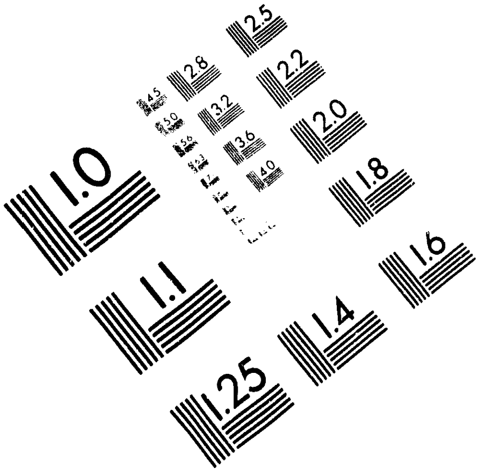

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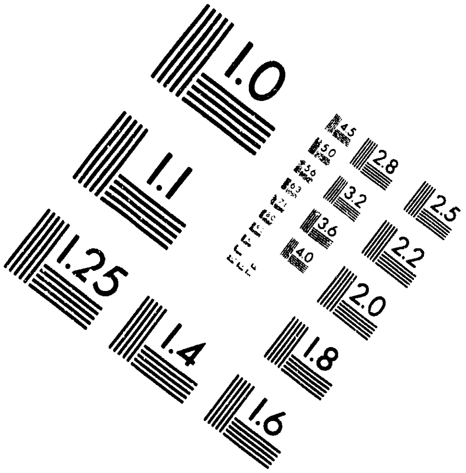

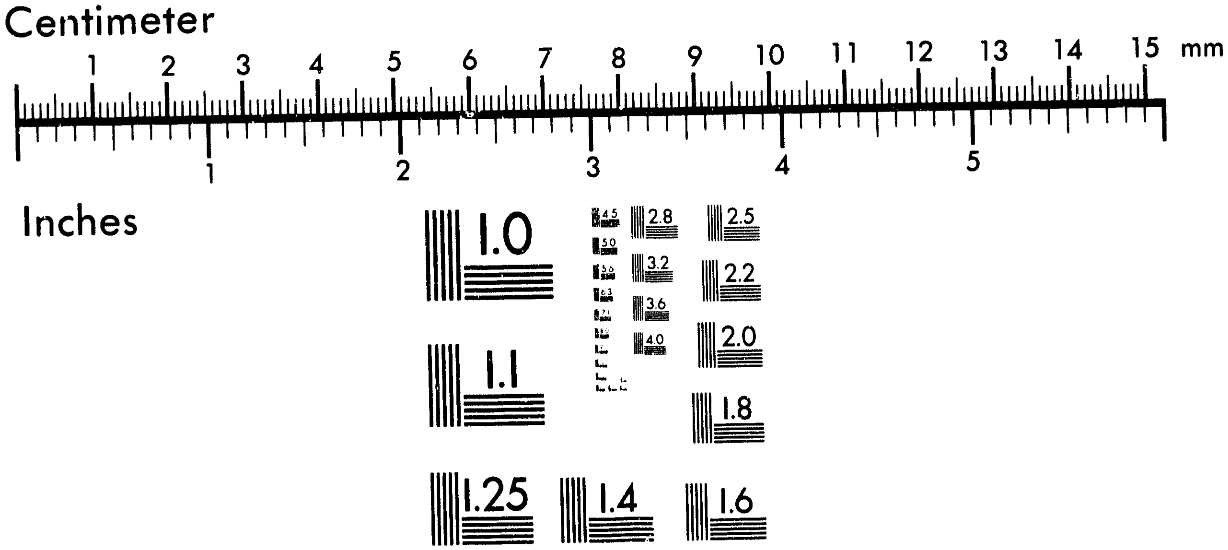

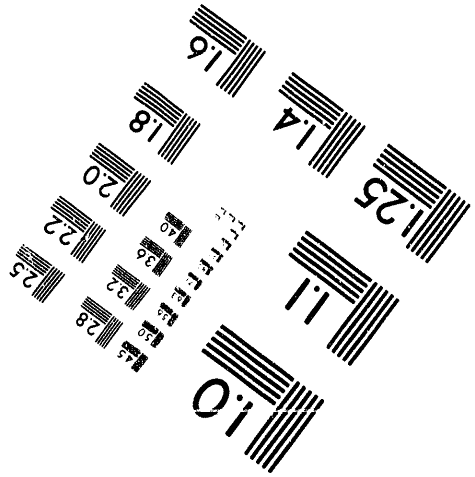

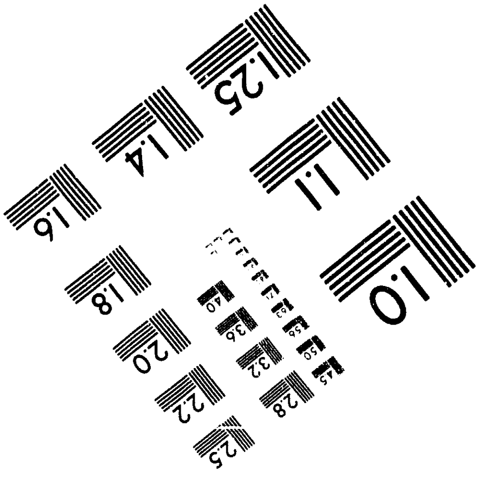

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PNL-8537
UC-721

Underground Storage Tank Integrated Demonstration

Evaluation of Pretreatment Options for Hanford Tank Wastes

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Summary

Separation science plays a central role in the pretreatment and disposal of nuclear wastes. The potential benefits of applying chemical separations in the pretreatment of the radioactive wastes stored at the various U.S. Department of Energy sites cover both economic and environmental incentives. This is especially true at the Hanford Site, where the huge volume (>60 Mgal) of radioactive wastes stored in underground tanks could be partitioned into a very small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). The cost associated with vitrifying and disposing of just the HLW fraction in a geologic repository would be much less than those associated with vitrifying and disposing of all the wastes directly. Furthermore, the quality of the LLW form (e.g., grout) would be improved due to the lower inventory of radionuclides present in the LLW stream.

In this report, we present the results of an evaluation of the pretreatment options for sludge taken from two different single-shell tanks at the Hanford Site—Tanks 241-B-110 and 241-U-110 (referred to as B-110 and U-110, respectively). The pretreatment options examined for these wastes included 1) leaching of transuranic (TRU) elements from the sludge, and 2) dissolution of the sludge followed by extraction of TRUs and ^{90}Sr. In addition, the TRU leaching approach was examined for a third tank waste type, neutralized cladding removal waste.

The major findings of this work are shown below:

- Carbonate/bicarbonate leaching (with or without oxidant) of tank sludges is not a promising approach to removing TRUs from the bulk waste components.

- After treatment of U-110 sludge with 2 M HNO_3 at 100°C, the bulk of the sludge meets the U.S. Nuclear Regulatory Commission Class C LLW criteria for TRUs, ^{90}Sr, ^{137}Cs, and ^{99}Tc.

- Extraction of TRUs from the U-110 acid leach solution with CMPO will require adjustment of the process chemistry in order to avoid the formation of interfacial crud.

- The SREX process can be used to extract Sr from dissolved B-110 sludge.

- The TRUEX process can be used to extract TRUs from dissolved B-110 sludge; in this case, minimal feed adjustment will be required to avoid interfacial crud.

Data on the extraction behavior of Bi in the TRUEX process are included as an appendix in this report. The data indicate that Bi does extract into the TRUEX process solvent. However, separation of Bi from the TRUs might be achieved by adjusting the stripping conditions.

Acknowledgments

This work was funded by the U.S. Department of Energy, Office of Technology Development. The authors would also like to thank J. L. Swanson of Pacific Northwest Laboratory (PNL) for his many helpful suggestions. The assistance of the staff in PNL's Analytical Chemistry Laboratory is gratefully acknowledged.

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1.0 Introduction

Methods are currently being developed to treat and dispose of large volumes of radioactive wastes, such as those stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site. The current baseline scenario for the treatment and disposal of the wastes at Hanford involves partitioning the wastes into a small volume of high-level waste (HLW) and a relatively large volume of low-level waste (LLW). The HLW will be vitrified into borosilicate glass and disposed of in a geologic repository offsite, while the LLW will be converted to grout and disposed of by shallow burial on the Hanford Site.

There are both economic and environmental reasons to separate various radionuclides from the bulk waste components. Because vitrification and disposal of HLW is considerably more costly than disposal of LLW, it is desirable to minimize the volume of HLW. This volume reduction can be achieved by separating the radionuclides from the waste, so that the bulk waste material can be handled as LLW. Furthermore, maximum removal of radionuclides from the LLW stream would minimize leaching of these radionuclides from the grout matrix into the surrounding environment.

There are approximately 2×10^7 Ci ^{137}Cs, 5×10^7 Ci ^{90}Sr, 2×10^4 Ci ^{239}Pu, 4×10^4 Ci ^{241}Am, and various other isotopes stored in waste tanks on the Hanford Site (DOE 1987). Most of the ^{137}Cs inventory is in the tank supernatant solutions. Most of the transuranics (TRUs) and ^{90}Sr are found in the tank sludges. The average concentration of all radioactive material in the Hanford tank waste is less than 20 ppm. The mass of radioactive components in the Hanford tank wastes is on the order of a few thousand kilograms, whereas the mass of nonradioactive components is approximately 300,000 tons.

