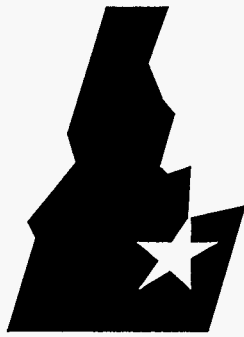


January 1996



**Idaho
National
Engineering
Laboratory**

**Actinide Partitioning Studies Using
Dihexyl-N,N-diethylcarbamoymethyl
Phosphonate And Dissolved Zirconium
Calcine**

RECEIVED

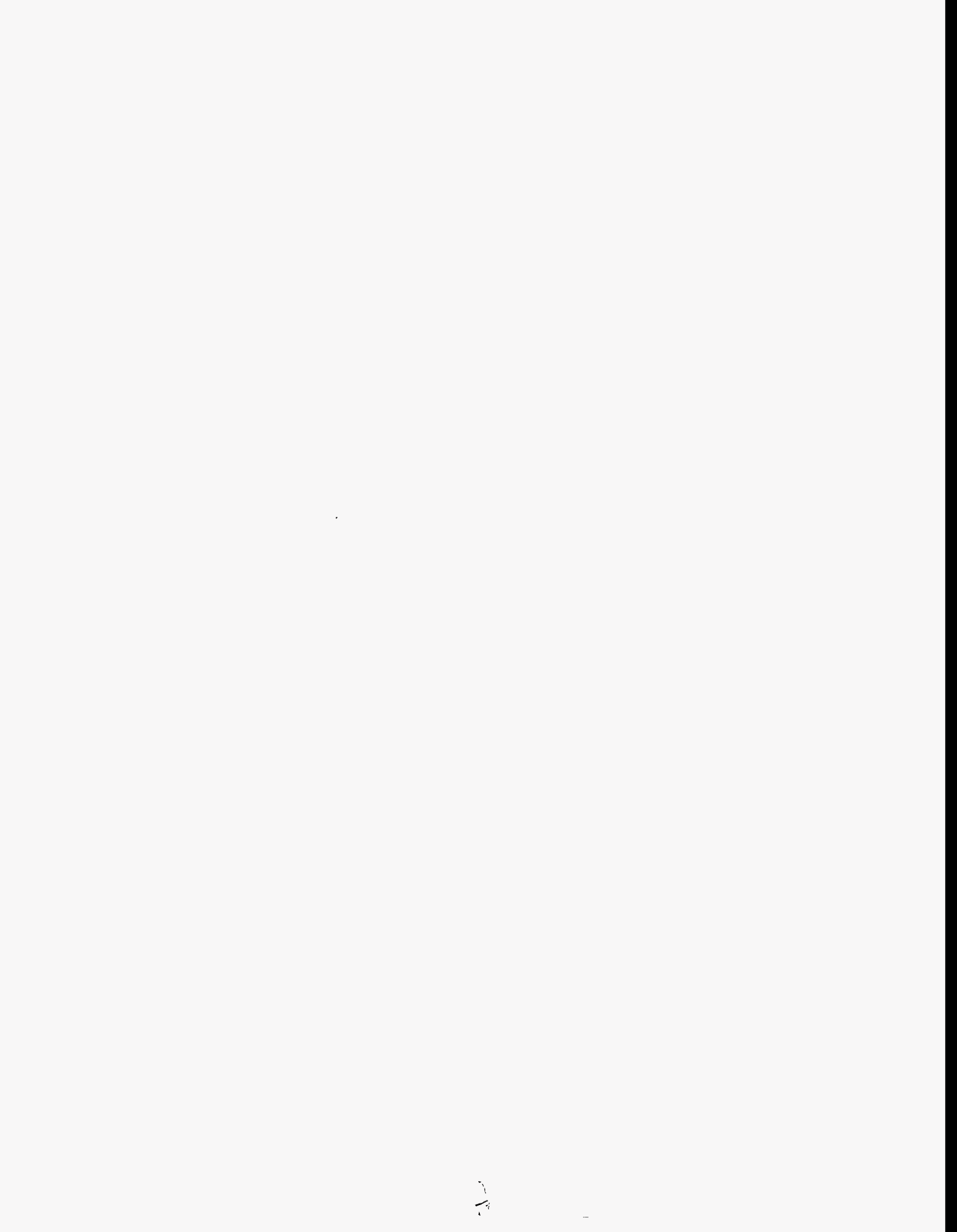
FEB 23 1996

OSTI

***K. N. Brewer
R. S. Herbst
J. D. Law
T. G. Garn
R. D. Tillotson
T. A. Todd***

 **Lockheed**
Idaho Technologies Company

MASTER



Actinide Partitioning Studies Using Dihexyl-N,N-diethyl-carbamoylmethyl Phosphonate And Dissolved Zirconium Calcine

K. N. Brewer
R. S. Herbst
J. D. Law
T. G. Garn
R. D. Tillotson
T. A. Todd

January 1996

Idaho National Engineering Laboratory
HLW Engineering and Projects Department
Lockheed-Martin Idaho Technologies Company
Idaho Falls, Idaho 83415

Prepared for the
U. S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

HH
MASTER.

1974

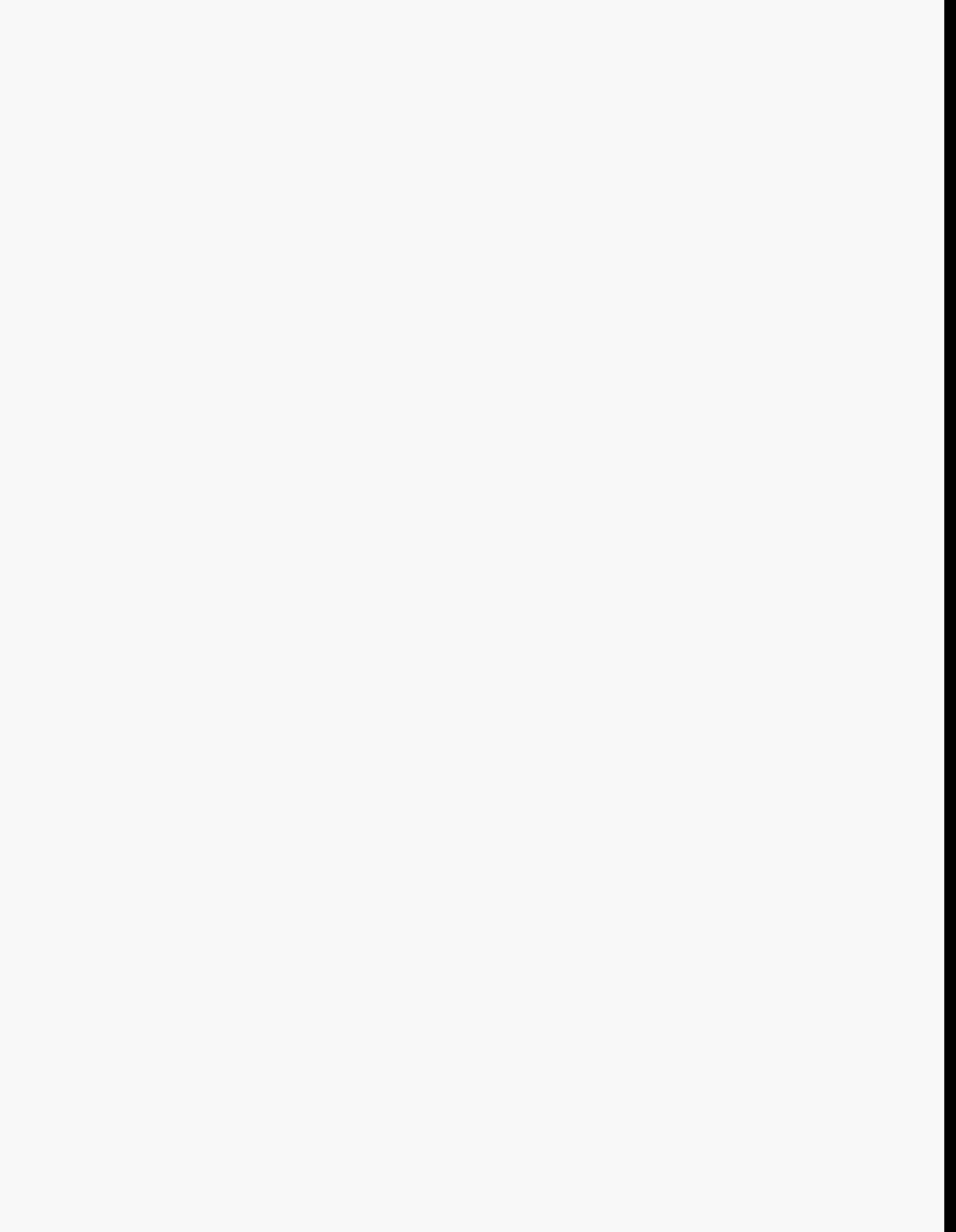
1974

SUMMARY

A baseline flowsheet capable of partitioning the TRansUranic (TRU) elements from dissolved zirconium calcines has been developed. The goal of the TRU partitioning process is to remove the TRUs from solutions of dissolved zirconium calcines to below the 10 CFR 61.55 Class A waste limit of 10 nCi/g. Extraction, scrub, strip, and wash distribution coefficients for several elements, including the actinides, were measured in the laboratory by performing equal volume batch contacts. A solvent containing dihexyl-N,N-diethylcarbamoylmethyl phosphonate (CMP), tributylphosphate (TBP), and a branched chain hydrocarbon as the diluent were used to develop this process. A non-radioactive zirconium pilot-plant calcine was spiked with the TRUs, U, Tc, or a radioactive isotope of zirconium to simulate the behavior of these elements in actual dissolved zirconium calcine feed.

Distribution coefficient data obtained from laboratory testing were used to recommend: 1) solvent composition, 2) scrub solutions capable of selectively removing extracted zirconium while minimizing actinide recycle, 3) optimized strip solutions which quantitatively recover extracted actinides, and 4) feed adjustments necessary for flowsheet efficiency. A solvent composition of 0.5 M CMP, 1.0 M TBP diluted with Isopar L[®] is recommended. Scrub solutions containing no more than 0.05 M H₂C₂O₄ or 0.1 M NH₄F, each in 3.0 M HNO₃, is recommended for selectively scrubbing zirconium from the solvent. A strip solution between 0.001 M and 0.04 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) is recommended for complete actinide recovery.

Laboratory distribution coefficients were used in conjunction with the Generic TRUEX Model (GTM) to develop and recommend a flowsheet for testing in the 5.5-cm Centrifugal Contactor Mockup. GTM results indicate that the recommended flowsheet should remove the actinides from dissolved zirconium calcine feeds to below the Class A waste limit of 10 nCi/g. Less than 0.01 wt% of the extracted zirconium will report to the high-activity waste (HAW) fraction using the 0.05 M H₂C₂O₄ in 3.0 M HNO₃ scrub, and greater than 99 % of the extracted actinides are recovered with 0.001 M HEDPA. Modeling results from the GTM indicate this to be a viable flowsheet for testing in the 5.5-cm Centrifugal Contactor Mockup.



ACKNOWLEDGEMENTS

Excellent analytical support was provided by the Idaho Chemical Processing Plant's Radiochemical and Spectrochemical Groups. Specifically, Troy Tranter, Chris Ortell, Brian Storms, Lee Hinkley and Mike Evens of the Radiochemical Group and Jeff Laug, Duane Lundholm, and Bryan Zaccardi of the Spectrochemical Group continuously provided quick sample turn around times during this testing. A barrage of tests were performed that inundated these two laboratories with samples. The work performed by these people restored order to the chaos.

