW glass produced for TRU disposal.

The mass balance for the major sludge components in the wash and dissolution steps is summarized in Table 6.1. The percentages of the sludge components dissolved in each step were derived from the experimental data presented in Table 3.2. The average composition of the NCRW sludge shown in the table was provided by WHC. The HNO₃ and HF additions shown in Figure 6.1 are based on this average composition. These values will vary depending on the actual composition of the particular batch of NCRW sludge undergoing pretreatment.^(a)

6.3 TBP Extraction of Uranium

The solutions from the primary and secondary dissolution steps are combined, and HF is added to adjust the F/(Zr+Al) ratio to 5. This feed adjustment prevents formation of interfacial crud; crud formation was observed at low F/(Zr+Al) ratios in the CMPO extraction stages (see Section 4) and might also be a problem under similar conditions in the TBP extraction stages. Next, ascorbic acid is added to adjust the Pu valence to +3, so that Pu is not extracted in the TBP cycle. This Pu valence adjustment is critical to the success of the flowsheet. After the solution is stored for ≥ 1 h, it is clarified by filtration and then sent through the TBP extraction cycle (see Figure 6.2). Any filtered solids are routed to the primary dissolver to be redissolved.

The TBP extraction cycle consists of three extraction stages, three scrub stages (0.2 M HNO₃), and two strip stages (0.25 M Na₂CO₃) with flow rates as indicated in Figure 6.2. Based on the data

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- (a) Because of the large volume of NCRW sludge present in Tanks 103-AW and 105-AW, it is unlikely that the entire inventory of NCRW sludge will be homogeneously mixed for feed to the pretreatment process. Rather, the sludge will be retrieved in layers. Each batch of NCRW sludge processed will consist of one or more of these layers. Because the composition of the sludge varies from layer to layer in the tanks, the composition of one batch will be different from other batches.

Table 6.1. Mass Balance of the Major NCRW Sludge Components for the Pretreatment Flowsheet (see Figure 6.1 and 6.2)

Source	Major Components										
	Al	Cr	Fe	La	Na ^(a)	U	Zr	Pu	Am		
Average Composition, g/L sludge	4.6	1.24	0.86	0.59	161	7	89	0.0094	0.000052		
Total kg in NCRW ^(b)	1.53E+04	4.13E+03	2.86E+03	1.96E+03	5.36E+05	2.33E+04	2.96E+05	3.13E+01	1.73E-01		
Wash Solution, % ^(c)	15	45	0	0	95	10	0	0	0		
Wash Solution, kg	2.30E+03	1.86E+03	0.00E+00	0.00E+00	5.09E+05	2.33E+03	0.00E+00	0.00E+00	0.00E+00		
1st Dissolver, %	25	45	75	95	5	85	80	(d)	(d)		
1st Dissolver, kg	3.83E+03	1.86E+03	2.15E+03	1.87E+03	2.68E+04	1.98E+04	2.37E+05	(d)	(d)		
2nd Dissolver, %	60	10	25	5	0	5	20	(d)	(d)		
2nd Dissolver, kg	9.19E+03	4.13E+02	7.16E+02	9.82E+01	0.00E+00	1.17E+03	5.93E+04	(d)	(d)		
TBP Strip, % ^(c)	0	0	0	0	0	85.5	0	0	0		
TBP Strip, kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.99E+04	0.00E+00	0.00E+00	0.00E+00		
CMPO Raffinate, % ^(c)	85	55	100	0	5	0	100	0.05	0.05		
CMPO Raffinate, kg	1.30E+04	2.27E+03	2.86E+03	0.00E+00	2.68E+04	0.00E+00	2.96E+05	1.57E-02	8.66E-05		
CMPO Strip, % ^(c)	0	0	0	100	0	4.5	0	99.95	99.95		
CMPO Strip, kg	0.00E+00	0.00E+00	0.00E+00	1.96E+03	0.00E+00	1.05E+03	0.00E+00	3.13E+01	1.73E-01		

(a) Includes Na added during the sludge wash procedure.

(b) Based on a total volume of 3.33E+06 L of NCRW sludge.

(c) The volumes of the various waste streams resulting from this process are as follows: 4 x 10⁷ L of wash solution, 3.5 x 10⁷ L of CMPO raffinate, 2.4 x 10⁷ L of CMPO strip solution, and 2.4 x 10⁶ L of 0.25 M Na₂CO₃. These volumes are based on 3.3 x 10⁶ L of NCRW sludge processed, and evaporation of the solutions is not taken into account.