For many Hanford tank sludges, it is the quantity of TRU material present that requires that the waste be handled as HLW. Thus, separation of the TRUs from the sludge material will allow the bulk of the sludge to be disposed of less expensively as LLW. The work discussed in this report was conducted by Pacific Northwest Laboratory (PNL)[a] to evaluate pretreatment options for separating TRUs and ^{90}Sr from tank sludges. This study was performed for the Underground Storage Tank Integrated Demonstration (USTID).[b] In this work, we consider two approaches towards separating TRUs from the bulk sludge material: 1) selective leaching of the TRUs from the sludge and 2) acidic dissolution of the sludge and extraction of the TRUs from the dissolved sludge solution using the TRUEX process developed at Argonne National Laboratory (ANL). The TRUEX process is a solvent extraction process in which the TRUs are extracted from acidic solution using octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (Horwitz et al. 1985). TRUEX experiments were conducted on solutions derived from Hanford tank sludge obtained from Tank 241-B-110 and Tank 241-U-110, hereafter referred to as B-110 and U-110, respectively.

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

(b) The USTID, sponsored by the DOE Office of Technology Development, is identifying and evaluating technologies that may be used to characterize, retrieve, treat, and dispose of hazardous and radioactive wastes contained in tanks on DOE sites.

Both alkaline (carbonate/bicarbonate solution) and acidic (dilute HNO_3) leach procedures were tested for the leaching of TRUs from the bulk waste material. Because Pu and Am are known to have some solubility in carbonate/bicarbonate media (Kim, Lierse, and Baumgartner 1983; Felmy, Rai, and Fulton 1990), an attempt was made to exploit this solubility to remove these elements from the bulk sludge components. Pu and Am are also known to be soluble in acid solution, thus leaching of certain sludges with dilute HNO_3 was also tried as a method to leach the TRUs. The Hanford tank wastes used in these leaching studies were 1) neutralized cladding removal waste (NCRW) and 2) U-110 sludge.

It is desirable to separate ^{90}Sr from the bulk sludge components in order to minimize the radioactivity and perceived risk in the LLW waste form. The SREX process, also developed at ANL, was investigated as part of this work for separating ^{90}Sr from the bulk sludge components. This process is also a solvent extraction process. In this case, Sr is extracted from acidic solution using di-t-butylcyclohexano-18-crown-6 (DtBC18C6) (Horwitz, Deitz, and Fisher 1991). Sludge from B-110 was chosen for testing the SREX process because this sludge contains approximately 7×10^6 nCi ^{90}Sr per gram of sludge.

This report describes the procedures used in the experiments, gives the results of the tests, and provides conclusions and recommendations. The appendix contains data on the extraction of Bi with CMPO.

2.0 Experimental

The experimental methods used in this work are described in this section. The experiments conducted included 1) leaching of TRUs from NCRW sludge and from U-110 sludge (see Figures 2.1 and 2.2); 2) extraction of TRUs from the U-110 sludge acid leach solution using the TRUEX process; and 3) extraction of ^{90}Sr and TRUs from dissolved B-110 sludge using the SREX and TRUEX processes, respectively. Descriptions of the analytical methods used can be found in Swanson (1991a).

2.1 Leaching of TRUs from NCRW Sludge

A 1.104-g portion of NCRW sludge (composite of Segments 3 to 6 from the May 1990 core sampling of Tank 105-AW) was slurried with 5 mL water. One mL of this slurry was withdrawn for use in these experiments. This portion contained 0.215 g of dry sludge (assuming complete homogeneity of the slurry).

The sludge was first washed with a strongly alkaline solution in an attempt to remove the Al present. The sludge was heated at 100°C with 2.2 mL (~ 10 mL/g sludge) of 1.0 $\underline{M}$ NaOH for 2 h. After cooling to room temperature, the mixture was centrifuged, and the supernatant solution was decanted. The sludge was then washed with one 2.5-mL portion of water.

The washed sludge was slurried in 2.5 mL water and was divided into three approximately equal portions (76B, 76C, and 76D). Portion 76B was leached with bicarbonate/carbonate, then with HNO_3; Portion 76C was leached with bicarbonate/carbonate plus permanganate; and Portion 76D was leached with bicarbonate plus ozone.

2.1.1 Leaching of TRUs from NCRW Sludge with Carbonate/Bicarbonate

One mL of water and 0.1 mL of 1 $\underline{M}$ K_2CO_3 were added to 76B and 76C, and saturated $KHCO_3$ was added until the pH was 8.05 for both. Next, 0.2 mL of 0.02 $\underline{M}$ $KMnO_4$ was added to 76C, then 76B and 76C were heated (100°C) and stirred for 5 h. After the mixtures had cooled, 76B and 76C were centrifuged, and the supernatant solutions were decanted. A second strike with carbonate/bicarbonate was done in a similar manner on the remaining sludges in 76B and 76C.

The washed NCRW sludge 76D was leached with bicarbonate and ozone. One mL of water and 2.0 mL of saturated $KHCO_3$ were added to 76D, and 0.4 mL of 1 $\underline{M}$ HNO_3 was added to lower the pH to 7.96. With the mixture stirring, ozone was bubbled through for 1 h. Then the mixture was heated with stirring at 100°C for 4 h. After cooling, the mixture was centrifuged. The supernatant solution was decanted, and the residue was dissolved in 10 $\underline{M}$ HCl/2 $\underline{M}$ HF at 100°C for analysis.

2.1.2 Acid Leaching of TRUs from NCRW

To determine if the NCRW sludge could be made non-TRU by leaching with acid, the carbonate/bicarbonate leached sludge from 76B was leached with dilute HNO_3. Two mL of water