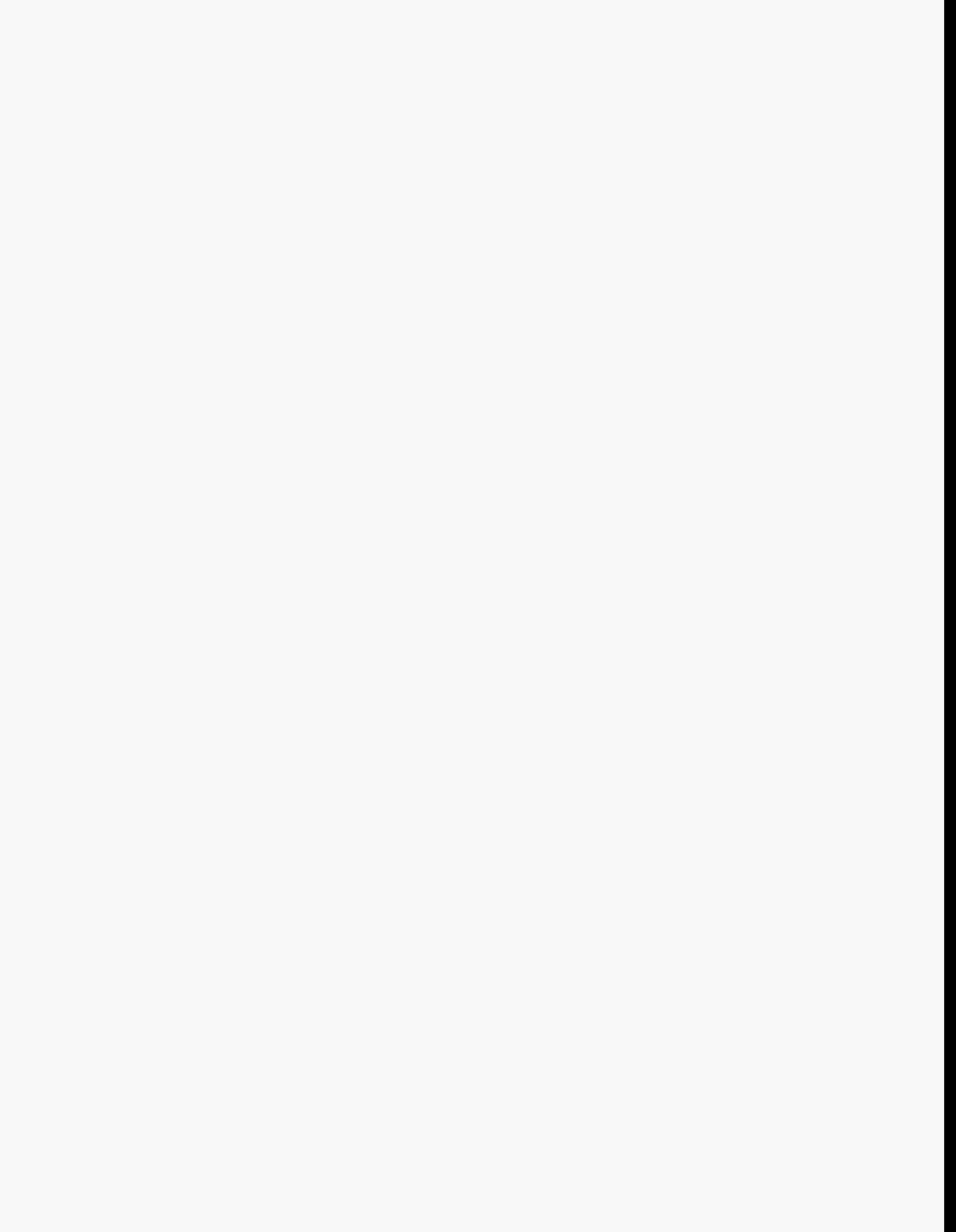
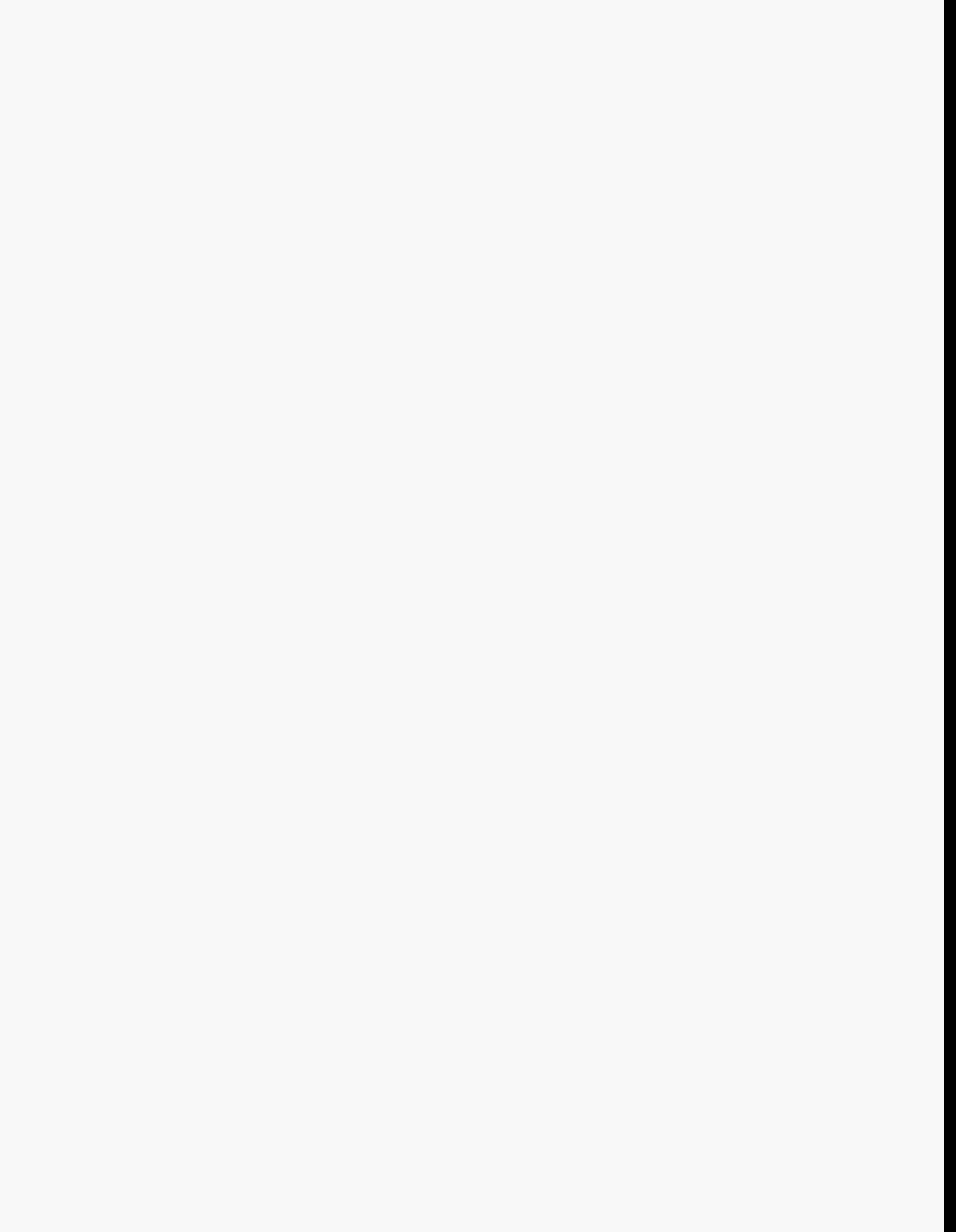


TABLE OF CONTENTS

SUMMARY	iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vii
LIST OF FIGURES	ix
LIST OF TABLES	ix
INTRODUCTION	1
BACKGROUND	5
EXPERIMENTAL	7
Run 74 Calcine Feed	7
Reagents/Chemicals	7
Experimental Methodology	10
Analytical Methods	12
RESULTS/DISCUSSION	15
0.75 M CMP Tests	15
0.5 M CMP Tests	21
Feed Adjustments	27
Chromium Extraction	27
Zirconium Extraction	30
0.5 M CMP Tests Using Reduced Calcine Feed	30
Extraction From Reduced Run 74 Feed	31
HEDPA Strip Concentration	33
RECOMMENDATIONS	37
Flowsheet Development Using the Generic TRUEX Model	37
CONCLUSIONS	39
REFERENCES	41

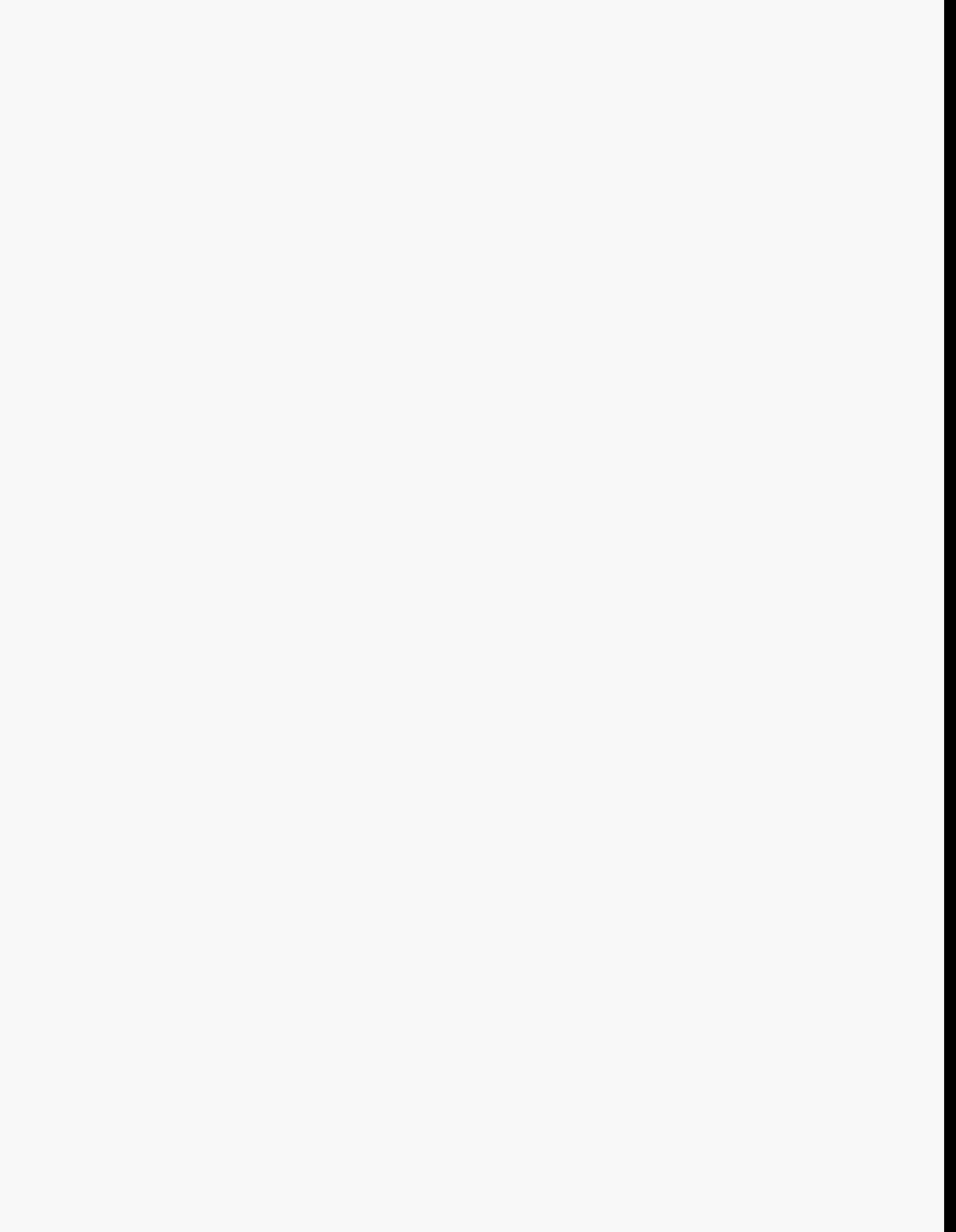


LIST OF FIGURES

Figure 1: Experimental Procedure used for testing Simulated ICPP Dissolved Zirconium Calcine	12
Figure 2: D_{Am} as a function of $[HNO_3]$ using 0.5 M CMP and 1.0 M TBP in Isopar L [®]	24
Figure 3: D_{Zr} as a function of $[HNO_3]$ using 0.5 M CMP and 1.0 M TBP in Isopar L [®] ..	24
Figure 4: CMP Flowsheet for the Treatment of ICPP Dissolved Zirconium Calcine	38

LIST OF TABLES

Table 1: TRU Activity in Actual Dissolved Zirconium Calcine	3
Table 2: Dissolved Run 74 Calcine Feed Composition	8
Table 3: Extraction Distribution Coefficients Using 0.75 M CMP and 1.0 M TBP in Isopar L [®]	15
Table 4: Zirconium Scrubbing With 0.05 M $H_2C_2O_4$ in 3 M HNO_3 or 1.5 M HNO_3 ...	18
Table 5: Zirconium and Actinide Scrubbing With 0.1 M NH_4F in 3 M HNO_3	18
Table 6: Technetium and Actinide Scrub D's Using 0.05 M $H_2C_2O_4$ in 3 M HNO_3	19
Table 7: Feed Stability Test	20
Table 8: Stripping Distribution Coefficients Using 0.04 M HEDPA in 0.04 M HNO_3 ..	21
Table 9: Stripping Distribution Coefficients Using 0.05 M $H_2C_2O_4$ in 0.01 M HNO_3 ...	21
Table 10: Zirconium and Americium Extraction Distribution Coefficients as a Function of CMP Concentration	23
Table 11: Uranium and Plutonium Distribution Coefficients Using 0.5 M CMP	26
Table 12: D_{Cr} for Extraction, Scrub, Strip, and Wash Contacts	28
Table 13: Zr, Tc, and Actinide Extraction into 0.5 M CMP from Reduced Run 74 Feeds	31
Table 14: Scrub Distribution Coefficients from 0.5 M CMP Using 0.05 M $H_2C_2O_4$ in 3.0 M HNO_3	33
Table 15: Strip Distribution Coefficients from 0.5 M CMP using 0.001 M HEDPA	34



INTRODUCTION

Actinide separation processes are being evaluated at the Idaho Chemical Processing Plant (ICPP) to minimize the volume of high-level radioactive waste requiring disposal in a geological repository. A solvent extraction process using dihexyl-N,N-diethyl-carbamoylmethyl phosphonate (CMP) as the primary actinide extractant is being evaluated at the ICPP to separate the actinides from the high activity calcines and sodium-bearing waste (SBW). The goal of actinide separation processes applied to these two wastes is a resulting aqueous raffinate stream that meets the 10 CFR 61.55 Class A transuranic (TRU) waste limit of <10 nCi/g. The purpose of this document is to report the results of applying the CMP extractant to ICPP dissolved zirconium pilot-plant calcine. Extraction, scrub, and strip distribution coefficients of the actinides, Zr, Cr, and Tc were obtained from batch contacts with the dissolved pilot-plant zirconium calcine. These distribution coefficients, as well as the physical characteristics of the CMP solvent, will eventually be compared to other solvent extraction processes (TRUEX). Data generated from this study will be used to recommend a flowsheet for testing in a 5.5 cm Centrifugal Contactor Mock-up located at the ICPP and to satisfy some of the criteria for selecting a solvent extraction process for treating ICPP calcines.

