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**TRUEX PARTITIONING STUDIES APPLIED
TO ICPP SODIUM-BEARING WASTE**

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May 1994

**Westinghouse Idaho
Nuclear Company, Inc.**

PREPARED FOR THE
DEPARTMENT OF ENERGY
IDAHO OPERATIONS OFFICE
UNDER CONTRACT DE-AC07-84ID12435

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ACKNOWLEDGEMENTS

The authors express their appreciation to Lee Hinkley, Dean Goodwin and Brian Storms of the Radiochemistry Group; also to Jeff Laug and Duane Lundholm of the Spectrochemistry Group. It was their tireless efforts to report accurate data in a timely fashion which enhanced the development process and made the results herein both possible and meaningful.

ABSTRACT

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 HLW raffinates from the combined PUREX/REDOX type uranium recovery process were converted to solid oxides (calcine) in a high temperature fluidized bed. Liquid effluents from the calcination process were combined with liquid sodium bearing waste (SBW) generated primarily in conjunction with decontamination activities. Due to the high sodium content in the SBW, this secondary waste stream is not directly amenable to solidification via calcination. Currently, approximately 1.5 million gallons of liquid SBW are stored at the ICPP in large tanks. Several treatment options for the SBW are currently being considered, including the TRansUranic Extraction (TRUEX) process developed by Horwitz and co-workers at Argonne National Laboratory (ANL), in preparation for the final disposition of SBW. Herein described are experimental results of radionuclide tracer studies with simulated SBW using the TRUEX process solvent (0.2 M CMPO, 1.4 M TBP in n-dodecane).

Due to the unique and complex composition of the liquid SBW, a non-radioactive simulant was prepared, and the partitioning behavior of the TRUEX solvent was studied for several radioisotopes in tracer experiments. The SBW simulate used in all tracer experiments was prepared to be representative of an average composition of the cold matrix materials contained in the SBW tank farm. Included in these tests were the actinides uranium, americium, neptunium and plutonium. The fission product, technetium, was also examined. Mercury distribution data was collected due to the high Hg composition (used as a catalyst in Al clad fuel dissolution) in the SBW and the lack of Hg distribution data in the open literature.

The purpose of the experimental procedure was to examine the extraction distribution coefficient, D , for the isotope in question as well as the stripping distribution coefficient with several potential stripping reagents. The behavior of the TRUEX solvent, with regard to potential problems such as third phase formation and solvent cleanup, as applied to SBW was also evaluated. The results of these experiments were compared with those predicted by the Generic TRUEX Model (GTM) developed by Vandegrift and co-workers at Argonne National Laboratory (ANL). The GTM is a computer modelling tool which can be used to estimate the anticipated performance of the TRUEX process with a user specified feed for both experimental and process flowsheets. This comparison of experimental with GTM results indicated reasonable agreement considering the complex composition of SBW. These experiments are currently being extended to examine the extraction and stripping behavior of other metals in the SBW matrix. From all indications to date, the TRUEX process is expected to be compatible with SBW and processing problems are not anticipated. Currently, preparations are being made for small scale, batch contact tests on samples of actual SBW. Finally, distribution coefficients generated during these tracer experiments have been used in conjunction with the GTM to develop a potential process flowsheet for the large scale treatment of ICPP SBW.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
ABSTRACT	v
LIST OF TABLES	ix
LIST OF FIGURES	xi
INTRODUCTION	1
SCOPE AND PURPOSE	3
METHODOLOGY/EXPERIMENTAL PROCEDURE	6
SBW Simulant	6
Radioisotopes Studied	7
TRUEX Solvent	7
Contacting Procedure	8
Solvent Pre-equilibration	9
Contacting Methodology	9
Calculations	10
Sample Titration	12
Analytical Methods	12
RESULTS AND DISCUSSION	14
Actinide Tracer Studies	14
Uranium Results	17
Plutonium Results	24
Americium Results	30
Neptunium Results	36
Non-actinide Elements	41
Technetium Results	41
Mercury Results	48
Chromium Results	59
Iron Results	61
Zirconium Results	62
Other Inert Elements	62
Comparison of Experimental Data	63
POTENTIAL FLOWSHEETS FOR TREATMENT OF SBW	67
CONCLUSIONS & RECOMMENDATIONS	71
REFERENCES	72

LIST OF TABLES

Table 1.	Composition of simulated sodium bearing waste (SBW)	6
Table 2.	Radionuclides used as tracers in the simulated SBW	7
Table 3.	Results of the uranium extractions	19
Table 4.	Results of the uranium scrub contacts.	20
Table 5.	Results of the uranium stripping contacts with the TUCS reagent	21
Table 6.	Results of the uranium stripping contacts with 0.1 M oxalic acid	21
Table 7.	Results of uranium stripping with dilute nitric acid and solvent washing with sodium carbonate	22
Table 8.	Summary of experimental extraction results with the Pu-238 traced SBW simulant	25
Table 9.	Pu-238 0.2 M HNO ₃ scrub distribution coefficients	26
Table 10.	Pu-238 stripping distribution coefficients using TUCS and oxalic acid	28
Table 11.	Pu-238 stripping and washing distribution coefficients with 0.01 M HNO ₃ and 0.25 M Na ₂ CO ₃	29
Table 12.	Extraction distribution coefficients for Am-241 spiked into SBW simulant	31
Table 13.	Am-241 scrub distribution coefficients	32
Table 14.	Am-241 stripping distribution coefficients using TUCS and oxalic acid	33
Table 15.	Am-241 stripping and washing distribution coefficients with 0.01 M HNO ₃ and 0.25 M Na ₂ CO ₃	35
Table 16.	Summary of experimental results with the Np-239 traced SBW simulant	39
Table 17.	Extraction D _{Tc} from SBW simulant	43
Table 18.	Scrub D _{Tc} for SBW contacted TRUEX solvent	45
Table 19.	Stripping D _{Tc} from loaded TRUEX solvent	46
Table 20.	Stripping D _{Tc} using oxalic acid	47
Table 21.	Results of the mercury extractions	50
Table 22.	Mercury results for 0.2 M HNO ₃ scrubs and 0.01 M HNO ₃ strips	51
Table 23.	Mercury results for 0.2 M HNO ₃ scrubs and oxalic acid strips	52
Table 24.	Results of mercury strips with 5 M HNO ₃	53
Table 25.	Results of mercury stripping with 5 M HNO ₃	54
Table 26.	Mercury stripping results with 0.01 M HCl	56
Table 27.	Mercury stripping results with 5 M HCl	57
Table 28.	Mercury stripping results with the TUCS reagent	58
Table 29.	Results of "cold" chrome (VI) extractions from SBW simulant and pure nitric acid solutions	60
Table 30.	Experimental versus estimated (GTM) distribution coefficients for TRUEX extractions from simulated SBW	64
Table 31.	Distribution coefficients used in the GTM.	70

LIST OF FIGURES

Figure 1. Schematic of a typical TRUEX process flowsheet . . .	4
Figure 2. Experimental schematic used to test the TUCS & oxalic acid stripping reagents (U, Pu, Am)	15
Figure 3. Experimental schematic used to test 0.01 <u>M</u> HNO ₃ , stripping solution and carbonate wash (U, Pu, Am) .	16
Figure 4. Experimental schematic used with neptunium tracer .	38
Figure 5. Experimental schematic used with technetium tracer	42
Figure 6. Experimental schematic used to test Hg stripping at high acid concentrations ([H ⁺] = 5 <u>M</u>)	50
Figure 7. TRUEX flowsheet for the treatment of SBW	68

INTRODUCTION

The Idaho Chemical Processing Plant is currently conducting development activities to evaluate several feasible alternatives for treatment and final disposition of liquid sodium bearing waste (SBW). This liquid waste was generated as a result of decontamination and solvent wash activities. The SBW has historically been blended with reprocessing raffinates and solidified by calcination in a fluidized bed operated at 500°C. The SBW solutions cannot be calcined directly, primarily due to the high sodium content, and therefore, must be blended with non-radioactive aluminum nitrate [1] or reprocessing raffinate solutions resulting from the dissolution of aluminum or zirconium clad fuels. As of November 1993, all raffinate solutions were calcined, thereby eliminating the option of blending to deplete the SBW inventory. SBW is being stored temporarily in underground storage tanks. Currently, approximately 1.5 million gallons of liquid SBW are stored at the ICPP.

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, remove sodium, or remove 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 purpose of this work was primarily to evaluate actinide partitioning from SBW using the TRansUranic EXtraction (TRUEX) process. The TRUEX process is a liquid-liquid solvent extraction scheme which was developed by E. P. Horwitz and co-workers at Argonne National Laboratory (ANL) [2]. The 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 n-dodecane. The process has been effectively used to remove actinides from acidic simulants and real waste solutions to well below the 10 nCi/gram Class A waste 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 practically every country with nuclear processing capabilities (U.S., Canada, India, Italy, and Japan).

The applicability of the TRUEX process for use with ICPP acidic sodium bearing waste 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 evaluate the TRUEX solvent extraction process as applied to sodium bearing waste (SBW) in two generic ways. The first, and most determinant method, was to evaluate the distribution coefficients of several radioactive species contained in the actual SBW with radioactive tracers and SBW simulant. Secondly, potential problems, i.e., third phase formation, solids precipitation, extraction, stripping or solvent cleanup difficulties, etc., could be observed and dealt with prior to bench scale or pilot plant testing with actual waste. This methodology allows the behavior of SBW during batch scale hot experiments and pilot plant testing to be anticipated, and is therefore cost effective.

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-level waste (HLW) product stream and a low-level waste (LLW) 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 an 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 as well as 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 single stripping agent, capable of removing all the actinides

Figure 1. Schematic of a Typical TRUEX Process Flowsheet

from the loaded organic solvent is advantageous. A Thermally Unstable Complexant (TUCS) reagent (Ionquest 201[®]), oxalic acid, and dilute nitric acid were evaluated as actinide stripping reagents.

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.

The scope of this study focused primarily on the determination of elemental distribution coefficients from the SBW matrix. The batch-wise contacting schemes adopted to measure distributions are quite different than evaluating a countercurrent process flowsheet such as show in Figure 1. However, such tests will provide a relative measure of the distributions that can be anticipated in a single contacting stage. These results can be used in conjunction with the GTM to develop a process flowsheet for the treatment of SBW.

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 the TRUEX process as applied to the SBW matrix. Such a study is the primary scope of these experiments.

METHODOLOGY/EXPERIMENTAL PROCEDURE

SBW Simulant

For the purposes of this study, the TRUEX process was evaluated primarily using radioactive isotopes, or tracers, spiked into simulated SBW waste solution. Using the analytical results obtained from SBW tank samples, a non-radioactive or "cold" simulant was prepared to represent the average chemical composition of the major non-radioactive matrix components in the SBW tanks [4,5]. The chemical composition of the SBW simulant is shown in Table 1.

Table 1. Composition of simulated sodium bearing waste (SBW).

Component	<u>M</u>	Component	<u>M</u>
Acid (H ⁺)	1.35	K	1.43E-1
Al	6.48E-1	Mn	1.42E-2
B	1.71E-2	Mo	1.49E-3
Cd	2.29E-3	Na	1.26
Ca	3.91E-2	NO ₃	4.46
Ce	3.88E-4	Ni	2.20E-3
Cl	3.52E-2	Pb	1.08E-3
Cs	7.52E-5	PO ₄	<9.18E-3
Cr	6.56E-3	Sr	1.70E-4
F	9.66E-2	SO ₄	3.86E-2
Fe	3.10E-2	Zr	1.00E-3
Hg	2.88E-3		

Radioisotopes Studied

The radioactive species to be partitioned from SBW by the TRUEX process include: uranium, neptunium, americium, plutonium and technetium. The affinity of the TRUEX solvent for several other elements, such as mercury, chromium, iron and zirconium was also studied. The specific isotopes of the various elements used as tracers in these tests are indicated in Table 2.

The isotope of interest was spiked into a known volume of the simulant and allowed to equilibrate for 24 hours prior to contact with the TRUEX solvent. Only one isotope was spiked into the waste simulant at a time to simplify analytical sample preparation and allow for rapid sample analysis turn around times. Small volumes of the tracer solutions were spiked into the simulant to minimize dilution effects as much as possible.

Table 2. Radionuclides used as tracers in the simulated SBW.

Isotope
Am-241
Np-237
Pu-239
Tc-95m
U-233
Hg-203
Cr-51
Fe-55

TRUEX Solvent

The active extractant in the TRUEX solvent is octyl(phenyl)-N-N-diisobutyl-carbamoylmethylphosphine oxide (CMPO), which was developed and extensively studied by Horwitz and co-workers at Argonne National Laboratory (ANL). Tributylphosphate (TBP) is

added to prevent the formation of a second organic phase (third phase formation) 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 n-dodecane. This composition was used in all extraction studies reported herein. TRUEX solvent preparation was performed by Quality Control (QC) Laboratory at the ICPP.

The purity and composition of the TRUEX solvent was established prior to use in extraction experiments. Horwitz [6] 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 is particularly sensitive to CMPO impurities [6]. To insure the purity of the CMPO used in these experiments, one pound of this material was purified by ANL. The results of CMPO purification and TRUEX solvent testing are presented elsewhere [7].

The distribution coefficient of americium was evaluated as a function of nitric acid concentration from HNO_3 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 used to test each freshly prepared batch of TRUEX solvent [7]. If the results were comparable to literature values [6], this indicated the solvent was suitable for extraction studies.

Contacting Procedure

All contacts were performed in test tubes for 1 minute at an O/A = 1. Phase disengagement was accomplished by centrifuging at 5000 rpm for one minute. Temperature control (i.e., a constant temperature bath) was not incorporated into the experimental procedure. Consequently, all phase contacts were performed at room temperature of $27 \pm 2^\circ\text{C}$.

