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Published February 1995

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ABSTRACT

Previous lab-scale work using batch contacts with sodium-bearing waste (SBW) simulant and samples of radioactive SBW from tank WM-185 suggested a potential flowsheet for partitioning actinides using solvent extraction (the TRUEX process). The suggested baseline flowsheet includes: an extraction section to remove actinides from liquid SBW into the TRUEX solvent (0.2 M CMPO, 1.4 M TBP in Isopar-L); a dilute nitric acid scrub (0.07-0.2 M HNO₃) to back extract co-extracted matrix materials (primarily Fe, Zr, and HNO₃) from the loaded solvent; thermally unstable complexants (TUCS) to back extract actinides; and a carbonate wash section for solvent cleanup. The purpose of the flowsheet development studies was to test and develop the baseline TRUEX flowsheet for ICPP SBW under continuous, countercurrent conditions using centrifugal contactors.

Two flowsheets were tested in four experiments using the Centrifugal Contactor Mockup which consists of sixteen stages of 5.5 cm diameter centrifugal contactors (procured from Oak Ridge National Laboratory). All testing was performed using non-radioactive SBW simulant. Potential flowsheets were evaluated with regards to the behavior of the non-radioactive components known to be extracted by the TRUEX solvent. Specifically, the behavior of the matrix components including iron, mercury, and zirconium was studied. In addition, neodymium was added to the SBW simulant as a surrogate for americium. In general, the behavior of the individual components closely paralleled that anticipated from batch testing. The results indicate that eight extraction stages are more than sufficient to reduce the actinide content in the SBW to levels well below the NRC Class A LLW criteria of 10 nCi/g. Iron was effectively scrubbed from the organic and 5% ended up in the high-activity waste (HAW) fraction. Zirconium scrubbing was not as effective and as much as 60% of the Zr in the feed could end up in the HAW fraction. The TUCS strip was effective at quantitatively stripping all metals except mercury from the TRUEX solvent. Carbonate washing effectively back extracted mercury from the stripped solvent, resulting in 99.4% of the mercury selectively partitioned from the SBW.

Potential problems, such as solids formation, which could arise because of solvent loading effects due to the countercurrent flow in the contactors, were not encountered. However, in the first experiment, flooding (aqueous in the organic) was encountered in at least two of the eight extraction stages. This problem was eliminated in the second experiment by increasing the rotor speed of the extraction section contactors from 3000 rpm (first experiment) to 3500 rpm. The countercurrent TRUEX flowsheets tested with non-radioactive SBW simulant will be used for future flowsheet development with actual SBW.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
ABSTRACT	v
LIST OF TABLES	ix
LIST OF FIGURES	xi
INTRODUCTION	1
SCOPE AND PURPOSE	3
EQUIPMENT DESCRIPTION	7
METHODOLOGY/EXPERIMENTAL PROCEDURE	13
SBW Simulant	13
TRUEX Solvent	13
Analytical	14
TRUEX Flowsheet Test #1	15
Solvent Wash Test #1	18
TRUEX Flowsheet Test #2	19
Solvent Wash Test #2	20
RESULTS AND DISCUSSION	21
TRUEX Flowsheet Test #1	21
Contactor Operation	21
Time To Reach Steady State	23
Steady-State Concentrations	27
Neodymium	29
Iron	29
Mercury	30
Zirconium	30
Flowsheet Changes	31
Solvent Wash Test #1	31
Contactor Operation	31
Steady-State Concentrations	31
Mercury	33
TRUEX Flowsheet Test #2	33
Contactor Operation	33
Steady-State Concentrations	34
Neodymium	34

Iron	37
Zirconium	38
Mercury	39
Solvent Wash Test #2	39
Contactor Operation	39
Steady-State Concentrations	41
Mercury	41
Solvent Degradation	41
Generic TRUEX Model Results	45
CONCLUSIONS AND RECOMMENDATIONS	47
Conclusions	47
Recommendations	48
REFERENCES	51

LIST OF TABLES

Table I.	Centrifugal Contactor Description	7
Table II.	Composition of Simulated Sodium-Bearing Waste (SBW)	14
Table III.	Flowrates and O/A Ratios From TRUEX Flowsheet Test #1	21
Table IV.	Percentage of Component in Each of the Product Streams for TRUEX Flowsheet Test #1	27
Table V.	Flowrates and O/A Ratios From Solvent Wash Test #1	32
Table VI.	Percentage of Component in Each of the Product Streams for Solvent Wash Test #1	32
Table VII.	Flowrates and O/A Ratios From TRUEX Flowsheet Test #2	33
Table VIII.	Percentage of Component in Each of the Product Streams for TRUEX Flowsheet Test #2	36
Table IX.	Component Distribution Coefficients for TRUEX Flowsheet Test #2	37
Table X.	Comparison of Distribution Coefficients to Laboratory Data	38
Table XI.	Flowrates and O/A Ratios From Solvent Wash Test #2	40
Table XII.	Percentage of Component in Each of the Product Streams for Solvent Wash Test #2	42
Table XIII.	Hg Distribution Coefficients for Solvent Wash Test #2	42
Table XIV.	Comparison of Experimental Results to GTM Results	46

LIST OF FIGURES

Figure 1.	Schematic of a Typical TRUEX Process Flowsheet . . .	4
Figure 2.	Centrifugal Contactor Mockup	8
Figure 3.	Simplified Flow Diagram of the Centrifugal Contactor Mockup	9
Figure 4.	Centrifugal Contactor Mockup Sampler Configuration	.11
Figure 5.	TRUEX Flowsheet for the Treatment of SBW	.16
Figure 6.	TRUEX Flowsheet Test #1	.17
Figure 7.	Solvent Wash Test #1 Flowsheet	.19
Figure 8.	Centrifugal Contactor Flooding Curve	.22
Figure 9.	H ⁺ Concentration Vs Time (TRUEX Flowsheet Test #1)	.24
Figure 10.	Nd Concentration Vs Time (TRUEX Flowsheet Test #1)	.24
Figure 11.	Fe Concentration Vs Time (TRUEX Flowsheet Test #1)	.25
Figure 12.	Hg Concentration Vs Time (TRUEX Flowsheet Test #1)	.25
Figure 13.	Zr Concentration Vs Time (TRUEX Flowsheet Test #1)	.26
Figure 14.	TRUEX Flowsheet Test #1 Steady-State Concentrations	28
Figure 15.	TRUEX Flowsheet Test #2 Steady-State Concentrations	35
Figure 16.	Solvent Purity Results	.44

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located in southeast Idaho at the US-DOE Idaho National Engineering Laboratory, formerly reprocessed highly enriched spent nuclear fuel to recover fissionable uranium. The radioactive raffinates from the combined PUREX/REDOX type uranium recovery processes were converted to granular solids (*calcine*) in a high temperature fluidized bed. During the course of reprocessing, a secondary waste stream, liquid sodium-bearing waste (SBW), was also generated primarily from equipment decontamination between campaigns and solvent wash activities. This SBW cannot be directly calcined due to the high sodium content and has historically been blended with reprocessing raffinates or non-radioactive aluminum nitrate [1] prior to calcination. As of November 1993, all raffinate solutions were calcined, thereby eliminating the option of waste blending to deplete the SBW inventory. Currently, approximately 1.5 million gallons of liquid SBW are stored at the ICPP in large stainless steel tanks.

A Notice of Noncompliance (NON) was filed by the Region 10 United States EPA and Idaho Department of Health and Welfare (IDHW) contending that the underground storage tanks at the ICPP do not meet the secondary containment requirements set forth in Title 40, Part 265.193 of the Code of Federal Regulations. The Department of Energy has agreed with the EPA and IDHW to remove the SBW from some of the underground storage tanks by 2009 and from the remaining tanks by 2015.

Several technologies are currently being evaluated to treat SBW. These include: 1) a numerous array of pretreatment options to concentrate the liquid or remove sodium nitrate, followed by direct calcination, and 2) partitioning of transuranics (TRUs), cesium, and strontium and immobilizing the resulting high- and low-activity segregated streams for final disposition. The TRans Uranic Extraction (TRUEX) process, developed by Horwitz and co-workers at Argonne National Laboratory (ANL) [2], is a potential TRU partitioning process for the SBW. Herein described are experimental results of TRUEX flowsheet development studies with simulated SBW using centrifugal contactors.