Approximately 3,800 m³ of high-level waste (HLW) calcine was generated from aluminum and zirconium fuel reprocessing raffinates and is currently stored at the ICPP [1]. The calcine is primarily made-up of inert metal oxides (Al₂O₃, ZrO₂, and CaO) and CaF₂ [2]. Fluoride is present in these raffinates from the addition of HF and HBF₄ during the dissolution of zirconium fuels and can volatilize as HF during calcination. HF is very corrosive to calcination equipment; therefore, calcium was added to some of the raffinates prior to calcination to inhibit fluoride (HF) volatility. TRU and fission product concentrations in the calcine are less than 1 wt% [3]. A significant volume reduction may be achieved if these radioactive constituents are partitioned from the non-radioactive components of the calcine, as opposed to direct disposal (vitrification) of this material.

Calcine used in the evaluation of the CMP solvent was generated in the 30-cm pilot-

plant calciner at the ICPP in February, 1979. This calcine is here after designated as Run 74 calcine which was generated from a simulated blend of wastes from tanks WM-188 and WM-189. Waste in these tanks were similar in composition; therefore, no blend ratios were performed. These tanks contained a combination of first-cycle zirconium raffinate and stainless steel sulfate waste diluted with non-fluoride wastes. Run 74 calcine was generated to evaluate the calcination of WM-188 and WM-189 tank wastes at the Waste Calcination Facility (WCF).

Run 74 calcine was chosen as a suitable waste simulant for radionuclide separations testing because it is similar to actual ICPP zirconium calcine. Actual ICPP zirconium calcine represents approximately 3,000 m³ of the current 3,800 m³ inventory [4]. ICPP zirconium calcines are expected to be the most challenging with regards to actinide separation flowsheet development because of their high zirconium, calcium, and fluoride content. Zirconium has historically presented problems by coextracting with the TRU elements. Zirconium extraction may result in physical problems associated with the solvent, such as third phase formation or interfacial crud. Zirconium recovery with the actinides may increase the volume of final high-level waste. Inhibiting zirconium extraction can be accomplished with complexing agents but high calcium concentrations, present in dissolved solutions of zirconium calcine, typically form undesirable insoluble salts with these complexants. Zirconium complexing agents may also prevent the extraction of the actinides to such an extent as to exceed the Class A TRU waste limit of 10 nCi/g in the aqueous raffinate. Successful actinide separations flowsheet development with the zirconium calcine would potentially result in a flowsheet applicable to the total ICPP calcine inventory.

A significant effort has been devoted at the ICPP to develop calcine dissolution flowsheets that result in feeds suitable for aqueous separation processes [4-7]. Suitable calcine solutions are defined as those that: 1) contain the smallest concentration of undissolved solids, 2) are stable with respect to precipitate formation after dissolution and after contact with the extractant, and 3) provide adequate actinide distribution coefficients with no (or a minimal amount of) feed adjustments. Dissolution parameters defined by Herbst, et al., [5] were used to dissolve the Run 74 pilot-plant calcine.

The dissolution parameters established by Herbst [5], were also evaluated on actual zirconium calcine [4]. Greater than 95 wt% of the calcine was dissolved and the resulting dissolved calcine solution had an approximate total alpha activity of 1250 nCi/g. The contribution of the individual TRUs to this activity are shown in Table 1.

Table 1: TRU Activity in Actual Dissolved Zirconium Calcine

Isotope	Am-241	Pu-238	Pu-239	Np-237
Activity (nCi/g)	104	1100	42	0.5

The total alpha activity in some dissolved calcine solutions could be as large as 10,000 nCi/g. Taking the range of 1,000 to 10,000 nCi/g total alpha into consideration, a TRU activity removal between 99% and 99.9% is required for the aqueous raffinate to contain <10 nCi/g total alpha activity.

is a surprising result, since McIsaac [8] reported the $D_{Zr} = 0.018$ in a test with zirconium fuel reprocessing raffinate simulant, indicating that small amounts of extracted zirconium may cause physical problems with the solvent.

The mixer-settler test was repeated by Baker and co-workers [10], but this time two of the mixer-settler stages in the hot cell were used to concurrently scrub the loaded solvent and the remaining six stages were used for extraction. The solvent was scrubbed with 3 M HNO_3 to remove the extracted zirconium. This eliminated the zirconium precipitation. Americium and plutonium decontamination factors of 170 and 2500 were achieved in this test. Greater than 99.98 % of the extracted TRUs were recovered from the solvent using 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ in 0.005 M HNO_3 ; however, a white precipitate formed in the first stripping stage after several

EXPERIMENTAL

Run 74 Calcine Feed

Run 74 calcine was dissolved according to the procedure developed by Herbst, et al. [5]. Herbst's work was scaled-up to evaluate those dissolution parameters defined in the small scale testing and to generate a large volume of dissolved Run 74 calcine for radionuclide separations testing. Dissolved Run 74 calcine generated in the dissolution pilot-plant was used as the dissolved calcine feed tested in this study. A 60:40 wt.% mixture of Run 74 calcine product and fines was dissolved at 90° C in 5 M HNO₃. One liter of 5 M HNO₃ was added to every 100 gm of the product:fines mixture. Approximately 1kg of the product:fines mixture was dissolved per batch. Each batch was allowed to be in contact with the hot acid for a minimum of 30 minutes while being well mixed. Approximately 200 L of dissolved Run 74 calcine feed were generated. Dissolved Run 74 calcine feed composition is shown in Table 2.

The feed was clarified by filtering through a 0.45 µm cellulose nitrate filter prior to testing. Tests were performed directly with the clarified feed, or with the clarified feed reduced with hydrogen peroxide prior to contact with the CMP solvent. Hydrogen peroxide was used to reduce Cr(VI) to Cr(III). Feed reduction was performed by "titrating" a specified feed volume with 30% H₂O₂ until the feed color changed from yellow {Cr(VI)} to blue {Cr(III)}. Less than 100 µL of 30% H₂O₂ was required to reduce 100 mL of feed. Holding reductants were not added to the feed because of the stability of Cr(III). The reduced feed was allowed to stand for 24 hours before use.

Reagents/Chemicals

Approximately 20 L of CMP was obtained from Sandia National Laboratory. The history of this CMP is unknown and is suspected to contain some organic impurities. Three CMP solvent concentrations were evaluated, 0.75 M, 0.5 M, and 0.25 M CMP, all in 1.0 M

Table 2: Dissolved Run 74 Calcine Feed Composition

Element	wt% in calcine before dissolution ¹	Feed concentration M
Al	11.2	4.2E-1
B	1.1	6.8E-2
Ca	25.0	6.5E-1
Ce	0.1	4.0E-4
Cr	0.4	5.7E-3
Cs	0.5	4.7E-3
Fe	0.1	1.3E-2
K	<0.1	6.0E-4
Mo	ND	1.8E-4
Na	0.4	8.5E-3
Ni	0.1	1.7E-3
Pb	<0.1	<1.9E-6
Sr	0.7	8.1E-3
Zr	16.6	2.1E-1
Cl ⁻	<0.2	<8.8E-2
F ⁻	17.4	8.9E-1
H ⁺	NA	3.5
NO ₃ ⁻	<0.1	6.0
PO ₄ ⁻³	ND	ND
SO ₄ ⁻²	5.4	5.0E-2
density	NA	1.2

NA = Not Applicable

ND = Not Determined

1. Remainder of mass balance is oxygen

TBP and an Isopar L[®] diluent. This range of CMP concentrations were chosen based on the hydraulic parameters of the 5.5-cm Centrifugal Contactor Mockup. A solvent containing 0.75 M CMP, 1.0 M TBP in an Isopar L[®] diluent resulted in flooding problems when tested in the 5.5 cm Centrifugal Contactor Mockup with an ICPP sodium-bearing waste simulant [13]. The flooding problems were eliminated when the CMP concentration in the solvent was reduced to 0.5 M.

Technical grade TBP (Baker Chem., Inc.) was used as a phase modifier in the solvent. Isopar L[®] (Exxon Chemical Co.), a branched chain hydrocarbon, was chosen as the diluent, as opposed to a normal paraffinic hydrocarbon (NPH), because it appears to be more effective at preventing third phase formation. Some third phase formation was observed when the TRUEX solvent (containing n-dodecane as the diluent) was contacted with the Run 74 dissolved calcine. The third phase was eliminated when the diluent was changed to Isopar L[®]. The Isopar L[®] diluent was chosen as the CMP diluent because of the experience with n-dodecane in the TRUEX solvent and Run 74 calcine [11]. The CMP solvent was prepared by the Quality Control (QC) Laboratory at the ICPP and was washed with three contacts of 0.25 M Na₂CO₃ (O/A = 5) prior to testing.

The gross strip reagent, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), was obtained from Albright & Wilson. Solutions of HEDPA were prepared by the QC Laboratory. Ammonium fluoride and oxalic acid scrub solutions were also prepared by the QC Laboratory.

The Zr-95 tracer was obtained from Isotope Products Laboratories and was received in 1 M H₂C₂O₄. Two Zr-95 tracers were used during this study. The first Zr-95 tracer (~5.4 μCi in 5 mL) was diluted to 100 mL with 2 M HNO₃. No attempt was made to destroy the oxalate in the tracer stock solution because the concentration of oxalate in the spiked Run 74 feeds was typically 0.005 M, compared to 0.2 M total Zr. Minimal zirconium complexing by oxalate would occur under these conditions. The second Zr-95 tracer was prepared by destroying the oxalate before use. The as received Zr-95 standard solution was evaporated to dryness and redissolved in 10 mLs of concentrated nitric acid. This solution was again evaporated to dryness. Oxalate solids were then destroyed by adding 0.5 mL of 30% H₂O₂

while the solids were still hot. The solids immediately disappeared. The Zr-95 was redissolved in 6 M HNO₃ and re-evaporated to verify the absence of oxalate in the tracer. Finally, 2 M HNO₃ was used to bring the tracer to a volume of 50 mLs. This tracer solution was used in all tests with 0.5 M CMP.

Am-241 tracer was obtained from Argonne National Laboratory. The Am-241 was dissolved in 1% nitric acid and brought up to a total volume of 100 mL. Am-241 activity in the stock solution was 1.69E+5 dps/mL. Np-239 was obtained in pure form from the ICPP's Isotopic Measurement Systems group by "milking" Np-239 from an Am-243 "cow" (Am-243 absorbed onto a cation exchange column). The Np-239 was eluted from the column with HIO₄ and HCl and converted to the nitrate form by evaporating to dryness twice in HNO₃. Residual americium was removed from the Np-239 tracer by passing the tracer through a TRU-Spec[®] column. Americium was retained on the column while a majority of the neptunium passed through. The absence of Am-241 and Am-243 was verified in the Np tracer by gamma spectroscopy.

U-233 tracer was prepared from a New Brunswick Certified Reference Material (CRM 111-A). The Th-229 daughter was separated from the U-233 by passing the tracer through an Aliquat 336N column. The radium daughter was removed from the U-233 by performing two sequential co-precipitations with BaSO₄. The U-233 standard was analyzed by gamma spectroscopy and by liquid scintillation counting (LSC) following purification to verify the absence of Th-229. The standard was counted by LSC at two and four week intervals to ensure absence of the radium daughter. Counting values obtained at these intervals agree with the initial activity determined by LSC following purification.

Pu-238 and Tc-99 tracers were obtained from the Radiochemistry Group at the ICPP and were used as made-up.

Experimental Methodology

Run 74 dissolved calcine spiked with a single radioactive isotope was typically tested. The only exception being tests conducted with Am-241 and Zr-95, which were tested together

because both isotopes have resolvable gamma energies. Isotopes were spiked into the feed 24 to 48 hours before contacting with the CMP solvent. Reduced feeds were prepared by reducing the feed twenty-four hours after addition of the tracer to the feed. The twenty-four hour interval between tracer addition and feed reduction allowed the tracer to reach an equilibrium oxidation state with the initial feed. Allowing the tracer to reach equilibrium in the reduced feed by permitting that feed to stand for an additional 24 hours before contacting with the CMP solvent provided time for the tracer to again reach equilibrium conditions. Effects of feed reduction on the TRUs being evaluated was considered to be more representative of actual waste processing conditions when performed in this manner.

The CMP solvent was pre-equilibrated three times with a tracer free feed prior to contact with the traced feed except in those tests involving Zr-95. Reduced, non-traced feed was used to pre-equilibrate the solvent when tests were performed with reduced feed. When Zr-95 traced feed (either reduced or non-reduced) was to be contacted with the CMP solvent, the solvent was pre-equilibrated with 3.4 M HNO₃. Acid was used instead of tracer free feed to prevent the extraction of stable zirconium into the solvent while still loading the solvent with acid. Pre-equilibrating the solvent prior to contacting with the traced feed allows for the measurement of distribution coefficients under close to equilibrium conditions by minimizing perturbations of the distribution coefficient caused by the extraction of acid or other species.