Solvent Pre-equilibration

The TRUEX solvent was contacted (pre-equilibrated) with non-spiked waste simulant prior to extraction with the spiked feed. Pre-equilibration was performed by contacting the solvent three times, fresh simulant being used each time, at an organic to aqueous phase ratio of one ($O/A = 1$). In this manner, the TRUEX solvent was "loaded" with inert, extractable species, such as zirconium, iron or chromium as well as nitric acid present as macro constituents in the simulant. This provision insured that the isotope of interest was the only species quantitatively transferred between phases.

Contacting Methodology

An aliquot of tracer spiked SBW feed was first contacted with the pre-equilibrated solvent to determine the extraction distribution coefficient. This first extraction step is typically labelled as E1. The aqueous raffinate from the first forward extraction was used as the feed in a second extraction (E2) where it was contacted with an equal volume of fresh pre-equilibrated TRUEX solvent, again to examine the forward extraction coefficient. This process of using the aqueous raffinate as the feed to another extraction contact was typically repeated three times.

The organic from the first extraction, E1, now loaded with extracted species was often scrubbed with 0.2 M nitric acid. The purpose of scrubbing is to back-extract any inert materials, such as Zr, Fe, and Cr, and lower the acidity of the organic by scrubbing nitric acid. Typically, the loaded organic was scrubbed in three consecutive contacts denoted as Sc1 through Sc3. Depending on the distribution coefficient of the radionuclide in question, some of the actinides may also be scrubbed from the organic. This is not a problem, however, since in an actual TRUEX process, the scrub solution is combined with the feed to the extraction section. Thus, back-extracted actinides are recycled and not lost from the high-level waste product.

The scrubbed organic was generally contacted with one of several aqueous reagents to determine which of these solutions best removed or *stripped* the species of interest from the TRUEX solvent. Stripping reagents tested included dilute (0.01 M) nitric acid, dilute (0.1 or 0.01 M) oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, and a TUCS reagent.

The TUCS reagent (Albright & Wilson, tradename Ionquest 201®) is a derivative of diphosphonic acid. Although proprietary, it is believed to be 1-hydroxyethane-1,1-diphosphoric acid (HEDPA). TUCS refers to a class of alkylphosphonic acids which have proven useful as stripping reagents from the TRUEX solvent [8]. The composition of the TUCS stripping solution used in these experiments was 0.25 M Ionquest 201® in 0.05 M HNO_3 .

Finally, the organic raffinate from the 0.01 M HNO_3 strip contacts was subjected to one or more washes with 0.25 M sodium carbonate, Na_2CO_3 , to evaluate the applicability of this reagent for solvent cleanup.

Calculations

The *distribution coefficient* or *distribution ratio*, D , for the radionuclide of interest was determined by:

$$D_x = \frac{[\text{Activity of } X]_{\text{org}}}{[\text{Activity } X]_{\text{aq}}} \quad (1)$$

where X is the isotope of interest. The distribution coefficient is a measure of the partitioning efficiency for species X between the organic and aqueous phases. It is apparent from equation (1) that larger distribution coefficients represent a greater propensity for species X to be transferred to or remain in the organic phase. If the distribution ratio is large for the forward extraction of species X , the organic solvent is readily loaded with this element. Conversely, large distribution coefficients during scrubbing, stripping or washing contacts

indicate the extracted species largely remains in the organic phase. Typically, distributions greater than one are necessary in the extraction stages of a TRUEX process to remove the species of interest and larger distributions translate to fewer contacting stages. For the stripping section, distributions much less than one are desired and smaller D values correlate with fewer stripping stages.

The use of material balances can be used in radioisotope tracer studies to evaluate the accuracy of a particular contact. Material balances were calculated by dividing the total activity of the feed (organic or aqueous) by the sum of the total activities of both phases after contact:

$$\% \text{ Material Balance} = \frac{\text{Total Activity In}}{\text{Total Activity Out}} \times 100\% \quad (2)$$

where the ratio of activities is given by:

$$\frac{\text{Total Activity In}}{\text{Total Activity Out}} = \frac{(\text{dps/ml feed})(\text{ml feed})}{(\text{dps/ml aq. phase})(\text{ml aq phase}) + (\text{dps/ml org. phase})(\text{ml org. phase})} \quad (3)$$

Material balances were typically within $100 \pm 5\%$ and were used as a secondary check on the experimental procedure. In cold tests, the organic phase cannot typically be analyzed directly. Thus, the material balance is used to establish the concentration of species X in the organic, which in turn, is used determine the distribution coefficient:

$$D_x = \frac{[X]_{\text{Org.}}}{[X]_{\text{Aq. Raff.}}} = \frac{[X]_{\text{Feed}} - [X]_{\text{Aq. Raff.}}}{[X]_{\text{Aq. Raff.}}} \quad (4)$$

In equation (4), [X] is the molar concentration of species X in the respective feed, aqueous raffinate or organic phase.

Sample Titration

Aqueous samples were titrated to determine the free acid concentration. Due to metal hydrolysis associated with the high concentrations of metal species in the SBW simulant, the titrations were performed in potassium oxalate solution. A standard $K_2C_2O_4$ solution (prepared by the QC laboratory) was first titrated with standardized sodium hydroxide solution to a phenothalien endpoint. An appropriate aliquot (typically 0.1 to 0.5 ml) of the sample to be titrated was pipetted into this solution. Standardized NaOH was then used to titrate to a phenothalien endpoint. In a few instances, the organic phase was also titrated in accord with this same procedure.

Analytical Methods

Samples of the aqueous feed, loaded organic and aqueous raffinates from each batch contact (extraction, scrub, strip or solvent wash) were taken for radiochemical analysis. The sample activity was determined by the appropriate method and the distribution coefficient of the isotope being studied was determined for each individual contact.

Two analytical methods were employed to determine activity in the appropriate samples. The particular method was dependent on the type of decay the isotope of interest undergoes. Alpha (α) emitting isotopes (Pu-238, U-233, Np-239 and Am-241) were analyzed via liquid scintillation (LSC). Gamma (γ) emitters (Tc-95m, Hg-203) were analyzed with the γ -spectroscopy technique.

For gamma spectroscopy, a known amount of the appropriate sample (0.1 to 1 ml) was accurately pipetted into a 5 dram glass vial with a calibrated geometry. A total volume of 1 ml was always counted by gamma spectroscopy, regardless of the original sample size. The vial was centered against a High Purity Germanium detector with a relative counting efficiency of 73%. The appropriate photopeak (isotope dependent) was used to determine sample activities. Measurement uncertainties for LSC and gamma techniques were calculated as two standard deviations

of the count rate only and are strictly a function of the total activity in the sample. Overall uncertainties in laboratory technique were not propagated since this bias would be expected to cancel in distribution and material balance calculations. Counting uncertainties were calculated as follows:

$$\sigma_{\text{count}} = (\text{total counts})^{1/2} * (1/\text{total count time})$$

RESULTS AND DISCUSSION

Actinide Tracer Studies

TRUEX extractions from the simulated SBW were performed with uranium, plutonium, americium, and neptunium. Because experimental programs are dynamic, the batch-wise contacting schemes, or experimental "flowsheet", varied from test to test and was different for many of the isotopes studied. The two experimental flowsheets used for the batch-wise contacts with uranium, plutonium and americium are shown in Figures 2 and 3. The difference between these two test procedures is in the stripping and solvent wash steps: the schematic in Figure 2 was used to test TUCS and oxalic acid as stripping solutions; the schematic in Figure 3 was used to test dilute nitric acid stripping and sodium carbonate solvent cleanup. Three consecutive forward extractions were performed with the aqueous feeds. These extractions are labelled E1 through E3 in Figure 2 and E4 through E6 in Figure 3. Note that fresh, pre-equilibrated solvent was used in each forward extraction. The loaded organic solvents from the first forward extractions, E1-O and E4-O, were subjected to three consecutive scrub contacts with 0.2 M HNO_3 , Sc1 through Sc3 (Figure 2) and Sc4 through Sc6 (Figure 3). The extraction and scrub portion of the two experimental schemes were the same. Consequently, replicate observations were obtained (since each experiment was performed independently), thus experimental reproducibility was readily ascertained.

Referring to Figure 2, the loaded organic phase from the final scrub, Sc3-O, was split into equal volumes. The first aliquot was contacted with TUCS in three consecutive stripping contacts labelled St1 through St3. The second aliquot was contacted three consecutive times with oxalic acid and are labelled St4 through St6.

Figure 2. Experimental Schematic used to test the TUCS & Oxalic Acid Stripping Reagents (U, Pu, Am)

Figure 3. Experimental Schematic used to test the 0.01 M HNO₃ Stripping Solution and Carbonate Wash (U, Pu, Am)

In Figure 3, the scrubbed organic, Sc6-O, was used as a feed for three successive stripping contacts with dilute (0.01 M) nitric acid. The organic from the final strip, St9-O, was washed in two successive contacts with 0.25 M sodium carbonate to emulate the solvent cleanup process.

It is pertinent at this point to consider the convention adopted in presenting subsequent distribution ratio results. Note that in either of the experimental procedures, appropriate size samples of the respective organic and aqueous phases were taken for analysis. Subsequent tracer results for plutonium, americium and uranium are reported in accord with the conventions used in Figures 2 and 3. Thus, Sc1-A represents the analysis of the aqueous raffinate from the first scrub contact shown in Figure 2. A sample designation of St9-O corresponds to the organic phase from the ninth stripping contact with dilute nitric acid as shown in Figure 3.

Uranium Results

Uranium concentrations in SBW range from 25 to 160 ppm. Although it is unclear as to the allowable uranium concentration limit in the low-level waste stream (aqueous raffinate) resulting from the TRUEX separation, uranium separation must take place and is therefore an element of concern.

A ^{233}U standard was prepared from a New Brunswick Certified Reference material (CRM 111-A). The ^{229}Th daughter was separated by passing the standard over a column loaded with Aliquat 336N as the stationary phase. The radium daughter was separated by two sequential co-precipitations with BaSO_4 . The initial uranium activity of the standard prior to purification was 1.011×10^8 dpm. After purification, the uranium standard solution was analyzed by liquid scintillation and found to be 9.918×10^7 dpm which indicates a recovery of 98.1%. Aliquots of the standard were analyzed by gamma spectrometry to verify the absence of ^{229}Th . No ^{229}Th contamination was found. Aliquots of the standard were also analyzed by LSC at two and four week intervals after

purification. These analyses agreed with the value obtained just after separation which confirms that radium and its daughters were successfully separated. All uranium feed solutions used in the TRUEX tests were prepared from this purified stock solution.

Uranium-233 is an α emitter, consequently, liquid scintillation was used for sample analysis. Due to an oversight during the experiments, blank organic and aqueous samples were not taken, counted, and used as a correction. In most cases, the lack of "blanks" was unimportant due to the high radioactivity (where a blank correction would make little or no difference) or extremely low activities (where the counts due to uranium were essentially at or below background).

Uranium extraction, scrubbing and stripping distribution coefficients were determined from the simulated SBW solution spiked with ^{233}U . The concentration of ^{233}U spike in the simulant was 4×10^{-4} M. The two experimental methods previously outlined and discussed in accord with Figures 2 and 3 were used to examine the uranium distribution coefficients.

The results of the uranium forward extractions are presented in Table 3. It is apparent from the sample analysis that virtually all of the uranium in the aqueous feed was extracted into the TRUEX solvent during the first contact. The average uranium distribution coefficient for the two initial forward extractions, E1 and E4, is $D_0 = 1709$, indicating that extracting the uranium from the sodium waste should not be difficult. This is not unexpected since the TRUEX solvent is essentially identical to the solvent used in the PUREX process (30 vol% TBP in dodecane) for uranium separation. It is also possible that CMPO and TBP could even act synergistically to extract uranium.

Activities for E1-O and E4-O are slightly larger than the activities of the initial feeds. This is probably due to the slightly larger volume pipetted when taking the 1 ml organic aliquot. Small volume differences resulting from slight inaccuracies associated with pipetting the organic solvent (due to the density and viscosity of the solvent being different than

Table 3. Results of the uranium extractions.

Sample	Volume (ml)	Activity (dpm/ml)	Aqueous [HNO ₃] (M)	D ₀	Material Balance (In/Out)
Feed-1	18	6.04E5	ND	---	---
E1-O	18	6.12E5	ND	1760	101%
E1-A	18	3.48E2	1.51		
E2-O	7	BDL	ND	NA	NA
E2-A	7	BDL	1.46		
E3-O	3	BDL	ND	NA	NA
E3-A	3	BDL	1.44		
Feed-2	20	6.03E5	ND	NA	NA
E4-O	20	6.14E5	ND	1659	102%
E4-A	20	3.70E2	1.48		
E5-O	6	BDL	ND	NA	NA
E5-A	6	BDL	1.53		
E6-O	3	BDL	ND	NA	NA
E6-A	3	BDL	1.45		

BDL = Below Detection Limits

ND = Not Determined

NA = Not Applicable

that of water) are particularly noticeable when working with high activities.

The two loaded organic raffinates, E1-O and E4-O, were scrubbed with 0.2 M HNO₃. The result of the scrub contacts are summarized in Table 4.

Scrubbing distribution coefficients for uranium decreased for both sets of experiments as the number of scrub contacts increased. The decrease in D₀ is attributed to the decreasing acid concentration of the organic associated with back-extraction or scrubbing of nitric acid. Distribution data for both sets of experiments agree favorably; however, some uranium does back-extract to the aqueous scrub solution. The activity of uranium stripped from the solvent may have been reduced if a more realistic scrub organic-to-aqueous ratio (O/A) had been used.

Table 4. Results of the uranium scrub contacts.