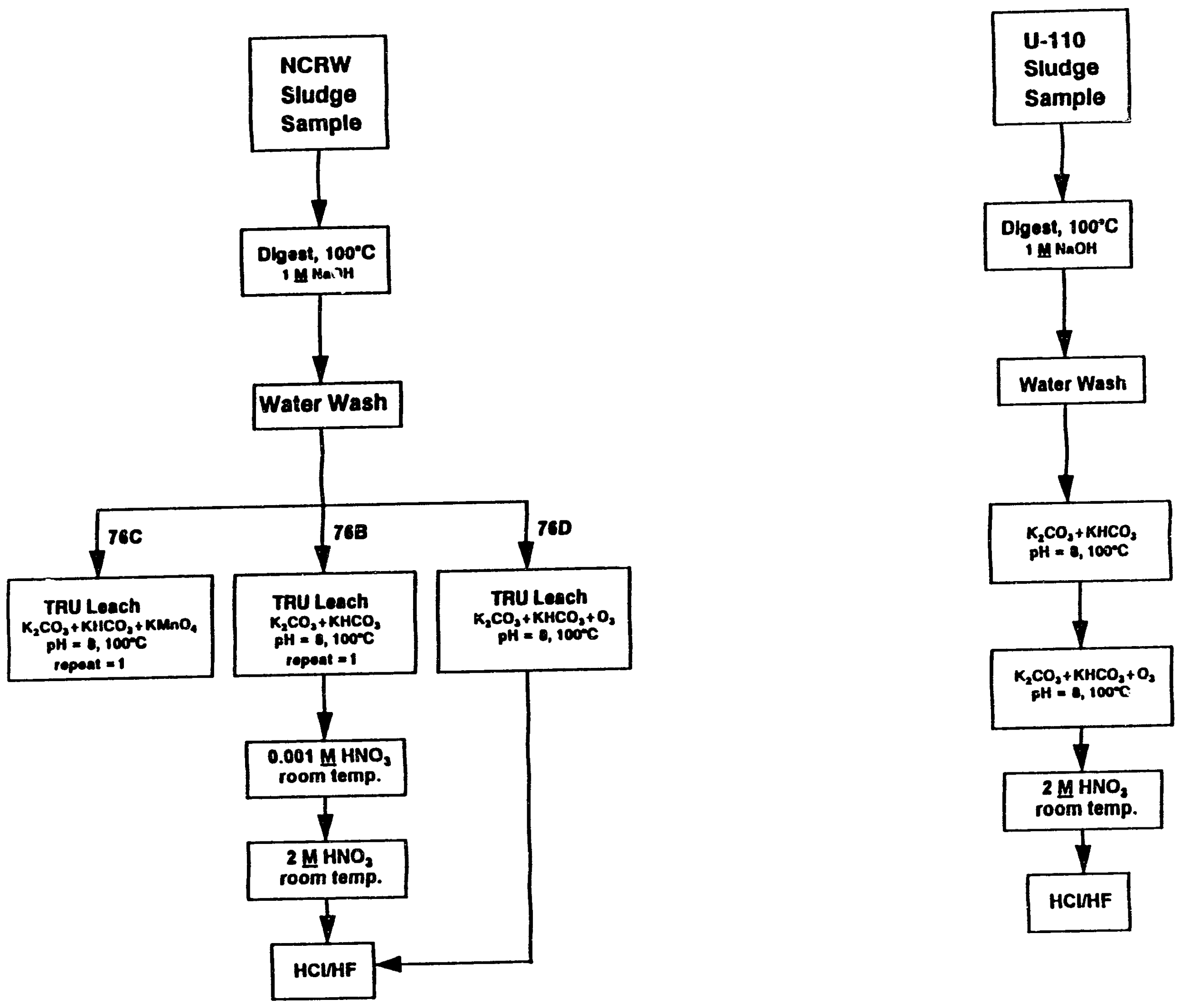

Figure 2.1. Selective Leaching of NCRW and U-110 Waste

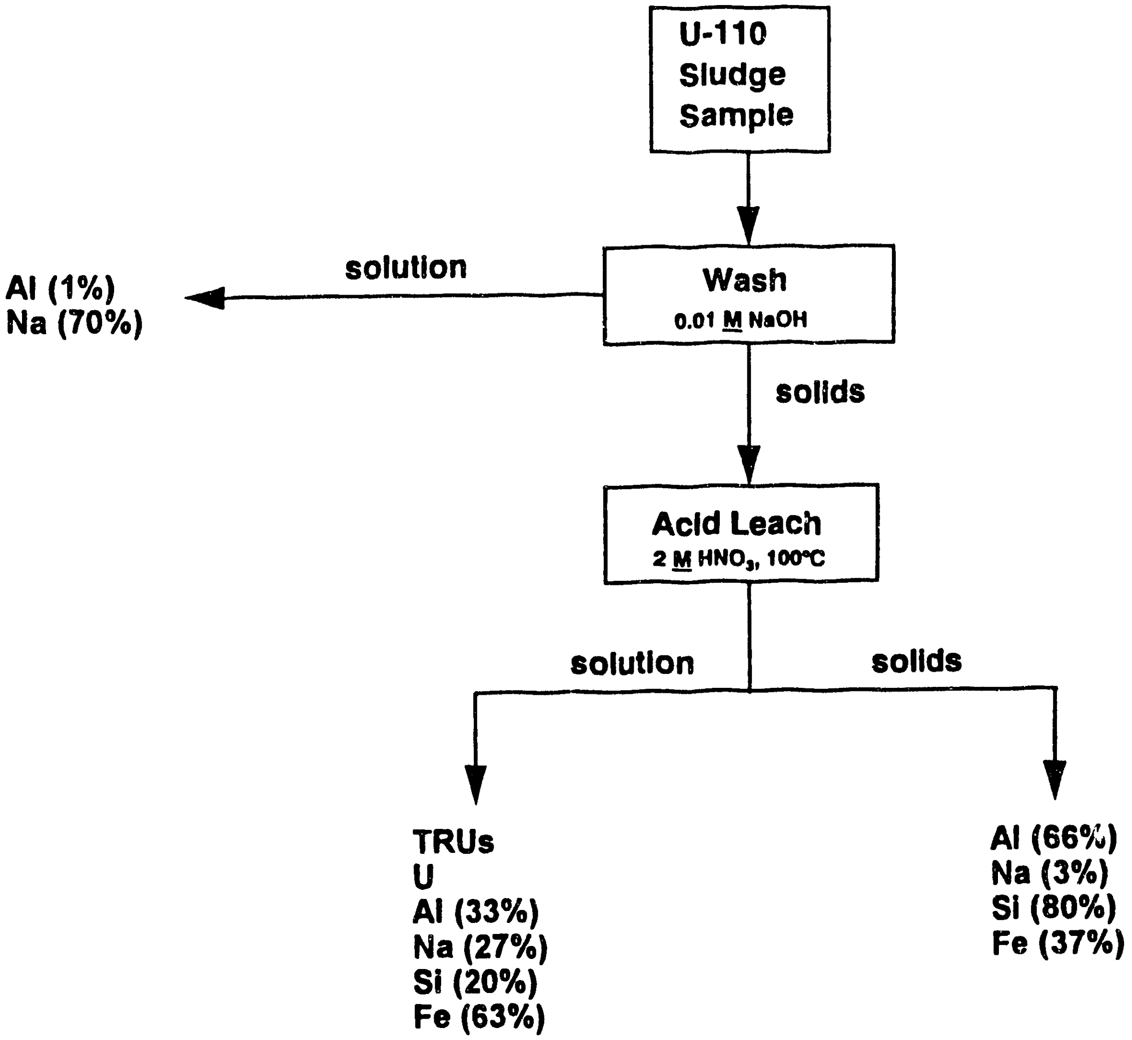

Figure 2.2. Acid Leaching of U-110 Waste

were added to leached sludge 76B, then 0.26 mL of 1.0 M HNO_3 was added to lower the pH to 2.9. After stirring for 2.5 h, the mixture was centrifuged, and the solution was decanted. Two mL of 2 M HNO_3 were added to the sludge, and the mixture was stirred for 2.25 h. After the mixture was centrifuged, the supernatant solution was decanted. The remaining solid was dissolved in 5.4 M HCl/0.9 M HF at 100°C for analysis.

2.2 Leaching of TRUs from Tank U-110 Sludge

The experiments involved both alkaline and acid leaching.

2.2.1 Alkaline Leaching of TRUs from U-110 Sludge

A 2.204-g portion of dried sludge from U-110 (composite from Core # 12) was suspended in 5.033 g of 0.01 M NaOH, and 2.398 g of the resulting slurry were withdrawn for use in this experiment. This portion contained 0.729 g of the dry sludge (assuming complete homogeneity of the slurry).

The sludge was first washed with a strongly alkaline solution in an attempt to remove the Al present. The sludge was stirred with 2.2 mL of 1 M NaOH for 1 h at 100°C; then the mixture was centrifuged, and the yellow supernatant solution decanted. This sludge wash procedure was repeated a second time combining the second wash solution with the first wash solution.

The washed sludge was slurried in 2.0 mL of water and was divided into two equal portions. One portion was used in acid leaching tests, while the other was used for this alkaline leaching experiment.

The alkaline-washed sludge was washed with 3.0 mL of water to lower the free hydroxide content. The sludge was then slurried with 0.9 mL water, and 0.1 mL of 1.0 M K_2CO_3 plus 2 mL of saturated $KHCO_3$ were added. Also added was 1 M HNO_3 (0.9 mL) to lower the pH from 9.34 to 8.21. The mixture was stirred and heated at 100°C for 6.25 h, then was allowed to cool to room temperature. After centrifuging, the supernatant solution was decanted. One mL of water and 2 mL of saturated $KHCO_3$ were added to the sludge. The pH was lowered from 8.72 to 8.00 by adding 0.6 mL of 1 M HNO_3. Ozone was bubbled through the mixture while stirring for 1 h; the mixture was then stirred and heated at 100°C for 5 h. The mixture was centrifuged after cooling, and the supernatant solution decanted. The residue was leached repeatedly (four 1.5-mL portions) with 2 M HNO_3. The remaining sludge was dissolved in concentrated HCl and 10 M HF for analysis.

2.2.2 Acid Leaching U-110 Sludge

A 0.355-g portion of dry U-110 sludge (composite sample from Core # 12) was washed twice with 1-mL portions of 0.01 M NaOH at room temperature. The washed sludge was treated four successive times with 2-mL portions of 2 M HNO_3 at 100°C. The remaining residue was treated with concentrated HCl, then 10 M HF to dissolve the solids for analysis. Each solution was analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The solutions were also analyzed for TRUs (as total alpha), ^{137}Cs, ^{90}Sr, and ^{99}Tc.

In a second acid leaching experiment, a 0.328-g portion of dry U-110 sludge (composite sample from Core # 14) was washed once with 1.8 mL of 0.1 M NaOH at room temperature. The sludge was then treated four successive times with 2, 1, 1, and 1 mL of 2 M HNO_3, respectively, at 100°C. The remaining residue was treated with concentrated HCl, then 10 M HF to dissolve the solids for analysis. In this case, the solutions were only analyzed for total alpha activity.

2.3 TRUEX Experiments on the Tank U-110 Sludge Acid Leach Solution

A series of batch TRUEX contacts were performed using aqueous solutions derived from the acid leaching of U-110 sludge. In certain cases, oxalic acid or HF was added to the acid leach solution to determine the effects of these components on interfacial crud (see Table 3.6). The aqueous feed solutions were contacted for 30 s with the TRUEX process solvent [0.2 M CMPO plus 1.4 M tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH)] at an organic-to-aqueous phase ratio of 0.33. The mixtures were centrifuged to facilitate phase disengagement. In most cases interfacial crud was observed (see Section 3.3). For the contact that did not contain crud, the aqueous phase was sampled before and after the contact for ICP/AES and for total alpha analyses.

2.4 SREX and TRUEX Processing of Tank B-110 Sludge

A test of the SREX process was conducted on actual B-110 sludge. This process involves the dissolution of the sludge in acid followed by extraction of Sr with DtBC18C6. Also, batch TRUEX contacts were performed to obtain preliminary data in the use of the TRUEX process for separating TRUs from this waste.