(d) Data unavailable for percentage of TRUs dissolved in each step.

STATUS: PPT

Figure 6.2. TBP and CMPO Cycles for Extraction of U and TRUs From Dissolved NCRW Sludge

presented in HAPO (1955), this cycle should extract >95% of the U from the dissolved sludge solution, while leaving 100% of the Am and Pu.^(a) Improved U extraction could be achieved with additional extraction stages. For the purpose of this discussion, 95% U extraction from the dissolved sludge is conservatively estimated in the mass balance calculations. The mass balance for the major sludge components during the TBP cycle is given in Table 6.1. The U is stripped from the TBP solvent with Na_2CO_3 , which also serves to wash the solvent. The U is routed to the LLW stream, while the raffinate is routed to the CMPO extraction cycle.

6.4 CMPO Extraction of TRUs

The CMPO extraction cycle consists of extraction, scrubbing, stripping, and solvent washing operations. The extraction and scrubbing operations involve three extraction stages, two scrub stages using $0.04 \text{ M H}_2\text{C}_2\text{O}_4 + 1.2 \text{ M HNO}_3$ (to scrub out Zr), four scrub stages using 1.7 M HNO_3 (to scrub out $\text{H}_2\text{C}_2\text{O}_4$), and three scrub stages using 0.01 M HNO_3 (to lower the HNO_3 content). The stripping and solvent washing operations involve two strip stages using 0.01 M HNO_3 , four strip stages using $0.01 \text{ M H}_2\text{C}_2\text{O}_4$, and two solvent wash stages using $0.25 \text{ M Na}_2\text{CO}_3$. The relative flow rates for each stream are shown in Figure 6.2. Regarding the two strip steps (using HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$, respectively), the dilute HNO_3 strip removes the trivalent actinides and lanthanides from the CMPO solvent, while the dilute $\text{H}_2\text{C}_2\text{O}_4$ strip removes any Pu(IV) that might be present. In this step, the $\text{H}_2\text{C}_2\text{O}_4$ was chosen rather than HEDPA (Section 5) to avoid adding P to the HLW stream.^(b) The use of $\text{H}_2\text{C}_2\text{O}_4$ to strip Pu(IV) from the CMPO solvent had been suggested by Argonne National Laboratory (Horwitz et al. 1985), and the GTM indicates that this approach is viable (see Section 6.5). With the high concentration of La in the NCRW sludge, lanthanum oxalate may potentially precipitate in the strip stages (i.e., stage 13). If this were the case, the aqueous phase from stage 15 could be collected as an effluent rather than be fed into stage 14 or the $0.01 \text{ M H}_2\text{C}_2\text{O}_4$ solution can be replaced with 0.001 M HEDPA .^(b) Note that evaporation of the CMPO strip stream will result in the concentration of Pu into a relatively small volume. Thus, the issue of criticality safety must be addressed in the design and implementation of this process.

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- (a) Under the conditions described here, the TBP extraction cycle would partially remove Th from tank wastes high in this actinide element. However, the Th extraction could be improved by performing the TBP extraction at higher HNO_3 concentrations. Th is not an issue in processing NCRW sludge.
 - (b) Note that a 0.001 M HEDPA solution could be used as the second stripping solution without causing production of additional HLW glass canisters. This would reduce the potential for oxalate precipitation in the stripping stages.

Table 6.3. Results of the GTM Calculation for Stage 1, Final Extraction and for Stage 13, Final Strip of the CMPO Cycle of the Flowsheet Depicted in Figure 6.2

Components	GTM Calculation Results					
	Aqueous, <u>M</u>		Organic, <u>M</u>		Distribution Coefficient ^(a)	
	Stage 1	Stage 13	Stage 1	Stage 13	Stage 1	Stage 13
La	5.85E-07	4.46E-04	1.62E-05	1.77E-05	2.77E+01	3.97E-02
Na	3.05E-02	1.62E-24	3.05E-05	1.62E-27	1.00E-03	1.00E-03
U	1.47E-09	1.43E-04	3.26E-07	1.20E-04	2.21E+02	8.37E-01
Zr	9.16E-02	4.86E-24	9.16E-05	4.86E-27	1.00E-03	1.00E-03
Pu(IV)	8.30E-09	7.72E-08	4.70E-08	3.46E-10	5.67E+00	4.48E-03
Pu(III)	2.77E-10	8.03E-07	1.28E-08	5.32E-08	4.62E+01	6.62E-02
Am	3.07E-10	8.92E-07	1.42E-08	5.91E-08	4.62E+01	6.62E-02

(a) Distribution coefficient is the organic phase concentration divided by the aqueous phase concentration.

