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**Pretreatment of Neutralized Cladding
Removal Waste Sludge: Results of
the Second Design Basis Experiment**

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Summary

An experiment was performed by Pacific Northwest Laboratory to test a solvent extraction flow-sheet for pretreating Hanford neutralized cladding removal waste (NCRW) sludge. A sample of actual NCRW sludge was used in this experiment. The sludge was washed with 0.1 M NaOH and then was dissolved under acidic conditions. The dissolved sludge solution was subjected to a series of batch solvent extraction contacts, first using tributyl phosphate (TBP) to separate U, then using octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) to separate the transuranic (TRU) elements from the bulk sludge components. The TBP and CMPO extracts were then scrubbed and stripped.

The results of this test follow:

- The combination of sludge washing and acid dissolution dissolved 96 wt% of the NCRW sludge, including 98% of the Zr.
- Approximately 98% of the U was separated from the TRU portion of the waste, and thus could be handled as low-level waste (LLW) if this pretreatment option is used.
- Greater than 99% of the TRUs was extracted by CMPO, and the TRUs were easily stripped from the CMPO solvent using dilute HNO_3 and dilute $\text{H}_2\text{C}_2\text{O}_4$.
- The trivalent lanthanides (La, Nd, and Eu) were extracted along with the TRUs, and they would remain in the high-level waste (HLW) stream.
- Other sludge components (e.g., Na, Zr, Cr, etc.) were not extracted, and would be routed to the LLW stream.
- The proposed flowsheet would result in the production of ~500 canisters (1,650 kg each) of HLW glass, compared to an estimated 2,400 canisters if only sludge washing was performed.

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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 was conducted at the request of Westinghouse Hanford Company (WHC), and the results have been published (Swanson 1991a, 1991b, 1991c; Lumetta and Swanson 1993a, 1993b). A design basis experiment (DBE1) was performed in FY 1991 to test the NCRW pretreatment flowsheet as it was envisioned at that time (Swanson 1991c). Subsequent to DBE1, the NCRW pretreatment flowsheet was modified as described by Lumetta and Swanson (1993a). A second design basis experiment (DBE2) was performed to test the modified NCRW pretreatment flowsheet. The results of the DBE2 are presented in this report.

In the past, Zircaloy-clad metallic 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 insoluble Zr hydroxides and/or oxides and NaF. Significant quantities of Al, La, U, as well as other insoluble minor constituents are present in the sludge, along with sodium and potassium nitrates, nitrites, and hydroxides in the interstitial liquid. The sludge contains about 2,000 nCi of transuranic (TRU) material per gram of dry sludge, and mixed fission products. Therefore, the sludge must be handled as high-level waste (HLW).

The NCRW sludge must be pretreated before treatment (e.g., vitrification) and disposal, so that the overall cost of disposal can be minimized. The NCRW pretreatment flowsheet tested in DBE2 is illustrated in Figures 1.1 and 1.2. The flowsheet was designed to achieve the following objectives:

- to separate Am and Pu from the major sludge constituents (Na, Zr)
- to separate Am and Pu from U
- to concentrate Am and Pu in a small volume for immobilization in borosilicate glass, based on Hanford Waste Vitrification Plant (HWVP).

The flowsheet involves: 1) sludge washing, 2) sludge dissolution, 3) extraction of U with tributyl phosphate (TBP), and 4) extraction of TRUs with octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO).

As presented in the flowsheet, the NCRW sludge is first washed with 0.1 M NaOH to remove interstitial liquid and soluble salts from the sludge including sodium and potassium fluorides, carbonates, hydroxides, nitrates, and nitrites. The washed sludge is then subjected to two dissolution steps to achieve near complete dissolution of Zr.

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Figure 1.1. Sludge Dissolution and Feed Adjustment Flowsheet for Pretreating Neutralized Cladding Removal Waste Sludge

DSEI-3.PPT

Figure 1.2. Solvent Extraction Flowsheet for Pretreating NCRW Sludge

Ascorbic acid and HF are then added to the dissolved sludge solution. The ascorbic acid is added to adjust the Pu valence to Pu(III) so that this transuranic element is not extracted by TBP. The HF addition prevents formation of interfacial crud in the CMPO extraction stages (Lumetta and Swanson 1993a). After storing the adjusted dissolved sludge solution for an hour or more (to ensure the reactions necessary to avoid crud formation are complete), the solution is filtered and fed to the solvent extraction process.

The solvent extraction portion of the flowsheet involves two extraction cycles (Figure 1.2). In the first cycle, U is extracted with TBP. The TBP extract is scrubbed with 0.2 M HNO_3 , then the U is stripped from the TBP solvent with 0.25 M Na_2CO_3 (which also serves as a solvent wash), and the TBP solvent is recycled to the extraction section. For the second extraction cycle, the raffinate from the TBP extraction section serves as feed to the CMPO extraction cycle, where the TRUs are separated from the bulk sludge components (e.g., Zr and Na). The CMPO extract is subjected to three different scrub streams. The functions of these scrub streams are to 1) remove extracted Zr and F with oxalic acid, 2) remove extracted oxalic acid with HNO_3 , and 3) remove excess HNO_3 with a dilute solution of HNO_3 . The trivalent actinides (and lanthanides) are stripped from the scrubbed CMPO extract with 0.01 M HNO_3 containing a low concentration of $\text{H}_2\text{C}_2\text{O}_4$. Any Pu(IV) present in the CMPO extract is stripped with 0.01 M $\text{H}_2\text{C}_2\text{O}_4$. Finally, the stripped CMPO solvent is washed with 0.25 M Na_2CO_3 and recycled to the extraction section. The raffinate from the CMPO extraction section contains the Zr, Na, F, and other nonradioactive sludge components and can be handled as LLW.^(a) The CMPO stripping solution contains the TRUs and trivalent lanthanides, so this solution must be handled as HLW.

(a) Strontium-90 and ^{137}Cs separation might be necessary to handle the LLW stream in the recently proposed lightly shielded LLW vitrification facility.

2.0 Experimental

2.1 Methods and Materials

The composite NCRW sludge sample (NCRW-78) used in this experiment was prepared from portions of the five sludge segments obtained in the 1990 core sampling of Tank 105-AW. The segments had dried during the storage period preceding this work. The quantity of each segment used to make up NCRW-78 is given in Table 2.1. The total weight of the composite sample was 15.07 g.