2.4.1 Dissolution of Tank B-110 Sludge

A 5.24-g portion of sludge from B-110 (Composite #2 from Core Sample #3) was washed twice with 10-mL portions of 0.1 M NaOH at room temperature. These washes involved mixing the sludge with 0.1 M NaOH for 1 to 2 h, centrifuging, then decanting the wash liquor from the sludge.

Water was added to the washed sludge to give a total volume of 10 mL. Nitric acid (2.9 mL of 15.7 M) and HF (0.15 mL of 10 M) were added along with enough water to give a total volume of 15 mL. After stirring at 100°C for 1 h, another 0.15 mL of 10 M HF was added. The dissolver mixture was heated for another 2 h, then was allowed to cool. After centrifuging, the solution (Solution 1) was decanted. Water (5 mL) and 10 M HF (1 mL) were added to the undissolved solid. This mixture was stirred at room temperature overnight, which resulted in dissolution of most of the solid. Further dissolution was achieved by heating for 1 h at 100°C. The solution (Solution 2) was cooled and centrifuged, then was decanted from the small amount of residual solid. Solutions 1 and 2 were filtered through 0.2-μm membrane filters.

2.4.2 SREX Experiment on Dissolved B-110 Sludge

The solvent extraction contacts performed to test the SREX process for dissolved B-110 sludge are summarized in Table 2.1. For each contact, the two phases were mixed for 30 s. Dispersion numbers (N_{Di}) were determined by measuring the total height of the aqueous plus organic phases before mixing, then measuring the time required for the two phases to break after mixing.

Table 2.1. Solvent Extraction Contacts Performed to Test the SREX Process on Dissolved Tank B-110 Sludge

Contact #	Aqueous Phase	Aq. Vol., mL	Organic Phase	Org. Vol., mL
SREX-1	Adjusted Feed	9	SREX Solvent	3
SREX-2	0.5 M HNO_3	0.83	Organic from SREX-1	2.5
SREX-3	0.5 M HNO_3	0.67	Organic from SREX-2	2
SREX-4	0.01 M HNO_3	1.50	Organic from SREX-3	1.50
SREX-5	0.01 M HNO_3	1.00	Organic from SREX-4	1.00
SREX-6	0.01 M HNO_3	0.50	Organic from SREX-5	0.50
SREX-7	Aqueous from SREX-1	3.00	SREX Solvent	1
SREX-8	Aqueous from SREX-7	1.50	SREX Solvent	0.5

The dispersion numbers were calculated from the following equation:

$$N_{D_I} = \frac{1}{t}\sqrt{\frac{\Delta Z}{g}}$$

where t is the time (in seconds) for the phases to disengage, ΔZ is the total height of the two phases (in meters), and g is the acceleration due to gravity (9.81 m/s^2) (Leonard et al. 1981).

The feed solution was prepared by mixing 2.5 mL of Solution 1, 2.5 mL of Solution 2, 1 mL of 15.7 M HNO_3, and 4 mL of water. This solution was contacted with 3 mL of SREX process solvent,(a) then portions of each phase were taken for subsequent contacts, as outlined in Table 2.1.

Samples were drawn from the aqueous phase from each contact. The concentrations of the bulk sludge components were determined by ICP/AES. Acid concentrations were determined by potentiometric titration with standard NaOH. Fluoride concentrations were determined potentiometrically using a fluoride-selective electrode. Radiochemical analyses were done to determine ^{90}Sr concentrations for the feed solution and each aqueous phase. Alpha energy analyses were performed for the feed solution and the aqueous phase from the first extraction.

2.4.3 TRUEX Experiment on Dissolved B-110 Sludge

For this experiment, $H_2C_2O_4$ (0.09 mL of 1 M) was added to a 4.5-mL portion of the aqueous phase from the first SREX extraction (Contact # SREX-1). This solution was then contacted three

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(a) The SREX process solvent consisted of 0.2 M di-t-butylcyclohexano-18-crown-6 dissolved in 1-octanol. The di-t-butylcyclohexano-18-crown-6 was purchased from Parish Chemical Company (Orem, Utah) and was derived from Lot # 3ISQ.

successive times with the TRUEX process solvent at an organic-to-aqueous phase ratio of 0.33. In all cases, the phases separated rapidly (within 60 s), and no interfacial crud was observed. The mixtures were centrifuged to ensure complete phase separation. The aqueous phase from each contact was analyzed by ICP/AES and for total alpha activity.

3.0 Results and Discussion

The results of experiments on pretreatment of Hanford tank sludges are presented in this section. The discussion is divided into five parts: 1) leaching of TRUs from NCRW sludge, 2) leaching of TRUs from U-110 sludge, 3) TRUEX processing of the acid leach solution from U-110 sludge, 4) SREX processing of dissolved B-110 sludge, and 5) TRUEX processing of dissolved B-110 sludge.

3.1 Leaching of TRUs from NCRW Sludge

Experiments were conducted to determine if the TRU elements (Pu and Am) could be leached from NCRW sludge so that the bulk of the sludge could be disposed of as LLW. Two approaches were taken: 1) leaching with carbonate/bicarbonate solution and 2) leaching with HNO_3. The carbonate/bicarbonate leach procedure involved mixing the sludge with a solution of K_2CO_3, then adjusting the pH to 8 by adding $KHCO_3$ and HNO_3. The leach was done at pH 8 because literature data suggest that the Pu solubility should be relatively high at this pH (Kim, Lierse, and Baumgartner 1983). The acid leach was considered because of the known solubilities of Pu and Am in acidic solution.

3.1.1 Leaching of TRUs from NCRW Sludge with Carbonate/Bicarbonate

The solutions generated from the washing of NCRW sludge with 1 M NaOH at 100°C contained very little TRU material; the amount of alpha activity in these solutions was below the detection limit. The total alpha activity in the various leach solutions from Experiments 76B and 76C and in the dissolved sludge solutions from 76B are listed in Table 3.1. Clearly, very little TRU material was leached under the conditions used here. It did appear that a slight increase in the amount of TRU material leached was achieved by adding an oxidant ($KMnO_4$); however, this would not be sufficient to render the sludge non-TRU (i.e., less than 100 nCi/g[a] TRU). The vast bulk of the TRU material (94.6%) remained in the sludge during the carbonate/bicarbonate leach portion of Experiment 76B. The sludge sample used contained 2285 nCi TRU/g of dry sludge. Thus, this method does not hold great promise for decontaminating NCRW sludge to the point where it can be considered a non-TRU waste.

Leaching TRUs from NCRW sludge with bicarbonate solution plus ozone (Table 3.2) also does not appear promising. Ozone did not affect the leaching behavior of the bicarbonate solution. About 4% of the TRUs was dissolved at pH 8 with (76D) or without (76B) ozone present.

3.1.2 Acid Leaching of TRUs from NCRW Sludge

Very little Zr in the NCRW sludge dissolved in HNO_3 in the absence of F^- ion. Greater than 93% of the Zr still remained in the sludge after treatment with 2 M HNO_3. This offered the

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[a] Class C limit set by the U.S. Nuclear Regulatory Commission (NRC) in 10 CFR 61.

Table 3.1. Results of TRU Leach from NCRW Sludge without Oxidant (76B) and with Oxidant, $KMnO_4$ (76C)

	76B		76C
Solution	Total alpha, dpm/mL	% of total	Total alpha, dpm/mL
First leach[a]	3926	3.6	5844
Second leach[a]	1407	1.8	2325
Dilute HNO_3 (pH = 3)	2567	1.6	
2 M HNO_3	12,155	6.6	
5.4 M HCl/0.9 M, HF[b]	147,527	86.4	

(a) Leached with carbonate/bicarbonate solution (pH 8) at 100°C for 5 h. In the case of 76C, the solution also contained 0.0001 M $KMnO_4$.

(b) Complete dissolution of the leached sludge for analysis.

Table 3.2. Results of TRU Leach from NCRW Sludge with Bicarbonate and Ozone (76D)

Solution	Total alpha, dpm/mL	% of total
Ozone Leach[a]	3322	4.2
Dissolved Sludge	65,685	95.8

(a) The sludge was slurried with carbonate/bicarbonate solution (pH 8), and ozone was bubbled through the solution for 1 h. The mixture was then heated (100°C) for 4 h.

possibility of leaching the TRUs from NCRW with an acid solution. However, acid leaching of NCRW sludge was not promising, since 86.4% of the TRU material remained in the sludge after the 2 M HNO_3 treatment (Table 3.1).

This result did not agree with results obtained earlier in which leaching of water-washed NCRW sludge with dilute (0.2 to 0.4 M) HNO_3 was found to dissolve greater than 90% of the Am and approximately 50% of the Pu (Swanson 1991b). In the present case, the sludge was washed with 1 M

NaOH at 100°C, whereas in the earlier work the sludge was washed with water at ambient temperature. This suggests that continued aging of the NCRW waste under alkaline conditions such as those found in the waste tanks may lead to the formation of TRU species that are increasingly difficult to leach with dilute nitric acid. Thus, acid leaching of TRUs from NCRW (following a hot alkaline wash) is not a viable pretreatment option.