6.5 Modeling of CMPO Cycle With the Generic TRUEX Model

The CMPO cycle of the flowsheet has been modeled using the GTM (Vandegrift et al. 1990). The input parameters for the model are given in Table 6.2, and the results are presented in Tables 6.3 and 6.4 and Figures 6.3 and 6.4. The model indicates that the trivalent actinides^(a) and lanthanides are extracted to very low levels, with a DF of 3250. The DF for Pu(IV) was predicted to be only 12, but based on the results of the DBE (see Section 2) a greater DF (~900) for Pu(IV) would be expected. Furthermore, the Pu valence going into the process is +3 due to reduction by ascorbic acid; some oxidation to Pu(IV) will likely occur in the scrub stages, but this would not affect extraction performance. For mass balance calculations, the DF for Pu was assumed to be the same as that for Am. The model indicates that the actinides and lanthanides will remain in the organic phase during the scrub steps and will be quantitatively stripped from the CMPO solvent at stage 13 (see Tables 6.3 and 6.4 and Figures 6.3 and 6.4).

Based on the GTM results, the number of glass canisters required to dispose of the TRU portion of the NCRW sludge can be estimated from the mass balance values in Table 6.1. Due to the rigorous dissolution of the NCRW sludge and the high selectivity of the CMPO extraction process for the actinides and lanthanides, the only metals in the HLW stream (i.e., the CMPO strip solution) are La, U,

(a) The model predicts that the behavior of Am(III) and Pu(III) are identical.

Table 6.4. Distribution Coefficients Calculated by the GTM for Each Stage of the CMPO Cycle of the Flowsheet Depicted in Figure 6.2

Stage	Function	Distribution Coefficients									
		Al	Cr	Fe	La	Na	U	Zr	Pu(IV)	Pu(III)	Am
1	Extraction	0.001	0.001	7.70E-03	2.77E+01	0.001	2.21E+02	0.001	5.67E+00	4.62E+01	4.62E+01
2	Extraction	0.001	0.001	6.76E-03	3.04E+01	0.001	2.38E+02	0.001	5.82E+00	5.07E+01	5.07E+01
3	Extraction	0.001	0.001	4.07E-03	2.95E+01	0.001	2.26E+02	0.001	5.43E+00	4.91E+01	4.91E+01
4	Scrub 1	0.001	0.001	1.64E-03	2.30E+01	0.001	1.52E+02	0.001	4.68E+00	3.84E+01	3.84E+01
5	Scrub 1	0.001	0.001	1.60E-03	2.02E+01	0.001	1.54E+02	0.001	6.13E+00	3.36E+01	3.36E+01
6	Scrub 2	0.001	0.001	2.12E-03	2.15E+01	0.001	3.99E+02	0.001	1.88E+01	3.58E+01	3.58E+01
7	Scrub 2	0.001	0.001	4.70E-03	2.06E+01	0.001	6.43E+02	0.001	3.25E+01	3.44E+01	3.44E+01
8	Scrub 2	0.001	0.001	9.42E-04	1.99E+01	0.001	8.02E+02	0.001	4.86E+01	3.31E+01	3.31E+01
9	Scrub 2	0.001	0.001	9.42E-04	1.92E+01	0.001	9.06E+02	0.001	7.43E+01	3.21E+01	3.21E+01
10	Scrub 3	0.001	0.001	9.41E-04	1.65E+01	0.001	3.54E+02	0.001	1.48E+01	2.75E+01	2.75E+01
11	Scrub 3	0.001	0.001	9.35E-04	1.04E+01	0.001	1.66E+02	0.001	4.57E+00	1.73E+01	1.73E+01
12	Scrub 3	0.001	0.001	9.44E-04	3.29E+00	0.001	5.00E+01	0.001	1.35E+00	5.49E+00	5.49E+00
13	Strip 1	0.001	0.001	0.001	3.97E-02	0.001	8.37E-01	0.001	4.48E-03	6.62E-02	6.62E-02
14	Strip 1	0.001	0.001	0.001	0.001	0.001	6.32E-02	0.001	0.001	1.62E-03	1.62E-03
15	Strip 2	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
16	Strip 2	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
17	Strip 2	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
18	Strip 2	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
19	Wash	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
20	Wash	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