Single batch, equal-volume contacts of the aqueous and organic phases were performed. Both phases were sampled after the phases were contacted for 1 minute on a vortex mixer and centrifuged for five minutes at 3500 RPM. All tracer tests were performed at 25° C ± 2° C. A schematic of the experimental procedure used in this study is shown in Figure 1.

Three extraction, scrub, and strip contacts were performed. Extraction contacts are designated E1-E3, scrub contacts Sc1-Sc3, and strip contacts St1-St3. Two wash contacts W1 and W2 were performed in some tests. Several scrub and strip solutions were evaluated during this testing.

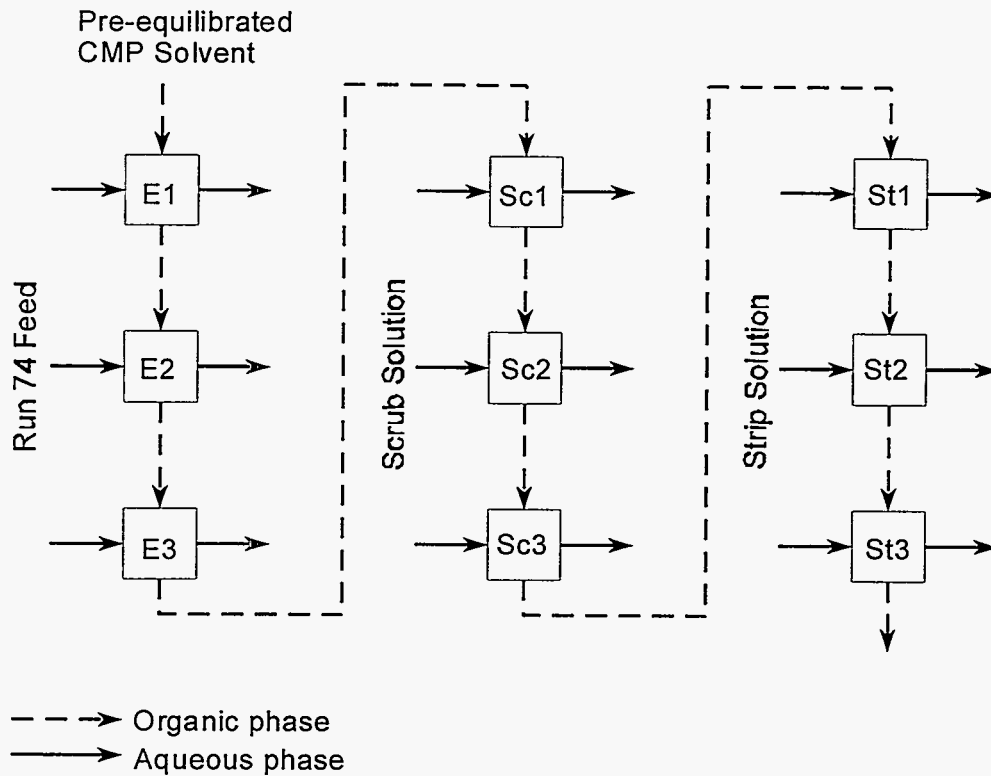


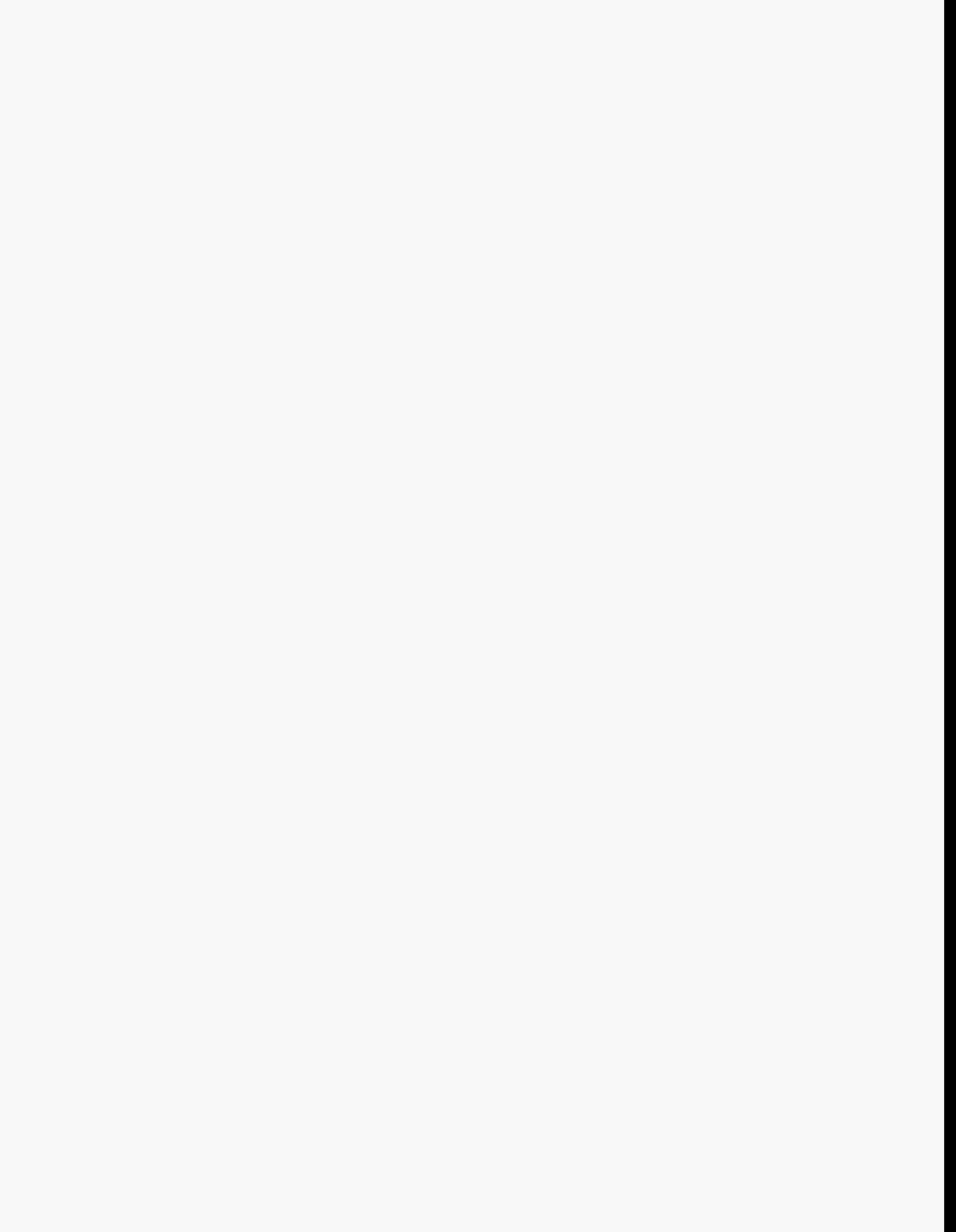
Figure 1: Experimental Procedure used for testing Simulated ICPP Dissolved Zirconium Calcine

Analytical Methods

Zr-95 and Am-241 analyses were performed by gamma spectroscopy using a high purity p-type coaxial germanium detector rated at 80% relative efficiency. The 59.5 keV photopeak was used to determine the Am-241 activity for all samples containing mixed isotopes of zirconium and americium. Zr-95 activities were determined from the 756.7 keV photopeak. Niobium-95, daughter of Zr-95 can potentially cause interferences with analysis

of Zr-95. Nb-95 primary energy is located at 765.8 keV. However, evaluating the Zr-95 activity using its 724 keV gamma energy as a confirmatory measurement produced results within 1% of those determined using the 756.7 keV energy. This indicates that scattering events or any other possible spectral interferences did not cause a bias in the Zr-95 at its primary energy. All Zr-95 results were decay corrected to the feed count time because of the short Zr-95 half-life (64 days). All samples were counted in sealed vials which were loaded onto a sample autochanger which included a large background shield around the gamma detector. The detector was calibrated for this geometry using a 1 ml mixed radionuclide NIST-traceable standard. Quality control was monitored by counting a traceable point source before, during, and after the sequence of sample counts.

Liquid Scintillation Counting (LSC) was used to determine activities of samples containing single isotopes. LSC spectrometry is a gross activity measurement since it has no capability to resolve emissions of different energies. A xylene "cocktail" was added to 1 mL aqueous and organic samples. Aqueous and organic blanks were prepared with each sample set. Blank activities were subtracted from the total sample activity prior to determining distribution coefficients for a given contact. The samples were counted on a Packard Bell LS 6000.



RESULTS/DISCUSSION

Several tracer tests were conducted to select: 1) solvent composition, 2) scrub reagent, 3) gross actinide stripping reagent, and 4) optimized scrub and strip concentrations. Batch contacts were conducted to develop a flowsheet for treating actual dissolved calcine. Results from batch contact tests with spiked Run 74 dissolved calcine feed were used in the Generic TRUEX Model (GTM) to simulate counter-current process conditions. GTM results were used to validate the recommended flowsheet for scale-up testing in the 5.5-cm Centrifugal Contactor Mockup.

0.75 M CMP Tests

Initial testing with the CMP solvent was performed using the CMP and TBP concentrations described by Rapko and Lumetta [14] (0.75 M CMP and 1.0 M TBP). Rapko and Lumetta [14] used a straight chain hydrocarbon as the diluent; Isopar L[®], a branched chain hydrocarbon, was used in these tests. Tracer tests were performed by spiking the clarified non-reduced Run 74 calcine with either Zr-95, Tc-99, U-233, Np-239, Pu-238, or Am-241. The spiked Run 74 feed was contacted with pre-equilibrated CMP solvent after the feed itself was allowed to equilibrate for at least 24 hours. Table 3 shows the extraction distribution coefficients for contacts, E1, E2, E3; where the solvent was contacted three times with fresh spiked feed being used for each contact.

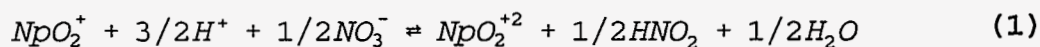
Table 3: Extraction Distribution Coefficients Using 0.75 M CMP and 1.0 M TBP in Isopar L[®]

Contact	D_{Zr}	D_{Tc}	D_U	D_{Pu}	D_{Np}	D_{Am}
E1	0.24	0.88	242	81	>133	15
E2	0.26	0.91	265	91	280	15
E3	0.29	0.92	265	96	350	15

Desirably large uranium and TRU extraction distribution coefficients were achieved with this solvent composition, while a small extraction distribution coefficient for zirconium was also observed ($D_{Zr} < 0.3$). Less than 20 % of the zirconium extracted in the first extraction contact E1, while >98 % of the Pu, >99 % of the Np, and > 90 % of the Am extracted in this contact. Uranium was also quantitatively extracted (>99 %).

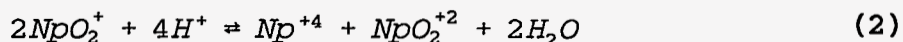
The large D_{Np} obtained in all three extraction contacts is interesting. Even though neptunium is a minor contributor to the total alpha activity in the calcine (Table 1), these large distribution coefficients were not expected and should be explained. H. R. Maxey, et. al., [15] reports Np(IV) and Np(VI) distribution coefficients from solutions of pure nitric acid into 30 % CMP (~0.7 M CMP) in diisopropylbenzene (DIPB). Maxey reports distribution coefficients for Np(IV) and Np(VI) from 6.0 M HNO₃ to be approximately 800 and 60, respectively. Krupa, et. al. [16], performed tests with simulated zirconium-aluminum fuel co-processing waste and 20 % CMP in DIPB. The simulated waste used by Krupa was 1.5 M HNO₃ and 2.4 M total NO₃⁻. Krupa reports a distribution coefficient for Np(V) of $D_{Np} = 0.55$ [16]. Based on the Np distribution coefficients reported by Maxey and Krupa, and the D_{Np} shown in Table 3, it would appear that neptunium is partitioned between the +4 and +6 oxidation states in the dissolved Run 74 zirconium calcine. Neptunium added to the Run 74 feed was expected to be in the +5 oxidation state; not partitioned between the +4 and +6 oxidation states.

Katz, Seaborg, and Morss report that Np(V) is oxidized to Np(VI) by nitric acid containing small amounts of nitrite (NO₂⁻) [17]. Nitrite in turn can reduce Np(VI) to Np(V). The mechanism for the oxidation-reduction reaction for neptunium by nitric acid and nitrite is shown in Equation 1.



The equilibrium of Equation 1 is shifted to the right during solvent extraction processes because NpO₂⁺² is preferentially extracted over NpO₂⁺. The large acid concentration in Run 74 dissolved calcine feed may be enough to shift the equilibrium to the right during

contacts with the CMP solvent resulting in significant Np(VI) extraction. However, a comparison of Maxey's data to D_{Np} shown in Table 3 would indicate the presence of Np(IV) in the dissolved Run 74 feed. Katz also describes the partitioning of Np(V) to Np(IV) and Np(VI) in highly acidic solutions [17]. This partitioning is shown in Equation 2.



Partitioning of Np(V) to Np(IV) and Np(VI) in highly acidic solutions may also provide a plausible explanation for the large D_{Np} shown in Table 3. A combination of the mechanisms shown in Equations 1 and 2 is also likely.