The volumes of the various process solutions indicated in Figure 1.1 are based on 1 L of wet sludge settled in-tank. To determine the proper volumes of wash and dissolution solutions needed in this experiment, it was necessary to convert sample NCRW-78 into a wet form. Conversion was accomplished by adding 15.055 g of water to the sludge, mixing thoroughly, then centrifuging for 15 min. The volume of the centrifuged sludge was 10.9 mL, which was assumed to be the volume of in-tank settled sludge; the density of this sludge was approximately 1.5 g/mL. Based on the total amount of Zr found in the wash liquor and dissolved sludge solutions, the centrifuged sludge contained ~ 1.4 M Zr.

After the supernatant liquid was decanted, the sludge was washed four successive times with 33-mL volumes of 0.1 M NaOH. For each wash step, the sludge and 0.1 M NaOH mixture was stirred at 100°C for 30 min, then allowed to cool to room temperature. The mixture was centrifuged for 5 min, and the wash liquor was decanted. The four wash liquors were combined and filtered^(a) before analysis. The total volume of the wash liquor was 131 mL.

Table 2.1. Description of the Composite Sludge Sample Used in the Second NCRW Design Basis Experiment

<u>Segment^(a)</u>	<u>Weight Used, g</u>
3	3.02
4	3.01
5	3.02
6	3.00
7	3.02

(a) Segment taken from the 1990 core sampling of Tank 105-AW. Segments 1 and 2 were tank supernatant liquid; these were not included in the composite.

(a) The solids filtered from the wash liquor were transferred back to the vessel containing the washed sludge for dissolution.

In the first of two dissolution steps, the following were added to the washed sludge: 1) 11.34 mL of 12.3 M HNO_3 , 2) 2.51 mL of 10.2 M HF, and 3) 17.5 mL of water. The volumes of these reagents were based on the original centrifuged sludge volume of 10.9 mL and the volumes indicated in Figure 1.1 for 1 L of sludge. The added solution consisted of ~ 31 mL of ~ 4.5 M HNO_3 and ~ 0.8 M HF. A procedural difficulty was remedied by removing $\sim 20\%$ of the dissolving solution so that the reaction tube could be capped. The quantity of removed dissolving solution was added back to the primary dissolver solution after it was filtered (*vide infra*). The remaining solution was mixed with the sludge by stirring for 2 h at room temperature.

After centrifuging was conducted for 5 min, the supernatant solution was very cloudy. The mixture was centrifuged for an additional 30 min, which resulted in a clearer, yet still cloudy solution. This solution was decanted from the undissolved solids and filtered through a $0.45\text{-}\mu\text{m}$ membrane filter. The filtration step did not proceed smoothly. The membrane filter unit clogged and had to be changed repeatedly to filter all the solution. The filtered solution, which will be referred to as the primary dissolver (PD) solution, had a total volume of 44 mL (after addition of the 20% of the dissolver solution removed earlier). The PD solution contained 0.26 M Zr, 0.39 M F, and 2.34 M HNO_3 . The filtered solids were transferred to the 50-mL centrifuge tube containing the rest of the undissolved solids, so that the second dissolution step could be performed.

For the second dissolution step, the remaining solids were slurried in 6.1 mL of a solution consisting of 1.6 M HNO_3 and 1.8 M HF. Again, the volumes of these reagents were based on the original centrifuged sludge volume of 10.9 mL and the volumes indicated in Figure 1.1 for 1 L of sludge. This secondary dissolver mixture was stirred at 100°C for 1 h. After cooling, the mixture was centrifuged for 5 min, yielding a clear solution and a solid residue. The solution was decanted and filtered through a $0.45\text{-}\mu\text{m}$ membrane filter. This solution, which will be referred to as the secondary dissolver (SD) solution, had a total volume of 5.9 mL. The SD solution contained 0.29 M Zr, 1.2 M F, and 2.06 M HNO_3 .

The undissolved residue was washed with four 5-mL portions of water, then dried to a constant weight by heating at 80°C . The weight of the undissolved residue was 0.631 g, representing 4.2% of the starting sludge weight.

A precipitate formed in the PD solution after standing at room temperature for 2 days. However, this precipitate redissolved when HF was added to adjust the solution before the solvent extractions steps (*vide infra*). The PD and SD solutions were combined and allowed to stand for 4 days at room temperature. The combined dissolved sludge solution was then adjusted before the solvent extraction steps. Hydrofluoric acid was added to increase the $\text{F}/(\text{Zr} + \text{Al})$ ratio to ~ 3.8 , and ascorbic acid was added to a concentration of 0.01 M. Adjustment resulted in a clear solution that was allowed to stand at room temperature for 65 min. The solution was then filtered through a $0.45\text{-}\mu\text{m}$ membrane filter before the solvent extraction tests were begun. The filtered solution contained ~ 0.25 M Zr, ~ 1.1 M F, and ~ 2.4 M HNO_3 .

The following general procedure was followed to perform the solvent extraction contacts. The aqueous and organic phases were placed in an appropriately sized vial. The total height of the mixture was measured to determine the dispersion number. The two phases were mixed by shaking for 30 s. The phases were allowed to separate, and the time required for the two phases to separate was measured. The dispersion number was calculated using the following equation (Leonard et al. 1981):

$$N_{DI} = \frac{1}{t} \sqrt{\frac{h}{g}} \quad (2.1)$$

where t is the time required 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/s^2 . The mixture was then centrifuged to ensure complete separation of the two phases. Both phases were sampled as appropriate for inductively coupled plasma atomic emission spectroscopic (ICP), radiochemical, titrimetric, and fluoride analyses. In the case of the aqueous phase, aliquots were diluted in either 0.01 M HNO_3 (for ICP, radiochemical, and fluoride analyses) or in water (for titrimetric analysis). For the organic phase, aliquots were mixed with 0.01 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) to back-extract the elements and radionuclides of interest. The HEDPA solutions were analyzed. For the titrimetric analysis of the organic phase, an aliquot was dissolved in ethanol, and the resulting solution was potentiometrically titrated with standard aqueous NaOH.