Sample	Volume (mℓ)	Activity (dpm/mℓ)	Aqueous [HNO ₃] (M)	D _{ij}	Material Balance (In/Out)
E1-O (Feed)	16	6.12E5	ND	---	---
Sc1-O	16	6.31E5	ND	450	103%
Sc1-A	16	1.40E3	0.84		
Sc2-O	13	6.31E5	ND	229	101%
Sc2-A	13	2.75E3	0.39		
Sc3-O	11	6.22E5	ND	161	99%
Sc3-A	11	3.85E3	0.26		
E4-O (Feed)	18	6.14E5	ND	---	---
Sc4-O	18	6.26E5	ND	476	102%
Sc4-A	18	1.32E3	0.83		
Sc5-O	15	6.33E5	ND	256	102%
Sc5-A	15	2.48E3	0.40		
Sc6-O	13	6.32E5	ND	156	100%
Sc6-A	13	4.06E3	0.26		

ND = Not Determined

Typically, organic to aqueous flows are maintained at an O/A = 3 in the scrub section [6] which maintains the acid concentration of the organic high enough to hinder the actinide stripping during the scrub contacts.

The scrubbed organic raffinate from Sc3-O was split into two equal volume aliquots which were used for the TUCS and oxalic acid stripping tests in accord with Figure 2. One aliquot was successively contacted with equal volumes of the TUCS reagent, (0.25 M Ionquest 201[®] in 0.05 M HNO₃). The other aliquot was contacted three successive times with equal volumes of 0.1 M H₂C₂O₄ in 0.01 M HNO₃. Uranium stripping distributions determined for the TUCS and oxalic acid contacts are shown in Tables 5 and 6, respectively.

Table 5. Results of the uranium stripping contacts with the TUCS reagent.

Sample	Volume (ml)	Activity (dpm/ml)	Aqueous [H ⁺] (M)	D _{ij}	Material Balance (In/Out)
SC3-O (Feed)	5	6.22E5	ND	---	---
St1-O	5	1.56E2	ND	2.5E-4	100%
St1-A	5	6.23E5	0.77		
St2-O	3	BDL	ND	NA	NA
St2-A	3	BDL	0.69		
St3-O	1.5	BDL	ND	NA	NA
St3-A	1.5	BDL	ND		

BDL = Below Detection Limits

ND = Not Determined

NA = Not Applicable

Table 6. Results of the uranium stripping contacts with 0.1 M oxalic acid.

Sample	Volume (ml)	Activity (dpm/ml)	Aqueous [H ⁺] M	D _{ij}	Material Balance (In/Out)
Sc3-O (Feed)	5	6.22E5	ND	---	---
St4-O	5	4.33E5	ND	2.4	99 %
St4-A	5	1.82E5	0.14		
St5-O	3	1.91E5	ND	0.8	99 %
St5-A	3	2.37E5	0.16		
St6-O	1.5	6.74E4	ND	0.6	95 %
St6-A	1.5	1.13E5	0.20		

ND = Not Determined

From the distribution data shown in Tables 5 and 6, oxalic acid and TUCS are both effective at stripping uranium from the TRUEX solvent. The TUCS reagent does seem to be more efficient in uranium stripping than the oxalic acid; virtually all of the uranium was stripped from the organic in the first contact. The oxalic acid did become more effective as the acid concentration decreased; however, a white precipitate was observed after

centrifuging the phases from the first contact. The excellent material balance (99%) suggests this precipitate did not contain uranium, but solid formation, regardless of its nature, is unwanted in solvent extraction processes. Decreasing the oxalic acid concentration or using ammonium oxalate in the stripping solution may eliminate this precipitation.

Dilute nitric acid strips followed by sodium carbonate washes were performed on Sc6-O according to the experimental method depicted in Figure 3. Uranium distributions obtained from these contacts are shown in Table 7.

Even though D_o decreases with each successive dilute acid strip, the distribution coefficients are probably too high to effectively strip uranium from the TRUEX solvent. These results are not unexpected and agree favorably with literature values

Table 7. Results of uranium stripping with dilute nitric acid and solvent washing with sodium carbonate.

Sample	Volume (ml)	Activity (dpm/ml)	Aqueous [HNO ₃] (M)	D_o	Material Balance (In/Out)
Nitric Acid Strips Sc6-O (Feed)	11	6.32E5	ND	---	---
St7-O	11	6.12E5	ND	33.4	100%
St7-A	11	1.84E4	0.069		
St8-O	8	5.40E5	ND	7.6	100%
St8-A	8	7.15E4	0.17		
St9-O	6	4.13E5	ND	3.3	100%
St9-A	6	1.25E5	0.01		
Carbonate Washes W1-O	4	1.22E3	ND	3.1E-3	97%
W1-A	4	3.99E5	ND		
W2-O	2	6.83E2	ND	1.33	98%
W2-A	2	5.15E2	ND		

ND = Not Determined

found for stripping uranium from the TRUEX solvent using dilute nitric acid [11]. In fact, it is the inability of dilute nitric acid to strip uranium that results in typical TRUEX flowsheets (see Figure 1) incorporating a separate uranium stripping section, commonly with TUCS as the stripping solution.

It is apparent that washing the solvent with 0.25 M Na_2CO_3 is also effective in removing uranium. The first contact with sodium carbonate resulted in a $D_U = 0.0031$. The uranium distribution for the second contact, W2, is much larger and therefore inconsistent with that observed in the first contact. This inconsistency could be due to cross-contamination of the organic and aqueous phases. However, the reasonable material balance (98%) indicates this is probably not the case.

Data obtained during the uranium tracer experiments indicate the potential for a simplified TRUEX flowsheet that allows the gross separation of actinides from SBW. Since gross actinide separation is currently desired, the TUCS reagent may prove beneficial when used to collectively strip the actinides from the TRUEX solvent. This would eliminate the dilute nitric acid stripping section and potentially reduce the number of scrub stages required to remove co-extracted acid and inerts. A reduction in the number of scrubbing stages could result due to the higher acidity of the TUCS reagent ($\sim 0.7 \text{ M H}^+$). In order for a reduction in the number of scrubbing stages to occur, it is necessary for the TUCS reagent to effectively strip each of the actinides, as well as nitric acid, from the organic phase. Oxalic acid could conceivably provide similar flowsheet simplification, provided the precipitate formation issue can be resolved. Further work is required prior to development of a flowsheet that allows for the gross separation of the actinides using either TUCS or oxalic acid.

Plutonium Results

The total plutonium content, as the sum of several Pu isotopes, averages approximately $2.3\text{E-}5 \text{ M}$ in actual SBW [4,5]. Consequently, it is necessary to fractionate this material from the SBW and immobilize it in a suitable waste form for final disposition.

For tracer tests with Pu-238, 28 ml of the SBW simulant was spiked with 2 ml of NIST traceable Pu²³⁸ standard (37,400 dps/ml) in 1 wt. % HNO₃. Radiochemical analyses were performed on the feed using the liquid scintillation method. Feed analysis indicated a count rate of 102,611.4 dpm/ml. A 1 ml sample of the pre-equilibrated TRUEX solvent and 1 ml of the SBW simulant were counted as organic and aqueous "blanks", respectively. These activities, 107.98 dpm/ml for the organic and 85.85 dpm/ml for the aqueous, were subtracted from the each respective organic or aqueous sample analysis as a blank correction. Consequently, the corrected analysis of the spiked Na waste feed solution was 102,525.55 dpm/ml. Based on this feed analysis, the concentration of Pu-238 in the spiked feed was calculated to be $1.133\text{E-}08 \text{ M}$ Pu or roughly three orders of magnitude below the average concentration of actual SBW.

The results of the forward extractions with Pu-238 are summarized in Table 8. The first forward extraction, E1, resulted in a Pu distribution coefficient of $D_{\text{Pu-238}} = 500$, which compared favorably to that of E4 where $D_{\text{Pu-238}} = 471$. Distribution coefficients for the second forward extractions (E2 & E5) were also consistent with $D_{\text{Pu}} = 5.2$ and 11, respectively, but were much smaller than observed for the first forward extractions. This lowering of the distribution ratio is a consequence of the affinity of the TRUEX solvent for Pu. The interpretation is simply that most of the Pu was extracted from the feed during the first extraction step, leaving little or none to be removed in subsequent contacts. This is substantiated by the material balances, which vary from 100% by significant amounts for E2, E3, and E5. Virtually complete plutonium extraction from the feed in

Table 8. Summary of experimental extraction results with the Pu-238 traced SBW simulant.

Organic Blank = 107.98 dpm/ml			Aqueous Blank = 85.85 dpm/ml		
Sample	Volume Contacted (ml)	Corrected Count (dpm/ml)	Aqueous [HNO ₃] (M)	D _{Pu}	Material Balance (In/Out)
Feed-1	---	1.03E5	ND	---	---
E1-O	18	1.03E5	ND	500	100%
E1-A	18	2.05E2	1.43		
E2-O	5	1.56E2	ND	5.2	114%
E2-A	5	2.98E1	ND		
E3-O	3	BDL	ND	NA	89%
E3-A	3	2.80E1	1.21		
Feed-2	---	1.03E5	ND	---	--
E4-O	20	1.05E5	ND	471	97%
E4-A	20	2.23E2	1.44		
E5-O	7	2.71E2	ND	11	75%
E5-A	7	2.49E1	1.37		
E6-O	3	BDL	ND	NA	102%
E6-A	3	2.45E1	1.38		

BDL = Below Detection Limits

ND = Not Determined

NA = Not Applicable

a single contact verifies the applicability of the TRUEX process for plutonium removal from the SBW.

The loaded organics from initial contacts (E1 & E4) were used in subsequent tests to evaluate the effects of dilute acid scrubs and the efficiency of different stripping reagents. These organic raffinates were scrubbed three consecutive times with 0.2 M HNO₃. Scrubbing is typically associated with back extraction of both inert materials (Zr, Fe, Cr, etc.) and nitric acid, which are co-extracted with the actinides from the feed, thereby alleviating these components from the actinide rich aqueous effluent. The results of these dilute acid scrubs are presented

in Table 9. The distribution coefficient decreased with each consecutive scrub from $D_{Pu} \sim 95$ in the first contact to $D_{Pu} \sim 20$ in the final scrub. These distributions are sufficiently high to insure most of the plutonium remains in the organic during scrubbing contacts. Note that the acid concentration in the aqueous raffinate consistently decreases toward the scrub acid concentration of 0.2 M HNO_3 for each contact, attesting to the back-extraction of nitric acid from the loaded organic.

Table 9. Pu-238 0.2 M HNO_3 scrub distribution coefficients.

Organic Blank = 107.98 dpm/ml Aqueous Blank = 85.85 dpm/ml Results are Blank Corrected					
Sample	Volume Contacted (ml)	Corrected Count (dpm/ml)	Aqueous [HNO_3] M	D_{Pu}	Material Balance (In/Out)
E1-O (Feed)	---	1.03E5	ND	---	---
Sc1-O	16	1.04E5	ND	96	97%
Sc1-A	16	1.08E3	0.820		
Sc2-O	14	1.03E5	ND	43	99%
Sc2-A	14	2.40E3	0.391		
Sc3-O	12	9.90E4	ND	17	98%
Sc3-A	12	5.72E3	0.260		
E4-O (Feed)	---	1.05E5	ND	---	---
Sc4-O	18	1.01E5	ND	93	103%
Sc4-A	18	1.08E3	0.838		
Sc5-O	15	1.06E5	ND	46	93%
Sc5-A	15	2.29E3	0.405		
Sc6-O	13	1.01E5	ND	24	101%
Sc6-A	13	4.23E3	0.263		

ND = Not Determined

The scrubbed organic from the first experiment, E1-O, was split into equal volume fractions for stripping studies with TUCS (0.25 M Ionquest 201[®] in 0.05 M HNO₃) and with 0.1 M H₂C₂O₄ in 0.01 M HNO₃ as indicated in Figure 2. The results of these strips are listed in Table 10. Note that the distribution ratio in the first TUCS stripping contact, St1, was $D_{Pu} = 2.1E-03$, indicating virtually all the plutonium in the organic was removed in a single contact. The increased D value in the subsequent TUCS contacts, St2 and St3, for which $D_{Pu} = 2.8$ and 2.1, respectively, is attributed to the greatly decreased plutonium activity in the feed. As a result, the detection limits of the analytical instrument were approached. Regardless, TUCS is obviously very effective at removing plutonium from the organic phase. The final stripping contact shown in Table 10, St4, is for a 0.01 M oxalic acid strip of the loaded organic. The distribution coefficient was $D_{Pu} = 0.24$ for this contact. Note, however, that the material balance indicates some discrepancy in the data. This is attributed to the formation of a white precipitate which settled in the aqueous phase at the bottom of the test tube. Much of the plutonium is postulated to have been "carried out" of solution due to entrainment in the precipitate. The solid is currently pending characterization. Unfortunately, the quantity of organic raffinate from ST4 was insufficient to permit second and third oxalic acid extractions. It should be noted that precipitate formation during initial oxalate stripping contacts is a recurring theme and this behavior was also observed during the americium and uranium tracer tests.

Table 10. Pu-238 stripping distribution coefficients using TUCS and oxalic acid.