The extraction distribution coefficients shown in Table 3 indicate that uranium and the TRUs will be removed from zirconium calcine feeds to below the 10 CFR 61.55 Class A non-TRU waste limit. Technetium's extraction distribution coefficient is expected to be large enough to partially remove Tc-99 from the dissolved calcine feed. This will have to be confirmed by performing counter-current tests with actual dissolved calcine since a suitable non-radioactive Tc surrogate has not been found to predict Tc behavior in the 5.5-cm Centrifugal Contactor Mockup. Even though D_{Zr} is desirably small, a significant mass of zirconium will extract with the actinides. If the extracted zirconium is allowed to be stripped with the actinides, a drastic increase in the final HLW glass or glass-ceramic waste volume may occur. The lack of success in preventing zirconium extraction necessitated the need to scrub zirconium from the solvent without causing significant actinide recycle (specifically for Am-241).

Zirconium scrubbing tests were performed using the 0.75 M CMP solvent loaded with Zr-95 and Am-241 from three successive contacts with the spiked Run 74 feed. Stable zirconium from the feed was also extracted. The loaded solvent was then contacted with either 0.05 M $H_2C_2O_4$ in 3 M HNO_3 or 1.5 M HNO_3 . These scrub compositions were chosen based on the work performed by Baker [10] and on D_{Am} as a function of $[HNO_3]$ using 0.75 M CMP [18]. Table 4 shows the results from Zr and Am scrubbing tests.

Table 4: Zirconium Scrubbing With 0.05 M H₂C₂O₄ in 3 M HNO₃ or 1.5 M HNO₃

	0.05 M H ₂ C ₂ O ₄ in 3 M HNO ₃			1.5 M HNO ₃		
	Sc1	Sc2	Sc3	Sc1	Sc2	Sc3
D _{Zr}	0.054	<<1	NA	0.26	0.29	1.18
D _{Am}	7.05	7.39	7.49	5.58	4.02	3.74

NA = No detectable activity in either phase

Dilute ammonium fluoride (0.1 M NH₄F) was also evaluated as a zirconium scrub reagent. Uranium, plutonium, americium, and zirconium were extracted into the CMP solvent from spiked Run 74 feed. The loaded solvent was then contacted three times with equal and fresh volumes of 0.1 M NH₄F in 3 M HNO₃. Results from this test are shown in Table 5.

Table 5: Zirconium and Actinide Scrubbing With 0.1 M NH₄F in 3 M HNO₃

Contact	D _U	D _{Pu}	D _{Am}	D _{Zr}
Sc1	23.1	93.7	8.06	0.027
Sc2	5.30	45.1	6.81	0.77
Sc3	4.94	39.3	6.73	<1

The 0.05 M H₂C₂O₄ in 3 M HNO₃ scrub solution was found to be more effective than 1.5 M HNO₃ at removing zirconium from the solvent while also minimizing americium recycle (D_{Am} is larger in the oxalic acid scrub contacts). The increase in D_{Zr} in the final scrub contact, Sc3, may be due to solvent impurities. Dilute ammonium fluoride results are comparable to the those obtained with dilute oxalic acid, and should be considered as a viable scrub reagent. The uranium scrub distribution coefficients are smaller than desired with the 0.1 M NH₄F but D_U could be increased in the scrub section by optimizing (decreasing) the NH₄F concentration. Uranium concentrations in the dissolved calcine feed are expected to be minimal since uranium separation processes were performed on these solutions prior to calcination. Therefore, the small scrub D_U may be of little consequence. The NH₄F

concentration evaluated in this test could possibly be decreased below 0.1M and still quantitatively remove zirconium from the solvent.

Further scrub testing was performed with 0.05 M H₂C₂O₄ in 3 M HNO₃ to evaluate the scrub distribution coefficients of U, Pu, Np, and Tc. Again, the CMP solvent that was contacted three times with Run 74 dissolved calcine spiked with either U-233, Pu-238, Np-239, or Tc-99 was contacted three times with equal volumes of 0.05 M H₂C₂O₄ in 3 M HNO₃. Scrub distribution coefficients from this test are shown in Table 6.

Table 6: Technetium and Actinide Scrub D's Using 0.05 M H₂C₂O₄ in 3 M HNO₃

Contact	D _U	D _{Pu}	D _{Np}	D _{Tc}
Sc1	106	31.4	77.2	1.74
Sc2	90.5	24.0	58.5	2.12
Sc3	86.2	22.9	32.7	2.20

Scrub distribution data shown in Table 6 indicate that very little actinide or technetium loss will occur with the 0.05 M H₂C₂O₄ in 3 M HNO₃ scrub solution. This scrub solution would appear to be effective at accomplishing the goal of selectively removing zirconium while minimizing actinide recycle. The only concern with this scrub solution is the formation of precipitates when combined with the aqueous feed. These precipitates will not only reduce contactor performance but may also carry down actinides. Previous tests have shown that a small amount of oxalate in the feed may result in a visible calcium oxalate precipitate. Reduced contactor performance and precipitates containing actinides may result in aqueous raffinates contaminated with TRUs above the 10 CFR 61.55 Class A limit of 10 nCi/g.

Precipitate formation was addressed by adding different volumes of the 0.05 M H₂C₂O₄ in 3 M HNO₃ scrub solution to constant volumes of Run 74 calcine spiked with Am-241. Run 74 feed to 0.05 M H₂C₂O₄ in 3 M HNO₃ ratios of 8:1, 8:2, 8:3, and 8:4 were tested to simulate a range of feed to scrub flowrates. This test was performed by adding 9 mLs of Run 74 to four test tubes. Am-241 was spiked into each test tube by adding 0.05 mL of the Am-241 standard having an activity of 1.65E+5 dps/mL. Each test tube was mixed for 1

minute on a vortex mixer and a 1 mL sample was taken to ascertain the initial Am-241 activity. The 0.05 M H₂C₂O₄ in 3 M HNO₃ scrub solution was added to each test tube after sampling to provide the above stated ratios. The solutions were again mixed for 1 minute on a vortex mixer and allowed to stand for 1 hour. Samples were taken from each test tube after 1 hour and analyzed for Am-241 activity to determine if any activity was lost. No visible precipitates were observed in any of the test tubes; therefore the solutions were not centrifuged or filtered prior to sampling. Results from this test are shown in Table 7.

Table 7: Feed Stability Test for 0.05 M H₂C₂O₄ in 3 M HNO₃ Scrubs

Feed:Scrub Ratio	Initial Am-241 Activity (dps/mL)	Am-241 Activity After Scrub Dilution (dps/mL)	Final Am-241 Activity (dps/mL)	Material Balance†
8:1	57,800	51,378	51,627	99.5%
8:2	58,183	46,546	45,950	100%
8:3	58,483	42,533	41,736	102%
8:4	58,432	38,955	38,160	102%

† (Am-241 activity after scrub dilution/final Am-241 activity) x 100

Data shown in Table 7 show that no Am-241 activity was lost in any of the feed scrub mixtures after 1 hour, which would indicate the feed and scrub mixture to be stable with regards to precipitation. Even though the test duration of 1 hour is well beyond the expected residence time of the feed/scrub mixture in the extraction section of a counter current system, this test should be repeated by allowing the spiked feed and scrub mixture to set for an extended period of time to ensure that precipitate formations are not kinetically slow.

The 0.05 M H₂C₂O₄ in 3.0 M HNO₃ scrubbed solvents used to obtain data in Tables 4 and 6 were contacted with either 0.04 M HEDPA in 0.04 M HNO₃ or 0.05 M H₂C₂O₄ in 0.01 M HNO₃ to evaluate the stripping behavior of the actinides and technetium from the 0.75 M CMP solvent. Selective stripping of the actinides from the solvent is not desirable; therefore, stripping reagents capable of a gross actinide recovery were evaluated. Stripping distribution

coefficients for the actinides and technetium using these two stripping reagents are shown in Tables 8 and 9.

Table 8: Stripping Distribution Coefficients Using 0.04 M HEDPA in 0.04 M HNO₃

Contact	D _U	D _{Pu}	D _{Np}	D _{Am}	D _{Tc}
St1	0.04	0.06	0.047	0.32	20
St2	0.004	0.01	0.155	0.01	40
St3	<<1	0.035	No Data	<<1	59

Table 9: Stripping Distribution Coefficients Using 0.05 M H₂C₂O₄ in 0.01 M HNO₃

Contact	D _U	D _{Pu}	D _{Np}	D ¹ _{Am}
St1	12.73	0.93	0.43	0.50
St2	1.39	0.49	0.25	0.03
St3	0.46	0.19	<0.25	<<1

1. Am-241 stripping distribution coefficients obtained with 0.1 M H₂C₂O₄ in 0.01 M HNO₃

The data shown in Tables 8 and 9 indicate that dilute HEDPA is much more efficient at stripping the actinides, especially uranium, than dilute oxalic acid; however, HEDPA did not strip Tc. No data is available regarding H₂C₂O₄ ability to strip Tc. Based on data from this test, HEDPA in dilute nitric acid was chosen as the stripping reagent of choice.

0.5 M CMP Tests

During the development of the CMP flowsheet, an evaluation of the dispersion numbers indicated that the 0.75 M CMP solvent may cause flooding problems when tested in the centrifugal contactor design currently available at the ICPP [19,20] . Dispersion numbers

are unitless values that provide an indication of how well the solvent and aqueous phases separate from one another. The larger the dispersion number the more difficult one phase separates from the other, which indicates that flooding may occur in the contactor. The dispersion numbers were evaluated to determine which solvent composition would have the best hydraulic properties for use in the 5.5 cm contactor design being used at the ICPP. Contactor design can be tailored around the hydraulic properties of a given solvent. The ICPP 5.5 cm contactor design was based on the TRUEX solvent (0.2 M CMPO and 1.4 M TBP in an NPH diluent) and not the CMP solvent. Rather than purchasing new contactors capable of efficient use with the 0.75 M CMP solvent, adjustments were made to the CMP solvent that would allow for testing in the current contactor system. The primary adjustment in the solvent was varying the CMP concentration until the hydraulic properties of the solvent were conducive to the 5.5 cm contactors.

Solvent composition was also adjusted around the extraction D_{Zr} and D_{Am} values. A solvent having desirable hydraulic properties but inefficient at extracting americium would be unacceptable. Two solvents, 0.5 and 0.25 M CMP, both in 1.0 M TBP, were shown to have acceptable dispersion numbers with the feed, scrub, strip, and wash solutions and were chosen for further testing. Extraction D_{Zr} and D_{Am} were determined for these two solvents from spiked Run 74 feeds by contacting each solvent three times with equal volumes of the fresh feed. The loaded solvent was then scrubbed with three equal volumes of 0.05 M $H_2C_2O_4$ in 3 M HNO_3 . Extraction and scrub data from this test are shown in Table 10. The 0.75 M CMP data are also shown for comparison.

Little difference in D_{Zr} was observed between the 0.75 M and 0.5 M CMP solvents. The 0.25 M CMP solvent extracted approximately 66% less zirconium than either the 0.75 M or 0.5 M CMP solvents. Even though this is a desirable attribute of the 0.25 M CMP solvent, the extraction and scrub D_{Am} may be too small for efficient Am removal. Almost 50% of the americium is lost in the scrub contacts and the relatively small extraction $D_{Am} \sim 2.5$ indicates relatively poor americium removal. Since >99% of the americium must be removed from the dissolved calcine feeds, it is doubtful that the extraction and scrub D_{Am} for the 0.25 M CMP solvent would result in an aqueous raffinate waste capable of consistently meeting the Class

A waste limit criteria. The 0.5 M CMP solvent does exhibit extraction and scrub D_{Am} suitable for americium removal from the dissolved calcine feed and was chosen as an acceptable solvent for further testing.

Table 10: Zirconium and Americium Extraction Distribution Coefficients as a Function of CMP Concentration

Contact	0.75 M CMP		0.5 M CMP		0.25 M CMP	
	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}	D_{Zr}	D_{Am}
E1	0.22	14.3	0.18	8.6	0.08	2.3
E2	0.24	14.6	0.19	8.5	0.09	2.5
E3	0.25	14.3	0.19	8.3	0.1	2.6
Sc1	0.054	7.05	0.05	3.4	<0.1	1.0
Sc2	<<1	7.39	<0.6	3.8	NA	1.1
Sc3	NA	7.41	NA	3.7	NA	1.1

NA = no activity in either phase

Figures 2 and 3 are distribution coefficient profiles for the extraction of americium and zirconium into the 0.5 M CMP solvent as a function of equilibrium aqueous phase HNO_3 concentration. Favorable americium extraction D 's are observed when the $[HNO_3] > 2$ M HNO_3 , where D_{Am} are > 2 . Americium can be stripped from the 0.5 M CMP solvent using solutions < 1 M HNO_3 , but favorable americium stripping D 's occur when the $[HNO_3] < 0.1$ M HNO_3 . Zirconium significantly extracts from pure nitric acid solutions when $[HNO_3] > 0.5$ M HNO_3 where D_{Zr} are > 1 . Extrapolating the zirconium distribution profile from the curve shown in Figure 5 also indicates that removing zirconium from the 0.5 M CMP solvent will be difficult using very dilute nitric acid solutions.