The solvent extraction contacts that were performed are summarized in Table 2.2. For the initial solvent extraction contact, 36 mL of the adjusted feed solution was mixed with 4.4 mL of 0.2 M HNO_3 . The resulting solution represented a blend of the aqueous streams entering stage 3 of the solvent extraction process (Figure 1.2); the composition of this solution is given in Table 2.3. After withdrawing samples for analysis, the solution was contacted with 30% TBP at an organic-to-aqueous volume ratio of 0.2. The aqueous phase was subjected to two additional extractions with TBP, and the organic phase was subjected to scrub and strip steps as described in Table 2.2. Thirty milliliters of the aqueous phase from the last TBP extraction was mixed with 4.8 mL of $0.15 \text{ M H}_2\text{C}_2\text{O}_4$, 4.8 mL of 5.0 M HNO_3 , and 9.6 mL of 0.01 M HNO_3 . The resulting solution represented a blend of the aqueous streams entering stage 11 of the solvent extraction process; the composition of this solution is given in Table 2.3. After withdrawing samples for analysis, the solution was contacted with 14.2 mL of $0.2 \text{ M CMPO}/1.4 \text{ M TBP}$ in normal paraffin hydrocarbon (NPH). The aqueous phase was subjected to two additional extractions with $0.2 \text{ M CMPO}/1.4 \text{ M TBP}$, and the organic phase was subjected to scrub and strip steps as described in Table 2.2.

2.2 Analytical Methods

Nitric acid concentrations were determined by potentiometric titration with standard NaOH. For certain aqueous phase samples, there were multiple equivalent points. Because HNO_3 was assumed to be the strongest acid present in the solutions, the first equivalent point in each titration curve was used to calculate the HNO_3 concentration. Fluoride concentrations were potentiometrically determined using a fluoride-selective electrode (Swanson 1991c) or were determined by ion chromatography.

The following determinations were made: bulk metal ion concentrations by ICP, U by laser fluorimetry, gamma-emitting radionuclides by counting with a gamma spectrometer equipped with a GeLi detector, and alpha-emitting radionuclides by counting directly mounted samples with an alpha spectrometer equipped with a silicon surface barrier detector. The total alpha, $^{239+240}\text{Pu}$, and $^{238}\text{Pu} + ^{241}\text{Am}$ concentrations were determined from these alpha spectra. To obtain the ^{241}Am concentrations, the Pu was separated by extraction with thenoyltrifluoroacetone, and the separated Pu was counted. The ^{238}Pu concentrations were determined from the Pu alpha spectra, and the ^{241}Am concentrations were calculated by subtracting the ^{238}Pu concentrations from the $^{238}\text{Pu} + ^{241}\text{Am}$ concentrations. For the organic

Table 2.2. Solvent Extraction Contacts for Testing the Solvent Extraction Flowsheet (Figure 1.2)

Stage ^(a)	O/A ^(b)	Aqueous Phase	Organic Phase
3	0.20	See note ^(c)	8.0 mL 30% TBP
2	0.20	37.5 mL aq from stage 3	7.5 mL 30% TOP
1	0.20	35 mL aq from stage 2	7.0 mL 30% TOP
11	0.29	See note ^(d)	14.2 mL CMPO ^(e)
10	0.29	5.0 mL aq from stage 11	1.45 mL CMPO
9	0.29	2.5 mL aq from stage 10	0.725 mL CMPO
12	0.75	16 mL scrub solution 1 ^(f)	12 mL org from stage 11
13	0.75	14.7 mL scrub solution 1	11 mL org from stage 12
14	1.00	10 mL scrub solution 2 ^(g)	10 mL org from stage 13
15	1.00	9 mL scrub solution 2	9.0 mL org from stage 14
16	1.00	8 mL scrub solution 2	8.0 mL org from stage 15
17	1.00	7 mL scrub solution 2	7.0 mL org from stage 16
18	1.50	4 mL 0.01 M HNO ₃	6.0 mL org from stage 17
19	1.50	3.67 mL 0.01 M HNO ₃	5.5 mL org from stage 18
20	1.00	4.5 mL strip solution 1 ^(h)	4.5 mL org from stage 19
21	1.00	4.0 mL strip solution 1	4.0 mL org from stage 20
22	3.00	1.17 mL 0.01 M H ₂ C ₂ O ₄	3.5 mL org from stage 21
23	3.00	1.0 mL 0.01 M H ₂ C ₂ O ₄	3.0 mL org from stage 22
24	3.00	0.83 mL 0.01 M H ₂ C ₂ O ₄	2.5 mL org from stage 23
25	3.00	0.67 mL 0.01 M H ₂ C ₂ O ₄	2.0 mL org from stage 24
26	9.60	0.16 mL 0.25 M Na ₂ CO ₃	1.5 mL org from stage 25
See note ⁽ⁱ⁾	3.33	1.5 mL 0.2 M HEDPA	0.5 mL org from stage 26
4	2.00	3.0 mL 0.2 M HNO ₃	6.0 mL org from stage 3
5	2.00	2.5 mL 0.2 M HNO ₃	5.0 mL org from stage 4
6	2.00	2.0 mL 0.2 M HNO ₃	4.0 mL org from stage 5
7	3.33	0.9 mL 0.25 M Na ₂ CO ₃	3.0 mL org from stage 6
8	3.33	0.6 mL 0.25 M Na ₂ CO ₃	2.0 mL org from stage 7
See note ⁽ⁱ⁾	0.33	1.5 mL 0.2 M HEDPA	0.5 mL org from stage 8

(a) Refers to the stage numbers indicated in Figure 1.2.

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

(c) The aqueous phase for stage 3 consisted of 36 mL of adjusted feed solution plus 4.4 mL 0.2 M HNO₃.

(d) The aqueous phase for stage 11 consisted of 30 mL of the aqueous phase from contact stage 1 plus 4.8 mL 0.15 M H₂C₂O₄, plus 4.8 mL 5.0 M HNO₃, plus 9.6 mL 0.01 M HNO₃.

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

(f) Scrub solution 1 consisted of 0.04 M H₂C₂O₄ in 1.3 M HNO₃.

(g) Scrub solution 2 consisted of 1.67 M HNO₃.

(h) Strip solution 1 consisted of 0.0025 M H₂C₂O₄ in 0.0075 M HNO₃.

(i) Contacts with 0.2 M HEDPA were done to ensure complete recovery of metal ions for mass balance calculations.

Table 2.3. Compositions of the Initial Aqueous Phases for the First TBP (stage 3) and First CMPO (stage 11) Extractions

Component	Initial Aqueous Phase Concentration	
	Stage 3	Stage 11
HNO ₃ , <u>M</u>	2.20	1.70
F, <u>M</u>	0.96	0.62
Al, <u>M</u>	0.034	0.020
Na, <u>M</u>	0.19	0.11
U, <u>M</u>	0.014	0.00018
Zr, <u>M</u>	0.22	0.13
TRU, μ Ci/mL	0.60	0.35
^{239,240} Pu, μ Ci/mL	0.28	0.12
²⁴¹ Am, μ Ci/mL	0.28	0.22

phase samples, ²⁴¹Am concentrations could not be determined by this technique, because the HEDPA, which was used to back-extract metal ions and radionuclides from the CMPO solvent, interfered with the Pu separation. The organic phase ²⁴¹Am concentrations were obtained by a material balance calculation using the aqueous phase concentration and assuming all the Am was stripped from the solvent after stage 22. The ²⁴¹Am concentrations were also obtained from the gamma spectra, using the 59.5-keV gamma emission. The results from the gamma spectra agreed with those from the alpha spectra.

