CMP FLOWSHEET DEVELOPMENT FOR THE SEPARATION OF ACTINIDES FROM ICPP SODIUM-BEARING WASTE USING CENTRIFUGAL CONTACTORS

J. D. Law
R. S. Herbst
A. M. Rodriguez

Published August 1995

Idaho National Engineering Laboratory
HLW Engineering and Projects
Lockheed Martin Idaho Technologies
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

HH

ABSTRACT

Previous results of lab-scale batch contacts with sodium-bearing waste (SBW) simulant suggested a potential flowsheet for partitioning actinides using solvent extraction with dihexyl-N,N-diethylcarbamoylmethyl phosphonate (DHDECMP or simply CMP) as the extractant. The suggested baseline flowsheet includes: an extraction section to remove actinides from liquid SBW into the CMP solvent (0.75 M CMP, 1.0 M TBP in Isopar-L®); a thermally unstable complexant (TUCS) strip section to back-extract actinides; a sodium carbonate wash section for solvent cleanup; and a dilute HNO_3 rinse section to re-acidify the solvent. The purpose of these studies was to test and develop a baseline CMP flowsheet for Idaho Chemical Processing Plant (ICPP) SBW under continuous, countercurrent conditions using centrifugal contactors.

This flowsheet was tested in two experiments using the Centrifugal Contactor Mockup which consists of sixteen stages of 5.5 cm diameter centrifugal contactors (procured from Oak Ridge National Laboratory). All testing was performed using non-radioactive SBW simulant. Potential flowsheets were evaluated with regard to the behavior of the non-radioactive components potentially extracted by the CMP solvent. Specifically, the behavior of the matrix components, including Fe, Hg, and Zr, was studied. In addition, Nd was added to the SBW simulant as a surrogate for ^{241}Am. In general, the behavior of the individual components closely paralleled that anticipated from batch testing. Based on the assumption that the behavior of Am will be very similar to the behavior of the Nd surrogate, eight extraction stages are more than sufficient to reduce the actinide content in the SBW to levels well below the NRC Class A LLW criteria of 10 nCi/g. Very little Fe or Zr were extracted from the SBW simulant, resulting in only 1% of the Fe and 4% of the Zr exiting in the high-activity waste (HAW) fraction. The CMP solvent extracted 99% of the Hg from the SBW. The TUCS strip was effective at quantitatively stripping all metals, except Hg, from the CMP solvent. Sodium carbonate washing was only effective in back-extracting 74% of the Hg from the stripped solvent. An 8.0 M HNO_3 wash was also tested for separating Hg from the stripped solvent, resulting in 63% Hg removal with four stages of wash.

Potential problems, such as solids formation, which could arise because of solvent loading effects due to the countercurrent flow in the contactors, were not encountered. However, when washing the CMP solvent with dilute HNO_3, flooding (organic in the aqueous) was encountered. It has been determined that this flooding is a result of poor phase separation (low dispersion numbers) when the CMP solvent is contacted with dilute HNO_3. This problem was subsequently eliminated by reducing the CMP concentration in the solvent to 0.5 M.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Troy Garn, Rich Tillotson, and Earlen Wade for their assistance in operation of the Centrifugal Contactor Mockup, chemical makeup, and sample preparations; and also to the Spectrochemistry Group for analytical support.

CONTENTS

FIGURES

TABLES

INTRODUCTION

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

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

Several technologies for partitioning the actinides, cesium, and strontium, and ultimately immobilizing the resulting high- and low-activity fractions for final disposition are currently being evaluated as treatments for SBW. Various derivatives of carbamoylmethylphosphonate (CMP) have been extensively investigated for the extraction of actinides from acidic waste solutions [2-6]. Consequently, dihexyl-N,N-diethylcarbamoylmethyl phosphonate (DHDECMP) is currently being considered at the ICPP for partitioning actinides from SBW. DHDECMP was the predecessor of the actinide extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide, commonly known as CMPO, the active extractant in the TRans Uranic EXtraction (TRUEX) process, developed by Horwitz and Schulz. The potential applicability of the TRUEX and CMP processes for use with ICPP acidic wastes was identified in a Peer Review attended by a group of internationally known separation experts [7]. 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. Based on the recommendations from the Peer Review, a comparison of CMP and TRUEX flowsheets as potential TRU partitioning processes for SBW was initiated at the ICPP.

Initial investigations were completed utilizing batch contacts with radionuclide spiked SBW simulant and the DHDECMP solvent [8]. Distribution coefficients of Am, Pu, U, Np, Tc, Hg, and Zr were measured in extraction and stripping contacts during these experiments. The results indicated the applicability of the CMP process to SBW and a potential flowsheet was recommended utilizing a thermally unstable complexant (TUCS) as the strip solution. The batch experiments also indicated an organic scrub section was unnecessary due to the low extraction of most matrix components, including Zr, and the ability to strip Am with ~ 1 M or less HNO_3. Finally, it was determined that either 8 M HNO_3 or 0.25 M Na_2CO_3 were suitable reagents to selectively back-extract mercury from the organic phase. Based on the recommended flowsheet, pilot plant extraction studies with CMP were initiated. Herein described are experimental results of the CMP flowsheet studies with simulated SBW under continuous, countercurrent flow conditions in centrifugal contactors.

DHDECMP (or simply CMP in this report) is the active extractant used to partition the actinides from acidic solutions in the CMP process solvent. Tributyl-phosphate (TBP) is used in the solvent to prevent third phase formation (second organic phase) and a paraffinic hydrocarbon is used as the diluent. The composition of the CMP solvent initially used in this study, and in the preliminary laboratory batch experiments, was based on literature reports [2-6] and was 0.75 M CMP and 1.0 M TBP in Isopar-L®. During the contactor tests, unsuitable hydrodynamic properties were observed with this solvent composition based on extensive flooding, presumably due to poor phase disengagement, encountered during solvent re-acidification with dilute nitric acid. These problems were not identified in laboratory batch contacts. Consequently, the composition of the organic phase was altered to enhance the hydrodynamics of the solvent without compromising extraction of the actinides. The final solvent composition was 0.5 M CMP, 1.0 M TBP in Isopar L®. Batch equilibrium data are currently being collected with the altered solvent composition.