Figure 6.3. Concentration Profile for Am in the CMPO Cycle as Predicted by the Generic TRUEX Model

Figure 6.4. Concentration Profile for Pu(IV) in the CMPO Cycle as Predicted by the Generic TRUEX Model

Table 6.5. Components of the HLW Stream and the Number of Borosilicate Glass Canisters Required for Disposal

	Components					
	F	La	Na ^(a)	U	TOC	Am, Pu
Maximum Wt% ^(b)	1.7	1.7	3.8	6.8	2.8	1
Weight in HLW, kg	1.5×10^3	2×10^3	2.2×10^4	1×10^3	2.6×10^2	3.2×10^1
Number of Canisters ^(c)	55	70	350	9	6	2

- (a) Na present only if the HLW stream is neutralized. The GTM predicts that the $[H^+]$ in the CMPO strip solution will be 0.04 M. The quantity of Na listed is based on the neutralization of this amount of acid.
- (b) Allowable addition to waste feed, assuming 25 % waste oxide loading in glass.
- (c) Based on 1650 kg glass/canister.

Am, and Pu. If the HLW stream is neutralized with caustic before vitrification, Na will also be present. Table 6.5 lists the quantities of the HLW stream components and the volume of glass produced by vitrifying these components. Clearly, if the HLW stream is neutralized before vitrification, the amount of Na added would dictate the number of glass canisters produced (350). The 350 canisters that would be produced far exceeds the objective of less than 100 canisters. Thus, it would be preferable to store the HLW stream as an acidic solution before vitrification, rather than to neutralize it.^(a) If the HLW stream is not neutralized, La would dictate the volume of glass needed. The resulting 70 glass canisters would meet the objective of less than 100 canisters required to dispose of the TRU portion of the NCRW sludge.

The concentration of TRU elements in the LLW grout stream may be determined from the quantity of TRU material in the CMPO raffinate and from the size of the LLW grout stream. The 8.66×10^{-5} kg of Am and 1.57×10^{-2} kg of Pu in the raffinate from the CMPO cycle are equivalent to 1.3×10^9 nCi of TRU.^(b) An estimation of the size of the LLW grout stream is based on two assumptions: 1) the grout quantity is limited by Na at a concentration of 3.6 M, and 2) the grout density is 1.7 g/mL. If the CMPO raffinate is neutralized for disposal without further treatment, the resulting LLW grout quantity would then be $\sim 3.5 \times 10^7$ kg, and the TRU concentration would be ~ 0.04 nCi TRU/g grout. If the raffinate is treated to remove a portion of its HNO_3 (e.g., by partial denitration) the required grout quantity would be lowered by some factor, and the TRU concentration would be increased by the

- (a) If the HLW stream is neutralized for interim storage before vitrification, it is likely that most of the Na added during neutralization could be washed from the precipitated TRUs and La. Thus, the 350 canisters indicated for Na in Table 6.5 should be viewed as a worst-case scenario.
- (b) The Pu was assumed to be ^{239}Pu for this calculation.

same factor. This factor has not been defined, but it is probably no greater than 10. In either case, the TRU concentration in the LLW form is well below the 100 nCi/g objective indicated in Section 6.1.

Based on the GTM, then, the flowsheet illustrated in Figures 6.1 and 6.2 should easily meet the objectives outlined in Section 6.1. That is, >99% of the nonradioactive sludge material and $\geq 95\%$ of the U will be routed to the LLW stream, and the resulting LLW form will contain less than 100 nCi/g TRU. Vitrification of the HLW stream will result in the production of less than 100 glass canisters.