3.0 Results and Discussion

The results of the DBE2 are presented in this section. The results are presented in terms of 1) sludge washing and dissolution, 2) phase disengagement in the solvent extraction tests, 3) HNO_3 extraction, 4) U extraction, 5) TRU extraction, and 6) extraction of other NCRW sludge components. Finally, the impact of the pretreatment process on waste volumes is discussed.

3.1 Sludge Washing and Dissolution

The results of the sludge washing and dissolution steps are summarized in Tables 3.1 and 3.2. Approximately 96 wt% of the sludge was dissolved by sludge washing and acid dissolution; Na and Zr were the most abundant metallic elements in the NCRW sludge. After sludge washing, 89% of the Na was removed from the sludge. On the other hand, Zr was not removed from the sludge by washing with dilute NaOH. The first acid dissolution step dissolved ~73% of the Zr, and the second dissolution step dissolved an additional ~25%. Thus, only 2% of the Zr remained undissolved. The two acid dissolution steps dissolved almost all the remaining Na, leaving only 0.1% in the residue.

The supernate and wash solutions were non-TRU. If these two solutions were combined and concentrated to 5 M Na for LLW disposal, the resulting solution would contain $< 1.1 \times 10^{-3}$ μCi TRU/mL, 0.29 $\mu\text{Ci/mL}$ ^{90}Sr , and 0.22 $\mu\text{Ci/mL}$ ^{137}Cs .

Elements found in significant quantities in the undissolved residue included Si (0.058 g/g residue), Al (0.054 g/g residue), Fe (0.016 g/g residue), Cr (0.0094 g/g residue), and P (0.012 g/g residue). The undissolved residue also contained 2.05 μCi TRU/g, 43.6 μCi $^{90}\text{Sr/g}$, and 260 μCi $^{137}\text{Cs/g}$; this material would likely require handling as HLW. Vittrification of the undissolved solids will be discussed in Section 3.7. Uranium was not detected in the undissolved residue, indicating that this element can easily be dissolved for processing.

Filtration of the PD solution through a 0.45- μm filter was hampered by clogging of the filter. In most previous tests with NCRW sludge, filtration of the acid-dissolved sludge solutions proceeded smoothly. An exception to this occurred when a portion of segment 3 from the 1990 core sampling of Tank AW-105 was dissolved in HNO_3 media; solutions derived from that segment were observed to clog filters. A portion of that segment was included in the composite used in this test (Table 2.1) and may be responsible for the difficulty in filtering the PD solution. Filtering aids might be needed to prevent filter clogging under processing conditions.

3.2 Phase Disengagement

The success of a solvent extraction process depends on aqueous and organic phase separation after the phases have been mixed. Phase separation can be quantitatively expressed by the dispersion number (Leonard et al. 1981), which may be calculated using Equation (2.1). A viable solvent extraction process using centrifugal contractors can be designed for systems in which the dispersion number is

Table 3.1. Results of Sludge Washing and Acid Dissolution of NCRW Sludge

Components	g/g Sludge	Supernate, % ^(a)	Wash, %	PD, % ^(b)	SD, % ^(c)	Residue, %
Na	1.80E-01	17.6	71.6	9.0	1.7	0.1
Zr	9.44E-02	0.0	0.0	73.3	24.5	2.2
U	1.47E-02	0.0	0.2	89.5	10.3	0.0
Si	1.14E-02	14.1	28.3	35.2	1.2	21.2
Al	8.33E-03	0.2	8.9	29.9	33.9	27.1
Fe	5.07E-03	0.0	0.0	64.8	21.9	13.4
Cr	3.48E-03	11.1	20.6	30.8	26.1	11.3
P	$\geq 1.67\text{E-}03, \leq 1.70\text{E-}03$	$\geq 25.1, \leq 25.4$	$\geq 34.5, \leq 35.1$	$\geq 8.6, \leq 8.7$	≤ 1.5	$\geq 30.3, \leq 30.8$
Ca	$\geq 1.52\text{E-}03, \leq 1.63\text{E-}03$	$\geq 3.1, \leq 3.3$	≤ 4.0	$\geq 74.7, \leq 79.9$	$\geq 15.7, \leq 16.8$	≤ 2.6
Mn	$\geq 1.44\text{E-}03, \leq 1.46\text{E-}03$	≤ 0.1	≤ 0.9	$\geq 68.4, \leq 69.1$	$\geq 28.8, \leq 29.1$	1.8
La	$\geq 6.36\text{E-}04, \leq 7.12\text{E-}04$	≤ 0.9	≤ 9.2	$\geq 73.8, \leq 82.7$	$\geq 15.5, \leq 17.3$	≤ 0.6
Nd	$\geq 3.40\text{E-}04, \leq 4.18\text{E-}04$	≤ 1.5	≤ 15.7	$\geq 68.0, \leq 83.6$	$\geq 13.4, \leq 16.4$	≤ 1.5
Pb	$\geq 2.43\text{E-}04, \leq 3.43\text{E-}04$	≤ 2.2	≤ 23.0	$\geq 59.5, \leq 84.0$	$\geq 11.4, \leq 16.0$	≤ 3.8
Ni	$\geq 2.03\text{E-}04, \leq 3.22\text{E-}04$	$\geq 17.2, \leq 27.4$	$\geq 21.2, \leq 33.7$	$\geq 18.8, \leq 30.0$	$\geq 5.6, \leq 8.9$	≤ 3.7
Cu	$\geq 9.29\text{E-}05, \leq 9.56\text{E-}05$	$\geq 16.3, \leq 16.8$	$\geq 8.6, \leq 8.8$	$\geq 58.3, \leq 60.0$	$\geq 13.9, \leq 14.3$	≤ 2.8
Ba	$\geq 1.40\text{E-}05, \leq 3.26\text{E-}05$	≤ 3.9	≤ 40.2	$\geq 37.6, \leq 87.7$	$\geq 12.3, \leq 12.8$	≤ 5.4
Sr	$\geq 1.03\text{E-}05, \leq 2.77\text{E-}5$	≤ 4.6	≤ 47.4	$\geq 33.8, \leq 90.9$	$\geq 9.1, \leq 12.3$	≤ 1.8

(a) This refers to the supernatant liquid that was formed by adding water to the dry sludge, mixing, and centrifuging.