3.2 Leaching of TRUs from Tank U-110 Sludge

The results of both alkaline and acid leaching are discussed here.

3.2.1 Alkaline Leaching of TRUs from U-110 Sludge

The results of the bicarbonate/carbonate leaching of TRUs from U-110 sludge are given in Table 3.3. A significant fraction (15.1%) of the total TRU material present in the sludge was leached in the initial treatment with bicarbonate/carbonate (without oxidant present). Introduction of ozone resulted in only a modest increase in the amount of TRU leached (an additional 7.0%). Although some TRU material was solubilized in the bicarbonate/carbonate solution, not enough TRU was removed to render the sludge a non-TRU waste. The sample of U-110 sludge used contained 530 nCi TRU/g sludge; removal of 22% by the bicarbonate/carbonate leaching would leave 410 nCi TRU/g, which exceeds the 100 nCi/g limit for TRUs.

3.2.2 Acid Leaching of U-110 Sludge

A portion of U-110 sludge was washed with 0.01 M NaOH and then leached with 2 M HNO_3. The amounts of TRU, ^{137}Cs, and ^{90}Sr found in the sludge wash, in the 2 M HNO_3 leach, and in the leached sludge are given in Table 3.4. The results indicate that there were 600 nCi TRU/g of dry U-110 sludge. Very little TRU material was found in the wash solution (below detection limit). Ninety-nine percent of the TRU activity was in the acid leach solution.

Table 3.3. Results of TRU Leach from U-110 Sludge with Bicarbonate/Carbonate and Ozone

Solution	Total Alpha, dpm	% TRU
Alkaline Wash	349	0.08
Water Wash	0	0
Carbonate/Bicarbonate Leach	65,640	15.1
Bicarbonate/Ozone Leach	30,300	7.0
2 M HNO_3 Leach	330,700	76.2
HCl Dissolution	4303	1.0
HF Dissolution	2718	0.6

Table 3.4. Results of Acid Leaching of Tank U-110 Sludge

Radionuclide	nCi in Wash	nCi in 2 M HNO_3 Leach	nCi in Leached Sludge
TRU	<0.14	211	2.2
^{137}Cs	1810	16,700	17
^{90}Sr	20	182,000	14,790

The weight of the wet sludge remaining after the acid leach step was 0.478 g. Thus, this residue contained 5 nCi TRU/g. If we assume that 50% of the weight of this residue is due to water (which we have often found for NCRW), this works out to 10 nCi/g dry residue, which is well below the 100 nCi/g NRC Class C limit for TRUs (10 CFR 61).

The U-110 sludge sample used here contained 52,100 nCi ^{137}Cs/g dry sludge. Ninety percent of the ^{137}Cs activity was in the acid leach solution. The other 10% was primarily in the sludge wash solution. The leached solids contained only 36 nCi ^{137}Cs/g of wet solids. The NRC Class A LLW limit (10 CFR 61) for ^{137}Cs is 1000 nCi/cm^3. Thus, if the acid-leached U-110 sludge were cast into grout, the resulting grout waste form would certainly fall below the Class A limit for ^{137}Cs.

The dry U-110 sludge contained 555,000 nCi ^{90}Sr/g sludge. Ninety-two percent of the ^{90}Sr was in the acid leach solution; the other 8% was in the leached solids. The leached solids contained 31,000 nCi ^{90}Sr/g wet solids. If the acid-leached sludge were cast into grout, the resulting grout waste form would exceed the Class A LLW limit (40 nCi/cm^3) for ^{90}Sr, but would be 2 orders of magnitude below the Class C LLW limit (7 x 10^6 nCi/cm^3) for this isotope.

Very little ^{99}Tc is present in the U-110 sludge. The amounts of ^{99}Tc in the samples analyzed were all below the detection limit. The analyses indicate that there is <40 nCi ^{99}Tc/g dry U-110 sludge, so Tc does not appear to be an issue for this particular waste type.

The behavior of the bulk sludge components is summarized in Table 3.5. A large fraction of the sludge did not dissolve in 2 M HNO_3. In particular, most of the Al and Si did not dissolve. The high molar ratio of Al to Si (the Al to Si ratio was ~3) suggested that there is an insoluble Al species present that is not an aluminosilicate. A significant fraction of the Fe also did not dissolve.

Most of the Na dissolved in the wash step, and less than 5% of the Na originally in the sludge remained after the 2 M HNO_3 leach step. All of the U present reported to the acid leach solution; this would have to be addressed when considering any further processing of this solution. On the other hand, all of the P present in the sludge was removed in the wash step, so this would not be

Table 3.5. Behavior of the Bulk Sludge Components in the Leaching of U-110 Sludge with Acid

Component	g/g sludge	% in wash	% in leach	% in residue
Al	1.47E-01	1.0	33.2	65.8
Na	1.13E-01	69.5	27.0	3.5
Si	4.03E-02	0.0	20.5	79.5
Fe	2.05E-02	0.0	62.9	37.1
U	1.32E-02	0.0	100.0	0.0
P	7.77E-03	100.0	0.0	0.0
Mn	5.08E-03	0.0	55.1	44.9
B	3.56E-03	3.9	1.9	94.2
Co	1.38E-03	0.0	74.3	25.7
Cr	1.26E-03	60.2	34.5	5.3
Ca	1.03E-03	22.7	63.8	13.4

routed to the Hanford Waste Vitrification Plant (HWVP).(a) Likewise, most of the Cr was also removed in the sludge wash step; only 34.5% of the Cr present might be routed to HWVP. Because Cr is a relatively minor component of the waste, it is not expected to present a major problem with regards to vitrification of the TRU-bearing acid leach solution.

The acid-leached sludge was analyzed for crystalline material by x-ray diffraction. Boehmite, $AlO(OH)$, was the dominant crystalline phase present. Gibbsite, $Al(OH)_3$, likely was also present, but this could not be confirmed unequivocally. At least one other minor crystalline phase was present, but could not be identified.

A second acid leaching experiment was conducted on a U-110 sludge sample derived from a different core. In this case, a small portion of sludge (0.328 g dry sludge) was washed with 0.1 M NaOH at room temperature, then leached with 2 M HNO_3 at 100°C. All of the detectable alpha activity was found in the acid leach solution. The alpha activities in the sludge wash solution and in the leached sludge were below detection limits. The weight of wet sludge remaining after the leaching step was 0.352 g, and this material contained less than 1 nCi of TRU.

Because the acid-leached sludge contains less than 100 nCi/g TRU, it can be concluded that a large fraction of the waste in Tank U-110 can be made suitable for grout feed by first washing with dilute NaOH, then leaching with 2 M HNO_3. The wash solution could be grouted along with the leached sludge. Unless the ^{137}Cs is separated from the wash solution, about 10% of the ^{137}Cs originally present in the sludge would be in the LLW form. The acid leach solution must be either

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(a) Phosphorus is known to cause problems in liquid fed ceramic melters such as those to be used in the HWVP; the maximum loading in glass for this element is 4 g P_2O_5/100 g of nonvolatile oxides.

vitrified directly, or treated further (e.g., TRUEX) to separate the TRU material for vitrification. A discussion of initial tests on the TRUEX processing of the leach solution is given in Section 3.3.

Obviously, leaching of U-110 sludge with 2 M HNO_3 was more successful in removing TRUs than was the acid leaching of NCRW sludge. The reason for this difference is not known, but there are two likely explanations: 1) the chemical form of the Pu in NCRW sludge might be more refractory towards acid dissolution than that in U-110 sludge, or 2) the TRUs are imbedded within the sludge particles in NCRW and are thus not accessible to the leaching solution.

3.3 TRUEX Experiments on the Tank U-110 Sludge Acid Leach Solution

An initial screening study was conducted on the applicability of the TRUEX process for extracting the TRUs from the U-110 acid leach solution. This study involved performing a series of batch contacts of the adjusted leach solutions with the TRUEX process solvent. The initial compositions of the aqueous phases are given in Table 3.6. The organic-to-aqueous phase ratio was 0.33 in each contact.

This screening study was plagued by the formation of interfacial crud. This crud may have been due to saturation of the organic phase with inert sludge components such as Fe or Al. Oxalic acid was added to complex these components in an attempt to prevent crud formation. The addition of oxalic acid had mixed effects with regards to the amount of crud formed. For example, Contact SXU110-1 ($[H_2C_2O_4]$ = 0.05 M) had much more crud than Contact SXU110-2 ($[H_2C_2O_4]$ = 0.1 M), but Contacts SXU110-3 and -4 ($[H_2C_2O_4]$ = 0.15 M and 0.2 M, respectively) had more crud than SXU110-2. As an alternative to oxalate, fluoride ion was added to complex bulk sludge components.