SCOPE AND PURPOSE

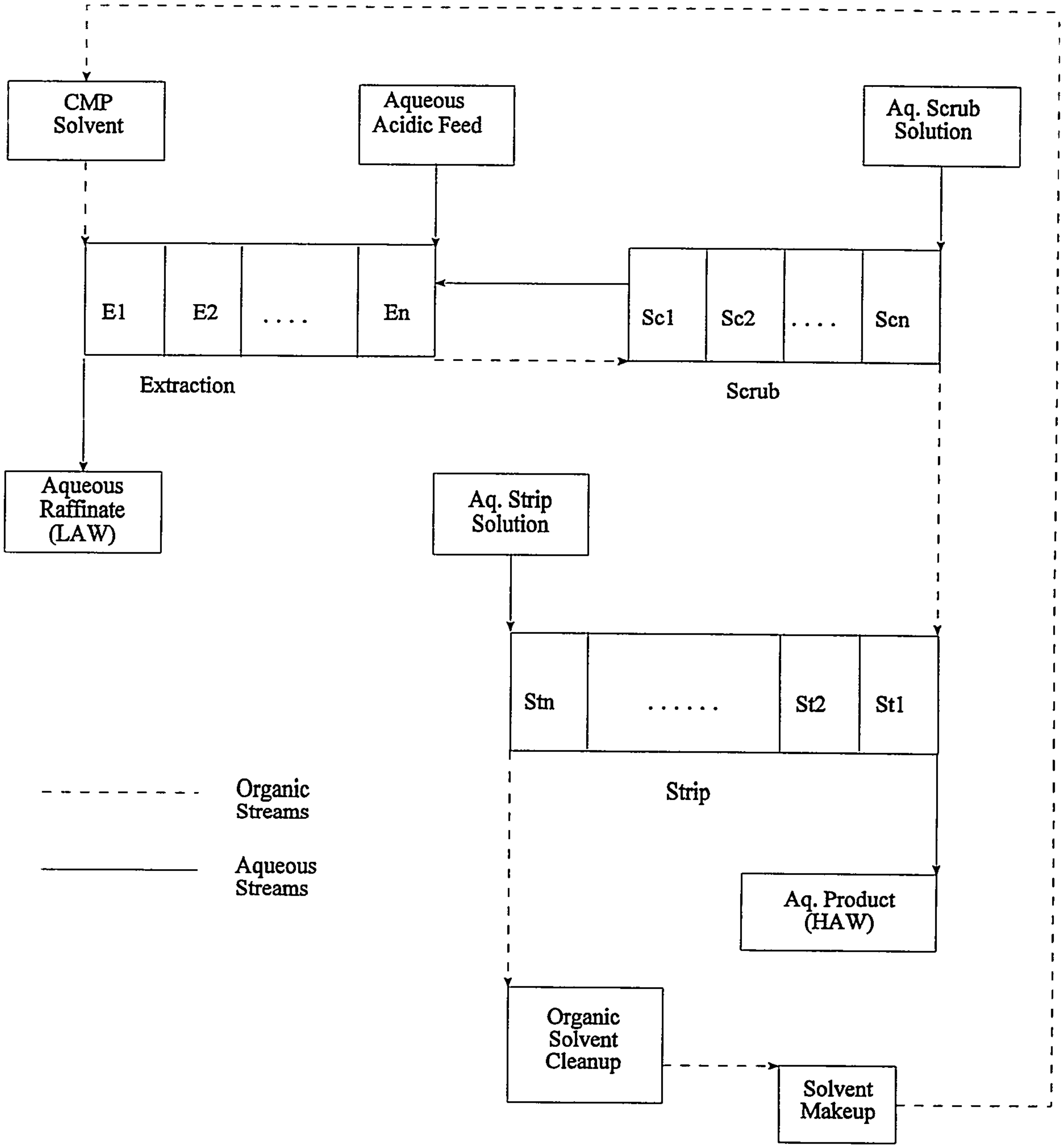
The purpose of these studies was to develop potential CMP solvent extraction flowsheets for ICPP SBW using centrifugal contactors. Sixteen stages of 5.5 cm diameter centrifugal contactors were procured from Oak Ridge National Laboratory and set up as part of the Centrifugal Contactor Mockup. The location of the mockup precludes the use of radioactive solutions. Therefore, all testing was performed using non-radioactive SBW simulant. Potential flowsheets were evaluated with regards to the behavior of the non-radioactive components. In addition, neodymium was added to the SBW simulant as a surrogate for ^{241}Am. This allowed the separation efficiency of the actinides to be predicted. Potential problems, such as solids precipitation, which were not apparent with batch contacting experiments, but could arise because of the solvent loading effects due to the countercurrent solution flow in the centrifugal contactors, were also evaluated. The countercurrent CMP flowsheets developed with non-radioactive SBW simulant may be used for future countercurrent flowsheet development and testing with actual SBW.

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

Dilute oxalic acid or hydrofluoric acid in nitric acid can be used to scrub trace metals, such as Fe or Zr, from the CMP solvent. Since the concentrations of Fe and Zr in the SBW are low and the CMP solvent is only slightly effective in extracting these components (distribution coefficients less than 0.2), a scrub section was not incorporated into the CMP flowsheet testing with SBW.