The TRUEX process uses octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) as the active extractant to partition the actinides from acidic solutions. Tributylphosphate (TBP) is used in the TRUEX solvent to prevent third phase formation (second organic phase) and a normal paraffin hydrocarbon (NPH) is used as the diluent. The typical TRUEX solvent is 0.2 M CMPO and 1.4 M TBP in Isopar-L. The process has been effectively used to remove actinides from acidic simulants and real waste solutions to well below the 10 nCi/gram NRC Class A LLW requirements. Typical solvent extraction tests use small continuous countercurrent extractions and batch contacts [3] to evaluate the efficiency of the TRUEX process. Large scale application has, of yet, not been realized. However, the TRUEX process has received attention in a number of countries with nuclear reprocessing capabilities (U.S., Canada, India, Italy, and Japan).

The applicability of the TRUEX process for use with ICPP acidic SBW was established in a Peer Review attended by a group of internationally known separation experts [3]. This panel of experts also evaluated strontium and cesium partitioning technologies of which the strontium extraction (SREX) process and inorganic ion exchange technologies for the removal of strontium and cesium, respectively, were recommended [3]. Even though all three of these technologies (TRUEX, SREX, and Cs ion exchange) must be evaluated and shown to be effective with SBW, the scope of work reported herein includes only the TRUEX process.

SCOPE AND PURPOSE

The purpose of these studies was to develop potential TRUEX solvent extraction flowsheets for ICPP SBW using centrifugal contactors. Sixteen stages of 5.5 cm diameter centrifugal contactors were procured from Oak Ridge National Laboratory and set up as part of the Centrifugal Contactor Mockup. The location of the mockup precludes the use of radioactive solutions. Therefore, all testing was performed using non-radioactive SBW simulant. Potential flowsheets were evaluated with regards to the behavior of the non-radioactive components. In addition, neodymium was added to the SBW simulant as a surrogate for americium. This allowed the separation efficiency of the actinides to be predicted. Potential problems, such as solids precipitation, which were not apparent with batch contacting experiments, but could arise because of the solvent loading effects due to the countercurrent solution flow in the centrifugal contactors, were also evaluated. The countercurrent TRUEX flowsheets developed with non-radioactive SBW simulant will be used for future countercurrent flowsheet development and testing with actual SBW.

A typical TRUEX process flowsheet, as shown in Figure 1, functions to fractionate and concentrate the radionuclides in an acidic aqueous feed stream, such as SBW, producing an aqueous high-activity waste (HAW) product stream and an actinide free low-activity waste (LAW) aqueous raffinate. The liquid-liquid extraction scheme is facilitated by countercurrent flow of the organic and aqueous phases through suitable process equipment, typically centrifugal contactors. Several sections composed of individual contactors or stages are necessary to effect the separation, including extraction, scrubbing and one or more stripping sections. The required number of individual stages in a section will depend on the distribution coefficients of various species, stream flow rates and compositions, and the required decontamination factor (DF) for a given species.

Several stripping sections, each using a different strip solution, may be specified to selectively partition and recover the various radionuclides (i.e., produce both americium and plutonium enriched products). A gross actinide separation, rather than the selective partitioning described by Horwitz [2] will most likely be applied to ICPP waste streams. Therefore, a

Figure 1. Schematic of a Typical TRUEX Process Flowsheet

single stripping agent, capable of removing all the actinides from the loaded organic solvent is advantageous. Thermally unstable complexants (TUCS) have been demonstrated for gross actinide stripping, effectively removing all actinides from the loaded TRUEX solvent, without precipitate formation with ICPP SBW [4]. The TUCS reagents are typically derivatives of diphosphonic acid. The TUCS reagent used in this study was 1-hydroxyethane-1,1-diphosphonic acid (HEDPA).

During processing, the organic can be degraded due to hydrolysis or radiolysis. Furthermore, trace quantities of extracted species often remain in the organic after stripping. Degradation products and residual metals in the solvent can have a negative impact on process performance. Solvent cleanup of the stripped organic phase typically includes a sodium carbonate wash to remove final traces of extracted species and solvent degradation products. Consequently, stripped organic solutions were contacted with dilute sodium carbonate. In addition, a dilute nitric acid rinse typically follows the sodium carbonate wash in order to re-acidify the solvent prior to recycling it to the extraction section. Acidifying the solvent will prevent emulsion problems in the extraction section.

It is important to note that a great deal of previous research has been conducted with the TRUEX solvent for nitric acid solutions, simulated waste solutions, and some small scale studies with real wastes. However, previous endeavors have not examined countercurrent TRUEX process flowsheets as applied to the SBW matrix. Such a study is the primary scope of these experiments.

EQUIPMENT DESCRIPTION

All testing was performed in the Centrifugal Contactor Mockup. The Centrifugal Contactor Mockup, as shown in Figure 2, consists of sixteen stages of 5.5 cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, flowmeters, filters, AC and DC motor drives, and a sample system. A simplified flow diagram is given in Figure 3.

Four stages of centrifugal contactors (four-pack) were procured from Oak Ridge National Laboratory (ORNL) in 1986. Twelve additional stages were procured from ORNL in 1993. A description of the centrifugal contactors is provided in Table I. All sixteen stages of contactors are basically identical with the exception of the type of motor.

Table I. Centrifugal Contactor Description

	Original Four-Pack	Additional Twelve Stages
Size	5.5 cm diameter	5.5 cm diameter
Motor	DC	1/3 HP AC
Controller	Individual DC motor controllers for each motor. 0-5,000 RPM control.	AC variable speed motor drive. 0-3,500 RPM control.
Material of Construction	304L s.s.	304L s.s.
Sample Ports	Aqueous and organic exiting each stage. Bottom access only.	Aqueous and organic exiting each stage. Top and bottom access.
Aqueous Feed Stages	Stage 4 only	Stages 2,3,and 4 of each four-pack

Figure 2. Centrifugal Contactor Mockup

21

Solution is fed to the contactors using Masterflex pumps. Surge lines, consisting of an 18-inch section of 1-inch tubing, were placed on the outlet of the pumps to dampen the surging flow. Rotameters were calibrated and used to monitor solution flowrates. Flowrates are adjusted by changing the pump speed using a ten-turn potentiometer.

Aqueous and organic feed solutions are filtered with two in-line sintered metal filters in series (20 micron and 5 micron). The filters are installed in glass tubing so that the buildup of any solids can be observed. In addition, pressure gauges were installed to monitor the pressure drop across the filters as solids accumulate on the filters.

Clear flexible Teflon tubing is used for inlet and outlet connections to the centrifugal contactors. This allows solution flow to be observed and solution characteristics to be noted, i.e., color changes of the organic solution between contactor banks.

The Centrifugal Contactor Mockup has provisions for sampling the aqueous and organic solution exiting each stage. Solutions exiting the contactors and draining to the product tanks are sampled with a block valve and spigot located on the drain lines. Sample ports were installed in each four-pack of contactors on the outlet lines between stages. On the original four-pack, the sample ports connect to the bottom of the lines. On the newer four-packs, samples can be pulled from either the top or bottom of the outlet lines. The 1/2 inch sample ports out of the bottom of the lines are filled with solution when the contactors are operating, requiring this solution to be flushed through the sample lines prior to pulling a representative sample. With the top sample ports, this problem does not exist. For purposes of this testing, all samples from the newer contactors were pulled out of the top of the lines.

Samples are pulled from the contactors utilizing the vacuum sample system shown in Figure 4. A vacuum pump is used to pull a vacuum of 10 to 15 inches Hg on a ballast tank. This ballast tank is connected to a sampler. Opening and then closing a block valve connecting the sampler with the ballast tank evacuates the sample bottle. Opening the needle valve between the sampler and desired sample location draws solution from the contactor

Figure 4. Centrifugal Contactor Mockup Sampler Configuration

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into the bottle. The use of a needle valve allows the sample flowrate to be controlled. During sampling, it is important that the sample be pulled slowly so not to disrupt the flowrate significantly enough to affect steady-state conditions. The needle valves allow the samples to be pulled over several minutes instead of all at once.

An air purge system is connected to the contactor bearing housings. Purge air is required in order to protect the motor body, shaft, and bearings from corrosive process fumes. Air to the bearing housings passes through four rotameters, one for each contactor four-pack. The rotameters control the air flowrate from 0 to 5 scfh. Air from each rotameter is split to feed each of the four bearing housings. Orifices were placed in the lines to each bearing housing to keep the air flowrate into each housing approximately equivalent. The offgas from the bearing purge system combines with the offgas from the feed and product tanks and vents out of the building.