Table 3.6. TRUEX Contacts Using Tank U-110 Sludge Acid Leach Solution: Initial Concentrations in the Aqueous Phases and Interfacial Crud Observations

	Contact								
Component	SXU110-0 moles/L	SXU110-1 moles/L	SXU110-2 moles/L	SXU110-3 moles/L	SXU110-4 moles/L	SXU110-5 moles/L	SXU110-6 moles/L	SXU110-7 moles/L	SXU110-8 moles/L
Al	0.057	0.045	0.048	0.045	0.045	0.045	0.042	0.044	0.045
Fe	0.0072	0.0073	0.0077	0.0073	0.0072	0.0067	0.0000	0.0066	0.0067
K[a]	0.00	0.13	0.14	0.13	0.13	0.00	0.00	0.00	0.00
Na	0.0410	0.0071	0.0077	0.0073	0.0072	0.0558	0.0529	0.0554	0.0569
Si	0.0012	0.0071	0.0044	0.0053	0.0070	0.0177	0.0117	0.0302	0.0341
U	0.0013	0.0011	0.0010	0.0010	0.0009	0.0018	0.0019	0.0017	0.0018
HNO_3	2	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.2
$H_2C_2O_4$	0.2	0.05	0.1	0.15	0.2	0.1	0.15	0	0
HF	0	0	0	0	0	0	0	0.1	0.15
crud?	N	Y	Y	Y	Y	Y	Y	Y	Y

---

[a] The high K contents in Contacts SXU110-1 to -4 were due to the leaching of this particular sludge sample with $K_2CO_3/KHCO_3$ prior to the acid leaching (see Section 3.2.1).

The addition of HF seemed to decrease the amount of crud when compared with identical solutions prepared with $H_2C_2O_4$ (comparison of Contacts SXU110-5 and -6 with SXU110-7 and -8), but considerable amounts of crud were still observed.

Clearly, much more work is required to determine the conditions under which the TRUEX process can be applied to U-110 sludge acid leach solution without the formation of interfacial crud. The lack of crud formation in Contact SXU110-0 indicated that higher acid concentrations might help to alleviate the interfacial crud problem. The distribution coefficient for the alpha-emitting nuclides (primarily Am and Pu) in Contact SXU110-0 was 3; the extraction behavior would be improved at higher acid concentrations. Thus, future work should be directed at adjusting the feed solution to higher acid concentrations. Also, the effects of oxalic acid and HF on the extraction process should be explored in greater detail.

The Si content in Contact SXU110-0 was lower than in the other contacts; it is unclear if the Si content is related to crud formation. Isolation and characterization of the crud would be helpful in resolving this issue, but this proved to be difficult. Further attempts should be made because identification of the crud would assist in determining what adjustments should be made in the process chemistry to avoid this problem.

3.4 Test of the SREX Process on Dissolved Tank B-110 Sludge

The sludge in B-110 contains approximately 220 μCi of ^{90}Sr, so it was chosen for Sr removal studies. The process investigated for separating Sr from the bulk sludge waste was the SREX process (Horwitz, Dietz, and Fisher 1991). This process is a solvent extraction process in which Sr is extracted from HNO_3 solutions with a solvent consisting of 0.2 M DtBC18C6 dissolved in 1-octanol.

The SREX flowsheet tested in this experiment is shown in Figure 3.1. The flowsheet was tested by performing a series of batch contacts that were designed to simulate the countercurrent flow shown in Figure 3.1. The feed solution, which was prepared from dissolved B-110 sludge, was subjected to three successive contacts with the SREX process solvent. The organic phase from the first extraction contact was scrubbed twice with 0.5 M HNO_3, then was contacted three successive times with 0.01 M HNO_3 to strip the Sr.

The results from the extraction contacts are summarized in Figure 3.2 and Table 3.7. Greater than 99% of the Sr was extracted from the aqueous feed solution; the DF for ^{90}Sr was 250. Of the major sludge components present, only Na extracted to any extent, and this did not occur until the third extraction contact. Barium, which is a minor constituent of the waste, was extracted along with the Sr. Because the scrub steps were only tested on the organic phase from the first extraction contact, the behavior of Na in the scrubbing stages could not be determined. The amount of H^+ extracted was consistent with published data on the SREX process (Horwitz, Dietz, and Fisher 1991).

The concentration profile for ^{90}Sr is given in Figure 3.3. The behavior of ^{90}Sr can be summarized as follows:

- Greater than 99% of the ^{90}Sr was extracted from the aqueous solution.