(b) PD refers to the primary dissolver solution.

(c) SD refers to the secondary dissolver solution.

Table 3.2. Behavior of the Radionuclides in the NCRW Sludge Washing and Acid Dissolution Steps

Component	$\mu\text{Ci/g}$ Sludge	Supernate, % ^(a)	Wash, %	PD, % ^(b)	SD, % ^(c)	Residue, %
Total Alpha	2.62E+00	0.0	0.0	82.9	13.8	3.3
²⁴³ + ²⁴⁴ Cm	4.12E-02	0.0	0.0	100.0	0.0	0.0
²³⁸ Pu ^(d)	1.03E-01	0.0	0.0	84.4	9.2	6.5
²³⁸ Pu + ²⁴¹ Am ^(e)	1.33E+00	0.0	0.0	88.6	10.0	1.3
²³⁹ + ²⁴⁰ Pu ^(e)	1.26E+00	0.0	0.0	75.8	18.7	5.5
²³⁹ + ²⁴⁰ Pu ^(d)	1.10E+00	0.0	0.0	78.7	15.0	6.2
²⁴¹ Am (alpha) ^(f)	1.22E+00	0.0	0.0	89.0	10.1	0.9
²⁴¹ Am (gamma) ^(g)	1.34E+00	0.4	0.0	83.8	10.8	5.1
¹⁴⁴ Ce	3.08E-01	0.0	0.0	82.5	17.5	0.0
⁶⁰ Co	2.39E-01	13.2	14.2	43.0	12.1	17.5
¹³⁴ Cs ^(h)	1.35E-01	38.1	45.8	0.0	16.1	0.0
¹³⁷ Cs ^(h)	5.72E+01	3.8	50.5	23.5	3.2	19.0
¹⁵⁴ Eu	1.42E+00	0.0	0.0	80.1	14.7	5.2
¹⁵⁵ Eu	1.41E+00	0.0	0.0	80.5	14.6	4.8
¹⁰⁶ Ru	5.59E-01	14.0	0.0	39.5	6.4	40.0
¹²⁵ Sb	3.11E+00	0.0	0.0	24.8	19.0	56.2
⁹⁰ Sr	9.46E+01	0.1	0.0	69.2	28.7	1.9
⁹⁹ Tc	4.47E-02	37.9	52.3	6.3	2.9	0.6

(a) This refers to the supernatant liquid that was formed by adding water to the dry sludge, mixing, and centrifuging.

(b) PD refers to the primary dissolver solution.

(c) SD refers to the secondary dissolver solution.

(d) Determined by alpha energy analysis after separating Pu from the other alpha emitters.

(e) Determined by alpha energy analysis without separating Pu from the other alpha emitters.

(f) Determined by subtracting ²³⁸Pu, determined by alpha energy analysis after separating Pu from the other alpha emitters, from ²³⁸Pu + ²⁴¹Am, which was determined by alpha energy analysis without separating Pu from the other alpha emitters.

(g) Determined by gamma energy analysis.

(h) The differences in the behaviors of ¹³⁴Cs and ¹³⁷Cs are likely due to large counting uncertainties associated with the ¹³⁴Cs data. The ¹³⁷Cs data are more reliable.

greater than 3×10^{-4} .^(a) The dispersion numbers for each solvent extraction contact performed in this test are given in Table 3.3. In all cases, the dispersion numbers were greater than 3×10^{-4} . Thus, the phase disengagement properties are favorable for the TBP and CMPO solvent extraction processes tested here.

Table 3.3. Dispersion Numbers from the Solvent Extraction Contacts

Stage ^(a)	Description	Height, mm	Time, s ^(b)	Dispersion Number
3	First TBP Extraction	99	73	1.4E-03
2	Second TBP Extraction	93	88	1.1E-03
1	Third TBP Extraction	88	70	1.4E-03
4	First TBP Scrub	35	34	1.8E-03
5	Second TBP Scrub	47	41	1.7E-03
6	Third TBP Scrub	37	34	1.8E-03
7	TBP Carb. Strip 1A	25	60	8.4E-04
8	TBP Carb. Strip 1B	23	42	1.2E-03
11	First CMPO Extraction	46.5	40	1.7E-03
10	Second CMPO Extraction	40	40	1.6E-03
9	Third CMPO Extraction	27	33	1.6E-03
12	CMPO Scrub 1A	64	30	2.7E-03
13	CMPO Scrub 1B	58	90	8.5E-04
14	CMPO Scrub 2A	46	25	2.7E-03
15	CMPO Scrub 2B	42	23	2.8E-03
16	CMPO Scrub 2C	38	19	3.3E-03
17	CMPO Scrub 2D	53	20	3.7E-03
18	CMPO Scrub 3A	39	65	9.7E-04
19	CMPO Scrub 3B	36	107	5.7E-04
20	CMPO Strip 1A	35	76	7.9E-04
21	CMPO Strip 1B	32	68	8.4E-04
22	CMPO Strip 2A	29	90	6.0E-04
23	CMPO Strip 2B	26	80	6.4E-04
24	CMPO Strip 2C	27	62	8.5E-04
25	CMPO Strip 2D	22	63	7.5E-04
26	CMPO Carb. Wash	14	70	5.4E-04

(a) Refers to the stage numbers indicated in Figure 1.2.

(b) Time required for the two phases to separate.

(a) R. A. Leonard, Argonne National Laboratory, personal communication.

In many of the contacts, air bubbles formed at the surface of the organic phase. These air bubbles generally persisted for longer than 5 min. It is unknown if these air bubbles will impact processing.