METHODOLOGY/EXPERIMENTAL PROCEDURE

SBW Simulant

For the purposes of this study, the behavior of non-radioactive components in simulated SBW was evaluated. Using the analytical results obtained from characterization of SBW waste solution, a non-radioactive simulant was prepared to represent the average chemical composition of the major non-radioactive matrix components in the SBW tanks. In addition, neodymium was added to the simulant as a surrogate for americium. The chemical composition of the SBW simulant is shown in Table II. It should be noted that the Zr concentration in the prepared SBW simulant was $7.70\text{E-}05 \text{ M}$ which is much less than the desired concentration of $1.00\text{E-}03 \text{ M}$ due to a makeup error. This low Zr concentration resulted in indeterminate and/or inaccurate zirconium material balances and distribution coefficients in each of the contactor tests since many of the samples were on the borderline of analytical detection limits for Zr. Unfortunately, the low Zr concentration in the feed was not discovered until testing was nearly complete or additional Zr could have been added to the feed to provide more conclusive analytical results. The concentrations of all other components were very close to the desired values.

Prior to testing, the SBW simulant was filtered with a 2 micron sintered metal filter to prevent plugging of the filters on the aqueous feed line during operation. The specific components evaluated in this study include those species extracted by the TRUEX solvent: acid, neodymium, iron, mercury, and zirconium.

TRUEX Solvent

The TRUEX solvent composition used in all TRUEX flowsheet studies reported herein was 0.2 M CMPO and 1.4 M TBP in Isopar-L and was prepared by the ICPP Quality Control (QC) Laboratory. The purity and composition of the TRUEX solvent were established prior to use in the centrifugal contactors. Horwitz [5] reports that impurities in the CMPO, resulting from acid hydrolysis, radiolytic degradation, or residual manufacturing impurities, may hinder the ability to strip the actinides from the TRUEX solvent. The distribution coefficient for americium, D_{Am} , is particularly

Table II. Composition of Simulated Sodium-Bearing Waste (SBW)

Component	M	Component	M
Acid (H ⁺)	1.31	K	1.41E-1
Al	5.63E-01	Mn	1.42E-2
B	1.40E-02	Mo	1.49E-3
Cd	2.05E-06	Na	1.17
Ca	3.39E-02	NO ₃	4.46
Ce	3.63E-04	Ni	1.63E-03
Cl	3.52E-2	Pb	9.80E-04
Cs	7.52E-5	PO ₄	<9.18E-3
Cr	5.63E-03	Sr	5.28E-04
F	9.66E-2	SO ₄	3.86E-2
Fe	2.45E-2	Zr	7.70E-05
Hg	1.17E-03	Nd	3.71E-03

sensitive to CMPO impurities [5]. Therefore, D_{Am} was evaluated as a function of nitric acid concentration from HNO₃ solutions to evaluate CMPO purity and solvent composition. This method of determining americium distributions as a function of nitric acid concentration was established as a quality control procedure and was used to test the initial TRUEX solvent and the TRUEX solvent product from each flowsheet test [6]. If the results were comparable to literature values [5], the solvent was suitable for extraction studies.

Analytical

Experimental results obtained from batch contacts with SBW simulant indicate HEDPA is extremely effective at quantitatively back extracting all metals, except mercury, from the TRUEX solvent [4]. Mercury can be effectively stripped from the organic with >5 M HNO₃ or 0.25 M Na₂CO₃ [9,10]. Consequently, the organic samples were first contacted with 0.25 M HEDPA in 0.05 M HNO₃ and then with 0.25 M Na₂CO₃. To insure quantitative metal recovery in a single contact, an O/A ratio of 0.4 was used. The HEDPA was assumed to strip all of the Nd, Fe, and Zr, but not the Hg, out of the organic phase. The Na₂CO₃ was assumed to strip

all of the Hg out of the organic phase. The aqueous phase from the HEDPA strip was separated from the organic and submitted for Nd, Fe, and Zr analysis. The aqueous phase from the Na_2CO_3 strip was separated from the organic and submitted for Hg analysis. This procedure provided an indirect measure of organic phase compositions and allowed the use of material balances to validate experimental results. All aqueous sample analyses were performed by the ICPP Analytical Department using Inductively Coupled Plasma (ICP) Atomic Absorption Spectroscopy.

TRUEX Flowsheet Test #1

Based on the results of TRUEX testing performed utilizing radioactive tracers with simulated SBW and computer modelling with the Generic TRUEX Model (GTM), a potential TRUEX flowsheet was developed for the separation of actinides from SBW [4]. This flowsheet, as shown in Figure 5, consists of five stages of extraction, four stages of 0.2 M HNO_3 scrub, five stages of 0.25 M HEDPA strip, two stages of 0.25 M Na_2CO_3 solvent wash, and one stage of 0.1 M HNO_3 rinse. HEDPA was chosen over nitric acid and oxalic acid for the strip section due to the ability to effectively strip actinides without precipitate formation [4]. The simulated SBW, with an average composition of the ICPP SBW tanks, was used as the feed for the flowsheet.

This flowsheet was used as a basis for TRUEX Flowsheet Test #1. However, due to the limited flexibility in feed locations to the sixteen stages of centrifugal contactors, several changes were made. The Centrifugal Contactor Mockup was configured for eight stages of extraction, four stages of scrub, and four stages of strip. The concentration of HEDPA in the strip solution was reduced from 0.25 M to 0.04 M in order to minimize the quantity of phosphorus in the high activity waste stream. The resulting flowsheet used for TRUEX Flowsheet Test #1 is shown in Figure 6.

Prior to testing, the solvent was washed with four stages of 0.25 M Na_2CO_3 and four stages of 0.1 M HNO_3 rinse at O/A ratios of 4 and 3, respectively. The purpose of the solvent wash was to remove degradation products and manufacturing impurities which may have been in the fresh solvent and to acidify the solvent prior the extraction contacts. The solvent was acidified in order to be consistent with recycled solvent in the TRUEX

Figure 5. TRUEX Flowsheet for the Treatment of SBW

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Component	Sodium Waste Feed (Molar)	TRUEX Solvent Feed	LAW Raffinate (Molar)	Scrub Feed (Molar)	TUCS Strip Feed (Molar)	HAW Strip Product (Molar)	Carbonate Wash Feed (Molar)	Acid Rinse Feed (Molar)	Carbonate Wash Product (Molar)	Acid Rinse Product (Molar)
	1	2	3	4	5	6	7	8	9	10
HNO ₃	1.5		1.25	0.2	0.05	0.05		0.1		0.09
Na ₂ CO ₃							0.25		0.25	
HEDPA					0.25	0.25				
Fe	2.45E-02		2.18E-02			3.66E-08			2.62E-16	4.52E-19
Al	0.545		0.485			3.09E-10			1.24E-20	2.07E-23
Na	1.327		1.182			7.51E-10			3.02E-20	5.03E-23
Ca	4.35E-02		3.87E-02			2.46E-11			9.91E-22	1.65E-24
Cd	1.84E-03		1.64E-03			1.42E-08			5.73E-19	9.53E-22
Ag	1.76E-05		1.57E-05			9.97E-15			4.01E-25	6.67E-28
F	6.32E-02		5.62E-02			7.92E-05			4.85E-05	6.25E-09
SO ₄	3.23E-02		2.88E-02			7.41E-12			2.98E-22	3.60E-25
PO ₄	9.44E-03		8.41E-03			1.52E-09			6.12E-20	7.40E-23
B	1.56E-02		1.04E-02			1.05E-02			1.88E-13	3.12E-16
Hg	2.03E-03		1.79E-03			4.47E-05			4.43E-05	8.12E-05
Cr(VI)	5.74E-03		9.94E-04			1.23E-02			4.96E-13	8.25E-16
Radionuclides										
Sr	6.23E-06		5.55E-06			3.53E-15			1.42E-25	2.36E-28
Cs	3.10E-04		2.76E-04			1.76E-13			7.06E-24	1.17E-26
Ba	4.59E-05		4.09E-05			2.60E-14			1.05E-24	1.74E-27
Zu	1.57E-08		5.26E-15			4.19E-08			8.75E-19	1.42E-22
Ce	2.08E-10		3.37E-17			5.55E-10			2.88E-20	3.94E-24
Tc	1.01E-05		9.85E-07			1.30E-05			5.47E-05	2.38E-07
ACTINIDES										
Am	8.82E-08		1.18E-12			2.35E-07			6.13E-18	1.79E-21
Np	3.16E-06		1.59E-06			3.66E-06			1.09E-16	5.45E-17
Pu	2.29E-05		2.41E-14			6.11E-05			5.67E-15	1.83E-20
U	3.77E-04		4.44E-14			1.01E-03			2.08E-14	1.91E-19
Activity nCi/g	348.5		0.22			1109				
Volume	400.0	150.0	449.3	50.0	150.0	150.0	30.0	15.0	30.0	15.8

Figure 6. TRUEX Flowsheet Test #1

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process, which is acidified after the Na₂CO₃ wash to prevent emulsions from forming when it is recycled back to the extraction section.