Organic Blank = 107.98 dpm/ml			Aqueous Blank = 85.85 dpm/ml		
Results are Blank Corrected					
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [H ⁺] M	D _{Am}	Material Balance (In/Out)
TUCS Strips Sc3-O (Feed)	5	9.90E4	ND	---	---
St1-O	5	2.00E2	ND	2.1E-3	104%
St1-A	5	9.51E4	0.567		
St2-O	3	1.57E2	ND	2.8	94%
St2-A	3	5.66E1	0.704		
St3-O	1.5	6.19E1	ND	2.1	100%
St3-A	1.5	8.05E0	0.683		
Oxalic Strips Sc3-O (Feed)	5	9.10E4	ND	---	---
St4-O	5	8.44E3	ND	0.24	230% ppt formation
St4-A	5	3.46E4	0.144		

ND = Not Determined

The scrubbed organic from the second extraction experiment was subjected to three consecutive equal volume strips with 0.01 M HNO₃ solution (St7, St8 and St9) followed by two 0.25 M Na₂CO₃ solvent washes (W1 and W2). The results of this series of strips and washes are listed in Table 11. In the dilute acid strips, the plutonium distribution coefficient was in the range of D_{Pu} ~ 1.5 to 22, indicating 0.01 M HNO₃ is not very effective at stripping plutonium from the (scrubbed) organic phase. The distribution ratio from the first carbonate wash is quite small, with D_{Pu} = 2.6E-03, indicating effective Pu stripping from the organic. However, a rust colored precipitate was observed in the bottom of the test tube after this contact. The solid is currently being characterized. Based on the excellent material balance (101%) for the first carbonate wash, plutonium was obviously not entrained in the precipitate.

Table 11. Pu-238 stripping and washing distribution coefficients with 0.01 M HNO₃ and 0.25 M Na₂CO₃.

Organic Blank = 107.98 dpm/ml Aqueous Blank = 85.85 dpm/ml Results are Blank Corrected					
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [H ⁺] N	D _{Pu}	Material Balance (In/Out)
HNO ₃ Strips Sc6-O (Feed)	11	1.01E5	ND	---	---
St7-O	11	8.71E4	ND	6.0	99%
St7-A	11	1.47E4	0.070		
St8-O	9	5.28E4	ND	1.6	103%
St8-A	9	3.20E4	0.017		
St9-O	7	5.00E4	ND	22	101%
St9-A	7	2.32E3	0.011		
Carbonate Washes W1-O	5	1.27E2	ND	0.0026	101% ppt formation
W1-A	5	4.94E4	ND		
W2-O	3	4.69E1	ND	0.8	121%
W2-A	3	5.77E1	ND		

ND = Not Determined

The precipitation of the rust colored solid is a recurring theme in carbonate washing of the TRUEX solvent, having been observed during uranium, americium, as well as the plutonium tracer experiments. However, the formation of the precipitate was not observed during carbonate washing of TRUEX solvents which were previously stripped with the TUCS solution. A second carbonate wash of the organic, W2, with a distribution coefficient of $D_{Pu} = 0.8$, indicates further Pu removal from the organic phase. However, so much of the activity had been removed from the organic during the first carbonate wash as to make the second contact unnecessary, resulting in the low activity in the W2-O and W2-A samples. Analytical detection limits were approached as attested by the somewhat high material balance (121%) associated with W2.

In general, the data associated with plutonium behavior during TRUEX extraction and stripping from the SBW simulant is indicative of expected trends and conforms to literature reports for similar feed types [12]. Furthermore, these results are comparable to those generated by the Generic TRUEX Model developed at Argonne. In conclusion, the TRUEX process is a viable method for the removal of plutonium from sodium bearing waste. Finally, TUCS appears to have a great deal of utility for plutonium stripping from the loaded organic.

Americium Results

Americium-241 is present in the SBW at an average concentration of $8.8\text{E-}8 \text{ M}$ [4,5]. Consequently, this isotope must be removed from the liquid waste and immobilized for final disposal.

The extraction and stripping of americium by the TRUEX solvent was experimentally studied from simulated SBW. Trivalent americium is one of the more difficult transuranics to extract with and strip from the TRUEX solvent. The aqueous feed was prepared by spiking 38 ml of the simulated sodium waste with 2 ml of a Am^{241} standard ($1.69 \times 10^5 \text{ dps/ml}$ in 1% HNO_3). Liquid scintillation analysis of the spiked feed indicated an Am activity of 488,446 dpm/ml. An organic blank, counted at the same time as the feed, indicated a count rate 118 dpm/ml. This blank analysis was subtracted from all sample analyses. Thus, the blank corrected SBW feed analyzed at 488,328 dpm/ml. The molar concentration of americium spiked into the SBW feed simulant was $2.7 \times 10^{-7} \text{ M}$ Am-241, which is an order of magnitude more than the average concentration in the actual SBW [4,5].

The experimental methods shown in Figures 2 and 3 were used to determine extraction, scrubbing and stripping distribution coefficients for americium. The experimental results of the Am-241 extraction tests are summarized in Table 12.

Table 12. Extraction distribution coefficients for Am-241 spiked into SBW simulant.

Organic Blank = 118 dpm/ml			Results are Blank Corrected		
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [HNO ₃] M	D _{Am}	Material Balance (In/Out)
Feed	18	4.88E5	ND	---	---
E1-O	18	4.61E5	ND	33	102%
E1-A	18	1.40E4	1.34		
E2-O	5	1.36E4	ND	32	100%
E2-A	5	4.27E2	ND		
E3-O	3	3.94E2	ND	21	103%
E3-A	3	1.89E1	1.34		
Feed	20	4.88E5	ND	---	---
E4-O	20	4.80E5	ND	27	97%
E4-A	20	1.79E4	1.33		
E5-O	8	1.92E4	ND	28	90%
E5-A	8	6.93E2	1.37		
E6-O	5	6.62E2	ND	33	102%
E6-A	5	1.99E1	1.33		

ND = Not Determined

The americium extraction distributions ranged from D_{Am} = 21 to 33 for the six contacts performed with the SBW simulant. Fresh pre-equilibrated TRUEX solvent was used for each contact. For the first series of forward extractions, E1 through E3, 99.997% of the americium was extracted from the spiked simulant. Data from the second set of extractions, E4 through E6, show that 99.996% of the americium was extracted. Americium distribution coefficients determined in this test indicate that removing americium from the SBW is feasible.

The loaded solvents resulting from the first set of extractions, E1 and E4, were scrubbed with 0.2 M HNO₃. The americium distribution coefficients determined for each scrub contact are shown in Table 13. It is apparent that the americium

Table 13. Am-241 scrub distribution coefficients.

Organic Blank = 118 dpm/ml			Results are Blank Corrected		
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [HNO ₃] M	D _{Am}	Material Balance (In/Out)
E1-O (Feed)	16	4.61E5	ND	---	---
Sc1-O	16	4.67E5	ND	22	106%
Sc1-A	16	2.17E4	0.82		
Sc2-O	14	4.24E5	ND	10	100%
Sc2-A	14	4.34E4	0.38		
Sc3-O	12	3.54E5	ND	5	101%
Sc3-A	12	6.78E4	0.25		
E2-O (Feed)	18	4.80E5	ND	---	---
Sc4-O	18	4.65E4	ND	27	98%
Sc4-A	18	2.67E4	0.79		
Sc5-O	15	4.20E5	ND	17	99%
Sc5-A	15	4.87E4	0.38		
Sc6-O	13	3.46E5	ND	8.6	100%
Sc6-A	13	7.28E4	0.25		

ND = Not Determined

distribution coefficient decreases as the acid concentration in the organic decreases upon successive scrub contacts. The americium distribution, D_{Am} , for the scrub contacts could be kept favorably higher by changing the scrub O/A phase ratio. Increasing the scrub O/A would most likely keep the acid concentration of the organic phase high enough to prevent stripping large amounts of americium.

The scrubbed solvent, Sc3-O, was split into two equal volume aliquots. One of these aliquots was contacted with TUCS while the other aliquot was stripped with 0.1 M H₂C₂O₄ in 0.01 M HNO₃ in accord with Figure 2. Table 14 lists the results of the TUCS and oxalic acid americium strips.

Table 14. Am-241 stripping distribution coefficients using TUCS and oxalic acid.

Organic Blank = 118 dpm/ml Results are Blank Corrected					
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [H ⁺] N	D _{Am}	Material Balance (In/Out)
TUCS Strips S3-O (Feed)	5	3.54E5	ND	---	---
St1-O	5	1.67E2	ND	5E-4	101%
St1-A	5	3.50E5	0.77		
St2-O	3.5	8.23E1	ND	1.2	110%
St2-A	3.5	7.00E1	0.71		
St3-O	2	6.19E1	ND	7.7	118%
St3-A	2	8.05E0	0.73		
Oxalic Strips Sc3-O (Feed)	5	3.54E5	ND	---	---
St4-O	5	6.39E2	ND	0.09	2% ppt formation
St4-A	5	7.34E3	0.15		
St5-O	3.5	1.53E1	ND	0.02	100%
St5-A	3.5	6.22E2	0.15		
St6-O	2	0	ND	NA	NA
St6-A	2	0	0.19		

ND = Not Determined

NA = Not Applicable

The TUCS reagent stripped 99% of the americium from the loaded TRUEX solvent, Sc3-O, during the first stripping contact, St1. The americium distribution coefficient for the second and third TUCS strips, St2 and St3, are considerably larger ($D_{Am} = 1.2$ and 7.7 , respectively) than the distribution of $D_{Am} = 5E10^{-4}$ for St1. Reasons for the difference in TUCS stripping distributions may be: 1) low americium activities in both phases of the St2 and St3 contacts resulting in poor counting statistics, 2) cross contamination of phases during sampling, 3) acidity of the TUCS reagent (0.7 M H^+), 4) small amounts of impurities in the CMPO, or 5) the TUCS reagent is unable to completely strip americium from the TRUEX solvent. Of these

reasons, cross contamination and the TUCS acidity seem to be the most likely cause of the discrepancy found in the americium distribution coefficients associated with the TUCS strips.

Oxalic acid was also found to be effective in stripping americium from the TRUEX solvent. A poor material balance was obtained on the first oxalic acid strip, St4. Undoubtedly, this is due to the formation of an insoluble americium complex with oxalate. Neglecting the activity of americium lost to the precipitate, a $D_{Am} = 0.09$ was achieved for the first oxalate strip. Assuming the activity is lost from the aqueous phase, an even smaller D_{Am} is realized if all the activity from Sc3-O is used in a material balance:

$$D_{Am} = \frac{[St4-O \text{ (dpm)}]}{[Sc3-O \text{ (dpm)}] - [St4-O \text{ (dpm)}]} = \frac{6.39E2 \text{ dpm/ml}}{[3.54E5 \text{ dpm/ml}] - [6.39E2 \text{ dpm/ml}]} = 0.002$$

Material balance data for St5 indicates that americium was not lost and a precipitate was not visibly observed for this contact. No activity was detected in either phase after the last oxalic acid strip, St6. Even though oxalic acid is effective in stripping americium from the TRUEX solvent, its use as a gross actinide stripping agent is not appealing due to the formation of insoluble complexes that normally form in the presence of most of the actinides. Again, the use of ammonium oxalate as a stripping reagent may alleviate the precipitate problem.

Scrubbed organic, Sc6-O, from the second set of contacts was stripped with 0.01 M HNO_3 and washed with 0.25 M Na_2CO_3 in accord with Figure 3. Results from the stripping and washing contacts are summarized in Table 15.

Ninety-seven percent of the americium in St6-O was stripped after three contacts with 0.01 M HNO_3 . As expected, the distribution ratio decreases as the acid concentration of the strip decreases, except for the final strip contact, St9. An unexpectedly high $D_{Am} = 0.9$ was observed with an acid concentration of 0.01 M HNO_3 . Material balance data for this

Table 15. Am-241 stripping and washing distribution coefficients with 0.01 M HNO₃ and 0.25 M Na₂CO₃.

Organic Blank = 118 dpm/ml			Results are Blank Corrected		
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Aqueous [H ⁺] N	D _{Am}	Material Balance (In/Out)
Nitric Acid Strips Sc6-O (Feed)	11	3.46E5	ND	---	---
St7-O	11	1.35E5	ND	0.69	104%
St7-A	11	1.97E5	0.07		
St8-O	9	2.02E4	ND	0.18	104%
St8-A	9	1.10E5	0.02		
St9-O	7	9.28E3	ND	0.91	184%
St9-A	7	1.01E4	0.01		
Carbonate Washes W1-O	5	2.47E1	ND	0.003	124% ppt formation
W1-A	5	7.45E3	ND		
W2-O	3	BDL	ND	NA	NA
W2-A	3	BDL	ND		

BDL = Below Detection Limit

ND = Not Determined

NA = Not Applicable

contact indicates cross contamination is the probable cause of this high distribution coefficient. This distribution does not correlate to americium distribution coefficients cited in the literature [2] nor with those determined previously at the ICPP [7]. Earlier but unreported stripping tests, performed with TRUEX solvent contacted with americium spiked SBW simulant, indicated a steady decrease in D_{Am} as the acid concentration decreases. Therefore, D_{Am} observed for St9 is inconsistent with previous experimental data. Dilute nitric acid is expected to be an effective americium stripping agent.

As in previous tracer experiments, a precipitate was noticed after the first sodium carbonate wash, W1. Material balance data suggest that some of the americium was lost to this precipitate. The chemical characteristics of the precipitate is not known at

this time, however a precipitate sample has been sent to Analytical Chemistry for XRD analysis. No precipitate was observed in the second carbonate wash, W2.

Neptunium Results

The average Np-237 concentration in SBW is 454 nCi/l or $2.7\text{E-}6$ M Np [4,5]. As a result, Np must be removed from the SBW and immobilized in an appropriate waste for final disposition.

Neptunium, primarily in the pentavalent oxidation state, Np(V), is reportedly one of the more difficult transuranics to extract with the TRUEX process solvent [12]. A series of extraction and stripping experiments were performed to evaluate the behavior of Np-239 in the sodium bearing waste under TRUEX processing conditions. The Np-239 standard was prepared and purified by the ICPP Radiochemistry group. Np-239 was first milked from a Am-243 "cow" (Am-243 absorbed onto a cation exchange column) with HIO_4 and HCl. The Np-239 fraction was taken to dryness twice in HNO_3 and converted to the nitrate form. The Np-239, as Np^{+5} , was then further purified by passing it over a TRU-SPEC column to remove any residual americium.