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 will most likely be applied to ICPP waste streams. Therefore, a single stripping agent, capable of removing all the actinides from the loaded organic solvent is advantageous. The use of thermally unstable complexants (TUCS) have been demonstrated for gross actinide stripping, effectively removing all actinides from the loaded CMP solvent, without precipitate formation with ICPP SBW [8]. The TUCS reagents are typically derivatives of diphosphonic acid. The TUCS reagent used in this study was 1-hydroxyethane-1,1-diphosphonic acid (HEDPA).

Figure 1. Schematic of a Typical CMP Process Flowsheet



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

Countercurrent CMP flowsheet testing, as applied to acidic waste streams such as SBW, has not been previously performed using CMP and TBP in Isopar-L®. Such a study is the primary scope of these experiments.

EQUIPMENT DESCRIPTION

All tests were performed in the Centrifugal Contactor Mockup located in building CPP-637. The Centrifugal Contactor Mockup, as shown in Figure 2, consists of sixteen stages of 5.5 cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, flowmeters, filters, AC and DC motor drives, and a sample system. A simplified flow diagram is shown in Figure 3.

Four stages of centrifugal contactors (assembled as a single unit or four-pack) were procured from Oak Ridge National Laboratory (ORNL) in 1986. Twelve additional stages were procured from ORNL in 1993 (as 3 four-packs). A description of the centrifugal contactors is provided in Table I. All sixteen stages of contactors are basically identical with the exception of the type of motor.

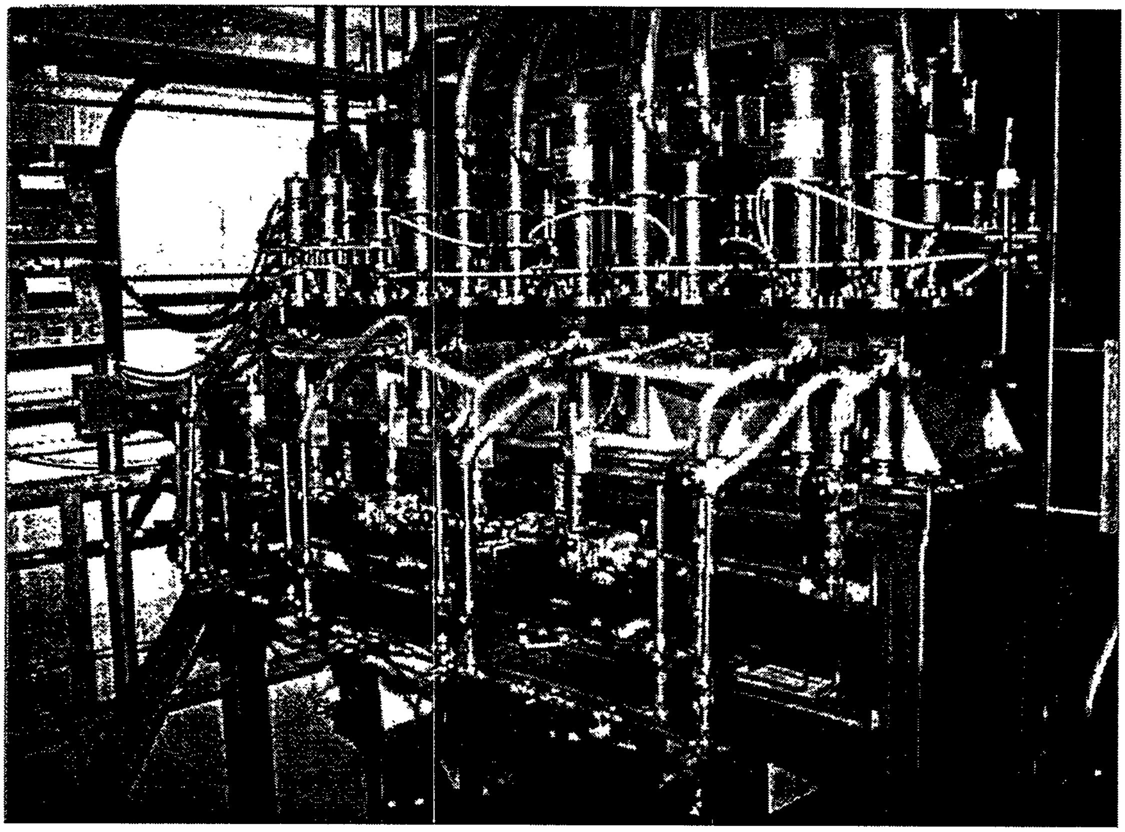
Solution is fed to the contactors using Masterflex® pumps. Surge lines, consisting of an 18-inch section of 1-inch stainless steel tubing, were placed on the outlet of the pumps to dampen the surging flow. Rotameters were calibrated and used to monitor solution flowrates. Flowrates are adjusted by changing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