The purpose of TRUEX Flowsheet Test #1 was to 1) evaluate the overall operability of the centrifugal contactors, 2) determine the operational time required for the mass transfer in the contactors to reach steady-state, 3) determine the concentrations of H⁺, Nd, Fe, Hg, and Zr at steady-state, and 4) determine if any precipitation or third phase formation problems exist with this flowsheet. The time required to reach steady-state was determined by sampling aqueous and organic product streams from each contactor four-pack at ten minute intervals and determining when component concentrations were no longer changing. These data are required in order to determine how long to operate the contactors prior to taking steady-state samples. Based on previous experience, it was expected that steady-state would be reached in about 20 minutes.

TRUEX Flowsheet Test #1 was performed as follows. Based on the results of hydraulic performance of the centrifugal contactors with PUREX solvent, the contactors were started at 3000 RPM. The scrub and strip solution flows were then established. Once aqueous solution was seen exiting the

extraction and strip sections, organic flow was started. When organic solution was seen exiting the last stage of the strip section, simulated SBW feed solution flow was started. At intervals of approximately 20, 30, 40, and 50 minutes after the start of SBW feed, samples were taken from each of the streams (aqueous and organic) exiting each four-pack. Sightglass readings on each of the feed tanks were also taken in order to determine actual solution flowrates based on tank depletion rates. After the last samples were taken, the simulated SBW feed solution flow was stopped. After approximately 10 minutes, organic solution flow was stopped. When organic solution could no longer be seen exiting the contactor four-packs, the scrub and strip solution flows were stopped. The contactor motors were then turned off when aqueous solution no longer was seen exiting the contactor four-packs.

Solvent Wash Test #1

The centrifugal contactors were flushed with water and set up for the solvent wash portion of the testing as shown in Figure 7. The solvent wash testing was also performed at a rotor speed of 3000 rpm. After starting the contactors, the carbonate wash and acid rinse solution flows were established. When the aqueous solution was seen exiting the two four-packs, organic solution flow was started. Forty minutes after the start of organic feed, samples were taken from each of the streams (aqueous and organic) exiting each contactor four-pack. Feed tank sightglass readings were also taken to determine actual solution flowrates based on tank depletion rates. Operation of the contactors was continued until all of the TRUEX solvent had been processed. When organic solution could no longer be seen exiting the contactor four-packs, the carbonate wash and acid rinse solution flows were stopped. The contactor motors were then turned off when aqueous solution no longer was seen exiting the contactor four-packs. The centrifugal contactors were then flushed with water.

The purpose of Solvent Wash Test #1 was to 1) determine how well Hg in the solvent from TRUEX Flowsheet Test #1 was stripped with 0.25 M Na_2CO_3 , 2) evaluate the effectiveness of the solvent wash in removing any degradation products which may have formed in the TRUEX solvent, and 3) prepare the solvent for additional TRUEX testing. The effectiveness of the solvent wash in removing degradation products was evaluated by experimentally determining

Figure 7. Solvent Wash Test #1 Flowsheet

D_{Am} as a function of nitric acid concentration using the TRUEX solvent before and after the solvent wash [6]. The results were then compared to literature values and values obtained with the initial organic feed solution.

TRUEX Flowsheet Test #2

Based on the results of TRUEX Flowsheet Test #1, the SBW TRUEX flowsheet was modified and a second test was performed. The rotor speed of the contactors was increased from 3000 rpm to 3500 rpm to prevent flooding in the extraction section. Also, the scrub flowrate was increased from 0.125 LPM to 0.20 LPM and the nitric acid concentration of the scrub feed was reduced to 0.07 M to increase the amount of Fe scrubbed from the TRUEX organic.

The purpose of TRUEX Flowsheet Test #2 was to 1) determine if observed flooding problems in the extraction section during TRUEX Flowsheet Test #1 could be alleviated by increasing the

rotor speed, 2) determine if the amount of Fe scrubbed out of the organic was increased with this flowsheet, 3) determine the steady-state concentrations of H⁺, Nd, Fe, Hg, and Zr with this modified flowsheet, and 4) determine distribution coefficients of H⁺, Nd, Fe, Hg, and Zr in the extraction, scrub, and strip sections of the flowsheet. Distribution coefficients were determined by sampling the aqueous and organic phases exiting one stage in each of the contactor four-packs.

This flowsheet test was performed in the same manner as TRUEX Flowsheet Test #1 except samples were taken only once, 40 minutes after the start of the SBW simulant flow, ensuring steady-state operation was obtained.

Solvent Wash Test #2

The organic product from TRUEX Flowsheet Test #2 was washed under the same conditions as Solvent Wash Test #1 with the following exceptions. The O/A ratio in the sodium carbonate wash section was increased from 1.0 to 1.5 in order to reduce the quantity of sodium carbonate waste generated. In addition, solution exiting the first and second sodium carbonate stages was sampled in order to determine Hg distribution coefficients.

The purpose of Solvent Wash Test #2 was to 1) determine distribution coefficients of Hg in the solvent wash section of the flowsheet, 2) evaluate the effectiveness of the solvent wash in removing any degradation products which may have formed in the TRUEX solvent, and 3) prepare the solvent for additional TRUEX testing. The effectiveness of the solvent wash in removing degradation products was evaluated by experimentally determining D_{Am} as a function of nitric acid concentration using the TRUEX solvent before and after the solvent wash. The results were then compared to literature values and values obtained with the initial organic feed solution.

RESULTS AND DISCUSSION

TRUEX Flowsheet Test #1

Contactor Operation

Actual solution flowrates for TRUEX Flowsheet Test #1 were calculated from feed tank depletion rates and are compared to the desired flowrates in Table III. The aqueous and organic feed flowrates were lower than the desired flowrates. The scrub and strip flowrates were as expected. The resulting O/A ratio in each section was only slightly different from the desired value.

Table III. Flowrates and O/A Ratios From TRUEX Flowsheet Test #1

Section	Feed	Flowrate (LPM)		O/A Ratio		Total Flow
		Desired	Actual	Desired	Actual	
Extraction	Org	0.375	0.32	0.33	0.346	1.24 LPM
	Aq	1.0	0.80			
Scrub	Aq	0.125	0.124	3.0	2.58	0.44 LPM
Strip	Aq	0.50	0.49	0.75	0.65	0.81 LPM

At the flowrates the contactors were operated, and at the rotor speed of 3000 rpm, flooding problems were not anticipated. However, the solution exiting the stage four organic weir contained approximately 50% aqueous solution and the solution exiting the stage eight organic weir contained approximately 2% aqueous solution. No flooding was seen in any other solutions exiting each four-pack. Samples were not taken between stages within a contactor four-pack so it is not known if any other stages in the extraction section were flooded.

Prior to performing this test, hydraulic testing was performed using 0.1 M HNO_3 and 30% TBP in n-dodecane (PUREX solvent). The resulting flooding curves are shown in Figure 8. The area below the lines represents flooded conditions. Flooding was defined as greater than 1% cross phase entrainment. At an

Figure 8. Centrifugal Contactor Flooding Curve

O/A of 0.35, a rotor speed of 3000 rpm, and a total throughput of 1.24 LPM it was expected that the centrifugal contactors would be well within an acceptable range of operation. Two possibilities were identified which could have caused the flooding problems; 1) the residence time in the centrifugal contactors was not sufficient for the aqueous/organic dispersion to break due to poor phase separation in the extraction section of the flowsheet, or 2) the higher organic densities associated with the TRUEX solvent, combined with the weir system design, resulted in aqueous solution exiting the organic weir. The density of the TRUEX solvent in the extraction section was in the range of 0.90 to 0.915 kg/L, whereas the PUREX solvent density is approximately 0.82 to 0.85 kg/L.

Phase separation can be quantitatively expressed by calculating a dispersion number using the following equation [7]:

$$N_{Di} = \frac{1}{t} \sqrt{\frac{h}{g}}$$

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). Using washed TRUEX solvent and SBW simulant, a dispersion number of 0.0012 was obtained. With this large of a dispersion number ($> 8.0\text{E-}04$), poor phase separation is not likely to be the cause of the flooding problem [7]. More likely, the higher densities associated with the TRUEX solvent, along with the weir system which was originally designed for the PUREX process, are believed to have caused the flooding problem. If this is the case, increasing the centrifugal contactor rotor speed would move the dispersion band away from the organic weir overflow and prevent aqueous solution from exiting with the organic. The rotor speed was increased to 3500 rpm for TRUEX Flowsheet Test #2.