Due to the short $1/2$ life of Np-239 ($t_{1/2} = 2.355$ days), all analyses were, of necessity, corrected for decay and for background. The spiked aqueous feed was prepared by adding 5.5 ml of the Np-239 standard to 10 ml of the SBW simulant. A sample of the aqueous feed was analyzed at an activity of 1,641.03 dpm/ml, which, when blank and decay corrected equated to 2,205.18 dpm/ml. A blank organic sample analysis indicated a count of 118.78 dpm/ml, and was used for blank correction of all subsequent analyses. Thus, the Np-239 concentration in the spiked SBW simulant feed solution was $1.99\text{E-}14$ M Np, which is much less than the average concentration in actual SBW.

The experimental procedure for tracer studies with neptunium was somewhat different than those presented in Figures 2 and 3 for uranium, plutonium and americium. The schematic of the

experimental TRUEX extractions with neptunium is indicated in Figure 4. As before, three consecutive forward extractions, E1-E3, were performed with the aqueous feed using fresh, pre-equilibrated organic for each contact. The loaded organic from the first extraction was contacted three consecutive times with dilute (0.01 M) HNO_3 , and a fourth contact was performed with 0.1 M oxalic acid in water. Scrubbing contacts with dilute nitric acid were not performed in this set of experiments.

Consequently, stripping contacts St1 through St3 served the dual purpose of scrubbing and stripping. Consequently, larger distribution coefficients were anticipated for these strips than would be expected if several 0.2 M HNO_3 scrub steps had been included. As with previous results, sample results are labelled in a manner consistent with those indicated in Figure 4.

Experimental results of the Np-239 extractions and strips are summarized in Table 16. The distribution coefficient in the first forward extraction (E1) was $D_{\text{Np-239}} = 2.28$. Subsequent forward extractions indicated reasonable agreement with $D_{\text{Np-239}} = 1.20$ for E2 and $D_{\text{Np-239}} = 1.40$ in the third forward extraction, E3. These values are consistent with those available in the literature [12,13] and with GTM results for Np(V) , e.g., $D_{\text{Np-239}} \approx 1$ to 3 . Consequently, Np(V) is slightly extracted from SBW simulant, but not to the extent of Pu or Am. The material balances for the third extraction, E3, was somewhat high (129.7%) and is attributed to cross contamination of the aqueous and organic phases or poor counting statistics associated with the low activity of the samples. Material balances for E1 and E2 are reasonable and lend credibility to the results of these two contacts.

Stripping results with 0.01 M HNO_3 (St1, St2, St3, and St5) are consistent and indicate the same trend as with previous dilute acid strips for Pu and Am, e.g., the distribution ratio decreases with successive stripping contacts due to the effects of scrubbing acid from the organic phase. Especially for the third dilute acid strip, St3, where $D_{\text{Np-239}} = 0.366$, it is

Figure 4. Experimental Schematic used with Neptunium Tracer

Table 16. Summary of experimental results with the Np-239 traced SBW simulant.

Organic Blank = 118.78 dpm/ml Corrected for blank & decay time: $T_d = 9/22/93$ @ 1005 hrs					
Sample	Volume Contacted (ml)	Actual Count (dpm/ml)	Blank & Decay Corrected Count (dpm/ml)	D_{Np-239}	Material Balance (In/Out)
Feed	---	1641.03	2205.2	---	113.1%
E1-O	13	1122.26	1463.6	2.28	104.8%
E1-A	13	555.52	641.5		
St1-O	11	865.73	1104.8	2.60	95.7%
St1-A	11	403.91	424.7		
St2-O	9	588.43	704.4	1.83	101.4%
St2-A	9	373.95	385.3		
St3-O	7	241.82	187.1	0.366	100.9%
St3-A	7	452.57	511.0		
St4-O	5	96.98	-33.60	BDL'	124.0%
St4-A	5	237.63	184.4		
E2-O	6.5	371.19	394.4	1.20	106.5%
E2-A	6.5	251.00	208.0		
St5-O	2	239.5	193.9	1.01	102.0%
St5-A	2	273.91	192.7		
St6-O	2	149.25	49.62	0.155	106.8%
St6-A	2	313.69	319.6		
E3-O	2	177.82	93.53	1.40	129.7%
E3-A	2	160.73	66.92		

apparent that Np-239 is readily removed from the loaded organic phase. The material balances for the 0.01 M HNO_3 are all reasonable and lend credibility to the experimental data.

Stripping results with dilute oxalic acid (0.1 M $H_2C_2O_4$ in water), St4 and St6, are again less conclusive. Based on the distribution data, it appears that oxalate is effective at removing Np-239 from the organic phase. However, the data is

questionable in light of the high material balances in these two cases. The high material balances are postulated to have been due to precipitate formation, similar to those observed in previous oxalate strips. No precipitate was observed, however, this is not surprising considering the extremely dilute nature of Np in these solutions.

As with uranium, plutonium and americium tracer experiments, no severe limitations of the TRUEX process as applied to Np removal from SBW are anticipated.

Non-actinide Elements

Technetium Results

Technetium-99 is present in the actual SBW at an average concentration of 0.017 mCi/l or $1.01\text{E-}5$ M Tc [4,5]. Thus, the average Tc concentration in sodium bearing waste is well below the Class A limit of 0.3 Ci/m³. However, it could prove advantageous Tc from the SBW prior to final disposition.

Technetium - 95m was spiked into the sodium waste simulant to evaluate its distribution into the TRUEX solvent. ^{95m}Tc was used in this test because it is a gamma emitter and can be quantified non-destructively by gamma spectrometry. The 204 KEV and 582 KEV photopeaks were used to calculate ^{95m}Tc and have intensities of 64% and 36% respectively.

A NIST traceable ^{95m}Tc standard having an initial activity of 3476 dps/ml at T₀ = December 1, 1993 in 1 vol. % HNO₃ was prepared for these extractions. All activities were decay corrected back to T₀ due to the short half-life of ^{95m}Tc (61 days). The technetium activities were determined by gamma spectroscopy using ^{95m}Tc primary photopeak at 204.1 keV. The TRUEX solvent is reported to extract technetium as HTcO₄ [2,14]. To evaluate the extraction properties of ^{95m}Tc from the SBW simulant, 3 mls of the ^{95m}Tc standard was spiked into 12 mls of the simulant. The spiked solution was allowed to come to equilibrium over a 24 hour period. The activity of ^{95m}Tc in the spiked feed was 546 dps/ml, which corresponds to 6.89×10^{-12} M Tc in the feed. The experimental flowsheet shown in Figure 5 was used to evaluate the extraction, scrub, and stripping distribution coefficients for Tc.

Figure 5. Experimental Schematic used with Technetium Tracer

Results for the extraction of ^{95m}Tc from the SBW simulant into the TRUEX solvent are shown in Table 17. The technetium distribution coefficients for the forward extractions averaged $D_{\text{Tc}} = 4.2$ for the three forward contacts. Thus, after three contacts 99.3% of the activity had been removed from the feed. As is apparent from Table 17, the acid concentration of the aqueous raffinate tends to increase for each successive contact. This phenomenon is attributed to dilution of the feed when the Tc spike was added. Under ideal conditions, the HNO_3 concentration of the aqueous raffinate should have remained constant due to the pre-equilibration process. The acid concentration in the SBW simulant used for pre-equilibration of the organic was 1.45 M HNO_3 , while the acid concentration in the Tc spiked feed was 1.14 due to dilution of the simulant by the tracer solution. This apparently resulted in some of the acid in the organic to be stripped back into the spiked feed.

Literature reports [11] indicate $D_{\text{Tc}} = 6.1$ for a pure 1 M HNO_3 solution and a $D_{\text{Tc}} = 1.9$ for a 2 M HNO_3 solution. In those tests, the TRUEX solvent was pre-equilibrated with either 1 M or 2 M HNO_3 prior to determining D_{Tc} ; therefore, both phases were assumed to contain the respective equilibrium concentrations of nitric acid.

Table 17. Extraction D_{Tc} from SBW simulant.

Sample	Volume (ml)	Activity (dps/ml)	Aqueous [HNO_3] (M)	D_{Tc}	Material Balance (In/Out)
Feed	13	5.46E2	1.14	---	---
E1-O	13	4.29E2	ND	4.0	102 %
E1-A	13	1.07E2	1.27		
E2-O	11	8.55E1	ND	4.6	103 %
E2-A	11	1.87E1	1.3		
E3-O	3	1.53E1	ND	4.1	98%
E3-A	3	3.74E0	1.42		

ND = Not Determined

The equilibrium acid concentration of the SBW simulant ranged from 1.2 M to 1.4 M HNO₃, indicating the experimentally determined $D_{Tc} = 4.2$ is consistent with the literature reports.

The loaded TRUEX solvent from the first extraction, E1-O, was contacted with 0.2 M HNO₃ to determine technetium distribution coefficients during scrub contacts. The solvent was contacted three consecutive times with the scrub solution, fresh acid being used for each contact. Table 18 lists the results of these scrub contacts (Sc1 - Sc3). Analogous scrub contacts were also performed on the TRUEX solvent resulting from the second extraction contact (E2-O). These results are also presented in Table 18 (Sc4 - Sc6).

Small amounts of technetium activities were removed from the organic phases in the scrubbing contacts. Seventeen percent of the activity in E1-O was lost after three contacts with 0.2 M HNO₃, while approximately 20% of the activity in E2-O was removed during scrubbing. The activity scrubbed from the organic phase might have been much less if a more realistic organic-to-aqueous phase ratio (O/A = 3) would have been used. At an O/A = 3, the acid concentration in the scrubs would have been higher (less acid back-extracted from the organic) than occurred at the O/A = 1 used in these experiments. Concentrated nitric acid has also been found to effectively strip technetium from the TRUEX solvent [6]. Therefore, increasing the scrub acid concentration too much may result in technetium being stripped from the solvent. Scrubbing distribution coefficients for ^{95m}Tc averaged $D_{Tc} = 11.7$ for all six scrubbing contacts.

A technetium distribution coefficient of $D_{Tc} = 9.5$ was determined by Tse [11] when technetium was spiked into the TRUEX solvent and contacted with 0.5 M HNO₃. Tse also reported a $D_{Tc} = 8.3$ when the spiked solvent was contacted with 0.2 M HNO₃. These values agree favorably with the experimentally determined scrub distributions of this work.

Table 18. Scrub D_{Tc} for SBW contacted TRUEX solvent.

Sample	Volume (ml)	Activity (dps/ml)	Aqueous $[HNO_3]$ (M)	D_{Tc}	Material Balance (In/Out)
E1-O (Feed)	11	4.29E2	ND	---	---
SC1-O	11	4.04E2	ND	11.4	98%
SC1-A	11	3.50E1	0.76		
SC2-O	9	3.63E2	ND	13.9	110%
SC2-A	9	2.61E1	0.38		
SC3-O	7	3.55E2	ND	13.8	95%
SC3-A	7	2.58E1	0.25		
E2-O (Feed)	9	8.55E1	ND	---	---
SC4-O	9	8.00E1	ND	9.8	97%
SC4-A	9	8.20E0	0.78		
SC5-O	7.5	7.38E1	ND	11.3	100%
SC5-A	7.5	6.56E0	0.37		
SC6-O	6	6.87E1	ND	9.7	97%
SC6-A	6	7.07E0	0.25		

ND = Not Determined

The scrubbed organic feed, E1-O, was stripped with three successive contacts with fresh 0.01 M HNO_3 . Results of these dilute nitric acid stripping tests are summarized in Table 19. It is apparent that the technetium distribution ratio decreases as the number of strip contacts increases. This trend is due to the decrease in acid concentration of the organic due to the back-extraction of acid by the stripping solution. The nitric acid concentration in St1-A was 0.07 M, while in St3-A it had decreased to 0.008 M HNO_3 .

Tse reports a technetium distribution coefficient of $D_{Tc} = 3.16$ when using 0.05 M HNO_3 to strip technetium from spiked TRUEX solvent [11]. This value agrees favorably with the experimentally determined $D_{Tc} = 7.8$ in the first strip, St1.

Note that the equilibrium nitric acid concentration for St1-A was 0.07 M HNO₃. The experimentally determined $D_{Tc} = 1.5$ ($[HNO_3] = 0.02$ M) for St2 also agrees with that of $D_{Tc} = 1.5$ ($[HNO_3] = 0.02$ M) determined by Tse. A Tc distribution of $D_{Tc} = 0.6$ was observed for the final strip contact, St3, which is consistent with the trends for technetium distribution ratio found in the literature [11] and suggests that 0.01 M HNO₃ should effectively strip technetium from the TRUEX solvent.

It should also be noted that Tse reports low technetium distributions (0.75 - 0.05) when the TRUEX solvent is stripped with 3-8 M HNO₃. Recent developments in the extraction chemistry of mercury, also present in the SBW, suggests 5 M HNO₃ may be required to strip mercury from the TRUEX solvent (*vide infra*). Accordingly, if mercury is stripped with 5 M HNO₃, technetium could possibly be stripped concomitantly.

The scrubbed solvent from the second forward extraction, E2-O, was stripped with 0.01 and 0.1 M H₂C₂O₄ in 0.01 M HNO₃ in accord with Figure 5. This test was designed to determine Tc distributions using different concentrations of oxalic acid. The results of these stripping experiments are shown in Table 20. The data indicate a Tc distribution of $D_{Tc} = 1.9$ when the organic was stripped with 0.1 M H₂C₂O₄. In the case of stripping with 0.01 M H₂C₂O₄, a distribution coefficient of $D_{Tc} = 3.14$ was

Table 19. Stripping D_{Tc} from loaded TRUEX solvent.