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

Table I. Centrifugal Contactor Description

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

Figure 2. Centrifugal Contactor Mockup



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

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

Figure 3. Simplified Flow Diagram of the Centrifugal Contactor Mockup

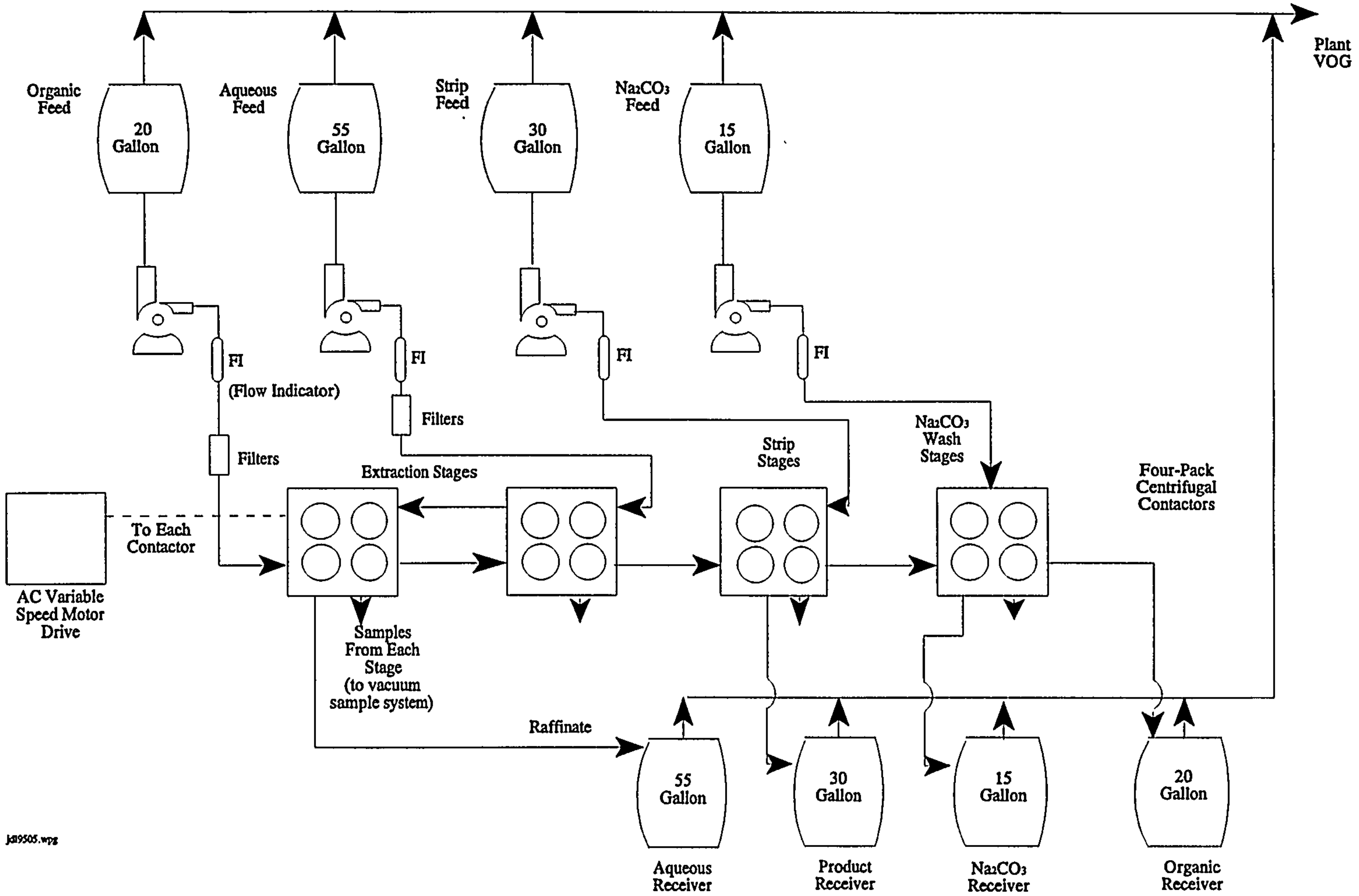
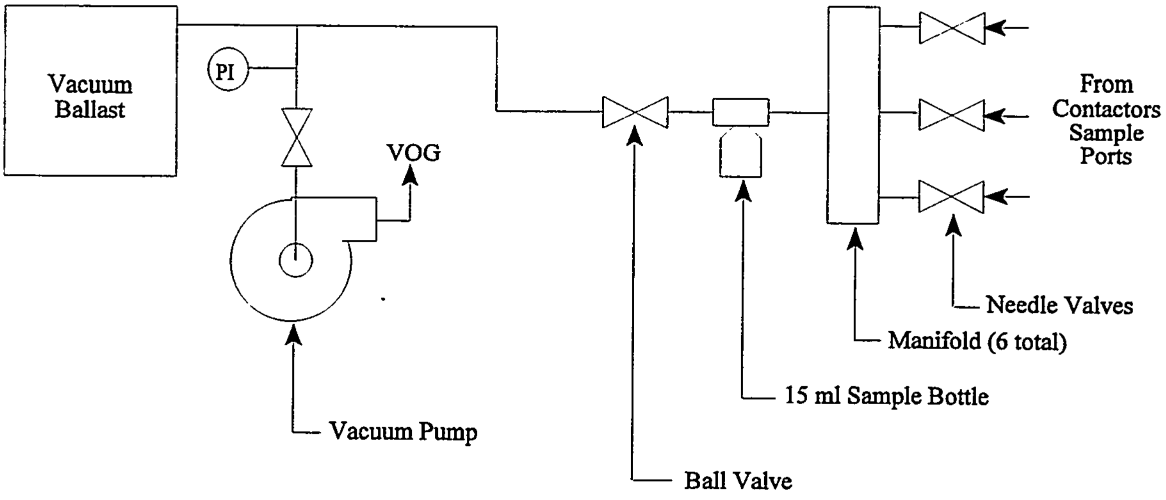


Figure 4. Centrifugal Contactor Mockup Sampler Configuration



prwin\jd9409.wpg

During operation, samples are pulled from the centrifugal contactors utilizing the vacuum sample system shown in Figure 4. A vacuum pump is used to pull 10 to 15 inches of Hg vacuum on a ballast tank. This ballast tank is connected to a sampler. Opening and then closing a block valve connecting the sampler with the ballast tank evacuates the sample bottle.

Opening the needle valve between the sampler and desired sample location draws solution from the contactor into the bottle. It is important to pull the samples slowly so the flowrate is not disrupted significantly enough to affect steady-state conditions. The use of a needle valve allows the samples to be pulled over several minutes instead of all at once.