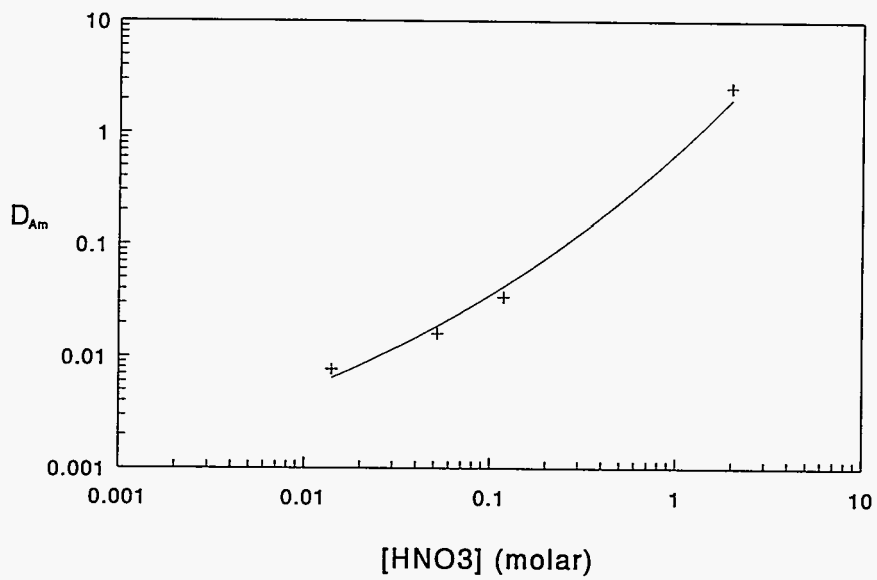


Figure 2: D_{Am} as a function of $[HNO_3]$ using 0.5 M CMP and 1.0 M TBP in Isopar L[®]

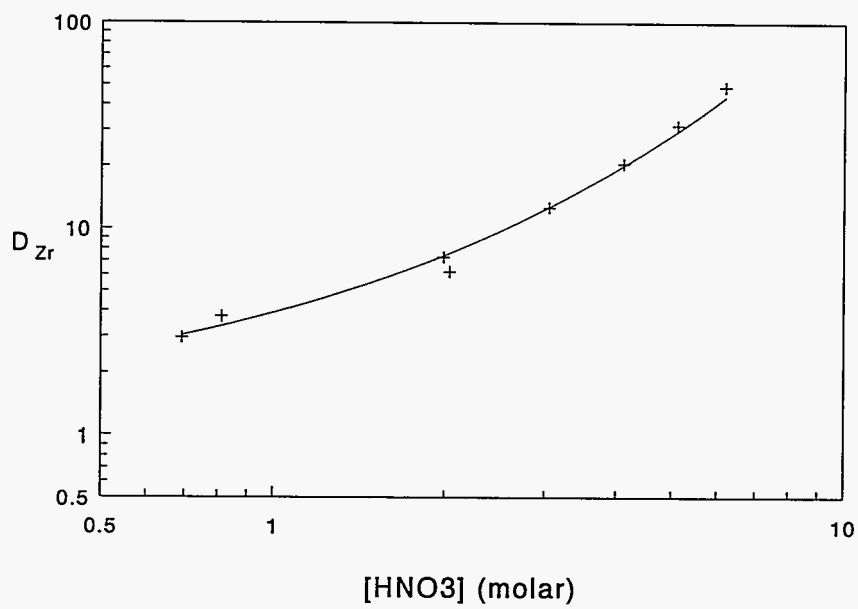


Figure 3: D_{Zr} as a function of $[HNO_3]$ using 0.5 M CMP and 1.0 M TBP in Isopar L[®]

D_{Am} and D_{Zr} data shown in Figures 2 and 3 suggest that selectively scrubbing zirconium from 0.5 M CMP using nitric acid is impossible to perform without causing significant americium stripping. Baker, et al., used 3 M HNO_3 to scrub extracted zirconium during a counter-current test performed with a Zr-Al first cycle raffinate and 20 vol.% CMP (dihexyl analogue) in decalin and DIPB [10]. Even though Baker does not report a D_{Zr} for the 3 M HNO_3 scrub, McIsaac [21] reports a $D_{Zr} = 0.016$ when also using 3 M HNO_3 to scrub Zr that extracted from a feed and into a solvent having compositions analogous to those used by Baker [10]. Schulz [22] also reports a scrub $D_{Zr} = 0.066$ when 6.0 M HNO_3 is contacted with 30 vol% CMP (dihexyl analogue) in xylene (the zirconium was loaded into the solvent from Zr-Al first cycle simulant). The zirconium scrub D's reported by McIsaac [21] and Schulz [22] seem to contradict the D_{Zr} data shown in Figure 3. This contradiction is explained by the difference in solvent compositions used by McIsaac, Schulz, and the present work. Therefore, a comparison of zirconium D's between previous work and those reported here is invalid because of the drastic differences in the solvents used.

The zirconium data shown in Figure 3 would also appear to contradict the data observed when contacting the dissolved calcine feed with the CMP solvent, where very small D_{Zr} were obtained ($D_{Zr} < 1$). The dissolved calcine feed is 3.5 M H^+ and 6.0 M NO_3^- ; therefore, the D_{Zr} would be expected to be > 10 (Figure 3). However, the majority of the zirconium in the dissolved calcine is complexed by fluoride (0.9 M) which inhibits zirconium extraction. Zirconium scrubbing data shown in Table 4, where 1.5 M HNO_3 and 0.75 M CMP were used, again seem to contradict the zirconium data shown in Figure 3. $D_{Zr} < 1$ were obtained for the first two scrub contacts using 1.5 M HNO_3 and a larger CMP concentration. A $D_{Zr} = 1.2$ was obtained in the final Sc3 scrub contact. Figure 3 shows a $D_{Zr} \sim 3.5$ for 1.5 M HNO_3 . This discrepancy may be due to a difference in the species of extracted zirconium.

Uranium and plutonium were spiked into Run 74 dissolved calcine in order to conduct tests to determine extraction, scrub, strip, and wash distribution coefficients for these two elements using 0.5 M CMP. The scrub and strip solutions used for this test were 0.05 M $H_2C_2O_4$ in 3 M HNO_3 and 0.04 M HEDPA in 0.04 M HNO_3 , respectively. A 0.25 M

performed with fresh aqueous phases being used for each contact. The data from this test are shown in Table 11.

A comparison of the uranium and plutonium distribution coefficients shown in Table 11 with those shown in Tables 3, 6, and 8 shows very little change in the extraction, scrub, and strip distribution coefficients for uranium and plutonium between the 0.75 M and 0.5 M CMP solvents.

The excellent hydraulic properties offered by the 0.5 M CMP solvent, and the distribution coefficient data shown in Tables 10 and 11 suggest this solvent composition as the primary candidate for further testing.

Table 11: Uranium and Plutonium Distribution Coefficients Using 0.5 M CMP

Contact	D_U	D_{Pu}
E1	210	71.4
E2	220	71.8
E3	224	71.7
Sc1	78.8	21.1
Sc2	67.6	15.6
Sc3	65.3	14.4
St1	0.016	0.027
St2	0.002	0.008
St3	NA	<0.3
W1	NA	<0.1
W2	NA	<0.3

NA = No activity detected in either phase

Feed Adjustments

Feed adjustments were evaluated during the development of actinide separations processes for dissolved zirconium calcine feeds. These feeds contain significant quantities of chromium and zirconium, both of which can extract and be recovered with the actinides. The extraction of these two elements have caused physical problems associated with the solvent and consume precious extractant to the point of suppressing actinide extraction. The recovery of these elements with the actinides may cause an increase in the HLW glass or glass-ceramic final waste volume, which is also undesirable. Even though scrubbing zirconium with 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ in 3 M HNO_3 suggests a plausible means of preventing its recovery with the actinides, a brief discussion of work performed to prevent its extraction is provided.

Chromium Extraction

Chromium has been known to extract into solvents containing TBP [23] as chromate at $\text{pH} < 6$. Most ICPP calcines will contain Cr which is most likely present as chromate (CrO_4^{-2}) because of the oxidizing environment in the calcination process. Run 74 calcine contained 0.4 wt% Cr prior to dissolution and 5.3×10^{-3} M Cr following dissolution. Chromium is most likely present as dichromate, $\text{Cr}_2\text{O}_7^{-2}$, in the acidic dissolved calcine. Physical problems, such as third phase formation during extraction contacts and interfacial crud formation during solvent wash contacts, were observed in early work performed with the TRUEX solvent (0.2 M CMPO, 1.4 M TBP in dodecane) and Run 74 dissolved calcine [11]. These problems were eliminated by reducing the calcine with either ascorbic acid, hydrogen peroxide, or ferrous sulfamate. Reducing the feed with any of these reductants caused the feed to change from the yellow dichromate color to the blue Cr(III) color, and also eliminated the third phase and interfacial crud problems. These data indicate that chromate extraction was the culprit causing the physical problems with the TRUEX solvent.

The success achieved by reducing the feed in the TRUEX process was applied to CMP process in order to inhibit dichromate extraction. Even though the CMP solvent contains 1.0 M TBP, as opposed to the 1.4 M TBP in the TRUEX solvent, the CMP solvent still extracted significant amounts of dichromate. Tests performed with reduced Run 74 dissolved calcine resulted in a "cleaner" solvent (the solvent remained opaque as opposed to dark yellow) throughout the extraction, scrub, strip, and wash contacts. Chromium distribution coefficients using reduced and non-reduced feeds with 0.5 M CMP solvent are shown in Table 12.

Table 12: D_{Cr} for Extraction, Scrub, Strip, and Wash Contacts

Contact	D_{Cr} Reduced Feed	D_{Cr} Non-Reduced Feed
E1	0.037	0.36
E2	0.066	0.49
E3	0.062	0.54
Sc1	0.082	1.34
Sc2	0.76	1.67
Sc3	0.75	7.84
St1	2.55	5.31
St2	0.70	8.41
St3	Aqueous value below detection limit ¹	7.09
W1	Aqueous value below detection limit ¹	0.044
W2	Aqueous value below detection limit ¹	0.0075

1. Analytical detection limit = 0.03 ppm

Chromium distribution coefficients shown in Table 12 were determined by assuming a material balance of 100% and calculating the organic phase Cr

concentration by difference ($Cr_{Org} = Cr_{Aq\ in} - Cr_{Aq\ out}$). Only the aqueous phases were sampled and analyzed for Cr. Using the material balance to calculate the organic phase Cr concentration causes greater uncertainty in D_{Cr} , especially in those samples with very little Cr, because the analytical error is compounded with each successive contact. However, these errors should be inconsequential when comparing D_{Cr} for a specific contact associated with the reduced and non-reduced feeds.

Chromium extraction distribution coefficients into the CMP solvent from the non-reduced feed are approximately an order of magnitude larger than the extraction distribution coefficients observed in the reduced feed. The difference in D_{Cr} between the two feeds is assumed to be the difference between Cr(VI) and Cr(III) extraction. The Cr extraction distributions are consistent with those observed by Schulz and McIsaac [24], where $Cr_2O_7^-$ is reported to extract considerably more strongly than Cr^{+3} into CMP solutions.

Scrub distribution coefficients, using 0.05 M $H_2C_2O_4$ in 3 M HNO_3 , indicate that dilute oxalic acid is ineffective in scrubbing Cr(VI) from the CMP solvent. Chromium scrub D's are smaller for those contacts with the CMP solvent previously contacted with the reduced feed. This may indicate that Cr(III) is scrubbed from the solvent using the dilute oxalic acid/high nitric acid scrub solution.

Stripping Cr(VI) from the solvent contacted with the non-reduced feed shows 0.04 M HEDPA to be ineffective in removing Cr(VI). Even though a $D_{Cr} < 1$ was obtained in the first strip contact in the reduced feed test, the Cr concentration analytically determined in the first strip solution was near the analytical detection limit. This may indicate that HEDPA is more effective at stripping Cr(III), as opposed to Cr(VI), provided the St_1 value is assumed realistic. Strip D_{Cr} from the test using non-reduced feed are > 1 and are much more reliable because of the higher Cr concentrations found in these samples.

Sodium carbonate (0.25 M) does seem to efficiently remove Cr from the solvent. Contacts with the non-reduced feed show the wash $D_{Cr} \ll 1$. Chromium concentrations were below the analytical detection limit of 0.03 ppm in the wash

samples from the reduced feed test.

Even though the Cr(VI) extraction distribution coefficient is small ($D_{Cr} < 1$), chromium reduction is recommended for dissolved calcine feeds prior to contact with the CMP solvent. This recommendation is based on the Cr problems observed in the TRUEX testing [11], where small amounts of chromium in the solvent caused physical problems during extraction and wash contacts.

Zirconium Extraction

Inhibiting zirconium extraction from dissolved zirconium calcines, such as Run 74, by adjusting the feed with zirconium complexing reagents was also investigated. Zirconium extraction into the CMP solvent is < 1 , but the large zirconium concentration in the feed may cause a significant zirconium mass in the solvent.

Several zirconium complexing reagents were evaluated during the TRUEX flowsheet development [11]. Fluoride, ammonium oxalate, ketomalonic acid, tetrahydrofuran carboxylic acid, and HEDPA were all evaluated as potential zirconium masking reagents. Most of these complexing agents caused precipitations to occur in the feed. Fluoride, HEDPA, and oxalate compounds caused severe precipitations (mostly calcium salts) in the feed even when small amounts were added. Those reagents that were stable in the feed did not reduce the D_{Zr} extraction into the TRUEX solvent. The lack of success in preventing zirconium extraction precluded the use of complexing reagents during CMP flowsheet development. Even though CMP is not as strong of an extractant as CMPO, other means of preventing zirconium from following the actinides into the HLW stream, such as selective scrubbing, were pursued.