Sample	Volume (ml)	Activity (dps/ml)	Aqueous [HNO ₃] (M)	D_{Tc}	Material Balance (In/Out)
Sc3-O (Feed)	5	3.55E2	ND	---	---
St1-O	5	3.18E2	ND	7.8	99 %
St1-A	5	4.07E1	0.07		
St2-O	3.5	1.89E2	ND	1.5	102 %
St2-A	3.5	1.23E2	0.02		
St3-O	2	7.71E1	ND	0.6	97 %
St3-A	2	1.18E2	0.008		

ND = Not Determined

observed. Even though these two distribution coefficients are not favorable for stripping technetium from the TRUEX solvent, they are smaller than the D_{Tc} obtained with the first 0.01 M HNO_3 strip listed in Table 19 ($D_{Tc} = 7.8$). Comparison of the first dilute nitric acid strip distribution ratio with the oxalic acid stripping distribution coefficients indicates oxalic acid may enhance the removal of Tc from the TRUEX solvent. Literature values were unavailable for the distribution coefficient of technetium for stripping with oxalic acid.

It should be noted that a white precipitate was observed at the bottom of both test tubes after each oxalic acid strip. The exact chemical nature of this precipitate is not known at this time. Since the technetium material balances are reasonable for both contacts, it was concluded that very little technetium was carried with this precipitate.

Table 20. Stripping D_{Tc} using oxalic acid.

Sample	Volume (ml)	Activity (dps/ml)	Aqueous $[HNO_3]$ (M)	D_{Tc}	Material Balance (In/Out)
Sc6-O (Feed)	2	6.87E1	ND	ND	---
0.01 M $H_2C_2O_4$ St1-O	2	5.28E1	ND	3.14	99 %
St1-A	2	1.68E1	ND		
0.1 M $H_2C_2O_4$ St2-O	2	4.55E1	ND	1.9	98 %
St2-A	2	2.35E1	ND		

ND = Not Determined

Mercury Results

In order to enhance the dissolution rate of aluminum clad fuels, mercury was added as a catalyst in the dissolution process. Consequently, high-level raffinates from reprocessing aluminum fuel types contained substantial quantities of dissolved mercury [15]. The liquid raffinates were subsequently solidified, or calcined, in a high temperature fluidized bed. At temperatures of nearly 500°C associated with the calcination process, much of the mercury was volatilized, scrubbed from the off-gas and accumulated in the SBW tanks. Analysis indicates the concentration of mercury in the SBW is typically between 100 and 900 mg/l Hg, which corresponds to $5\text{E-}4 \text{ M}$ and $4.5\text{E-}3 \text{ M}$ Hg, respectively. Consequently, an estimated 2 metric tons of mercury have accumulated in the SBW tank farm from reprocessing activities. References regarding the extraction of mercury by the TRUEX solvent are lacking in the literature. Due to the high mercury content and interest in the applicability of the TRUEX process to ICPP SBW, an experimental study on the behavior of mercury in the TRUEX solvent was undertaken. Results of experiments to examine the behavior of mercury, from both nitric acid solutions and simulated SBW have been presented elsewhere [16,17].

A NIST traceable Hg^{203} standard in HCl was purchased from Amersham. One milliliter of this standard was diluted to 100 ml with 2 M HNO_3 . The resulting activity of Hg^{203} in this solution was 14,864 dps/ml at T_0 = December 1, 1993 and contained 163 ppm Cl^- . Because of the short Hg^{203} half-life (46.8 days), all Hg^{203} results were decay corrected back to T_0 . Aliquots of the stock Hg^{203} solution were spiked into the SBW simulant. The spike was allowed to equilibrate with the SBW for approximately 24 hours prior to contacting with the TRUEX solvent.

Kinetic studies [16] have shown that mercury extraction into the solvent are rapid and that Hg^{203} quickly achieves equilibrium with stable mercury. The distribution coefficient of stable mercury was assumed to be that determined for Hg^{203} . Note that

during solvent pre-equilibration, cold mercury in the simulant is also extracted resulting in Hg loading of the organic prior to contact with the Hg^{203} spiked feed. Consequently, extractions with mercury containing solvent could conceivably skew distribution results. To alleviate this problem and to examine the extraction kinetics, a SBW simulant was prepared which contained no stable mercury. In certain tests, this solution was used for solvent pre-equilibration. This "mercury free" SBW feed was spiked with both stable Hg^{200} and radioactive Hg^{203} such that the mercury concentration was representative of the average for actual SBW. The distribution of mercury was always evaluated based on the Hg^{203} tracer analysis and was assumed representative of that for the cold mercury as well.

Two experimental schemes were utilized with mercury extractions from SBW. One scheme was similar to that used with technetium which was presented in Figure 5. The experimental flowsheet of Figure 5 was used to evaluate TUCS, dilute (0.01 M) nitric acid, dilute (0.01 M) hydrochloric acid, and dilute (both 0.1 and 0.01 M) oxalic acid as potential stripping reagents. Previous studies [16] predict 5 M HNO_3 would adequately strip mercury from the organic. A second flowsheet, shown in Figure 6, was used to test higher acid concentrations (5M) for both nitric and hydrochloric acids as stripping reagents. Carbonate washing was not performed during the mercury tests.

Multiple forward extraction contacts were performed on the spiked aqueous feed simulant. The results of these forward extractions are shown in Table 21. Extractions were repeated in several cases and the distribution coefficient was always consistent with the results in Table 21, averaging approximately $D_{\text{Hg}} = 3$ in all cases. These results indicate mercury can be extracted from SBW with the TRUEX process solvent.

Figure 6. Experimental Schematic Used to Test Hg Stripping at High Acid Concentrations ($[H^+] = 5\text{ M}$)

Table 21. Results of the mercury extractions.

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous $[HNO_3]$ (M)	D_{Hg}	Material Balance (In/Out)
Feed	15	1.57E3	1.47	---	---
E1-O	15	1.17E3	ND	3.0	101%
E1-A	15	3.88E2	1.49		
E2-O	12	2.77E2	ND	3.1	106%
E2-A	12	8.95E1	1.45		
E3-O	2	7.05E1	ND	3.1	96%
E3-A	2	2.29E1	1.47		

ND = Not Determined

The organic feed resulting from the first contact with the sodium waste (E1-O) was contacted three times with 0.2 M HNO₃ scrub solutions, followed by three contacts with 0.01 M HNO₃ strip solutions in accord with Figure 5. The results of the 0.2 M HNO₃ scrubs and 0.01 M HNO₃ strips are shown in Table 22. An increase in the distribution coefficient was observed in going from the first to the third scrub. This increase is attributed to decreasing organic acid concentration as nitric acid is back-extracted from the solvent on successive contacts. Recall that the acid concentration of scrub was 0.2 M HNO₃, the increase in scrub acid concentration above this initial value was due to the back-extraction of acid from the organic.

The mercury distribution was high, $D_{Hg} \sim 70$, for each of the dilute nitric acid strips. The large D_{Hg} values observed with the 0.2 M HNO₃ scrub and 0.01 M HNO₃ strip contacts indicate mercury is not significantly removed with these reagents.

Table 22. Mercury results for 0.2 M HNO₃ scrubs and 0.01 M HNO₃ strips.

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous [HNO ₃] (M)	D_{Hg}	Material Balance (In/Out)
E1-O (Feed)	13	1.17E3	ND	---	---
Sc1-O	13	1.15E3	ND	23.7	98%
Sc1-A	13	4.86E1	0.85		
Sc2-O	10	1.13E3	ND	46.7	100%
Sc2-A	10	2.42E1	0.39		
Sc3-O	8	1.13E3	ND	55.7	98%
Sc3-A	8	2.03E1	0.26		
St1-O	6	1.10E3	ND	71.4	101%
St1-A	6	1.54E1	0.068		
St2-O	4	1.09E3	ND	67.7	99%
St2-A	4	1.61E1	0.017		
St3-O	2.5	1.08E3	ND	67.2	99%
St3-A	2.5	1.61E1	0.0095		

ND = Not Determined

The loaded solvent resulting from the second feed contact (E2-O) was also scrubbed three times with 0.2 M HNO₃ in accord with Figure 5. The scrubbed solvent was then divided into two equal volume aliquots. One aliquot was stripped with 0.01 M H₂C₂O₄, the other aliquot was stripped with 0.1 M H₂C₂O₄. Table 23 lists the experimental results for these nitric acid scrubs and oxalic acid strips.

Mercury distribution coefficients for the two sets of 0.2 M HNO₃ scrub contacts listed in Tables 22 and 23 are in reasonable agreement. An increase in D_{Hg} is observed for each successive scrub. Again, this is attributed to a decrease in the organic acid concentration during successive scrubbing contacts.

It is apparent by the large distribution coefficients (D_{Hg} ~60) in Table 23 that oxalic acid did not effectively strip the mercury from the TRUEX solvent.

Table 23. Mercury results for 0.2 M HNO₃ scrubs and oxalic acid strips.

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous [HNO ₃] M	D _{Hg}	Material Balance In/Out
E2-O (Feed)	10	2.77E2	ND	---	---
Sc4-O	10	2.73E2	ND	25.5	98%
Sc4-A	10	1.07E1	0.84		
Sc5-O	7	2.69E2	ND	42.6	99%
Sc5-A	7	6.32E0	0.40		
Sc6-O	5.5	2.66E2	ND	57.8	99%
Sc6-A	5.5	4.60E0	0.25		
0.1 M H ₂ C ₂ O ₄ St4-O	2	2.59E2	ND	53.7	101%
St4-A	2	4.82E0	ND		
0.01 M H ₂ C ₂ O ₄ St5-O	2	2.64E2	ND	67.3	99%
St5-A	2	3.92E0	ND		

ND = Not Determined

Previous results for the extraction of mercury from pure nitric acid solutions [16] indicate the feasibility of stripping mercury from the loaded organic with nitric acid solutions $\geq 5 \text{ M HNO}_3$. Results of the experimental procedure described in Figure 6 for mercury stripping tests with 5 M nitric acid are shown in Table 24. Note that scrubbing is unnecessary since the acidity of the organic will increase during strip contacts with higher nitric acid concentrations. As in previous tests, the mercury distribution coefficient for the forward extraction was $D_{\text{Hg}} = 3$. The first strip contact with 5 M HNO_3 resulted in a distribution of $D_{\text{Hg}} = 0.66$, indicating the mercury was back-extracted from the organic. Similarly, low mercury distributions were observed for the second through sixth strip contacts. The Hg^{203} activity in the loaded solvent decreased from $1.11\text{E}3 \text{ dps/ml}$ after the initial forward extraction to 5.11 dps/ml after six strips.

Table 24. Results of mercury strips with 5 M HNO_3 .

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous M [HNO ₃]	D_{Hg}	Material Balance (In/Out)
Feed	15	1.57E3	ND	---	---
E1-O	15	1.11E3	ND	3.1	107%
E1-A	15	3.61E2	1.52		
St1-O	12	4.46E2	ND	0.66	99%
St1-A	12	6.76E2	4.68		
St2-O	9	1.73E2	ND	0.62	98%
St2-A	9	2.81E2	4.97		
St3-O	6	5.53E1	ND	0.53	109%
St3-A	6	1.04E2	4.91		
St4-O	4.5	2.63E1	ND	---	---
St4-A	4.5	ND	5.08		
St5-O	3	1.10E1	ND	0.33	60%
St5-A	3	3.32E1	ND		
St6-O	1.5	5.11E0	ND	0.84	98%
St6-A	1.5	6.06E0	5.22		

ND = Not Determined

To verify the accuracy of Hg distributions shown in Table 24, the experimental procedure shown in Figure 6 was repeated by pre-equilibration of the TRUEX solvent with the "mercury free" sodium waste simulant. Consequently, the TRUEX solvent was not pre-loaded with stable Hg^{200} prior to contact with the feed. The SBW for this experiment was prepared by spiking both stable Hg^{200} and radioactive Hg^{203} into the solution for the feed. This allowed the transfer of both stable and radioactive mercury between the organic and aqueous phases during the forward extraction. Results from this test are shown in Table 25. The distribution coefficients for the extraction and stripping of mercury agree favorably with those obtained from TRUEX solvent pre-equilibrated with SBW simulant which contained stable mercury (Table 24).

Table 25. Results of mercury stripping with 5 M HNO_3 (pre-equilibration with "mercury free" SBW simulant).

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous [HNO_3] M	D_{Hg}	Material Balance (In/Out)
Feed	17	1.60E3	ND	ND	ND
E1-O	17	1.24E3	ND	2.98	96.6%
E1-A	17	4.16E2	1.57		
St1-O	14	5.11E2	ND	0.72	101%
St1-A	14	7.15E2	4.78		
St2-O	12	1.94E2	ND	0.62	101.2%
St2-A	12	3.11E2	4.88		
St3-O	10	7.10E1	ND	0.57	99.5%
St3-A	10	1.24E2	5.00		
St4-O	8	2.68E1	ND	0.60	99.4
St4-A	8	4.46E1	5.17		
St5-O	6	1.03E1	ND	0.81	99.3%
St5-A	6	1.67E1	5.05		
St6-O	3	4.87E0	ND	0.62	94.9%
St6-A	3	5.98E0	5.08		

ND = Not Determined

Stripping mercury from the TRUEX solvent is possible with solutions containing increased (≥ 5 M) nitric acid concentrations. This alleviates the concern of mercury build-up in the solvent, resulting in an eventual "poisoning" effect. Mercury build-up in the TRUEX solvent could lead to reduced TRU forward extraction distribution coefficients. Mercury stripping is potentially necessary if the TRUEX process is applied to ICPP's sodium bearing waste.