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

METHODOLOGY/EXPERIMENTAL PROCEDURE

SBW Simulant

For the purposes of this study, the behavior of the non-radioactive components in simulated SBW was evaluated. The analytical results obtained from characterization of SBW waste solution were utilized to prepare a non-radioactive simulant which represents the average chemical composition of the major non-radioactive matrix components in the SBW tanks. In addition, neodymium was added to the simulant as a surrogate for ^{241}Am. The chemical composition of the SBW simulant is shown in Table II.

Prior to testing, the SBW simulant was filtered with a 2 micron sintered metal filter to prevent plugging of the filters on the aqueous feed line during operation. The specific components evaluated in this study include H^+, Nd, Fe, Hg, Zr, Al, B, Ca, Ce, Cl, Cr, Cs, F, Pb, Ni, Na, K, Sr, and SO_4, .

CMP Solvent

The CMP solvent composition used in all CMP flowsheet studies reported herein was either 0.50 M or 0.75 M CMP and 1.0 M TBP in Isopar-L® and was prepared by the ICPP Quality Control (QC) Laboratory. The purity and composition of the CMP solvent were established prior to use in the centrifugal contactors. Impurities in the CMP, resulting from acid hydrolysis, radiolytic degradation, or residual manufacturing impurities, may hinder the ability to strip the actinides from the CMP solvent. The distribution coefficients for Am, D_{Am}, are sensitive to CMP impurities. Therefore, D_{Am} was evaluated as a function of nitric acid concentration from HNO_3 solutions to evaluate CMP purity and solvent composition. This method of determining Am distributions as a function of nitric acid concentration was established as a quality control procedure for CMPO [9] and is also being applied to the CMP solvent. This procedure was used to test the initial CMP solvent and the CMP solvent product from each flowsheet test. If the results were comparable to previous laboratory data, the solvent was deemed suitable for extraction studies.

Analytical

Experimental results obtained from batch contacts with SBW simulant indicate 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) is extremely effective at quantitatively back extracting all metals, except Hg, from the CMP solvent. Consequently, the organic samples were contacted with 0.25 M HEDPA in 0.05 M HNO_3. To insure quantitative metal recovery in a single contact, an O/A ratio of 0.4 was used. The aqueous phase from the HEDPA strip was separated from the organic and submitted for Nd, Fe, and Zr analysis. This procedure provided an indirect measure of organic phase compositions and allowed the use of material balances to validate experimental results. Organic phase Hg concentrations were determined by performing

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

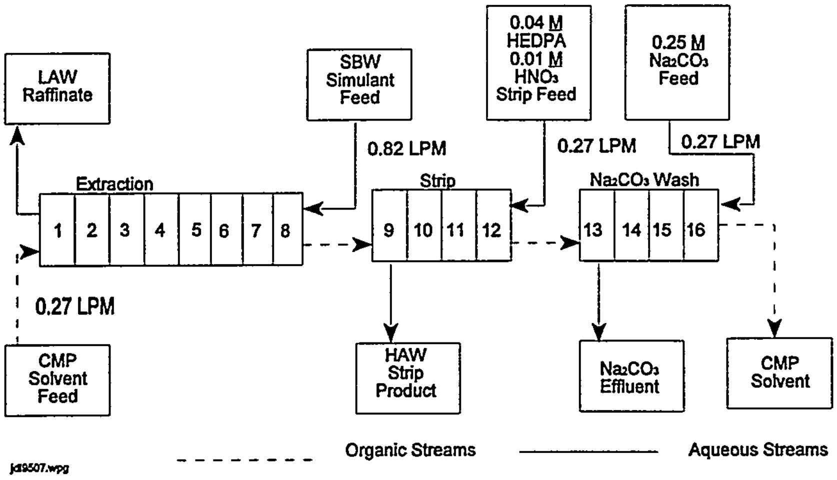
Component	M	Component	M
Acid (H^+)	1.31	K	1.48E-01
Al	5.56E-01	Mn	1.42E-02
B	1.34E-02	Mo	1.49E-03
Cd	2.05E-06	Na	1.13
Ca	3.27E-02	NO_3	4.22
Ce	3.60E-04	Ni	1.74E-03
Cl	3.52E-02	Pb	9.60E-04
Cs	9.78E-05	PO_4	<1.39E-04
Cr	6.14E-03	Sr	6.30E-04
F	9.66E-02	SO_4	3.84E-02
Fe	2.26E-02	Zr	5.12E-04
Hg	1.20E-03	Nd	3.75E-03

a material balance across each stage. All aqueous sample analyses were performed by the ICPP Analytical Chemistry Section using Inductively Coupled Plasma (ICP) Atomic Absorption Spectroscopy.

CMP Flowsheet Testing

Based on the results of CMP testing performed with radioactive tracers and simulated SBW, and computer modelling with the Generic TRUEX Model (GTM) [10-12], a CMP flowsheet was developed for the separation of actinides from SBW. This flowsheet consists of five stages of extraction at an O/A of 0.33, four stages of 0.04 M HEDPA strip at an O/A of 1.0, two stages of 0.25 M Na_2CO_3 solvent wash at an O/A of 1.0, and one stage of 0.1 M HNO_3 rinse at an O/A of 3.0. This flowsheet was used as a basis for the CMP flowsheet testing. However, due to the limited flexibility in feed locations to the sixteen stages of centrifugal contactors, several changes were made. The Centrifugal Contactor Mockup was configured for eight stages of extraction, four stages of strip, and four stages of Na_2CO_3 wash. A second run was then performed in which the CMP solvent was re-acidified with HNO_3. The resulting flowsheet used for CMP flowsheet testing is shown in Figure 5.