Time To Reach Steady State

The concentrations of H^+ , Nd, Fe, Hg, and Zr as a function of time after the start of SBW simulant feed is given in Figures 9 through 13 for each of the streams sampled. It was assumed that steady state was reached when the concentrations of the components varied by less than the analytical error associated

Figure 9. H+ Concentration Vs Time (TRUEX Flowsheet Test #1)

Figure 10. Nd Concentration Vs Time (TRUEX Flowsheet Test #1)

Figure 11. Fe Concentration Vs. Time (TRUEX Flowsheet Test #1)

Figure 12. Hg Concentration Vs. Time (TRUEX Flowsheet Test #1)

Figure 13. Zr Concentration Vs. Time (TRUEX Flowsheet Test #1)

with the sample analyses ($\pm 10\%$ for Zr, Nd, and Fe; $\pm 20\%$ for Hg). The H^+ , Nd, and Fe reached steady state within 20 minutes. The large analytical uncertainty associated with the Hg results makes it difficult to determine whether steady state was reached. The Zr did not appear to reach steady state as quickly, possibly due to the analytical detection limit problem previously mentioned. The concentration of Zr in the first sample pulled for each of the streams was higher than the concentration in the remaining samples. The Zr reached steady state in approximately 30 to 40 minutes. Based on these results, samples for future TRUEX flowsheet testing should be taken a minimum of 40 minutes after feed solution flow is started.

Steady-State Concentrations

The concentrations of H^+ , Nd, Fe, Hg, and Zr at steady state are given in Figure 14. A material balance for each of the components is given in Table IV. The values in Table IV were normalized to obtain an overall material balance of 100%. A discussion of the behavior of each of the components follows.

Table IV. Percentage of Component in Each of the Product Streams for TRUEX Flowsheet Test #1

Stream	Nd	Fe	Hg	Zr	H^+
Aq. Raffinate	< 0.17% (<0.16%)	83.5% (84.0%)	3.7% (3.5%)	23.5% (30.7%)	84.6% (86.1%)
Strip Product	108.5% (99.7%)	15.9% (16.0%)	2.5% (2.3%)	50.4% (65.6%)	13.4% (13.6%)
Organic Product	< 0.15% (<0.14%)	0.03% (0.03%)	101.3% (94.2%)	< 2.8% (<3.7%)	0.3% (0.3%)
Percent Recovery	108.8%	99.43%	107.5%	76.7%	98.3%

() = Normalized percentage

Figure 14. TRUEX Flowsheet Test #1 Steady-State Concentrations

	SBW Feed 1	Organic Feed 2	LAW Raff. 3	Stage 5 Aqueous 4	Stage 4 Organic 5	Stage 8 Organic 6	Stage 9 Aqueous 7	Scrub Feed 8	Stage 12 Organic 9	Strip Feed 10	Strip Product 11	Organic Product 12
H ⁺ M	1.31	0.0132	1.04	1.37	0.82	0.82	1.98	0.20	0.25	0.01	0.31	0.012
TUCS										0.04	0.04	
Nd M	3.71E-03		<5.6E-06	<5.6E-06	1.87E-04	9.49E-03	7.06E-04		9.58E-03		9.58E-03	<1.4E-05
Hg M	1.17E-03		3.77E-05	2.49E-04	5.14E-04	3.64E-03	4.04E-04		3.26E-03		4.73E-05	2.96E-03
Fe M	0.0245		0.0177	0.0227	0.0156	0.0181	0.0218		0.00877		0.00638	2.07E-05
Zr M	7.7E-05		1.57E-05	1.77E-05	1.75E-05	1.10E-04	1.19E-05		1.08E-04		6.33E-05	<5.5E-06
Flow LPH	0.8	0.32	0.924	0.924	0.32	0.32	0.124	0.124	0.32	0.49	0.49	0.32

Neodymium

Neodymium was added to the SBW simulant as a surrogate for americium. Less than 0.16% of the Nd remained in the aqueous raffinate. This equates to an overall decontamination factor, $DF = [Nd_{feed}]/[Nd_{raf}]$, of greater than 662. However, the analytical detection limit for Nd was reached with the stage five aqueous solution, so this DF was obtained with only four stages of extraction. The DF with all eight stages of extraction is expected to be much greater.

The four stages of HEDPA strip removed greater than 99.85% of the Nd from the organic. Again, the lower detection limit for Nd was reached.

The behavior of the Nd indicates that this flowsheet will be very effective in extracting americium from SBW and stripping the americium with HEDPA. In order to verify that Nd is a good surrogate for Am, samples were taken in TRUEX Flowsheet Test #2 to determine distribution coefficients of Nd in each of the flowsheet sections for comparison to experimental Am distribution coefficients obtained from batch contacts with actual SBW. In addition, Nd distribution coefficients will allow the actual removal efficiency of Nd to be calculated since the analytical detection limits were reached in the raffinate stream.

Iron

Eighty-four percent of the Fe in the SBW feed remained in the aqueous raffinate and 16% exited in the strip product. Fifty two percent of the Fe that was extracted into the organic phase was scrubbed back into the aqueous phase in the scrub section. Based on previous batch experiments with SBW, it was expected that nearly all of the Fe would scrub out of the organic [8]. It is desired to minimize the amount of Fe in the strip product in order to minimize the quantity of non-radioactive components in the final HAW form. The distribution coefficient of Fe decreases as the acid concentration decreases [8]. It is believed that the Fe was not scrubbed as well as expected due to the higher acid concentration in the organic phase resulting from the countercurrent solution flow. The acid concentration of the scrub feed was 0.2 M HNO_3 . The acid concentration of the aqueous exiting the scrub section was 1.98 M. As a result, the acid

concentration in the organic phase was only reduced to 0.25 M in the scrub section, whereas four batch contacts with 0.2 M HNO_3 are expected to reduce the acid concentration of the organic to less than 0.1 M HNO_3 . Adjustments were made to the scrub feed flowrate and acid concentration in TRUEX Flowsheet Test #2 to increase the amount of Fe scrubbed from the organic.

The HEDPA strip was very effective in back-extracting the Fe that was not scrubbed out of the organic phase. Essentially all of the Fe in the organic phase (99.8%) was removed with four stages of 0.04 M HEDPA strip.

Mercury

As expected, Hg was extracted from the SBW and remained in the organic phase. Only 3.5% of the Hg in the SBW feed remained in the aqueous raffinate and 2.3% exited with the strip product. Two strip solutions have been identified to back-extract Hg from the TRUEX solvent; sodium carbonate and concentrated HNO_3 (>5 M) [9,10]. The effectiveness of sodium carbonate in removing Hg was evaluated in the TRUEX solvent wash tests discussed later in this report.

Zirconium

Approximately 67% of the Zr in the SBW feed exited in the strip product and 33% remained in the aqueous raffinate. Greater than 95% of the Zr entering the strip section was stripped with four stages of 0.04 M HEDPA. The lower detection limits for Zr were reached in the organic product so it is unknown exactly how much of the Zr was stripped. It should be noted that a poor overall material balance was obtained for Zr (76.7%). The low material balance is attributed to analytical errors associated with the low Zr concentration and detection limits.

It was anticipated that adjustments made to the scrub feed flowrate and acid concentration for TRUEX Flowsheet Test #2 would increase the amount of Zr scrubbed from the organic; thereby reducing the amount of Zr in the strip product.

Flowsheet Changes

Based on the results of this test, several changes were made to the SBW TRUEX flowsheet for TRUEX Flowsheet Test #2. The rotor speed of the contactors was increased from 3000 rpm to 3500 rpm. It was expected this would prevent flooding from occurring in the extraction section. Also, the scrub flowrate was increased from 0.125 LPM to 0.20 LPM and the nitric acid concentration of the scrub feed was reduced to 0.07 M. It is expected that these changes will reduce the amount of Fe and Zr in the strip product.

Solvent Wash Test #1

Contactor Operation

Prior to performing Solvent Wash Test #1, a sample of the organic product from TRUEX Flowsheet Test #1 was contacted with 0.25 M Na_2CO_3 in the laboratory at O/A ratios of 3 and 1. The purpose of these contacts was to determine if a precipitate forms. A rust colored precipitate formed at an O/A of 3. Based on previous laboratory tests and analytical results, the precipitate is believed to be HgO [8]. No precipitate was observed at an O/A of 1. Consequently, to prevent precipitate formation in the contactors, the carbonate wash section was operated at an O/A of 1.