The experimental procedure shown in Figure 6 was repeated using 0.01 M HCl as the stripping solution. This series of extractions was designed to evaluate mercury stripping with HCl since it has been shown that Hg extracts as HgCl_2 [16]. This is analogous to stripping TRUs, which extract as nitrates from nitric acid solutions [2], with dilute (0.01 M) HNO_3 . Horwitz, et. al., has shown that the TRUs will also extract and strip with the TRUEX solvent from HCl solutions [18]. However, stripping mercury with dilute HCl after the TRUs have been stripped in dilute HNO_3 may offer an alternative Hg separation scheme. Results from the 0.01 M HCl stripping test are shown in Table 26.

The mercury forward distribution coefficient of $D_{\text{Hg}} = 3.2$ agrees with previous distributions of $D_{\text{Hg}} \sim 3$ obtained in previous tests. It is apparent from Table 26 that 0.01 M HCl is ineffective at stripping mercury from the TRUEX solvent. After the first stripping contact, the mercury distribution coefficient ranged from $D_{\text{Hg}} \sim 68$ to 79. The low D_{Hg} observed in the first stripping contact is probably due to the increased acid concentration in the strip solution resulting in the scrubbing of nitric acid from the TRUEX solvent.

Table 26. Mercury stripping results with 0.01 M HCl.

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous [H ⁺] N	D _{Hg}	Material Balance (In/Out)
Feed	15	1.57E3	ND	ND	ND
E1-O	15	1.16E3	ND	3.2	103%
E1-A	15	3.66E2	1.52		
St1-O	12	1.14E3	ND	35	99%
St1-A	12	3.56E1	0.68		
St2-O	9	1.23E3	ND	68	91%
St2-A	9	1.81E1	0.20		
St3-O	6	1.23E3	ND	79	99%
St3-A	6	1.55E1	0.046		
St4-O	4.5	1.21E3	ND	76	100%
St4-A	4.5	1.60E1	0.012		
St5-O	3	1.20E3	ND	77	100%
St5-A	3	1.56E1	0.010		
St6-O	1.5	1.14E3	ND	68	100%
St6-A	1.5	1.68E1	ND		

ND = Not Determined

The above experiment was repeated in accord with Figure 6, except 5 M HCl was used as the stripping agent. Results from this test are shown in Table 27. The extraction distribution coefficient was again $D_{Hg} = 3.05$, in accord with previous experiments. The mercury distribution coefficient increases with each successive stripping contact. A mercury distribution of $D_{Hg} = 1.08$ was observed for the first strip contact, while a $D_{Hg} = 10.1$ was obtained for the fifth and final strip contact. The increase in D_{Hg} during successive stripping contacts is attributed to changes in the acid concentration of the organic and aqueous strip solutions. The acid concentration of the aqueous raffinate from the first strip contact, St1-A, was 5.16 M H⁺. The acid concentration in the aqueous raffinate decreased to 5.01 M H⁺ after the fifth contact, St5, indicating that the

extracted acid (mostly as HNO_3) had been removed from the organic by the 5 M HCl solutions. Note that the acid concentration of the organic steadily decreased from 0.97 M H^+ in the feed (E1-O) to 0.58 M H^+ in the organic from the fifth strip, St5-O. These results verify that the organic acid concentration was decreasing, probably due to HCl stripping of HNO_3 from the organic phase.

The data indicate the extracted HgCl_2 can not be readily stripped from the TRUEX solvent with either dilute or fairly concentrated HCl . This behavior seems to be inconsistent with the extracted TRU-nitrates and TRU-chlorides which strip with dilute HNO_3 or HCl [18].

Table 27. Mercury stripping results with 5 M HCl .

Sample	Total Volume (ml)	Activity (dps/ml)	Acid $[\text{H}^+]$ N	D_{Hg}	Material Balance (In/Out)
Feed	11	1.55E3	ND	---	---
E1-O	11	1.22E3	0.97	3.05	96%
E1-A	11	4.00E2	1.53		
St1-O	9	6.17E2	0.87	1.08	102%
St1-A	9	5.74E1	5.16		
St2-O	7	4.69E2	0.75	3.13	100%
St2-A	7	1.50E2	5.42		
St3-O	5	4.01E1	0.67	5.80	100%
St3-A	5	6.91E1	5.18		
St4-O	3	3.58E2	0.60	8.14	100%
St4-A	3	4.40E1	5.18		
St5-O	1.5	3.23E2	0.58	10.13	101%
St5-A	1.5	3.19E1	5.01		

ND = Not Determined

Comparison of the mercury distribution coefficients obtained with 5 M HCl (Table 27) with those for 0.01 M HCl (Table 26) indicates 5 M HCl did result in a lower mercury distribution coefficient. However, stripping distribution coefficients for both HCl solutions are still too large to significantly remove mercury from the TRUEX solvent.

In accord with the experimental flowsheet shown in Figure 6, TUCS (0.25 M Ionquest 201[®] in 0.05 M HNO₃) was tested for stripping mercury from the TRUEX solvent. If the TUCS reagent were to remove mercury, there exists the possibility to strip mercury co-currently with uranium, perhaps simplifying some

Table 28. Mercury stripping results with the TUCS reagent.

Sample	Total Volume (ml)	Activity (dps/ml)	Aqueous [H ⁺] N	D _{Hg}	Material Balance (In/Out)
Feed	17	1.61E3	ND	---	---
E1-O	17	1.24E3	ND	3.1	98%
E1-A	17	4.00E2	1.51		
Sc1-O	15	1.23E3	ND	27.5	97%
Sc1-A	15	4.47E1	0.85		
Sc2-O	12	1.20E3	ND	53.3	101%
Sc2-A	12	2.25E1	0.41		
Sc3-O	10	1.20E3	ND	65.6	99%
Sc3-A	10	1.83E1	0.27		
St1-O	8	1.20E3	ND	114	99%
St1-A	8	1.05E1	0.78		
St2-O	6	1.18E3	ND	129	101%
St2-A	6	9.15E0	0.72		
St3-O	4	1.17E3	ND	133	100%
St3-A	4	8.79E0	0.70		
St4-O	2	1.13E3	ND	130	103%
St4-A	2	8.69E0	0.71		

ND = Not Determined

mercury extraction flowsheets. The results of the TUCS stripping experiment are listed in Table 28. In this test, the mercury loaded organic from the first forward extraction, E-1, was scrubbed three times with 0.2 M HNO₃ prior to the TUCS stripping contacts. Distribution coefficients for the mercury extraction and 0.2 M HNO₃ scrubs agree with results presented for previous tests (Tables 21-23).

The large mercury distribution coefficients for the TUCS stripping contacts indicate this particular reagent is ineffective at removing mercury from the TRUEX solvent. The mercury distributions for the TUCS strip contacts are almost twice that found for 0.01 M nitric or 0.01 M hydrochloric acids, as well as with 0.1 to 0.01 M oxalic acid.

Chromium Results

Pre-equilibration of the TRUEX solvent with sodium bearing waste simulant always results in a yellow coloration of the organic phase (which is not colored, or clear, when prepared or pre-equilibrated with varying concentrations of nitric acid). This coloration is indicative that one or more of the cold matrix elements in the simulant is extracted. Potential colored extractable species are limited to few elements including chromium or perhaps iron. An investigation of the color transfer was warranted. Chromium in the +6 oxidation state forms intensely colored yellow/orange solutions. Nitrate complexes of chromium in the +3 oxidation state are predominately blue. As a consequence of these observations, Cr(VI) was postulated to be responsible for the transfer of color to the organic.

Extraction results with stable or "cold" Cr(VI) nitrate solutions were performed from pure nitric acid solutions with varying HNO₃ concentrations and from the SBW simulant. These results are summarized in Table 29. It is apparent that Cr(VI) is readily extracted at higher nitric acid concentrations but not from the SBW simulant by the TRUEX process solvent.

Table 29. Results of "cold" chrome (VI) extractions from SBW simulant and pure nitric acid solutions.

Sample	[HNO ₃] (M)	[Cr(VI)] (mg/l)	D _{Cr}
F-1	0.01	5	0.19
F-2	0.04	20	0.83
F-3	0.5	250	4.1
F-4	1.0	500	3.7
F-5	2.0	1000	3.1
F-6	5.0	250	3.2
F-7	8.0	250	3.4
SBW Simulant	1.35	341*	-0-

*not conclusively Cr(VI)

Further experimentation was performed to determine the extraction of chromium from the SBW simulant. An aliquot of the TRUEX solvent was contacted three times with equal volumes of the SBW simulant containing 341 ppm Cr. The loaded TRUEX solvent was then scrubbed three times with equal volumes of 0.2 M HNO₃ and stripped with either: 1) 0.25 M TUCS in 0.05 M HNO₃, 2) 0.1 M H₂C₂O₄ in 0.01 M HNO₃, or 3) 0.01 M HNO₃. The stripped solvent was then washed with two equal volume contacts of 0.25 M Na₂CO₃. Samples of the aqueous phases were analyzed for Cr. These samples were also analyzed for iron and zirconium.

The chromium extraction distribution coefficient determined from these tests was D_{Cr} = 0.3 ([HNO₃] = 1.5 M). This extraction coefficient does not agree with those shown in Table 29 for Cr(VI) in pure nitric acid solutions. However, the Cr in the SBW simulant is most likely partitioned between Cr(III) and Cr(VI) with the vast majority being in the trivalent oxidation state. The SBW simulant was made up using Cr(NO₃)₃. The extraction coefficient of 0.3 determined for Cr could be due to the extraction of Cr(III) or from the extraction of Cr(VI). Since Horwitz and Schulz [12] report a D_{Cr(III)} < 0.05 in nitric acid solutions between 1 and 3 molar, it seems most likely that the

D_{Cr} determined in this test resulted from the extraction of Cr(VI).

Analysis of the scrub and strip solutions all showed < 50.5 ppm Cr, therefore, scrub and strip distribution coefficients were not determined. Since the TRUEX solvent was only loaded with approximately 100 ppm Cr after the three extraction contacts, this less than value does not suggest that Cr was not scrubbed or stripped from the solvent. It does suggest that the scrubbing distributions are > 2 in equilibrium nitric acid between 0.8 and 0.25 M HNO_3 . The data agree somewhat with the Cr(VI) extraction coefficients shown in Table 29. It should be noted that yellow color of the TRUEX solvent resulting from contact with the SBW simulant, is gone after one or two contacts with the 0.2 M HNO_3 scrub solution.

Iron Results

Extraction, scrubbing, and stripping coefficients of iron were also evaluated from the previously described test. Extraction coefficients for iron were determined to be $D_{Fe} = 2$. Horwitz and Schulz [12] report a $D_{Fe(III)} < 0.05$ in solutions of 1 to 3 M HNO_3 . This would indicate that the iron in the SBW simulant was not Fe(III) but Fe(II). The presence of Fe(II) in the SBW simulant is somewhat difficult to envision since the simulant was made-up using $Fe(NO_3)_3$ and there is no explanation as to how the iron would have been reduced to Fe(II).

Analysis of the scrub solutions shows that some of the iron is scrubbed from the TRUEX solvent, but only half of the iron that extracted was recovered in the three scrub solutions. Thus, a mass balance of 50% was achieved in these tests. No iron was found in the strip solutions. Further tests, using radioactive isotopes of iron, are required to determine the expected iron chemistry in the SBW and the TRUEX solvent.

Zirconium Results

Zirconium results of the aqueous feed (after contact), scrub, and strip solutions indicate that zirconium does not extract in sufficient amounts to warrant any concern. Analytical detection limits for zirconium were not low enough to determine zirconium concentrations in these solutions. More precise extraction, scrubbing, and stripping distribution coefficients for zirconium will be determined using a radioactive tracer.

Other Inert Elements

To ensure that the extraction of stable mercury matched that of Hg^{203} , the aqueous raffinate solutions from these tests were analyzed for mercury. Extraction coefficients for stable mercury ranged between $D_{\text{Hg}} = 6$ and 2 indicating that the stable mercury does behave like its radioactive isotope. Mercury analysis of the scrub and strip solutions were not performed because of the inherent waste problems associated with mercury analysis. The fact that the extraction ratios between the two isotopes were found to be consistent is thought to be sufficient evidence to deem further analysis warrantless at this time.

Major constituents of the sodium waste, such as Al, Ca, and Na, were found not to extract in sufficient quantities to warrant further evaluation.

Comparison of Experimental Data

The experimental distribution coefficients obtained in these tracer studies is summarized in Table 30. Also shown in this are the predicted values of the distribution coefficient from the Generic TRUEX Model (GTM), version 2.5, developed by Vandegrift and co-workers at Argonne National Laboratory (ANL) [9,10,11]. The GTM is a computer modelling tool which is useful to estimate and compare anticipated performance of the TRUEX process with user specified feeds for both experimental and process flowsheets. The GTM results were generated by modelling the experimental flowsheets in as exact a manner as possible, i.e., the SBW simulant composition was specified, fresh organic reflected pre-equilibration conditions with the unspiked SBW, actual molarity of tracers in the simulant was used in the aqueous feed, etc. Mercury is included in Table 30 for comparison, even though the GTM does not currently incorporate any distribution Hg data. Furthermore, none of the stripping solutions indicated in Table 30 are effective at removing mercury, which must be stripped from the loaded organic with concentrated (i.e. $\geq 5 \text{ M HNO}_3$) as was previously discussed.

The distribution coefficients determined experimentally for the forward extractions of U-233, Am-241, and Pu-238 from spiked SBW simulant are consistently lower than predicted by the GTM. Neptunium extraction results compare favorably with those predicted by the GTM while the experimental technetium extraction data is substantially higher than the GTM predicts. These trends are not surprising considering the complexity of the SBW matrix, and reflect the fact that the extraction chemistry is rather complicated. It is important to note that the experimental data indicates the capability of the TRUEX process for extraction of the radionuclides studied; the GTM simply confirms this point. Of singular importance is the key result that Tc is readily extracted from the SBW simulant, although the GTM predicts this radionuclide to be largely inextractable.