Figure 5. CMP Flowsheet Test



Prior to testing, the solvent was washed with four stages of 0.25 M Na_2CO_3 and four stages of 0.1 M HNO_3 rinse at O/A ratios of 4 and 3, respectively. The purpose of the solvent wash was to remove degradation products and manufacturing impurities which may have been in the fresh solvent. The solvent was re-acidified in order to be consistent with recycled solvent in the CMP process, which is acidified after the Na_2CO_3 wash to destroy residual carbonate carried over in the organic phase, and thereby prevent emulsions from forming when it is recycled back to the extraction section.

The purpose of the CMP flowsheet testing was to 1) evaluate the overall operability of the centrifugal contactors, 2) determine the operational time required for the mass transfer in the contactors to reach steady state, 3) determine the concentrations and distribution coefficients of H^+, Nd, Fe, Hg, and Zr at steady state, 4) evaluate the effectiveness of the CMP flowsheet in separating Nd (^{241}Am surrogate) from SBW, and 5) determine if any precipitation or third phase formation problems exist with this flowsheet. The time required to reach steady state was determined by sampling the aqueous raffinate, strip product, Na_2CO_3 wash product, and stage 8 organic product streams at ten minute intervals and determining when component concentrations were no longer changing. These data are required in order to verify steady state was achieved prior to sampling each stage. Based on previous experience with TRUEX flowsheet testing [13], it was expected that steady state would be reached in about 20 minutes.

CMP flowsheet testing was performed as follows. Based on the results of hydraulic performance of the centrifugal contactors with the TRUEX solvent, the contactors were started at 3500 RPM [13]. Both simulated SBW feed without Nd and strip solution flows were then established. Once aqueous solution was exiting the extraction and strip sections, organic flow was started. When organic solution exited the extraction section, simulated SBW feed containing Nd was started. At intervals of 20, 30, 40, and 50 minutes after the start of SBW feed, samples were taken from the aqueous raffinate, strip product, Na_2CO_3 wash effluent, and stage 8 organic effluent streams. Sightglass readings on each of the feed tanks were also noted in order to determine actual solution flowrates based on tank depletion rates. After the last samples were taken, the contactor mockup was shutdown by simultaneously stopping the contactor motors and feed pumps. With this type of shutdown, each stage remains at steady-state operating conditions. This allowed aqueous and organic samples to be taken from each stage and, therefore, distribution coefficients can be determined for each of the sixteen stages. The following procedure was used to obtain aqueous and organic samples from each stage; 1) 20 ml of aqueous was drained out of the contactor stage to flush the drain line, 2) 30 ml of aqueous sample was drained into a sample bottle for analysis, 3) The remaining aqueous and a portion of the organic was drained from the contactor stage, 4) 30 ml of organic was drained into a clean sample bottle. Any aqueous solution in the organic sample was pipetted out of the bottle. The centrifugal contactors were then flushed with water.

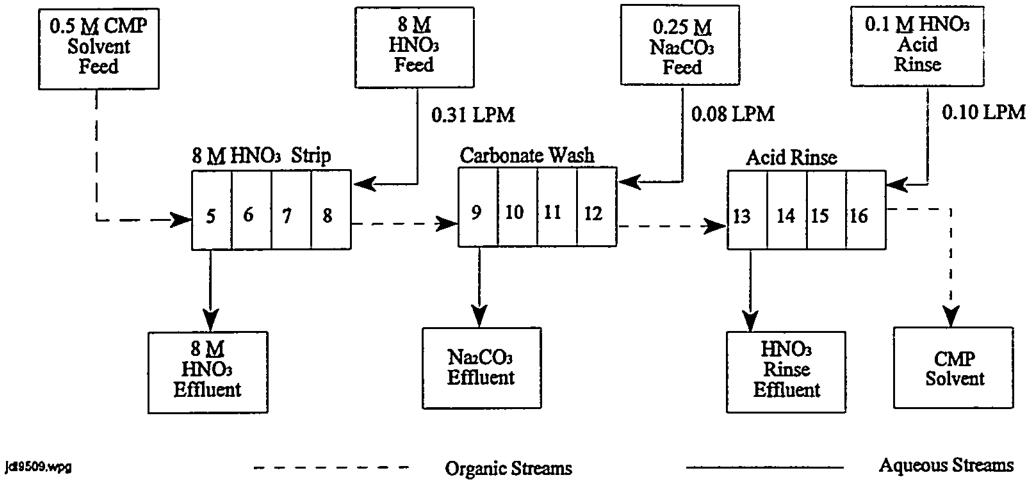
The acid rinse portion of the flowsheet was performed separately because only 16 stages of centrifugal contactors are available. The CMP solvent product from the flowsheet test was contacted with 2 $\underline{M}$ HNO_3 at an O/A of 3.0. The only purpose of the acid rinse was to acidify the solvent prior to performing additional testing. Therefore, samples from this test were not taken.

Additional Solvent Wash Testing

Based on the results of the CMP flowsheet test, additional solvent wash testing was performed. The solvent product from the CMP flowsheet test was washed with four stages of 8 $\underline{M}$ HNO_3 wash, four stages of 0.25 $\underline{M}$ Na_2CO_3 wash, and four stages of 0.1$\underline{M}$ HNO_3 acid rinse. The flowsheet tested is shown in Figure 6.

The solvent wash testing was performed at a rotor speed of 3500 rpm. After starting the contactors, the 8 $\underline{M}$ HNO_3 wash, carbonate wash, and acid rinse solution flows were established. When the aqueous solution was seen exiting the three four-packs of contactors, organic solution flow was started. Fifty minutes after the start of organic feed, samples were taken from the organic streams exiting each section and from the stage 3 aqueous and organic product streams for calculation of the Hg distribution coefficient in the 8 $\underline{M}$ HNO_3 wash section. Feed tank sightglass readings were also taken to determine actual solution flowrates based on tank depletion rates. Operation of the contactors was continued until all of the CMP solvent had been processed. When organic solution ceased exiting the contactor four-packs, the carbonate wash and acid rinse solution flows were stopped. The contactor motors were then turned off when aqueous solution quit exiting the contactor four-packs. The centrifugal contactors were then flushed with water.