3.3 Extraction of HNO_3

The behavior of HNO_3 is given in Table 3.4. In the table, the measured concentrations are presented along with the expected values based on the known distribution behavior of HNO_3 . The latter values were calculated from the HNO_3 concentrations found in the aqueous phases for the first TBP

Table 3.4. Behavior of Nitric Acid in the TBP and CMPO Solvent Extraction Tests

Stage	Description	O/A	Aqueous [HNO_3], M		Organic [HNO_3], M	
			Measured	Predicted ^(a)	Measured	Predicted ^(a)
--	First TBP Extr Initial Aq.	--	2.20	--	--	--
3	First TBP Extraction	0.2	2.07	2.11	0.41	0.46
2	Second TBP Extraction	0.2	2.01	2.02	0.43	0.44
1	Third TBP Extraction	0.2	1.96	1.94	0.34	0.42
4	First TBP Scrub	2.0	0.72	0.83	0.06	0.15
5	Second TBP Scrub	2.0	0.39	0.43	0.08	0.03
6	Third TBP Scrub	2.0	0.29	0.28	0.07	0.00
--	First CMPO Extr Initial Aq.	--	1.70	--	--	--
11	First CMPO Extraction	0.29	1.50	1.56	0.55	0.49
10	Second CMPO Extraction	0.29	1.30	1.43	0.46	0.45
9	Third CMPO Extraction	0.29	1.30	1.31	0.43	0.41
12	CMPO Scrub 1A	0.75	1.35	1.31	0.24	0.41
13	CMPO Scrub 1B	0.75	1.30	1.26	0.34	0.40
14	CMPO Scrub 2A	1.0	1.53	1.58	0.49	0.49
15	CMPO Scrub 2B	1.0	1.63	1.65	0.72	0.51
16	CMPO Scrub 2C	1.0	1.63	1.67	0.39	0.52
17	CMPO Scrub 2D	1.0	1.64	1.67	0.72	0.52
18	CMPO Scrub 3A	1.5	0.58	0.55	0.23	0.15
19	CMPO Scrub 3B	1.5	0.23	0.18	0.17	0.04
20	CMPO Strip 1A	1.0	0.06	0.05	0.08	~0
21	CMPO Strip 1B	1.0	0.02	0.02	0.12	~0
22	CMPO Strip 2A	3.0	0.01	0.01	(b)	~0
23	CMPO Strip 2B	3.0	0.02	0.01	(b)	~0
24	CMPO Strip 2C	3.0	0.03	0.01	(b)	~0
25	CMPO Strip 2D	3.0	0.04	0.01	(b)	~0

(a) The predicted HNO_3 concentrations were determined from the concentrations measured for the initial aqueous phases as described in Appendix A.

(b) Not determined.

(stage 3) and first CMPO (stage 11) extractions before contact with the organic solvents. The method by which these values were calculated is discussed in Appendix A.

For the aqueous phases, the measured values agreed well with the predicted values, except at very low acid concentrations (stages 23 to 25). At these low acid concentrations, the accuracy of the titration method is suspect. The agreement between the measured and predicted organic phase HNO_3 concentrations was not as good as for the aqueous phases. This is attributed to a poor analytical method. The organic phase HNO_3 concentrations were determined by diluting aliquots of the organic phase in ethanol and titrating with aqueous NaOH . The quality of the resulting titration curves was poor; thus, the measured organic phase HNO_3 concentrations have large errors associated with them.

3.4 Extraction of U

The U distribution coefficients for each solvent extraction contact are given in Figure 3.1, and the concentration profile for U in the TBP and CMPO cycles is presented in Figure 3.2. As expected, U was efficiently extracted by TBP. Ninety-seven percent of the U was extracted from the dissolved NCRW solution by three contacts with 30% TBP at an organic-to-aqueous phase ratio of 0.2. This result agrees with the >95% U removal predicted for the NCRW pretreatment flowsheet tested (Lumetta and Swanson 1993a).

Figure 3.1. Distribution Coefficients for U, TRUs, and Eu. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

Figure 3.2. Concentration Profile for U. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

The U distribution coefficients remained above 1 in the first two TBP scrub contacts (stages 4 and 5), but fell to ~ 0.9 in the final TBP scrub contact (stage 6). As indicated in Figure 3.3, published U distribution data indicate that the U distribution coefficient should have been ~ 1.6 in the final TBP scrub step under the conditions of this experiment (HAPO 1955). The reason for the slight discrepancy between the published data and the results obtained here is unknown; however, with the organic-to-aqueous phase ratio of 2 in the TBP scrub section the U extraction factor^(a) was ~ 1.8 , which is acceptable.

Carbonate effectively stripped the U from the TBP solvent. Essentially complete removal of U from the solvent was achieved in the two Na_2CO_3 contacts (stages 7 and 8). Uranium was not detected in either the aqueous or organic phases from the HEDPA strip contact used to strip residual metals from the solvent for analysis.

The U in the raffinate from the TBP cycle was completely extracted in the CMPO cycle. The U concentration in the raffinate from the CMPO cycle was $\leq 6 \times 10^{-7} \text{ M}$, indicating that $\geq 99.99\%$ of the U was removed from the dissolved NCRW solution. The U remained in the CMPO solvent during the CMPO scrub steps. In the first CMPO strip section (stages 20 and 21), the U distribution coefficient

(a) The extraction factor is defined as the distribution coefficient times the organic-to-aqueous phase ratio.

Figure 3.3. Uranium Distribution Coefficients Predicted from Data in the Literature (HAPO 1955) Compared to Those Found Here for the TBP Cycle

remained above 1. During the second CMPO strip section (stages 22 to 25), the U distribution coefficient was ~ 1 , which equates to a U extraction factor of ~ 3 . Thus, most of the U extracted by CMPO passed through the second strip section and was stripped during carbonate wash step (stage 26).

3.5 Extraction of TRUs

The behavior of the TRU elements was followed by measuring the total alpha activity in the various process solutions. The distribution coefficients for the total alpha emitters are given in Figure 3.1, and the concentration profile for the alpha emitters is presented in Figure 3.4. Very little TRU material was extracted by TBP. The total alpha concentration in the carbonate strip solution (stage 7) was $0.020 \mu\text{Ci/mL}$, which was $\sim 0.2\%$ of the TRU material in the feed solution.

The TRUs were effectively extracted with CMPO. The initial total alpha concentration in the aqueous phase for stage 11 was $0.35 \mu\text{Ci/mL}$, and in the aqueous phase for stage 9 the concentration was $0.0024 \mu\text{Ci/mL}$, giving a decontamination factor (DF)^(a) of ~ 150 . The TRUs were retained in the organic phase throughout the three CMPO scrub sections and were easily stripped. The total alpha

(a) The decontamination factor is defined as the quantity of TRU material present before treatment divided by the quantity present after treatment.

Figure 3.4. Concentration Profile for the Total Alpha Activity (TRUs). The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

distribution coefficient for the first stage (stage 20) of the first strip section was 0.069. The TRU concentration in the solvent was below the detection limit ($\leq 1.5 \times 10^{-4} \mu\text{Ci/mL}$) for the first stage (stage 22) of the second strip section.