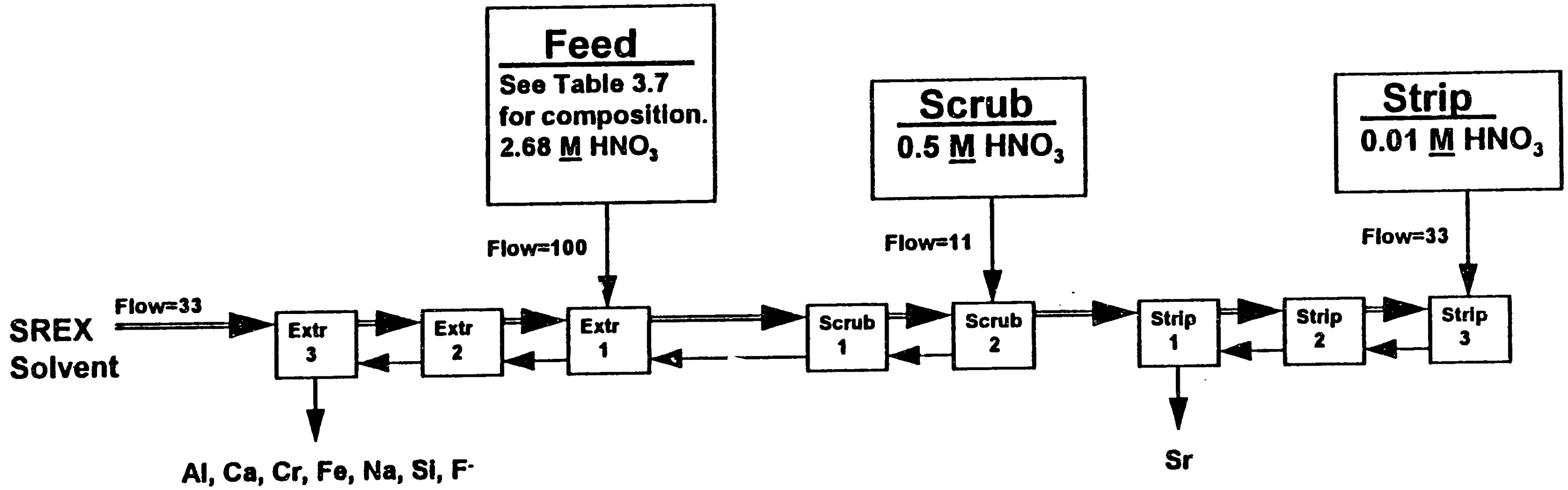

Figure 3.1. SREX Flowsheet Tested with Dissolved B-110 Sludge

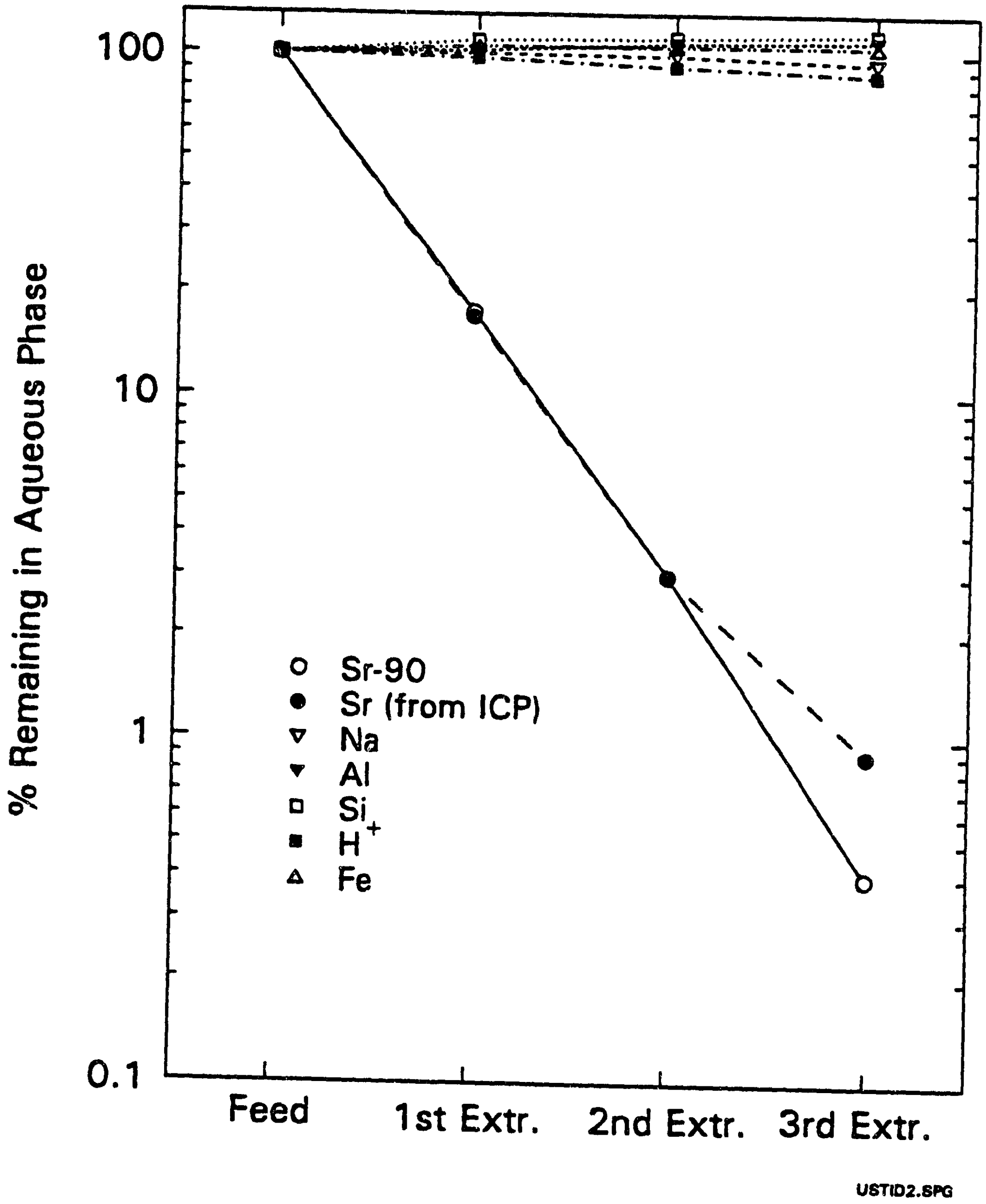

Figure 3.2. Results of SREX Extraction Contacts

- Eighty-eight percent of the extracted ^{90}Sr remained in the organic phase after the second scrub; this could likely be improved by using a more acidic scrub solution (e.g., 1 M HNO_3).
- Strontium-90 was stripped easily with 0.01 M HNO_3.

Table 3.7. Results of SREX Extractions for Dissolved Tank B-110 Sludge. The concentrations of each component in the feed are given in moles/L (except for ^{90}Sr, which is in nCi/mL).

Component	Feed Concentration	Extr. 1, % in feed[a]	Extr. 2, % in feed	Extr. 3, % in feed
Al	0.0042	102	107	109
Ba	1.4E-05	0	0	0
Ca	0.0027	104	104	100
Cr	0.0018	106	106	111
F	0.26	100	100	108
Fe	0.040	105	105	105
H^+	2.68	97.0	92.2	87.3
Na	0.105	100	99.0	94.3
Si	0.044	109	111	114
Sr	3.7E-4	16.8	3.0	0.9
^{90}Sr, nCi/mL	3000	17.3	3.0	0.4

(a) Percent of each component found in the aqueous phase after extraction.

Dispersion numbers were measured for each contact; these are summarized in the Table 3.8. Good phase disengagement was observed for all contacts except the two scrub contacts. The dispersion numbers for the two scrub contacts are at the lower limit for design of a workable process using centrifugal contractors. The reason for the low dispersion numbers in these two contacts is not known. Better phase disengagement might be achieved by modifying the composition of the scrub solution.

This experiment serves as a proof-of-principle that the SREX process can be used to separate ^{90}Sr from dissolved Hanford tank sludges. Further work will be needed to optimize the process flowsheet.

3.5 TRUEX Processing of Tank B-110 Sludge

The aqueous phase from the first SREX extraction done on the dissolved B-110 sludge was contacted three successive times with the TRUEX process solvent. The results are summarized in Table 3.9. Rapid phase disengagement was observed in all three contacts (N_{Di} = 0.0011 to 0.0017).

The low concentrations for the major sludge components (Al, Ca, Cr, Fe, Na, and Si) found in the aqueous phase from the third TRUEX extraction contact may have been due to an error in the analysis. These components showed little extraction in the first two extraction contacts, but the analysis of the aqueous phase from the third extraction indicated that approximately 20% of each of these components was extracted. This may be due to analytical error rather than a real phenomenon. Furthermore, the behavior of U is not reported because of suspected low quality of the U analysis data.

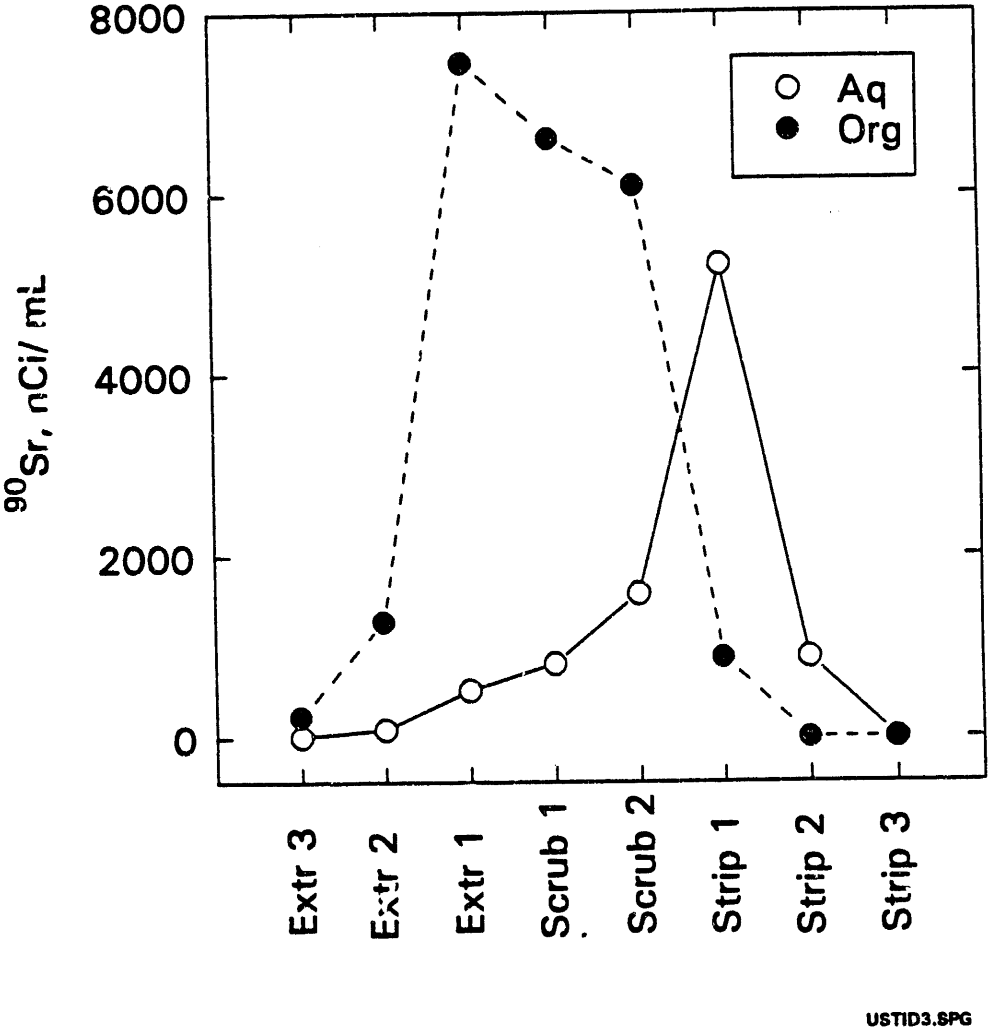

Figure 3.3. Concentration Profile for ^{90}Sr in the Extraction, Scrub, and Stripping Steps of the SREX Process

Despite the poor quality of the data from this TRUEX experiment, the following conclusions can be made:

- TRUs were extracted from the dissolved B-110 sludge (D_{TRU} was 37 in the first extraction contact).
- Bismuth was also extracted from the dissolved B-110 sludge (D_{Bi} was 7 in the first extraction contact).

Table 3.8. Dispersion Numbers for the SREX Solvent Extraction Contacts

Contact #	Phase height, mm	Break time, s	N_{Di}
SREX-1	26	50	0.0010
SREX-2	30	195	0.0003
SREX-3	22	150	0.0003
SREX-4	25	38	0.0013
SREX-5	17	40	0.0010
SREX-6	8	35	0.0008
SREX-7	25	52	0.0010
SREX-8	17	62	0.0007

Table 3.9. Results from the TRUEX Contacts with Dissolved Tank B-110 Sludge. Feed concentrations are given in moles/L.

Component	Feed Concentration	Extr. 1, % in feed[(a)]	Extr. 2, % in feed	Extr. 3, % in feed
Al	0.0043	102	100.0	83.7
Bi	0.0060	30.0	3.7	0
Ca	0.0028	96.4	96.4	78.6
Cr	0.0019	100	100	84.2
Fe	0.042	97.6	95.2	78.6
Na	0.105	99.0	96.2	80.0
Si	0.048	100	100	81.3
F^-	0.26	104	100	--
H^+	2.60	86.9	78.5	71.9
TRUs, nCi/mL	14.8	7.5	1.0	1.9

(a) Percent of each component found in the aqueous phase after extraction.