0.5 M CMP Tests Using Reduced Calcine Feed

Actinide, zirconium, and technetium extraction distribution coefficients were evaluated

from Run 74 feed reduced with 30% H₂O₂. The loaded solvent was scrubbed with 0.05 M H₂C₂O₄ in 3.0 M HNO₃ to remove zirconium. The scrubbed solvent was then stripped with 0.001 M HEDPA. The purposes of these tests were to determine if feed reduction adversely affected the extraction of these key elements and to optimize the HEDPA strip concentration. Optimization of the HEDPA strip solution is important to reduce the amount of phosphate reporting to the HAW fraction. Phosphate, like zirconium, may adversely increase the final HAW glass or glass-ceramic waste volume.

Extraction From Reduced Run 74 Feed

Run 74 calcine was spiked with either Pu-238, U-233, Np-239, Tc-99, Zr-95, or Am-241. The spiked feeds were allowed to equilibrate for at least 24 hours before reduction with 30% H₂O₂. Each feed was then reduced with 20 μL of 30% H₂O₂ and allowed to equilibrate for an additional 24 hours prior to contact with 0.5 M CMP. Three equal volume extraction contacts were performed with fresh reduced feed being used for each contact. Extraction distribution coefficients from these tests are shown in Table 13.

Table 13: Zr, Tc, and Actinide Extraction into 0.5 M CMP from Reduced Run 74 Feeds

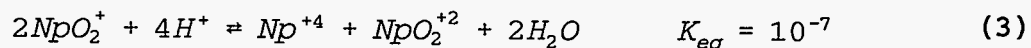
Contact	D _{Zr}	D _{Am}	D _{Pu}	D _U	D _{Np}	D _{Tc}
E1	0.19	7.4	73.5	143	>55	0.72
E2	0.22	7.0	78.5	195	>100	0.73
E3	0.22	7.1	78.5	195	58.3	0.72

A comparison of the Zr, Am, Pu, and U distribution coefficients shown in Tables 10 and 11 to those shown in Table 13 indicate little change in the extraction of these elements between non-reduced and reduced feeds. Tetravalent plutonium is reduced to trivalent plutonium by hydrogen peroxide in highly acidic solutions [25].

Tests conducted with plutonium spiked simulant before reduction have shown that the plutonium is partitioned between Pu(IV) and Pu(VI); 30% of the plutonium being Pu(IV) and 70% being Pu(VI). Hydrogen peroxide could also reduce Pu(VI) all the way to Pu(III) [17]. Even though the D_{Pu} indicate that plutonium was not extensively reduced to Pu(III) ($D_{Pu(III)} < D_{Pu(VI)} < D_{Pu(IV)}$), the likelihood of this is doubtful. Any reduced plutonium could have been re-oxidized by the dissolved calcine solution since no holding reductant was present. The redox chemistry of plutonium is complex in even simple solutions, the complicated matrix of the dissolved zirconium calcine adds to this complexity.

A comparison of the neptunium extraction data shown in Table 3 to those shown in Table 13 does indicate that neptunium may have been reduced. The D_{Np} in Table 3 were obtained with 0.75 M CMP rather than 0.5 M CMP which may make this comparison dubious. Comparing the extraction D's of the other elements listed in Tables 3 and 13 does not indicate such a drastic difference. D_{Am} did decrease from 15 in the 0.75 M CMP solvent to 7 in the 0.5 M CMP solvent, but D_{Np} went from 350 (E3) to 58 (E3). This 7 fold decrease in D_{Np} is expected to be from a combination of reduced CMP concentration and hydrogen peroxide reduction.

As previously mentioned, the large D_{Np} observed in tests using 0.75 M CMP were attributed to the disproportionation of Np(V) to Np(IV) and Np(VI). This conclusion is supported by Np(IV) and Np(VI) distribution coefficients into 30% CMP reported by Maxey [15]. The disproportionation of Np(V), shown in Equation 3, is not large [17] but is very dependant on the acid concentration.



The acid concentration in the dissolved calcine may be large enough to cause this disproportionation; however, the significant dichromate concentration prior to reduction may also contribute to Np(V) disproportionation. TBP does contribute to neptunium extraction but neptunium extraction into TBP is negligible compared to

CMP [17]. Katz [17] reports that the reduction of Np(VI) to Np(V) by H₂O₂ occurs very rapidly in nitric acid solutions, while the reduction of Np(V) to Np(IV) by H₂O₂ occurs very slowly in nitric acid. The re-oxidation of Np(IV) to Np(V) by NO₃⁻ also occurs very slowly. If equilibrium conditions are assumed, i.e., that the 24 hour equilibration period after feed reduction was enough time for any Np(V) to be reduced by H₂O₂ to Np(IV) and for Np(IV) to be re-oxidized to Np(V), then the decrease in D_{Np} can be attributed to the reduction of Np(VI) to Np(V) and the re-oxidation of Np(IV) to Np(V).

HEDPA Strip Concentration

The loaded solvent(s) from tests described above were scrubbed with 0.05 M H₂C₂O₄ in 3.0 M HNO₃ to remove extracted zirconium prior to performing HEDPA strip contacts. Three equal volume scrub contacts were performed with fresh scrub solution used in each contact. Scrub distribution coefficients are shown in Table 14. Scrub distribution coefficients shown in Table 14 are smaller than those obtained using 0.75 M CMP. Smaller scrub D's are expected with the less concentrated CMP solvent.

Table 14: Scrub Distribution Coefficients from 0.5 M CMP Using 0.05 M H₂C₂O₄ in 3.0 M HNO₃

Contact	D _{Zr}	D _{Am}	D _{Pu}	D _U	D _{Np}
Sc1	0.046	3.1	17.3	74.7	39.2
Sc2	<0.87	3.3	4.5	61.8	21.1
Sc3	NA	3.3	6.5	60.1	21.1

NA = No activity detected in either phase

The scrubbed solvent was stripped three times with 0.001 M HEDPA. Fresh HEDPA aliquots were used in each of the three contacts (St1-St3). The purpose of these contacts was to optimize the HEDPA strip concentration so that the phosphate

(from the HEDPA) concentration in the HAW fraction would be at a minimum while still quantitatively stripping the actinides from the solvent. Strip distribution data using 0.001 M HEDPA are shown in Table 15.

Americium, uranium, and neptunium were quantitatively stripped from the solvent with 0.001 M HEDPA. Not enough zirconium activity made it past the scrub contacts to determine its distribution coefficient with 0.001 M HEDPA. Plutonium stripping with 0.001 M HEDPA may be a concern. D_{Pu} is small for all three strip contacts, but because plutonium contributes to the majority of the activity, D_{Pu} may have to be much smaller to prevent significant plutonium activities from either being washed out in the sodium carbonate or from being recycled with the solvent. D_{Pu} obtained from 0.5 M CMP stripped with 0.04 M HEDPA (Table 11) are an order of magnitude smaller than these obtained with 0.5 M CMP and 0.001 M HEDPA. This data would indicate that an HEDPA concentration between 0.001 M and 0.04 M should efficiently strip plutonium.

Table 15: Strip Distribution Coefficients from 0.5 M CMP using 0.001 M HEDPA

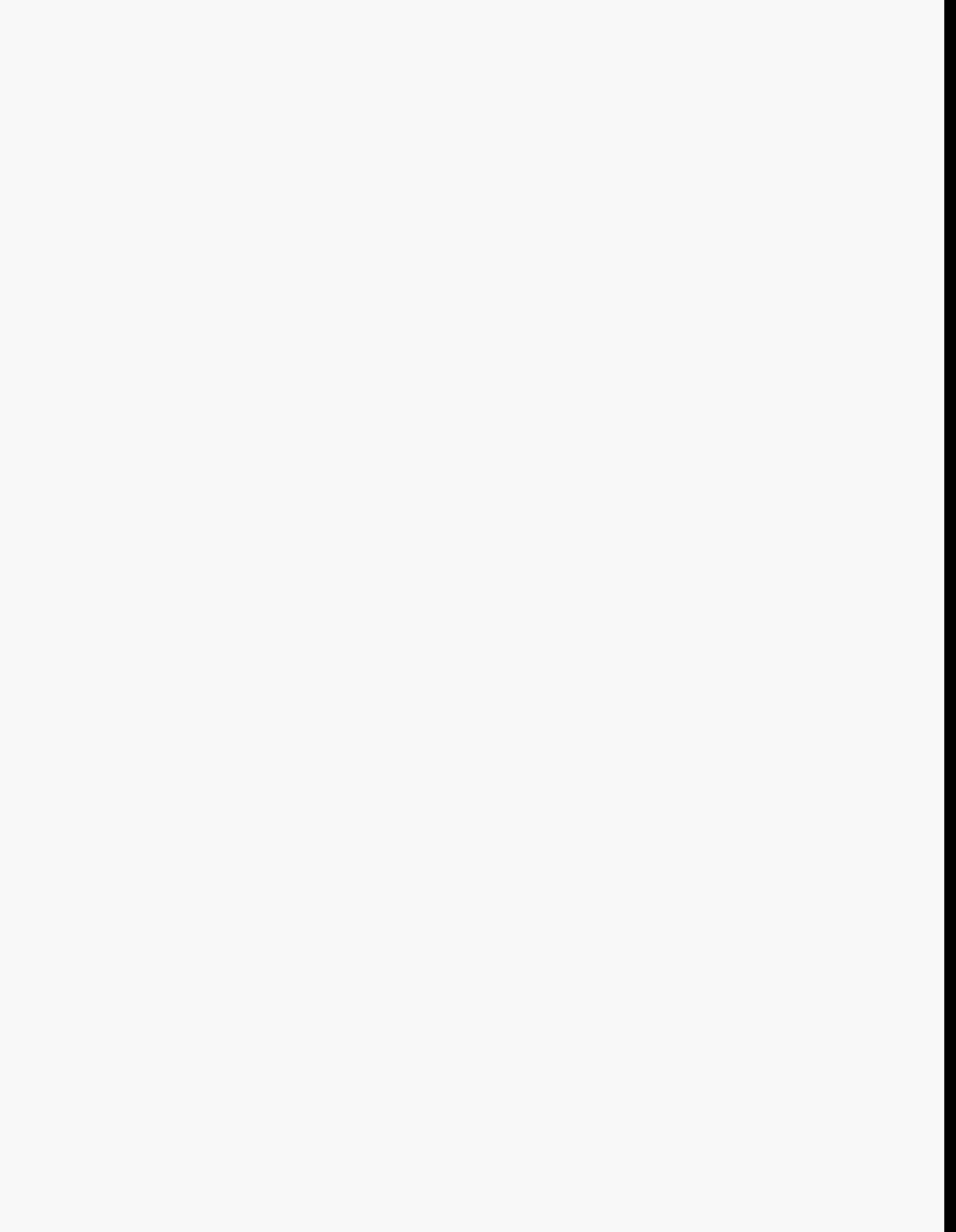
Contact	D_{Zr}	D_{Am}	D_{Pu}	D_U	D_{Np}	D_{Tc}
St1	NA	0.56	0.18	1.98	0.04	21.3
St2	NA	0.05	0.14	0.1	<0.2	40.2
St3	NA	NA	0.16	0.02	NA	61.6

NA = No activity detected in either phase

Technetium was not stripped with the 0.001 M HEDPA in 0.04 M HNO₃, which was expected. Scrubbing technetium from the 0.5 M CMP with 0.05 M H₂C₂O₄ in 3.0 M HNO₃ was not evaluated but based on the scrub data shown in Table 6 (0.75 M CMP), significant technetium loss in the scrub section is not expected. In addition, sodium carbonate does not strip technetium from the 0.5 M CMP. 0.25 M Na₂CO₃ contacts performed with the HEDPA stripped solvent, containing technetium, resulted

in technetium D's between 1 and 3. These data suggest that 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ in 3.0 M HNO_3 , 0.001 M HEDPA in 0.04 M HNO_3 , and 0.25 M Na_2CO_3 can not be used to strip technetium from the 0.5 M CMP solvent. Ideally, it would be desirable to extract and recover technetium with the actinides. The apparent inability of 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ in 3.0 M HNO_3 , and 0.25 M Na_2CO_3 to strip technetium is desirable but the lack of technetium stripping by 0.001 M HEDPA in 0.04 M HNO_3 does cause some concern.

Technetium stripping tests were performed with 5 M HNO_3 using 0.5 M CMP loaded with technetium from Run 74 calcine. Three sequential 5 M HNO_3 strip contacts were performed on unscrubbed solvent. An average $D_{\text{Tc}} = 0.26$ was obtained from these strip contacts indicating that technetium can be recovered from the 0.5 M CMP with 5 M HNO_3 .