The behavior of the individual TRU components was determined by alpha spectroscopy and by gamma spectroscopy in the case of ^{241}Am . The Am distribution coefficients are presented in Figure 3.1, and the concentration profile for Am is presented in Figure 3.5. In general, the concentrations determined by alpha spectroscopy compared favorably to those obtained by gamma spectroscopy. The Am DF was 140 in the CMPO cycle. Americium was retained in the organic phase during scrubbing and was easily stripped with dilute HNO_3 , as expected based on published Am distribution data (Horwitz et al. 1985).

The Pu concentration profile is depicted in Figure 3.6, based on the analysis of the $^{239,240}\text{Pu}$ peak in the alpha spectra. The Pu distribution coefficients are given in Figure 3.1. The results indicated favorable Pu behavior throughout the process. A Pu DF of 200 was achieved in the CMPO extraction cycle. In general, the Pu distribution coefficients in the CMPO scrub steps were larger than those for Am, indicating that a certain amount of Pu might have been present in the +4 oxidation state. The Pu distribution coefficients increased with each successive scrub step (Figures 3.1 and 3.7). This trend is further evidence for the presence of Pu(IV).

Figure 3.5. Concentration Profile for the ^{241}Am , Determined by both Alpha and Gamma Counting. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

Figure 3.6. Concentration Profile for Pu. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

Figure 3.7. Plutonium Distribution Coefficients in the CMPO Cycle as a Function of HNO_3 Concentration

Plutonium was effectively stripped in stage 20; Pu was not detected in the solvent at the first stage (stage 22) of the second strip section. If a certain percentage of the Pu in the scrubbed extract was in the +4 oxidation state, 0.01 M HNO_3 alone would not likely have stripped all the Pu from the solvent. However, the introduction of $\text{H}_2\text{C}_2\text{O}_4$ in the second scrub section ensured complete Pu stripping. Because the $\text{H}_2\text{C}_2\text{O}_4$ solution from the second strip section flows into the first strip section, sufficient $\text{H}_2\text{C}_2\text{O}_4$ was present in the first strip section to remove all the Pu from the solvent. The use of P-containing stripping agents was identified as a problem in earlier CMPO extraction flowsheets because they might introduce too much P into the HLW stream, resulting in an excessive quantity of HLW glass (Lumetta and Swanson 1993a). *This experiment clearly demonstrated that Pu can be stripped from the CMPO solvent without using P-containing stripping agents.*

3.6 Extraction of Other NCRW Sludge Components

None of the nonradioactive NCRW sludge components were extracted by TBP (Table 3.5). Although the test results indicated a Ca distribution coefficient of 0.26 in the first TBP extraction (stage 3), this measured value is suspected to be erroneously high because Ca was not detected in the organic or aqueous phases from the subsequent scrub and strip steps (stages 4 to 8). The concentration profile for F is presented in Figure 3.8. The F distribution coefficients were very low (~ 0.004) in the TBP extraction stages. Analyses of the organic phases from the TBP scrub contacts (stages 4 to 6) indicated that $\sim 90\%$ of the F extracted by TBP was removed in the scrub section. Fluoride was not detected in the TBP solvent after stage 7.

Table 3.5. Distribution Coefficients for Nonradioactive Metals in the First TBP (stage 3) and CMPO (stage 11) Extraction Steps

Component	Distribution Coefficient	
	Stage 3	Stage 11
Al	0.015	0.016
Ca	0.26	0.037
Cr	<0.009	0.014
Fe	<0.002	0.011
La	<0.053	5.0
Na	<0.003	0.005
Si	<0.17	0.020
Zr	0.002	0.062

Figure 3.8. Concentration Profile for F. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

Besides the actinides, the only other NCRW sludge components that were extracted by CMPO were the lanthanides. The behavior of Eu is illustrated in Figure 3.9 as an example. The concentration profile for ^{154}Eu is shown in this figure; the concentration profile for ^{155}Eu was almost identical. Ninety-six percent of the Eu was extracted from the dissolved NCRW solution. The behavior of La was very similar, >91% was extracted. Because the lanthanides were stripped in stage 20 and were not separated from the TRUs, they would be handled in the HLW stream.

Figure 3.9. Concentration Profile for the Eu. The stage numbers refer to those indicated in Figure 1.2 and Table 2.2.

Lanthanum was the only major nonradioactive NCRW sludge components extracted by CMPO. Distribution coefficients for the other major sludge components were less than 0.1 (Table 3.5). The small amounts of these nonradioactive elements that did transfer to the organic phase in the first CMPO extraction step (stage 11) were readily scrubbed from the solvent. For example, Zr was not detected in the organic phase after stage 12. The behavior of F is illustrated in Figure 3.8. The F distribution coefficients in the CMPO extraction stages were higher than in the TBP extraction stages, but were still low (~ 0.06). Analyses of the organic phases from the CMPO scrubs contacts (stages 12 to 17) indicated that $\sim 99\%$ of the extracted F was removed in the first two scrub sections; F was not detected in the CMPO solvent after stage 16. The F concentration in the aqueous phase at stage 20 was $< 10^{-4}$ M.

3.7 Impact on Waste Volumes^(a)

The HLW that would result from using the proposed NCRW pretreatment flowsheet will consist of the undissolved solids and the CMPO stripping solution. The estimated composition of the HLW stream is given in Table 3.6. This estimate is based on the dissolution and extraction data generated in this DBE and on the quantity and composition of NCRW sludge provided by WHC.^(b)

The amount of HLW glass produced from the HLW stream described in Table 3.6 was estimated using two methods. First, the minimum amount of glass produced by vitrification of the individual waste components was determined using the Hanford Waste Vitrification Plant (HWVP) feed specifications. This method of estimation has recently been described (Swanson 1993). Second, the amount of HLW glass was estimated using the Optimal Waste Loading (OWL) program.^(c) Both methods indicated the amount of HLW glass produced would be defined by the P content, resulting in ~ 500 canisters (8.25×10^5 kg) of glass. The amount of HLW glass produced might be decreased by 1) increasing the P loading in the glass, or 2) increasing P dissolution in the sludge. For certain single-shell tank sludges, leaching with 3 M NaOH can remove significant quantities of P from the sludge (Lumetta et al. 1994). Thus, performing a caustic leach before (or after) dissolving the NCRW in acid might decrease P in the undissolved residue and decrease the volume of HLW glass produced.