Figure 6. CMP Solvent Wash Test Flowsheet



The purpose of the 8 M HNO_3 solvent wash testing was to 1) evaluate the effectiveness of the 8 M HNO_3 in stripping Hg from the CMP solvent, 2) evaluate the effectiveness of the solvent wash in removing any degradation products which may have formed in the CMP solvent, and 3) prepare the solvent for additional CMP flowsheet testing.

RESULTS AND DISCUSSION

CMP Flowsheet Testing

Solvent Preparation

In preparation for CMP flowsheet testing with simulated SBW, the CMP solvent was washed in the Centrifugal Contactor Mockup with four stages of 0.25 M Na_2CO_3 at an O/A of 4 followed by four stages of acid rinse with 0.1 M HNO_3 at an O/A of 3. The purpose of the solvent wash was to remove any degradation products and/or impurities from the fresh CMP solvent. While performing the solvent wash, flooding problems in the acid rinse section occurred. The aqueous product from the acid rinse section was approximately 25% flooded. No flooding was observed in the carbonate wash section or with the CMP solvent in the acid rinse section. Initially the contactors were operated at a rotor speed of 3000 rpm. Increasing the speed to the maximum speed of 3500 rpm did not alleviate the flooding. The acid rinse feed flowrate was then increased to give an O/A of 1.5. This reduced the flooding of the aqueous product to approximately 10%. The acid rinse feed flowrate was then increased to give an O/A of 1. This reduced the flooding of the aqueous product to approximately 5%. The remainder of the solvent wash was conducted at this O/A.

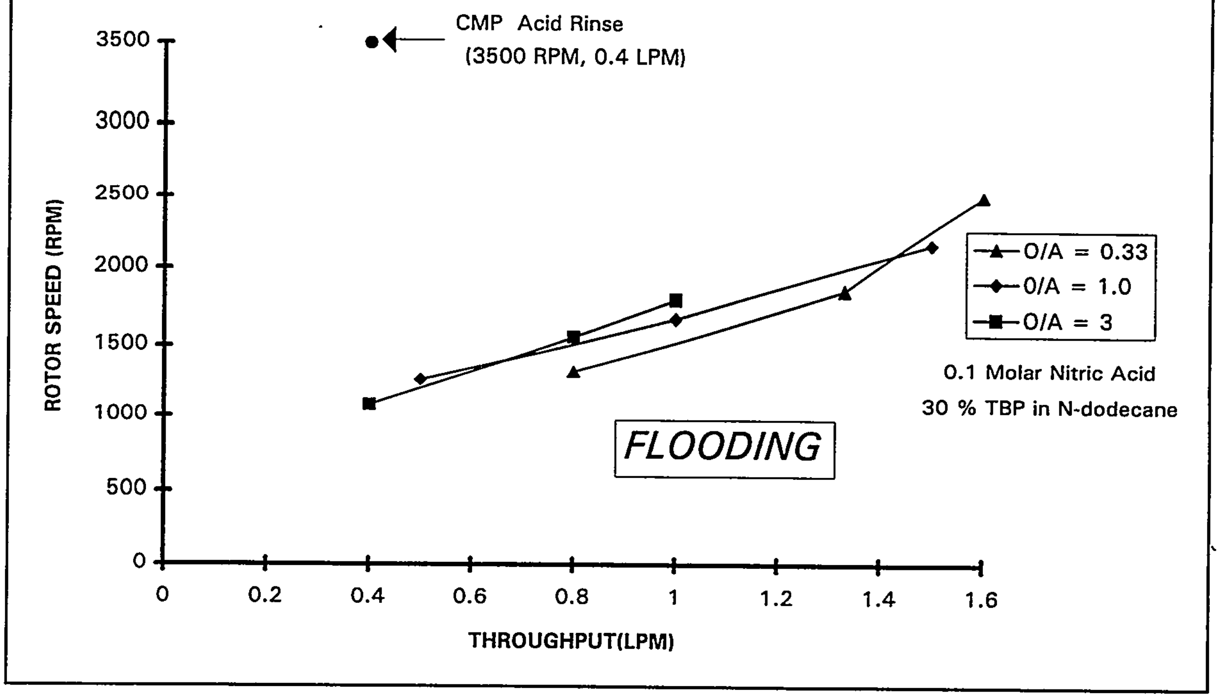
The total throughput (aqueous + organic flowrate) in the acid rinse section was 0.4 lpm. At this throughput and at a rotor speed of 3500 rpm, flooding problems were not anticipated. Prior to performing this test, hydraulic testing was performed using 0.1 M HNO_3 and 30% tributyl phosphate in n-dodecane (PUREX solvent). The resulting flooding curves are shown in Figure 7. The area below the lines represents flooded conditions. Flooding was defined as greater than 1% cross phase entrainment. At an O/A of 3.0, a rotor speed of 3500 rpm, and a total throughput of 0.4 lpm it was expected that the centrifugal contactors would be well within an acceptable range of operation. Also, previous TRUEX solvent wash flowsheet testing at a similar throughput did not result in any flooding problems in the acid rinse section [13]. The TRUEX solvent and the CMP solvent have similar densities (0.88 - 0.92 Kg/L) and, therefore, the hydraulic performance in the contactors was expected to be similar for the two flowsheets.

It was suspected that the flooding problems resulted from the residence time in the centrifugal contactors being too short for the organic/aqueous dispersion to break due to poor phase separation. Phase separation can be quantitatively expressed by calculating a dispersion number using the following equation [14]:

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

where t is the time required for the two phases to separate in seconds, h is the total height of the

Figure 7. Centrifugal Contactor Flooding Curve



two phases in meters, and g is the acceleration due to gravity (9.81 m/s^2). A dispersion number of approximately 8E-04 or larger indicates that the phase separation is adequate for proper operation with the centrifugal contactors being used.