The second observation is significant because most previous investigations of the TRUEX process have paid little attention to the behavior of Bi. The measured distribution coefficient for Bi in this example was lower than expected based on Bi distribution measurements made in our laboratory (see the appendix). Based on those data, the D_{Bi} was expected to be 30 to 40. The lower D_{Bi} may have been due to complexation of Bi by the F^- present in the feed solution.

This test demonstrates that the TRUEX process can be applied to the pretreatment of B-110 sludge. Optimization of the TRUEX flowsheet for the processing of this waste will be the subject of a future study.

4.0 Conclusions and Recommendations

In this work, we have evaluated various pretreatment options for Hanford tank wastes. Actual tank wastes were used in these studies. It is unknown how well the composite sludge samples used here represented the entire tank contents, so caution should be used in the interpretation of the results. However, the results do provide a basis for further development work. The major findings of this work are shown below:

- Carbonate/bicarbonate leaching (with or without oxidant) of tank sludges is not a promising approach to removing TRUs from the bulk waste components.
- After treatment of U-110 sludge with 2 M HNO_3 at 100°C, the bulk of the sludge meets Class C LLW criteria for TRUs, ^{90}Sr, ^{137}Cs, and ^{99}Tc.
- Extraction of TRUs from the U-110 acid leach solution with CMPO will require adjustment of the process chemistry in order to avoid the formation of interfacial crud.
- The SREX process can be used to extract Sr from dissolved B-110 sludge.
- The TRUEX process can be used to extract TRUs from dissolved B-110 sludge.

Considerable work would be required before any of the pretreatment options could be implemented. The following is a brief list of work that should be undertaken to further develop the promising pretreatment methods investigated here:

- Additional acid leaching studies should be conducted on U-110 sludge. Variables should include HNO_3 concentration, temperature, and time of leaching. The leached sludge should be thoroughly analyzed to ensure that it will meet grout specifications.
- Further work needs to be done to define the conditions under which interfacial crud will not form during the TRUEX processing of the U-110 acid leach solution; this would involve adjusting acidity, oxalate concentration, etc. Also, the crud should be isolated and characterized, so that methods to alleviate its formation can be devised in a logical manner.
- Alternative methods should be evaluated for separating the TRUs from the U-110 acid leach solution.
- The conditions for dissolution of B-110 sludge need to be optimized.
- The SREX flowsheet for the extraction of Sr from B-110 should be further defined and tested.
- A more vigorous test of the TRUEX process for the pretreatment of B-110 sludge needs to be conducted.

- The combined Sr and TRU process that is being developed at Argonne National Laboratory (Horwitz et al. 1992) should be tested for removal of Sr and TRUs from B-110 sludge. Although this process is still under development, significant benefits would be realized from process simplifications.

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Appendix

Extraction of Bismuth with CMPO

Appendix

Extraction of Bismuth with CMPO

One of the earliest processes used at Hanford for the production of Pu involved the coprecipitation of Pu with bismuth phosphate. The Bi-containing wastes from these early Pu production runs are now stored in single-shell tanks at Hanford. If these wastes are pretreated using the TRUEX process, it is essential to understand the behavior of Bi in this process. Because there was a paucity of information regarding the extraction of Bi^{3+} by CMPO, we measured the extraction of Bi^{3+} with the TRUEX process solvent (0.2 M CMPO plus 1.4 M TBP in NPH) from nitric acid solutions.

A series of batch contacts (organic-to-aqueous phase ratio of 0.33) were made in which nitric acid solutions (0.1 to 10 M) of $Bi(NO_3)_3$ (0.001 M and 0.01 M) were mixed with the TRUEX solvent for 60 s, then centrifuged. The aqueous solution was analyzed for Bi before and after contact with the TRUEX solvent by atomic absorption spectroscopy. The final concentration of Bi in the organic phase was determined by mass balance. The results are shown in Figure A.1.

The data indicate that Bi^{3+} is extracted to a great extent by the TRUEX solvent. This extraction is assumed to be due to CMPO, because Bi^{3+} is not extracted by TBP in NPH under similar conditions (Richardson and Schulz 1968). The D_{Bi} was maximum at approximately 1 M HNO_3. When the initial [Bi] was 0.01 M, the D_{Bi} was lower than when the initial [Bi] was 0.001 M. The reason for the lower D_{Bi} at higher Bi concentration is not known, but it may have been due to loading of the solvent with Bi and HNO_3.

In some cases, oxalic acid was added in an attempt to suppress the extraction of Bi. Oxalic acid did lower D_{Bi}, but it still remained greater than 1. When $[HNO_3]$ was less than 5 M, the addition of oxalic acid caused Bi to precipitate. Thus, tests with oxalic acid were not performed for solutions in which $[HNO_3]$ was less than 5 M.

Given these results, a more in-depth study of the behavior of Bi in the TRUEX process is needed. It is not known what impact Bi will have on the vitrification of the HLW stream generated in the TRUEX processing of Hanford tank wastes, but it should be assumed that the separation of Bi from the TRUs is desirable. Further work is needed to determine how this could be achieved in the TRUEX process.

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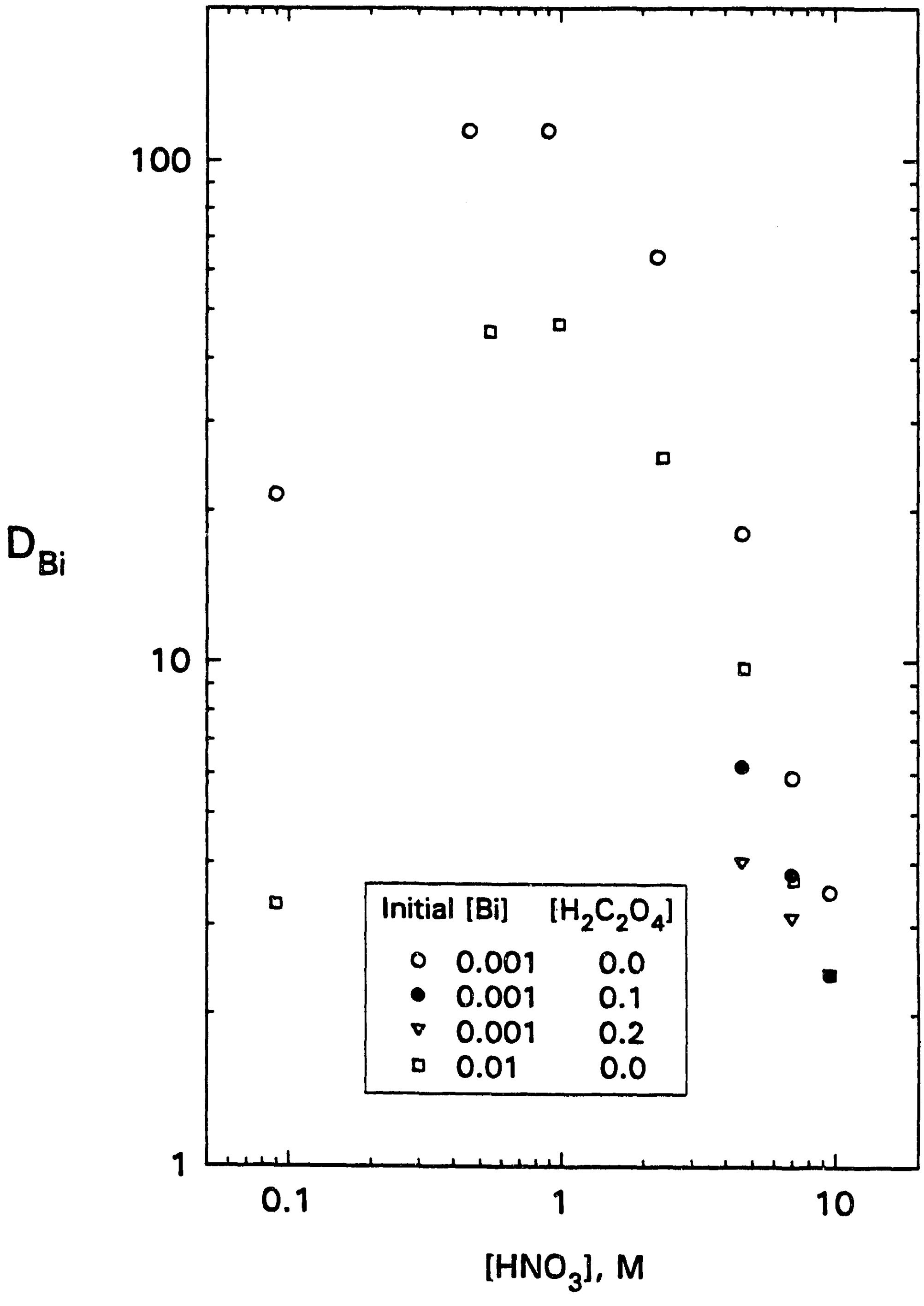

Figure A.1. Extraction of Bi With 0.2 M CMPO Plus 1.4 M TBP in NPH. Distribution coefficient (concentration of Bi in the organic phase divided by the concentration in the aqueous phase) as a function of equilibrium nitric acid concentration.

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