The TRUEX solvent product from TRUEX Flowsheet Test #1 was washed with four stages of 0.25 M Na_2CO_3 wash solution and four stages of 0.1 M HNO_3 rinse solution. The aqueous and organic product streams from each section were sampled in order to determine the steady-state Hg concentrations. The actual solution flowrates for this test were calculated from feed tank depletion rates and are compared to the desired flowrates in Table V. The flowrates and O/A ratios compare very well with the desired values. A flowrate based on tank depletion rate was not calculated for the acid rinse feed because the solution was fed out of a non-calibrated carboy.

Steady-State Concentrations

The concentrations of Hg at steady state and the overall material balance are given in Table VI.

Table V. Flowrates and O/A Ratios From Solvent Wash Test #1

Section	Feed	Flowrate (LPM)		O/A Ratio		Total Flow
		Desired	Actual	Desired	Actual	
Carbonate	Org	0.32	0.347			
Wash	Aq	0.32	0.320	1.0	1.08	0.67 LPM
Acid Rinse	Aq	0.11	NA	3.0	NA	0.46 LPM

Table VI. Percentage of Component in Each of the Product Streams for Solvent Wash Test #1

Stream	Hg Conc. (M)	Hg Material Balance
Organic Feed	1.8E-03	NA
Carbonate Wash Raffinate	1.98E-03	101.9% (98.8%)
Carbonate Wash Organic Product	3.95E-05	2.2%
Acid Rinse Raffinate	<7.4E-06	<.13% (<.13%)
Organic Product	<1.9E-05	<1.04% (<1.0%)
Percent Recovery	NA	103.1%

() = Normalized percentage

Mercury

The 0.25 M Na_2CO_3 solvent wash was very effective in removing Hg from the TRUEX solvent product. Less than 1.0% of the Hg remained in the organic after the solvent wash contacts. Less than 0.13% of the mercury in the TRUEX solvent product exited in the 0.1 M HNO_3 acid rinse raffinate. The analytical detection limits for Hg were reached with these samples so the actual Hg concentrations are not known.

TRUEX Flowsheet Test #2

Contactors Operation

Actual solution flowrates for TRUEX Flowsheet Test #2 were calculated from feed tank depletion rates and are compared to the desired flowrates in Table VII. All of the flowrates and O/A ratios compare very well with the desired values.

Table VII. Flowrates and O/A Ratios From TRUEX Flowsheet Test #2

Section	Feed	Flowrate (LPM)		O/A Ratio		Total Flow
		Desired	Actual	Desired	Actual	
Extraction	Org	0.30	0.30	0.33	0.33	1.21 LPM
	Aq	0.70	0.706			
Scrub	Aq	0.20	0.199	1.5	1.51	0.50 LPM
Strip	Aq	0.40	0.39	0.75	0.77	0.69 LPM

In TRUEX Flowsheet Test #1, the solution exiting the organic line from stage four was approximately 50% aqueous and the solution exiting the organic line from stage eight was approximately 2% aqueous. The contactors were not set up to sample the organic from any other stages in the extraction section so it is not known if any other stages were flooded. In TRUEX Flowsheet Test #2, the contactor rotor speed was increased

from 3000 rpm to 3500 rpm. At this rotor speed no flooding was observed in stages one, two, three, or eight. Approximately 5% flooding was noted in the stage four organic. The rotor speed of contactor stages one through four was increased to 3700 rpm for the remainder of the run. This slightly decreased the amount of flooding in the stage four organic. After all samples were taken, the rotor speed of contactor stages one through four was increased to 4000 rpm. At this rotor speed, flooding was alleviated in stage four.

Based on these results it is apparent that the operation of the centrifugal contactors is dependent upon the densities of the solutions processed. The weir system for the centrifugal contactors used in this testing was originally designed for the PUREX process. The density of the TRUEX solvent is considerably higher than the density of the PUREX solvent. Apparently the capacity of the centrifugal contactors with this weir system design is reduced when operating with the TRUEX solvent.

Steady-State Concentrations

The concentrations of H^+ , Nd, Hg, Fe, and Zr at steady state are given in Figure 15. A material balance for each of the components is given in Table VIII. Distribution coefficients were calculated for extraction stages four and eight, scrub stage twelve, and strip stage thirteen. The aqueous and organic phase concentrations, along with the resulting distribution coefficients, are given in Table IX. A comparison of these distribution coefficients with distribution coefficients obtained from laboratory testing with spiked SBW simulant and with actual WM-185 waste is given in Table X [4,8]. A discussion of the behavior of each of the components follows.

Neodymium

Less than 0.07% of the Nd in the SBW feed remained in the aqueous raffinate. This equates to an overall DF of greater than 1,815. Again, the analytical detection limit for Nd was reached with the stage five aqueous solution, so this DF was obtained with only four stages of extraction. The DF with all eight stages of extraction is expected to be much greater. Assuming the distribution coefficient of 33.4 obtained for extraction stage eight is constant for all extraction stages, a DF of $5E+6$

Figure 15. TRUEX Flowsheet Test #2 Steady-State Concentrations

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	SBW Feed 1	Organic Feed 2	LAW Raff. 3	Stage 5 Aqueous 4	Stage 4 Organic 5	Stage 8 Organic 6	Stage 9 Aqueous 7	Scrub Feed 8	Stage 12 Organic 9	Strip Feed 10	Strip Product 11	Organic Product 12
H ⁺ M	1.31	0.0142	1.00	1.28	0.84	0.82	1.21	0.072	0.108	0.01	0.18	0.007
TUCS										0.04	0.04	
Nd M	3.79E-03		<2.1E-06	<2.1E-06	<5.2E-06	8.98E-03	9.36E-04		9.64E-03		7.14E-03	<5.2E-06
Hg M	1.17E-03		1.19E-05	1.20E-04	2.02E-03	1.57E-03	1.90E-04		1.91E-03		1.35E-05	1.76E-03
Fe M	0.0245		0.0184	0.0204	8.28E-03	0.0107	0.0112		3.04E-03		2.45E-03	1.68E-05
Zr M	7.7E-05		3.46E-05	3.04E-05	1.67E-05	1.11E-04	1.62E-05		1.11E-04		8.47E-05	<1.9E-06
Flow LPH	0.706	0.30	0.905	0.905	0.30	0.30	0.199	0.199	0.30	0.39	0.39	0.30

Table VIII. Percentage of Component in Each of the Product Streams for TRUEX Flowsheet Test #2

Stream	Nd	Fe	Hg	Zr	H ⁺
Aq. Raffinate	<0.07% (<0.07%)	96.4% (94.6%)	1.3% (1.98%)	57.7% (48.3%)	93.3% (92.5%)
Strip Product	104.2% (99.9%)	5.5% (5.4%)	0.63% (0.97%)	60.8% (50.9%)	7.4% (7.3%)
Organic Product	<0.06% (<0.06%)	0.03% (0.03%)	63.7% (97.0%)	1.0% (<0.9%)	0.2% (0.2%)
Percent Recovery	104.2%	101.9%	65.7%	118.5%	100.9%

() = Normalized percentage

can be expected. This corresponds to 99.9999% removal of Nd. With an Am concentration of 88 nCi/g and a total actinide concentration of 350 nCi/g in the SBW [4], it is expected that operating with this flowsheet will reduce the actinide concentration well below the NRC Class A LLW limit of 10 nCi/g. Reduction of the number of extraction stages from eight to four should provide adequate actinide removal to meet the Class A limit.

The four stages of HEDPA strip removed greater than 99.95% of the Nd from the organic. Again, the lower detection limit for Nd was reached.

Distribution coefficients of 33.4, 3.6, and 0.015 were obtained for Nd in the extraction, scrub, and strip sections, respectively. As shown in Table X, these distribution coefficients compare very well with Am distribution coefficients obtained from batch contacts with SBW simulant spiked with Am-241 and with actual WM-185 waste. This indicates that Nd is an appropriate surrogate for Am.