Table 30. Experimental versus estimated (GTM) distribution coefficients for TRUEX extractions from simulated SBW.

Sample Description		D _{U-233}		D _{Am-241}		D _{Pu-238}	
		Exp.	GTM	Exp.	GTM	Exp.	GTM
Forward Extraction	E1	1710	3700	33	170	486	3400
	E2	170	3800	30	200	7.1	3500
	E3	'BDL	3900	27	230	'BDL	3500
0.2 M HNO ₃ Scrubs	Sc1	460	470	19.5	21.6	94.5	1100
	Sc2	240	258	9.3	10.3	44.5	430
	Sc3	160	154	4.9	5.55	20.5	220
0.01 M HNO ₃ Strips	St1-N	33	17.2	0.69	0.421	6.0	32.1
	St2-N	7.6	11.7	0.18	0.013	1.6	2.52
	St3-N	3.3	0.522	0.91	4.2E-03	22	1.15
0.1 M H ₂ C ₂ O ₄ Strips	St1-O	2.38	0.041	0.09	2.4E-02	0.24	1.0E-03
	St2-O	0.81	1.1E-03	0.02	1.0E-03	---	1.0E-03
	St3-O	0.59	1.1E-03	'BDL	1.0E-03	---	1.0E-03
TUCS Strips	St1-T	2.5E-04	1.2E-03	5.0E-04	7.0E-05	2.1E-03	3.5E-02
	St2-T	'BDL	1.2E-03	'BDL	7.0E-05	2.8	3.5E-02
	St3-T	'BDL	1.2E-03	'BDL	7.0E-05	2.1	3.5E-02
0.25 M Na ₂ CO ₃ Solvent Wash	St1-C	3.1E-03	8.8E-04	0.003	7.0E-05	2.6E-03	1.2E-3
	St2-C	'BDL	8.8E-04	'BDL	7.0E-05	0.8	1.2E-3
Sample Description		D _{Np-239}		D _{Tc-99m}		D _{Hg}	
		Exp.	GTM	Exp.	GTM	Exp.	GTM
Forward Extraction	E1	2.28	2.40	4.01	0.80	3.08	'NA
	E2	1.90	2.30	4.57	0.98	3.10	'NA
	E3	1.40	2.10	4.10	1.15	3.10	'NA
0.2 M HNO ₃ Scrubs	Sc1	---	0.217	10.7	7.6	27.5	'NA
	Sc2	---	0.116	12.6	10.4	53.3	'NA
	Sc3	---	0.083	11.7	10.3	65.6	'NA
0.01 M HNO ₃ Strips	St1-N	2.60	0.185	7.8	5.45	71.4	'NA
	St2-N	1.83	0.074	1.5	1.25	67.7	'NA
	St3-N	0.366	0.022	0.65	0.81	67.2	'NA
0.1 M H ₂ C ₂ O ₄ Strips	St1-O	---	0.18	1.94	4.51	53.73	'NA
	St2-O	---	6.8E-02	---	2.85	---	'NA
	St3-O	---	1.4E-02	---	2.92	---	'NA
TUCS Strips	St1-T	---	1.0E-03	---	1.9	114	'NA
	St2-T	---	1.0E-03	---	1.9	129	'NA
	St3-T	---	1.0E-03	---	1.9	133	'NA
0.25 M Na ₂ CO ₃ Solvent Wash	St1-C	0.155	0.0015	---	0.079	---	'NA
	St2-C	'BDL	---	---	0.079	---	'NA

'BDL = Below Detection Limits: Activity in either the organic or aqueous phase was below detection limits of the analytical instrumentation.

'NA = Not Applicable: The GTM does not incorporate Hg data.

With the exception of Pu-238, the 0.2 M HNO₃ scrub data from the experiments compare favorably with those predicted by the GTM. These results indicate the radioisotopes extracted will largely remain in the organic phase while acid and co-extracted metals are scrubbed from the organics. For strips with 0.01 M

HNO₃, the experimental data indicate americium, neptunium and technetium are somewhat back-extracted from the organic as apparent by distribution coefficients less than 1. At least for Am and Np, the GTM predicts much better stripping with dilute nitric acid than was experimentally obtained. In the case of uranium and plutonium, the 0.01 M HNO₃ strips were somewhat ineffective as stripping reagents. The GTM predicted this behavior since the distribution ratios were typically greater than 1.

Dilute oxalic acid, 0.1 M H₂C₂O₄, is effective at stripping each of the isotopes (except, of course, mercury) from the organic solvent. The GTM consistently predicts better stripping with this solution than was experimentally observed. Furthermore, at least for the actinides, oxalic acid was consistently found to cause a precipitate during the initial contact with the organic. In future work, it may be possible to control this problem by adjusting the oxalic acid concentration or using ammonium oxalate in the strip solution.

Of the stripping reagents studied, TUCS appears to have a great deal of potential for gross actinide separation. Except for mercury, TUCS was found to readily strip each of the studied species from the loaded organic phase. Table 30 clearly indicates very low distributions are anticipated for each of the species examined, even those which were not tested with TUCS stripping, with, of course, the exception of mercury. Future tests will be used to evaluate the potential to reduce the concentration of the TUCS reagent in the stripping solution. Such a reduction would lower the free acid content of the strip solution, decrease the quantity of chemical reagents required, and result in less phosphorus compounds in the high level waste product from a TRUEX process.

The use of sodium carbonate for solvent cleanup is feasible based on the experimental results in this study. The GTM results in Table 29 indicate 0.25 M Na₂CO₃ is quite effective at stripping trace metals from the TRUEX solvent. Unfortunately,

stripping mercury from the organic with carbonate has not yet been examined, but is scheduled in future experiments. The use of carbonate as a gross metal stripping reagent has been considered, but may not be feasible due to precipitate formation problems. The cause of difficulties associated with precipitate formation during carbonate washing is currently being evaluated. Solvent washing after organic stripping with TUCS has not as of yet been attempted. This arrangement is anticipated to alleviate the precipitation problem as TUCS is expected to strip virtually all residual extracted species from the TRUEX solvent [8].

Finally, the applicability of the TRUEX process for treatment of ICPP SBW will rely on tests with real waste. Such experiments are currently planned, and should be completed at the end of FY 94. The experiments described herein indicate the TRUEX process is applicable to SBW treatment and provide expectations of how the real waste will behave in future hot tests.

POTENTIAL FLOWSHEETS FOR TREATMENT OF SBW

The distribution coefficients generated during the tracer experiments have been used in conjunction with the GTM to develop a potential process flowsheet for the large scale treatment of ICPP SBW. The GTM allows input of user specified distribution coefficients to develop and compare potential flowsheets. A flowsheet for the treatment of SBW is given in Figure 7. The flowsheet consists of five stages of extraction, four stages of 0.2 M HNO_3 scrub, five stages of 0.25 M TUCS strip, two stages of 0.25 M Na_2CO_3 solvent wash, and one stage of 0.1 M HNO_3 rinse. TUCS was chosen over nitric acid and oxalic acid for the strip section of the flowsheet due to the ability of TUCS to strip all the actinides without forming a precipitate. The average chemical and radiochemical compositions of the ICPP SBW tanks were used as the feed for the flowsheet [5].

The concentration of inerts in the flowsheet, with the exception of mercury and chromium, were generated by the GTM using the existing data base of distribution coefficients. Experimental distribution coefficients, obtained from the tracer studies with SBW, were input into the GTM for americium, neptunium, plutonium, uranium, mercury, and technetium. Also, experimental distribution coefficients obtained from studies using cold Cr(VI) were input into the GTM. The distribution coefficients input for each stage of the flowsheet are given in Table 31. Where experimental data has not been obtained or where the experimental distribution coefficients are in very good agreement with the GTM (see Table 30), distribution coefficients as predicted by the GTM were used.

As is apparent from the flowsheet in Figure 7, the extraction section is very effective in removing actinides from the SBW. Greater than 99.99% of the americium, plutonium, and uranium are removed from the SBW feed. However, only 56.6% of the Np(V) is removed from the SBW feed due to the low distribution coefficient of Np(V) ($D_{\text{Np}}=1.9$). Reduction of the

Figure 7. TRUEX Flowsheet for the Treatment of SBW

Component	Sodium Waste Feed (Molar)	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
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	1.85E-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	2.38E-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
Eu	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	449.3	50.0	150	150	30.0	15.0	30.0	15.8

Components for which experimental distribution coefficients were used

Np(V) to Np(IV) in the SBW feed would greatly increase the neptunium distribution coefficient in the extraction section. Even with Np(V) in the SBW feed, the total activity of the actinides is reduced from 348.5 nCi/g to 0.22 nCi/g. This is well below the Class A limit of 10 nCi/g for actinides. The TUCS strip section removed essentially all of the actinides from the TRUEX solvent and only a very small fraction of the actinides are stripped in the carbonate wash and acid rinse sections.

The proposed flowsheet indicates 89% of the technetium and 81% of the Cr(VI) is extracted from the SBW feed. Essentially all of the Cr(VI) is stripped from the TRUEX solvent in the TUCS strip section. Finally, 54% of the technetium extracted from the SBW feed is stripped from the TRUEX solvent in the TUCS strip section and the remaining technetium is stripped in the carbonate wash section. The amount of technetium in the SBW feed is reduced from 0.017 Ci/M³ to 0.0017 Ci/M³, both of which are well below the Class A limit of 0.3 Ci/M³.

With a distribution coefficient of 3.1 for mercury in the extraction section, a considerable quantity of mercury is extracted into the TRUEX solvent. However, since mercury extracted from the sodium waste does not strip with TUCS, the mercury builds up to a steady-state concentration in the TRUEX solvent and 99% of the mercury exits in the LAW raffinate. If the quantity of mercury in the TRUEX solvent is determined to inhibit the extraction of actinides or if it is desired to partition the mercury from the low activity waste (LAW) raffinate, a 5 M HNO₃ strip section could be added after the extraction section to selectively strip the mercury from the TRUEX solvent.

The process flowsheet developed using the GTM with the experimental distribution coefficients obtained from the tracer studies indicates that large scale treatment of SBW with the TRUEX process is viable. As data becomes available from testing with actual ICPP SBW, this flowsheet will be revised as necessary.

Table 31. Distribution coefficients used in the GTM.

Stage No.	D(Pu)	D(Np)	D(Am)	D(Tc)	D(Cr)	D(U)	D(Hg)
1	486	1.9	30	4.23	3.0	1710	3.1
2	486	1.9	30	4.23	3.0	1710	3.1
3	486	1.9	30	4.23	3.0	1710	3.1
4	486	1.9	30	4.23	3.0	1710	3.1
5	486	1.9	30	4.23	3.0	1710	3.1
6	94.5	.9156 [†]	32.05 [†]	1.409 [†]	2.0	1074 [†]	48.8
7	94.5	.586 [†]	30.2 [†]	2.623 [†]	2.0	816.9 [†]	48.8
8	94.5	.3674 [†]	27.45 [†]	4.556 [†]	2.0	631.6 [†]	48.8
9	94.5	.2125 [†]	20.91 [†]	7.801 [†]	2.0	457.7 [†]	48.8
10	2.1E-3	1.0E-3 [†]	5.0E-4	1.9 [†]	1.0E-3 [†]	2.5E-4	125
11	2.1E-3	1.0E-3 [†]	5.0E-4	1.9 [†]	1.0E-3 [†]	2.5E-4	125
12	2.1E-3	1.0E-3 [†]	5.0E-4	1.9 [†]	1.0E-3 [†]	2.5E-4	125
13	2.1E-3	1.0E-3 [†]	5.0E-4	1.9 [†]	1.0E-3 [†]	2.5E-4	125
14	2.1E-3	1.0E-3 [†]	5.0E-4	1.9 [†]	1.0E-3 [†]	2.5E-4	125
15	2.6E-3	.155	3.0E-3	7.9E-2 [†]	1.0E-3 [†]	3.1E-3	125
16	2.6E-3	.155	3.0E-3	7.9E-2 [†]	1.0E-3 [†]	3.1E-3	125
17	86.64 [†]	3.7E-2 [†]	.9567 [†]	5.609 [†]	1.0E-3 [†]	34.51 [†]	68

† = GTM generated distribution coefficient

CONCLUSIONS & RECOMMENDATIONS

The results of this study indicate the TRUEX process is capable of adequate and selective removal of actinides from ICPP SBW. Furthermore, the GTM efficiently predicts the behavior of most matrix components in flowsheet simulations and will be useful as a process development tool.

Several stripping reagents are available for back-extraction of the actinides from the loaded TRUEX solvent. In particular, the TUCS reagent is exceptionally effective as a strip reagent. Several questions will be addressed in regards to TUCS, including the effect of phosphorus on the final waste form and the optimal concentration of the strip solution. Further tests will be designed to examine the later; however, the issue of phosphorus in the waste form must be addressed more extensively.

The formation of precipitates, particularly during oxalate strips and carbonate washes, is undesirable. However, this problem can be alleviated by selection of suitable strip and wash solutions. Thus, problems of this nature are not anticipated. Finally, potential problems such as third phase formation were not observed in these tests.

A full scale process must incorporate technologies for the removal of radioactive strontium and cesium which contribute significantly to the activity in the SBW. Methods currently being examined in this regard include solvent extraction, SREX and CSEX for strontium and cesium, respectively, and ion exchange for cesium removal. Once these technologies are determined feasible, an integrated flowsheet must be developed and tested.

Further work is required (and planned) to evaluate and verify TRUEX on samples of real ICPP SBW. Refinements of the process chemistry will be performed with continuing tracer and "hot" tests. Ultimately, dynamic flowsheet simulation tests will be incorporated through batch and pilot plant testing to verify and validate the applicability of the TRUEX process to ICPP SBW.

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