Because the LLW glass form has not currently been defined, the LLW volume cannot be estimated. The volume of LLW produced in disposing of NCRW sludge will likely be dictated by the quantity of Na present in the LLW stream. The LLW stream will consist of the sludge wash liquor, the raffinate from the CMPO cycle, and the carbonate washing/stripping solutions from the TBP and CMPO cycles. Based on the results of this DBE, an estimated 1.1×10^6 kg of Na would be present in the LLW stream if the CMPO raffinate is not neutralized for interim storage. If the CMPO raffinate must be neutralized, the quantity of Na in the LLW stream would be approximately 1.6×10^6 kg. These values can be used to estimate LLW glass volumes when feed specifications for the LLW glass become available.

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- (a) When this experiment was performed, the baseline scenario for disposal of Hanford tank wastes specified the disposition of HLW in borosilicate glass. Each canister of glass would contain 1,650 kg of HLW glass. The LLW would be disposed of in grout. The current scenario still specifies the disposition of HLW in borosilicate glass, but large, self-shielded casks have been proposed to reduce the disposal costs for the HLW glass. For the purposes of this discussion, HLW glass volume will be discussed in terms of the original 1,650 kg canisters. The current scenario specifies that the LLW will be disposed of in a glass waste form rather than grout. Because the LLW glass form has not been defined, LLW volumes will not be discussed in this report.
- (b) Lowe, S. S. 1991. *Preliminary Material Balances for Pretreatment of NCAW, NCRW, PFP, and CC Wastes*. WHC-SD-WM-TI-492, Revision 0. Westinghouse Hanford Company, Richland, Washington.
- (c) Hoza, M. 1993. *Optimal Waste Loading Models for Vitrifications of Hanford High-Level Waste*. PHTD-693.03.01M, Pacific Northwest Laboratory, Richland, Washington.

Table 3.6. Estimated Composition of the HLW Stream After Pretreating NCRW Sludge

Component	In Sludge, kg ^(a)	In Undissolved Residue		In CMPO Strip Solution		HLW Stream Total, kg
		% ^(b)	kg	% ^(b)	kg	
Al	1.53E+04	27	4.13E+03			4.13E+03
Am	1.73E-01	5	8.65E-03	100	1.73E-01	1.82E-01
Ba	5.33E+02	5	2.67E+01			2.67E+01
Ca	1.43E+03	3	4.29E+01			4.29E+01
Cr	4.13E+03	11	4.54E+02			4.54E+02
Fe	2.86E+03	13	3.72E+02			3.72E+02
La	1.40E+03	1	1.40E+01	96	1.34E+03	1.36E+03
Mn	9.99E+02	2	2.00E+01			2.00E+01
Na	4.43E+05	0.1	4.43E+02			4.43E+02
Nd	5.33E+02	2	1.07E+01	96	5.12E+02	5.22E+02
Ni	4.00E+02	4	1.60E+01			1.60E+01
P	7.66E+03	31	2.37E+03		1.27E+03 ^(c)	3.64E+03
Pu	3.13E+01	6	1.88E+00	100	3.13E+01	3.32E+01
Si	1.47E+04	21	3.09E+03			3.09E+03
U	2.33E+04	0	0.00E+00	2	4.66E+02	4.66E+02
Zr	2.86E+05	2	5.72E+03			5.72E+03
HNO ₃	N/A	N/A	N/A		7.04E+03	7.04E+03
TOC (oxalate)	N/A	N/A	N/A		9.00E+02	9.00E+02

(a) Lowe, S. S. 1991. *Preliminary Material Balances for Pretreatment of NCAW, NCRW, PFP, and CC Wastes*. WHC-SD-WM-TI-492, Revision 0. Westinghouse Hanford Company, Richland, Washington.

(b) Based on the results of the DBE.

(c) Based on the concentration of P in the aqueous phase from stage 20.

3.8 Conclusions

The DBE2 results indicated that the flowsheet illustrated in Figures 1.1 and 1.2 is capable of achieving the process objectives as outlined in Section 1.0. That is, the TRU components of the waste can be separated from the major sludge constituents (e.g., Na and Zr) and from the U in the sludge. Also, the TRUs can be concentrated into a relatively small volume for vitrification. However, improvements to the flowsheet can likely be made to both simplify use and to improve performance. First, addition of a caustic (3 M NaOH) leaching step (either before or after acid dissolution) might decrease the overall amount of P in the HLW stream to be vitrified which, in turn, would decrease the volume of HLW glass produced. Second, the TBP cycle could be eliminated if a scheme to selectively strip TRUs from U is employed. Methods for selectively stripping the CMPO solvent have been proposed (Lumetta et al. 1994, Horwitz et al. 1993).

4.0 References

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Appendix A

Calculated Nitric Acid Distribution

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Calculated Nitric Acid Distribution

Data for extracting HNO_3 by 30% TBP and the CMPO solvent (0.2 M CMPO plus 1.4 M TBP in NPH) have been published by Chaiko and Vandegrift (1988), Horwitz et al. (1985), and Lumetta and Swanson (1993). These data are plotted in Figure A.1.

The data for extracting HNO_3 by 30% TBP can be fit to the following second-order polynomial:

$$[\text{HNO}_3]_{\text{org}} = -0.0211[\text{HNO}_3]_{\text{aq}}^2 + 0.3046[\text{HNO}_3]_{\text{aq}} - 0.0932 \quad (\text{A.1})$$

The curve representing this polynomial is plotted in Figure A.1. This equation can be used to calculate the equilibrium concentrations of HNO_3 for a given batch contact if the initial aqueous and organic HNO_3 concentrations are known. For example, if an aqueous solution containing 2.0 M HNO_3 is contacted with fresh 30% TBP at an organic-to-aqueous phase ratio of 0.2, then according to Equation A.1, the equilibrium HNO_3 concentrations should be 1.92 M in the aqueous phase and 0.41 M in the organic phase. Note that this equation may not apply to the aqueous phase when the salt content is high.

Figure A.1. Extraction of HNO_3 with 30% TBP in NPH and 0.2 M CMPO/1.4 M TBP in NPH

The data for extracting HNO_3 by the CMPO process solvent can be treated in a similar manner. In this case, the data are divided into two sets. When the aqueous HNO_3 concentration is greater than 1 M, the data are fit to a second-order polynomial. But when the aqueous HNO_3 concentration is less than 1 M, the data are fit to a linear equation. These equations are listed below, and the corresponding curves for these equations are plotted in Figure A.1.

$$[\text{HNO}_3]_{\text{org}} = -0.0215[\text{HNO}_3]_{\text{aq}}^2 + 0.3511[\text{HNO}_3]_{\text{aq}} - 0.0091 \quad (\text{A.2})$$

$$[\text{HNO}_3]_{\text{org}} = 0.2972[\text{HNO}_3]_{\text{aq}} - 0.0097 \quad (\text{A.3})$$

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