Table IX. Component Distribution Coefficients for TRUEX
Flowsheet Test #2

Stage	Component	Aqueous Conc. (M)	Organic Conc. (M)	D
4 Extraction	Nd	<2.1E-06	<5.2E-06	NA
	Fe	1.99E-02	8.28E-03	0.42
	Hg	7.98E-04	2.02E-03	2.5
	Zr	3.91E-05	1.67E-05	0.43
	H+	1.30	0.84	0.64
8 Extraction	Nd	2.69E-04	8.98E-03	33.4
	Fe	2.22E-02	1.07E-02	0.48
	Hg	2.11E-04	1.57E-03	7.4
	Zr	4.25E-05	1.11E-04	2.62
	H+	1.31	0.82	0.63
12 Scrub	Nd	2.67E-03	9.64E-03	3.6
	Fe	3.19E-03	3.04E-03	0.95
	Hg	4.79E-05	1.91E-03	39.8
	Zr	1.58E-05	1.11E-04	7.0
	H+	0.26	0.11	0.42
13 Strip	Nd	7.14E-03	1.12E-04	0.016
	Fe	2.45E-03	1.35E-04	0.055
	Hg	1.35E-05	2.27E-03	168.5
	Zr	8.47E-05	2.11E-06	0.025
	H+	0.18	0.052	0.28

Iron

Increasing the scrub solution flowrate and decreasing the nitric acid concentration of the scrub solution resulted in 5% of the Fe in the SBW feed exiting in the strip product as compared to 16% obtained in TRUEX Flowsheet Test #1. If it is desired to further decrease the amount of Fe in the strip product, and therefore in the final HAW form, further adjustments to the scrub flowrate and nitric acid concentration could be made. However, these adjustments will also increase the amount of americium scrubbed out of the organic and into the LAW raffinate stream.

Table X. Comparison of Distribution Coefficients to Laboratory Data

Section	D_{Am}			D_{Fe}		
	Contactor Mockup (Nd)	Spiked Simulant	WM-185	Contactor Mockup	Spiked Simulant	WM-185
Extraction	33.4	~30	30	0.42-0.48	~0.8	~1.4
Scrub ¹	3.6	10	10	0.95	NA	~0.1
Strip ²	0.016	<<1	<<1	0.055	NA	NA

Section	D_{Zr}			D_{Hg}		
	Contactor Mockup	Spiked Simulant	WM-185	Contactor Mockup	Spiked Simulant	WM-185
Extraction	0.43-2.6	~60	>10	2.5-7.4	3.1	3-6
Scrub ¹	7.0	~15	>10	39.8	60	>>1
Strip ²	0.025	<<1	<<1	168.5	120	NA

¹ A 0.2 M HNO₃ scrub solution was used with spiked simulant and with WM-185 waste.

² A 0.04 M HEDPA strip was used with the spiked simulant and a 0.25 M HEDPA strip was used with WM-185 waste.

Distribution coefficients of 0.42 and 0.48 were obtained on stages four and eight of the extraction section, respectively, indicating the Fe is only partially extractable. The HEDPA strip was very effective in back-extracting the Fe that was not scrubbed out of the organic phase. Essentially all of the Fe in the organic phase (99.4%) was removed with four stages of 0.04 M HEDPA strip. A distribution coefficient of 0.055 was obtained for Fe in the first stripping stage.

Zirconium

Fifty-one percent of the Zr in the SBW feed exited in the strip product and 48% remained in the aqueous raffinate. Greater

than 98% of the Zr entering the strip section was removed with four stages of HEDPA strip. The lower detection limits for Zr were reached in the organic product so it is unknown exactly how much of the Zr was stripped.

Distribution coefficients of 0.4 and 2.6 were obtained in the extraction section, 7.0 in the scrub section, and 0.025 in the strip section. As shown in Table X, the extraction distribution coefficients are much lower than those obtained with spiked SBW simulant and with actual WM-185 waste. It is believed that this discrepancy is due to either different Zr speciation in the solutions or analytical error due to interferences.

Mercury

The Hg results from this test compare very well with the results obtained from TRUEX Flowsheet Test #1. The Hg was extracted from the SBW and remained in the organic phase. The amount of Hg in the TRUEX raffinate was reduced from 3.5% to 1.3% with this flowsheet. It is believed that more Hg was extracted with this flowsheet test because the flooding problem was alleviated allowing for eight complete stages of extraction. Only 0.6% of the Hg exited with the strip product. As shown in Table X, the distribution coefficients obtained for Hg in the extraction, scrub, and strip sections compared very well with laboratory data.

Solvent Wash Test #2

Contactors Operation

Prior to performing Solvent Wash Test #2, a sample of the organic product from TRUEX Flowsheet Test #2 was contacted with 0.25 M Na_2CO_3 in the laboratory at O/A ratios of 1, 2, and 3. The purpose of these contacts was to determine if a precipitate forms. A rust colored precipitate formed at O/A ratios of 3 and 2. However, at an O/A of 2 only a small amount of precipitate was observed. Based on previous laboratory tests and analytical results, the precipitate is believed to be HgO [8]. It is desired to minimize the flowrate of Na_2CO_3 in the solvent wash section in order to minimize the Na_2CO_3 waste generated. However, it is undesirable to have a precipitate form. The O/A was increased from 1 to 1.5 for this test to try to minimize the

solution flowrate without forming a precipitate.

The solvent product from TRUEX Flowsheet Test #2 was washed with four stages of 0.25 M Na_2CO_3 solution and rinsed with four stages of 0.1 M HNO_3 solution. The aqueous and organic product streams from each section were sampled in order to determine the steady-state Hg concentrations. In addition, interstage samples were taken from the first and fourth stages of the Na_2CO_3 wash section in order to calculate Hg distribution coefficients. The actual solution flowrates for this test were calculated from feed tank depletion rates and are compared to the desired flowrates in Table XI. The flowrates and O/A ratios compare very well with the desired values. A flowrate based on tank depletion rate was not calculated for the acid rinse feed because the solution was fed out of a non-calibrated carboy.

Table XI. Flowrates and O/A Ratios From Solvent Wash Test #2

Section	Feed	Flowrate (LPM)		O/A Ratio		Total Flow
		Desired	Actual	Desired	Actual	
Carbonate	Org	0.32	0.328	1.5	1.58	0.53 LPM
Wash	Aq	0.21	0.202			
Acid Rinse	Aq	0.10	NA	3.0	NA	0.43 LPM

While performing Solvent Wash Test #2, a rust colored precipitate, believed to be HgO , was noted in the aqueous product stream exiting the Na_2CO_3 wash section. The precipitate slowly accumulated in the corrugations on the Teflon line exiting the contactor bank. A precipitate was not observed in samples of this solution. After completion of the testing, the rotor was removed from the first Na_2CO_3 wash stage to determine if any precipitate was accumulating in the contactor rotors. A rust colored film was noted on the inside and outside of the rotor. No film was seen on the housing walls. The precipitate did not wipe off the contactors. The quantity of precipitate was too small to affect the operation of the contactors. However, continuous operation under these conditions could cause a significant quantity of precipitate to accumulate in the rotors

and cause operational problems. The precipitate was removed from the rotors by flushing 0.1 M HNO_3 through the contactors and leaving the solution in the contactors overnight.

Steady-State Concentrations

The concentrations of Hg at steady state and the overall material balances are given in Table XII. Distribution coefficients calculated for Hg are given in Table XIII.

Mercury

The 0.25 M Na_2CO_3 solvent wash was very effective in removing Hg from the TRUEX solvent product. Less than 0.12% of the Hg remained in the organic after the solvent wash contacts. Less than 0.031% of the mercury in the TRUEX solvent product exited in the 0.1 M HNO_3 acid rinse raffinate. The analytical detection limits for Hg were reached with these samples so the actual Hg concentrations are not known. Aqueous and organic samples were taken from the first and fourth stages of the Na_2CO_3 solvent wash section in order to determine the distribution coefficients of Hg in this section. Distribution coefficients of <0.0028 and <0.93 were obtained for stages 1 and 4, respectively, indicating that Na_2CO_3 is very effective as a stripping agent for Hg from the TRUEX solvent.

Based on TRUEX Flowsheet Test #2, only 1.3% of the Hg in the SBW feed exited in the HAW strip product. Essentially all of the Hg in the TRUEX solvent was stripped by the 0.25 M Na_2CO_3 solvent wash solution. Therefore, the flowsheets tested in TRUEX Flowsheet Test #2 and Solvent Wash Test #2 resulted in 98.7% of the Hg in the SBW feed being partitioned into the LAW streams.