6.6 Process Disadvantages and Alternatives

There are two primary disadvantages in using the NCRW pretreatment flowsheet (Figures 6.1 and 6.2). First, the flowsheet requires two solvent systems. The use of two systems is not deemed a problem, because the two solvents are compatible. Entrained TBP solvent that might be carried into the CMPO stages should not cause any performance problems in the CMPO extraction because the CMPO solvent already contains TBP. However, care should be taken to ensure the CMPO solvent will not be carried into the TBP extraction cycle, or the TRU extraction in that cycle could become excessive. The addition of the TBP cycle (as compared to the original CMPO extraction flowsheet, Figure 2.1) will increase the cost of implementing the pretreatment process, but this will likely be a small cost increase when compared to the overall pretreatment effort.

The second disadvantage is the relatively high volume of the TRU strip stream. This high volume is necessary to strike a balance between an acid content high enough in the final scrub stage to retain the TRUs in the organic phase and an acid content low enough to strip TRUs in the first strip stage. Although the volume of the strip stream is high, the volume of the HLW fraction can be easily reduced by evaporation. Furthermore, denitrating this solution with formic acid or sugar would allow further reduction of the volume of the HLW fraction.

An alternative TRU separation flowsheet is shown in Figure 6.5. In this flowsheet, the TBP extraction cycle has been eliminated, therefore, separation of U from the TRUs must be achieved in the strip stages. Two types of stripping solutions are shown: 1) dilute HNO_3 with a reducing agent (Fe^{2+} or ascorbic acid) and 2) dilute HNO_3 with HF.

Stripping the CMPO solvent under reducing conditions was discussed in Section 5. Under these conditions, the Pu(IV) would be reduced to Pu(III), which would then distribute to the aqueous phase. In theory, this method should work, but there are some questions regarding kinetics of the Pu reduction. Experimental results using FS as a stripping agent (see Section 5) suggest that a relatively long residence time in the stripping stages might be required. Furthermore, the ability of this flowsheet to satisfy the U split objective is questionable. Again, in the experiment using FS as a stripping agent, 12% of the U in the waste was found in the aqueous phases from the stripping contacts. This could be improved by including an organic scrub stream following the stripping stages, but it might be difficult to achieve separation of 95% of the U from the TRUs.

Figure 6.5. Alternative Flowsheet for the Extraction of U and TRUs From Dissolved NCRW Sludge

Stripping with dilute HNO_3 and HF should also remove the Am and Pu from the CMPO solvent (Horwitz et al. 1985). However, the goal of less than 100 glass canisters would be compromised by using HF unless additional process steps were added. If 0.01 M HF is used to strip the TRUs as indicated in Figure 6.5, the amount of F added ($\sim 3.9 \times 10^3$ kg) to the HLW stream would cause production of 140 canisters of glass, which does not meet the objectives outlined in Section 6.1. The number of canisters could be decreased by adding a process such as ion exchange or precipitation to separate the TRUs from the F. Depending on the economics of HLW disposal, the extra 40 canisters resulting from the use of HF might be tolerable.

Recent system analysis studies at WHC have assumed a CMPO process flowsheet in which the complexant tetrahydrofuran tetracarboxylic acid (THFTCA) is used to strip TRUs and lanthanides from the solvent, while stripping only a small (2%) portion of the U. The strip solution composition is 0.1 M THFTCA/0.01 M ascorbic acid/0.11 M HNO_3 . The stripped product solution is then concentrated to 6 M total nitrate before it is neutralized with NaOH for interim storage. The supernates are decanted during interim storage to remove much of the added Na. Such an approach appears to have merit. Workers at Argonne National Laboratory have indicated their preliminary results with THFTCA are encouraging, but tests conducted at PNL with this compound did not yield encouraging stripping results. The reason for this discrepancy is unknown, but it may be due to variations in the quality of the THFTCA.

7.0 Conclusion

The flowsheet described in Figures 6.1 and 6.2 is proposed for the NCRW pretreatment process. The flowsheet illustrates the pretreatment process, which includes sludge washing, primary and secondary sludge dissolution, feed adjustment and storage, and the CMPO and TBP extraction cycles. Although the flowsheet is not optimized, it should meet the following objectives (discussed in Section 6.1):

- separate the TRU components from the waste so that the bulk of the nonradioactive components may be disposed of as LLW
- route $\geq 95\%$ of the U to the LLW stream (or elsewhere for disposition)
- produce less than 100 canisters of glass for disposal of the TRU portion of the NCRW sludge.

A design basis experiment using actual NCRW sludge will be conducted in FY 1993 to test the proposed flowsheet.

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