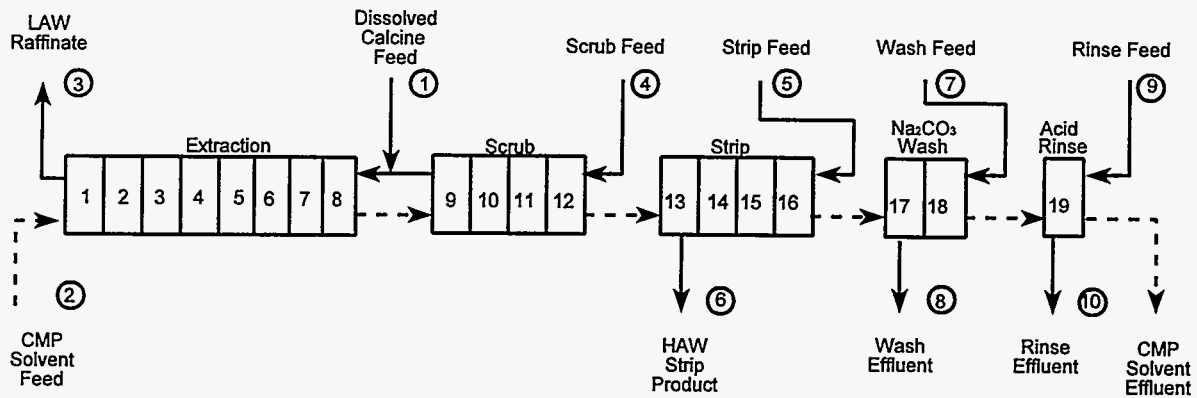
RECOMMENDATIONS

Flowsheet Development Using the Generic TRUEX Model

Experimental distribution coefficients were used in conjunction with the Generic TRUEX Model (GTM) to develop a flowsheet for the separation of the actinides from dissolved ICPP zirconium calcine using the CMP process. The experimental distribution coefficients for Am, Np, Pu, Tc, U, and Zr were input into the GTM and the GTM was used to evaluate several specific flowsheets. As a result of this modelling, the flowsheet shown in Figure 4 is recommended for future flowsheet testing in the 5.5-cm Centrifugal Contactor Mockup. The flowsheet consists of eight extraction stages at an O/A= 0.33, four scrub stages at an O/A= 2.0, four strip stages at an O/A= 1.0, two sodium carbonate wash stages at an O/A= 5.0, and one acid rinse stage at an O/A= 3.0.

With this flowsheet, the total activity of the actinides is reduced from 1246 nCi/g in the feed to 0.19 nCi/g in the raffinate, which is below the NRC Class A LLW requirement. The 0.001 M HEDPA strip removed 99.8% of the Pu from the CMP solvent. The remaining 0.2% of the Pu was stripped in the sodium carbonate wash section, resulting in a Pu activity of 17.6 nCi/g in the wash effluent. The use of a higher concentration of HEDPA in the strip is expected to result in more complete stripping of Pu, and a Pu concentration less than 10 nCi/g in the sodium carbonate effluent.

Zirconium was effectively scrubbed from the CMP solvent, resulting in less than 0.01% of the Zr exiting in the strip product. The Tc which was extracted from the dissolved calcine feed was not stripped, resulting in Tc building up to 0.023 Ci/m³ in the solvent and 96% of the Tc exiting in the aqueous raffinate.



Comp.	Dissolved Calcine Feed 1	CMP Solvent Feed 2	LAW Raff. 3	Scrub Feed 4	Strip Feed 5	Strip Product 6	Wash Feed 7	Wash Effluent 8	Rinse Feed 9	Rinse Effluent 10
HNO ₃ (M)	3.5		2.9	3.0					0.10	0.10
HEDPA (M)					0.001	0.001				
H ₂ C ₂ O ₄ (M)				0.05						
Na ₂ CO ₃ (M)							0.25	0.25		
Zr (M)	0.21		0.17			1.86E-05 ¹				
Am (nCi/g)	104		0.17			309				
Pu (nCi/g)	1142		0.02			3275		17.6		
U (nCi/g)	0.05		1.58E-07			1.5		0.011		
Np (nCi/g)	0.5		1.52E-06			1.5				
Tc (Ci/m ³)	0.06	0.023	0.048			0.0013		0.021		
Relative Flow	1.00	0.40	1.20	0.21	0.40	0.40	0.08	0.08	0.13	0.13

¹ Zr stripping data with 0.001 M HEDPA was not available so stripping data with 0.04 M HEDPA was used

Figure 4. CMP Flowsheet for the Treatment of ICPP Dissolved Zirconium Calcine

CONCLUSIONS

Conclusions drawn from tests conducted with the CMP extractant and dissolved Run 74 zirconium calcine are:

- A solvent composition of 0.5 M CMP and 1.0 M TBP in an Isopar L[®] diluent is recommended for use with the current contactor design. This solvent composition was tested in the 5.5 cm Centrifugal Contactor Mockup and provided good hydraulic properties and is expected to provide actinide decontamination below the 10 nCi/g NRC limit [26]. Extraction distribution coefficients for the actinides using this solvent are expected to be: $D_{Am} \sim 7$, $D_{Np} \sim 60$, $D_{Pu} \sim 80$ and $D_U \sim 200$. Zirconium extraction is minimal, $D_{Zr} < 0.3$, but is significant enough to make it desirable to prevent it from reporting to the HAW fraction. Comparable extraction D's for Nd (Am surrogate) and Zr were obtained in the 5.5 cm Centrifugal Contactor Mockup [26]. D_{Tc} is also small (~ 0.7) indicating complete extraction of technetium from the dissolved calcine feed may be difficult.
- A scrub solution containing 0.05 M H₂C₂O₄ in 3.0 M HNO₃ or 0.1 M NH₄F in 3.0 M HNO₃ should be used to selectively scrub extracted zirconium from the solvent. The high acid concentration of the scrub will inhibit actinide recycle. The 5.5 cm Centrifugal Contactor Mockup used the 0.05 M H₂C₂O₄ in 3.0 M HNO₃ scrub solution and the distributions were similar to those reported in this study [26]. Less than 0.1% of the Zr in the feed reported to the HAW fraction in the 5.5 cm Centrifugal Contactor Mockup [26]. Tc-99 is not expected to be significantly scrubbed from the solvent with 0.05 M H₂C₂O₄ in 3.0 M HNO₃.
- A strip solution concentration between 0.001 M and 0.04 M HEDPA in 0.04

M HNO_3 will remove the actinides from the 0.5 M CMP solvent. Even though D_{Act} were small using 0.001 M HEDPA, the $D_{Pu} \sim 0.2$ may be too large for complete plutonium stripping. This may result in greater than Class A plutonium activities in the sodium carbonate wash or may cause significant plutonium activities in the recycled solvent. 0.04 M HEDPA efficiently stripped the actinides from 0.5 M CMP; this was confirmed in the 5.5 cm Centrifugal Contactor Mockup [26]. The phosphate from 0.04 M HEDPA may increase the final HAW glass or glass-ceramic waste volume. Minimizing the phosphate concentration (or HEDPA concentration) will have a direct correlation in minimizing the final waste volume.

- Technetium is not stripped from the 0.5 M CMP with either 0.001 M HEDPA in 0.04 M HNO_3 or 0.25 M Na_2CO_3 . 5 M HNO_3 will efficiently strip technetium; thus allowing for technetium disposal with the actinides in the HAW fraction.
- Reducing the zirconium calcine feed with an extremely small volume of 30 % H_2O_2 will prevent the extraction of dichromate into the CMP solvent. Hydrogen peroxide reduces the extractable dichromate to the less extractable Cr(III). CMP solvent contacted with reduced feed remains opaque, as opposed to dark yellow/green. Inhibiting dichromate extraction will also decrease the likelihood of precipitation, interfacial crud, and third phase formation. These problems were observed (sporadically) when performing tests with unreduced feeds. In the 5.5 cm Centrifugal Contactor Mockup test, <0.2% of the chromium reported to the HAW fraction [26].
- The flowsheet shown in Figure 4 is expected to reduce the concentration of the actinides to below the 10 nCi/g Class A LLW requirements and minimize the quantity of zirconium reporting to the HAW strip product.

REFERENCES

1. J. A. Murphy, L. F. Pincock, and I. N. Christiansen, "ICPP Radioactive Liquid and Calcine Waste Technologies Evaluation Final Report and Recommendations", Lockheed Idaho Technologies Co., INEL-94/0119, April 1995.
2. J. R. Berreth, "Inventories And Properties Of ICPP Calcined High-Level Waste", Westinghouse Idaho Nuclear Co. Inc., WINCO-1050, February 1988.
3. B. A. Staples, G. S. Pomiak, and E. L. Wade, "Properties of Radioactive Calcine Retrieved From The Second Calcine Solids Storage Facility At ICPP", ICP-1189, March 1979.
4. K. N. Brewer, et al., "Dissolution Of Two NWCF Calcines: Extent Of Dissolution And Characterization of Undissolved Solids", Lockheed Idaho Technologies Co., INEL-95/0098, February 1995.
5. R. S. Herbst, et al., "Experimental Results: Pilot Plant Calcine Dissolution And Liquid Feed Stability", Lockheed Idaho Technologies Co., INEL-95/0097, February 1995.
6. P. C. Butler, and D. R. Trammell, "Technical Division Quarterly Progress Report, October 1 - December 31, Calcine Dissolution Experiments", Allied Chemical, February 1978.
7. B. E. Paige, "Leachability Of Aluminum Calcine Produced In The Idaho Waste Calcination Facility", IN-1011, July 1966.
8. L. D. McIsaac, J. D. Baker, J. W. Tkachyk, "Actinide Removal From ICPP Waste", Allied Chemical Corporation, ICP-1080, Aug. 1975.
9. W.W. Schulz, ARH, SA-203, 1974.
10. J. D. Baker, L. D. McIsaac, J. F. Krupa, D. H. Meikrantz, and N. C. Schroeder, "Experimental Mixer Settler Actinide Partitioning From ICPP Acidic Waste", Allied Chemical Idaho Chemical Programs, ICP-1182, Aug. 1979.
11. Experimental data; unpublished
12. B. J. Mincher, "Application Of TRUEX To Actual ICPP High-Level Waste", 15th Actinide Separations Conference, Charleston, SC, June 17-21, 1991.
13. J. D. Law, et. al., "CMP Flowsheet Development for the Separation of Actinides from ICPP Sodium-Bearing Waste using Centrifugal Contactors", Lockheed Idaho

Technologies Co., INEL-95/0414, August 1995.

14. B. M. Rapko and G. J. Lumetta, "Extraction of Transuranic Elements with a Dihexyl-N,N-diethylcarbamoylmethyl Phosphonate/Tributyl Phosphate System - Initial Investigations", Solvent Extraction and Ion Exchange, 12(5), 967-986, 1994.
15. H. R. Maxey, et. al., "Removal of Actinides from ICPP Fuel Reprocessing Wastes Engineering Studies Terminal Report", Exxon Nuclear Idaho Co., ENICO-1057, September 1980.
16. J. F. Krupa, et. al., "Actinide Partitioning from ICPP Waste: An Investigation of Methods to Eliminate Mercury Interference", Allied Chemical, ICP-1181, March 1979.
17. J. J. Katz, G. T. Seaborg, and L. R. Morss, The Chemistry of the Actinide Elements, 2nd Edition, Vol. 1, Chapman and Hall, New York, NY, 1986.
18. A. C. Muscatello, et. al., "Comparison Between CMPO and DHDECMP for Alpha Decontamination of Radioactive Liquid Waste", Los Alamos National Laboratory, LA-UR-90-1592.
19. J. D. Law, R. S. Herbst, and A. M. Rodriguez, "CMP Flowsheet Development for the Separation of Actinides from ICPP Sodium-Bearing Waste Using Centrifugal Contactors", Lockheed Idaho Technologies Co., INEL-95/0414, August 1995.
20. R. S. Herbst, A. M. Rodriguez, K. N. Brewer, T. G. Garn, and R. T. Tillotson, "Extraction of Actinides from Idaho Chemical Processing Plant Sodium-Bearing Wastes with 0.75 M DHDECMP", Lockheed Idaho Technologies Co., draft.
21. L. D. McIsaac, J. D. Baker, J. F. Krupa, D. H. Meikrantz, and N. C. Schoeder, "Flowsheet Development Work at the Idaho Chemical Processing Plant for the Partitioning of Actinides from Acidic Nuclear Waste", Actinide Separations Symposium Pacific Chemical Conference, Honolulu, Hawaii, April 1-6, 1979.
22. W. W. Schulz, and L. D. McIsaac, "Bidentate Organophosphorus Extractants: Purification, Properties, and Application to Removal of Actinides from Acidic Waste Solutions", Atlantic Richfield Hanford Co., ARH-SA-263, May 1977.
23. W.W. Schulz, L. L. Burger, and J. D. Navratil, Science and Technology of Tributyl Phosphate, Volume III, CRC Press, Inc., Boca Raton, Florida, 1990.
24. W. W. Schulz, and L. D. McIsaac, "Removal of Actinides from Nuclear Fuel Reprocessing Waste Solutions with Bidentate Organophosphorus Extractants", Atlantic Richfield Hanford Co., ARH-SA-217, August 1975.

25. D. S. Wisnubroto, et. al., "Solvent Extraction of Neptunium by n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine Oxide from Nitric Acid Solution Containing Hydrogen Peroxide", Solvent Extraction and Ion Exchange, 11(4), 569-583, 1993.
26. J. D. Law, R. S. Herbst, and K. N. Brewer, "CMP Flowsheet Development for the Separation of Actinides from Dissolved ICPP Calcine Using Centrifugal Contactors", Lockheed Idaho Technologies Co., INEL-95/0582, November 1995.