Solvent Degradation

Impurities in the TRUEX solvent, resulting from acid hydrolysis, may hinder the ability to strip the actinides. The distribution coefficient of Am is particularly sensitive to CMPO impurities [5]. D_{Am} was evaluated as a function of nitric acid concentration from HNO_3 solutions using the organic product from TRUEX Flowsheet Test #1 and again using the same organic solution after performing Solvent Wash Test #1. This process was repeated

Table XII. Percentage of Component in Each of the Product Streams for Solvent Wash Test #2

Stream	Hg Conc. (M)	Hg Material Balance
Organic Feed	1.51E-03	NA
Carbonate Wash Raffinate	2.64E-03	107.9% (100.0%)
Carbonate Wash Organic Product	<1.99E-06	<0.13%
Acid Rinse Raffinate	<7.98E-07	<0.033% (<0.031%)
Organic Product	<1.99E-06	<0.13% (<0.12%)
Percent Recovery	NA	107.9%

() = Normalized percentage

Table XIII. Hg Distribution Coefficients for Solvent Wash Test #2

Stage	Component	Aqueous Conc. (M)	Organic Conc. (M)	D
1 Na ₂ CO ₃ wash	Hg	2.64E-03	<7.48E-06	<0.0028
4 Na ₂ CO ₃ wash	Hg	2.15E-06	<1.99E-06	<0.93

using the organic product from TRUEX Flowsheet Test #2. In addition, a sample of the organic product from Solvent Wash Test #2 was washed with activated alumina and D_{Am} was evaluated. Activated alumina is used to remove potential diluent degradation products which may form. The distribution coefficients obtained for Am were compared to results obtained with the initial TRUEX solvent, in order to determine if any noticeable degradation of the solvent occurred during testing and to determine if the solvent wash was effective in removing any degradation products which may have formed. Results of this testing are given in Figure 16.

The distribution coefficients of Am at HNO_3 concentrations greater than 0.04 M remained approximately constant (within analytical error) for each test. However, with 0.01 M HNO_3 the distribution coefficients of Am varied slightly. D_{Am} is most sensitive to degradation products at 0.01 M HNO_3 . After washing the initial TRUEX solvent with Na_2CO_3 and HNO_3 , D_{Am} decreased from 0.020 to 0.014 indicating that some manufacturing impurities in the TRUEX solvent may have been removed. D_{Am} for the organic product from TRUEX Flowsheet Test #1 with 0.01 M HNO_3 increased to 0.033 indicating that CMPO degradation due to acid hydrolysis may be occurring. After this solvent was washed, D_{Am} decreased to 0.026. However, the distribution coefficient remained higher than with the initial washed solvent. After performing TRUEX Flowsheet Test #2, D_{Am} at 0.01 M HNO_3 increased to 0.05. After this solvent was washed, D_{Am} decreased to 0.037. Again, D_{Am} remained higher than after the previous solvent wash. A sample of the washed organic from Solvent Wash Test #2 was contacted with activated alumina. D_{Am} was only slightly decreased to 0.030 indicating that diluent degradation products are not causing the rise in Am distribution coefficients.

A general trend can be seen for D_{Am} at 0.01 M HNO_3 . After each TRUEX flowsheet test, D_{Am} increases. Washing the organic with sodium carbonate decreases this distribution coefficient, but not back to the original value. This indicates that there may be a slow buildup of degradation products which will eventually affect the ability to strip the actinides. As of yet, D_{Am} has not increased to a value high enough to cause stripping problems. D_{Am} will continue to be evaluated in future TRUEX flowsheet testing with dissolved pilot plant calcine to determine if D_{Am} continues to increase and any stripping problems result.

Figure 16. Solvent Purity Results

Generic TRUEX Model Results

Version 3.1 of the Generic TRUEX model was used to mathematically model the flowsheet tested in TRUEX Flowsheet Test #2 [11,12,13]. The flowsheet modelled was identical to the flowsheet tested, with one exception. A 0.25 M HEDPA strip in 0.05 M HNO_3 was used in the GTM instead of the 0.04 M HEDPA in 0.01 M HNO_3 used in the testing. This is the only composition of HEDPA strip allowed by the GTM. The percentage of each component in the raffinate and strip product streams, as predicted by the GTM and obtained experimentally, is presented in Table XIV.

Results predicted by the GTM were consistent with those obtained experimentally with the exception of Fe and Zr. The GTM predicted all of the Fe is scrubbed out of the organic and none exits with the strip product, whereas the experimental results indicate that 5% of the Fe is not scrubbed. Also, the GTM predicts that all of the Zr is extracted and exits with the strip product, whereas the experimental results indicate that only 51% of the Zr exits with the strip. It should be noted, however, that the results predicted by the GTM are consistent with results obtained experimentally with spiked SBW simulant and with actual WM-185 waste. At least in the case of Zr, this anomaly is attributed to the low Zr concentration in the feed, approaching analytical detection limits for this element.

For Al, Ca, Ce, Cr, F, Na, and Sr, only the raffinate stream was sampled. Therefore, it is expected that the percentages are less than 100 due to material balance errors and not because some of these species are extracting.

Table XIV. Comparison of Experimental Results to GTM Results

Component	% of Component in			
	LAW Raffinate		Strip Product	
	Actual	GTM	Actual	GTM
Nd	<0.07	0	>99.93	99.995
Fe	94.6	100	5.4	0
Zr	48.3	0	50.9	100
Al ¹	82	100	NA	0
B	94	100	0.1	0
Ca ¹	85	100	NA	0
Ce ¹	<0.8	0	NA	100
Cr ¹	103	100	NA	0
Na ¹	95	100	NA	0
Sr ¹	93	100	NA	0

¹ Only the raffinate stream was sampled for these components

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are based on the results of this testing.

Conclusions

1. A TRUEX flowsheet has been developed which is capable of sufficiently removing the actinides from SBW to meet NRC Class A LLW criteria (see Figure 15).
2. For this TRUEX flowsheet, no precipitation or third phase formation problems were observed or are anticipated with actual waste.
3. Mercury can be selectively partitioned from the HAW stream in the TRUEX process by using a 0.25 M Na_2CO_3 solvent wash solution to strip the extracted Hg from the TRUEX solvent. With the Na_2CO_3 strip, 0.6% of the Hg in the SBW feed exited with the HAW strip product.
4. An O/A ratio of 1.0 or less must be maintained in the 0.25 M Na_2CO_3 solvent wash section to prevent HgO from precipitating.
5. Nd, Fe, and Hg distribution coefficients obtained compared favorably with laboratory distribution coefficients obtained with spiked SBW simulant and actual WM-185 waste. Zr extraction distribution coefficients were considerably lower than those obtained in the laboratory. This anomaly in the contractor data is attributed to the low Zr concentration in the feed, approaching analytical detection limits.
6. A 0.04 M HEDPA strip solution is very effective in stripping Nd, Fe, and Zr from the TRUEX solvent.
7. The amount of iron scrubbed out of the TRUEX solvent can be increased by reducing the scrub nitric acid concentration and increasing the scrub flowrate. With a scrub concentration of 0.072 M HNO_3 and an O/A ratio of 1.5, only 5% of the Fe in the SBW exited with the HAW strip product.

8. A general upward trend in the Am distribution coefficients for the TRUEX solvent at 0.01 M HNO_3 was seen after each TRUEX flowsheet test. Washing the TRUEX solvent with 0.25 M Na_2CO_3 decreases the Am distribution coefficient, but not back to the original value. This indicates that there may be a slow buildup of degradation products in the solvent. As of yet, D_{Am} has not increased to a value high enough to cause stripping problems.
9. Steady state was reached in the Centrifugal Contactor Mockup for Nd, Fe, and H^+ within 20 minutes.
10. The weir system in the Centrifugal Contactor Mockup was designed for the PUREX process. The capacity of the contactors is significantly reduced with the TRUEX process due to the higher solvent density. Flooding problems can be avoided when operating with the TRUEX process by increasing the contactor rotor speed to the maximum allowable (3500 rpm).
11. No operational problems were noted with the centrifugal contactors. Even with 50% flooding on one stage during TRUEX Flowsheet Test #1, good overall results were obtained.
12. Results predicted by the GTM were consistent with the experimental results with the exception of Fe and Zr.

Recommendations

1. A flowsheet similar to the one tested in TRUEX Flowsheet Test #2 should be used as a baseline flowsheet for future TRUEX testing with actual SBW (see Figure 15).
2. Waste form studies should be performed to determine if the phosphorus in the 0.04 M HEDPA strip will adversely impact the development of a suitable waste form or produce excessive waste volumes.
3. Distribution coefficients of Am in the TRUEX solvent used for these tests should continue to be evaluated as future testing is performed in order to determine if D_{Am} continues to rise at low acid concentrations and if any stripping problems result.

4. For future TRUEX flowsheet testing, the Centrifugal Contactor Mockup should be operated a minimum of 40 minutes prior to sampling to ensure steady state has been reached.
5. To prevent flooding, the 5.5 cm diameter centrifugal contactors should be operated at ≥ 3500 rpm when using the TRUEX solvent.
6. Flooding curves should be generated for the TRUEX solvent and compared to theoretical flooding curves. Prior to performing future flowsheet testing in the Centrifugal Contactor Mockup with other solvents, the hydraulic performance of the contactors needs to be evaluated.

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