CMP solvent from the carbonate wash section was contacted with 0.1 $\underline{M}$ HNO_3 in a test tube and dispersion numbers were calculated. This process was also performed with fresh CMP and 0.25 $\underline{M}$ Na_2CO_3. The results are given in Table III. At O/A ratios of 1.0 and 3.0, dispersion numbers much less than 8E-04 were obtained with 0.1 $\underline{M}$ HNO_3 and carbonate washed CMP solvent. Therefore, poor phase separation is expected to be the cause of the flooding problems. Dispersion numbers greater than 8E-04 were obtained with fresh CMP solvent and 0.25 $\underline{M}$ Na_2CO_3 which explains why flooding problems were not observed in the carbonate wash section.

Prior to performing CMP flowsheet testing with SBW simulant, the flowsheet was simulated with batch contacts and dispersion numbers were calculated for each contact. Dispersion numbers >8E-04 were obtained for each of the extraction, strip, and carbonate wash contacts, indicating that acceptable phase separation was anticipated in the flowsheet testing. Testing in the Centrifugal Contactor Mockup was then performed with the flowsheet shown in Figure 5.

Table III. Dispersion Numbers with the CMP Solvent in the Solvent Wash Section

Aqueous	Organic	Contact	O/A	N_{Di}
0.1 M HNO_3	Carb. washed CMP	1	1.0	3.6E-04
0.1 M HNO_3	Org. from contact #1	2	1.0	4.2E-04
0.1 M HNO_3	Org. from contact #2	3	1.0	5.2E-04
0.1 M HNO_3	Carb. washed CMP	4	3.0	3.4E-04
0.1 M HNO_3	Org. from contact #4	5	3.0	4.3E-04
0.1 M HNO_3	Org. from contact #5	6	3.0	4.7E-04
0.25M Na_2CO_3	Fresh CMP	7	1.0	8.7E-04
0.25M Na_2CO_3	Fresh CMP	8	1.0	8.3E-04
0.25M Na_2CO_3	Fresh CMP	9	1.0	8.7E-04

Contactor Operation

Actual solution flowrates were calculated from feed tank depletion rates and are compared to the desired flowrates in Table IV. A tank depletion rate was not determined for the strip feed because a non-calibrated feed carboy was used. All of the flowrates and O/A ratios compare very well with the desired values.

Physical problems were not encountered while performing the CMP flowsheet testing. Flooding, third phase formation, and/or precipitation problems were not observed.

Time To Reach Steady State

The concentrations of H^+, Nd, Zr, Fe, and Hg as a function of time after the start of SBW simulant feed are given in Figures 8 through 12 for the aqueous raffinate, strip product, and stage 8 organic streams. It was assumed that steady state was reached when the concentrations of the components varied by less than the analytical error associated with the sample analyses (±10% for Zr, Nd, and Fe; ±20% for Hg). All components reached steady state within 20 minutes with the exception of Nd in the aqueous raffinate and Hg in the strip product, which reached steady state in 30 minutes and 40 minutes, respectively. Based on these results, samples for future CMP flowsheet testing at similar flowrates should be taken a minimum of 40 minutes after feed solution flow is started.

Table IV. Flowrates and O/A Ratios for the CMP Flowsheet Test

Section	Feed	Flowrate (LPM)		O/A Ratio		Total Flow
		Desired	Actual	Desired	Actual	
Extraction	Org	0.27	0.264	0.33	0.32	1.08 LPM
	Aq	0.82	0.819			
Strip	Aq	0.27	nd	1.00	nd	0.53 LPM[1]
Na_2CO_3 Wash	Aq	0.27	0.253	1.00	1.04	0.52 LPM

nd = not determined

[1] based on desired aqueous flowrate

Steady-State Concentrations

The concentrations of H^+, Nd, Fe, Hg, Zr, Al, B, Ca, Ce, Cl, Cr, Cs, F, Pb, Ni, Na, K, Sr, and SO_4 at steady state are given in Figure 13. A material balance for each of the components is given in Table V. The values in Table V were normalized to obtain an overall material balance of 100%. Distribution coefficients were calculated for H^+, Nd, Fe, Hg, and Zr on each of the 16 stages. The aqueous and organic phase concentrations, along with the resulting distribution coefficients, are given in Table VI. A comparison of these distribution coefficients with distribution coefficients obtained from laboratory testing with spiked SBW simulant is given in Table VII [8]. A discussion of the behavior of each of the components follows.

Neodymium

Neodymium was added to the SBW simulant as a surrogate for ^{241}Am. Less than 0.018% of the Nd remained in the aqueous raffinate. This equates to an overall decontamination factor, DF = $[Nd_{feed}]/[Nd_{raf}]$, of greater than 5410. However, the analytical detection limit for Nd was reached with the stage four aqueous solution, so this DF was obtained with only five stages of extraction. With an ^{241}Am concentration of 88 nCi/g and a total actinide concentration of 350 nCi/g in the SBW [15], it is expected that operating with this flowsheet will reduce the actinide concentration well below the NRC Class A LLW limit of 10 nCi/g. The DF with all eight stages of extraction is expected to be much greater. Distribution coefficients of 19.6 to 25.9 were obtained for stages five through eight of the extraction section. Using these distribution coefficients for stages five through eight and assuming a distribution coefficient of 19.6 for stages one through four, the GTM predicts an overall DF of 100,000 for Nd. This corresponds to 99.999% removal of Nd. Reduction of the number of extraction stages from eight to four should provide adequate actinide removal to meet the Class A limit.

Figure 8. H +Concentration Vs. Time

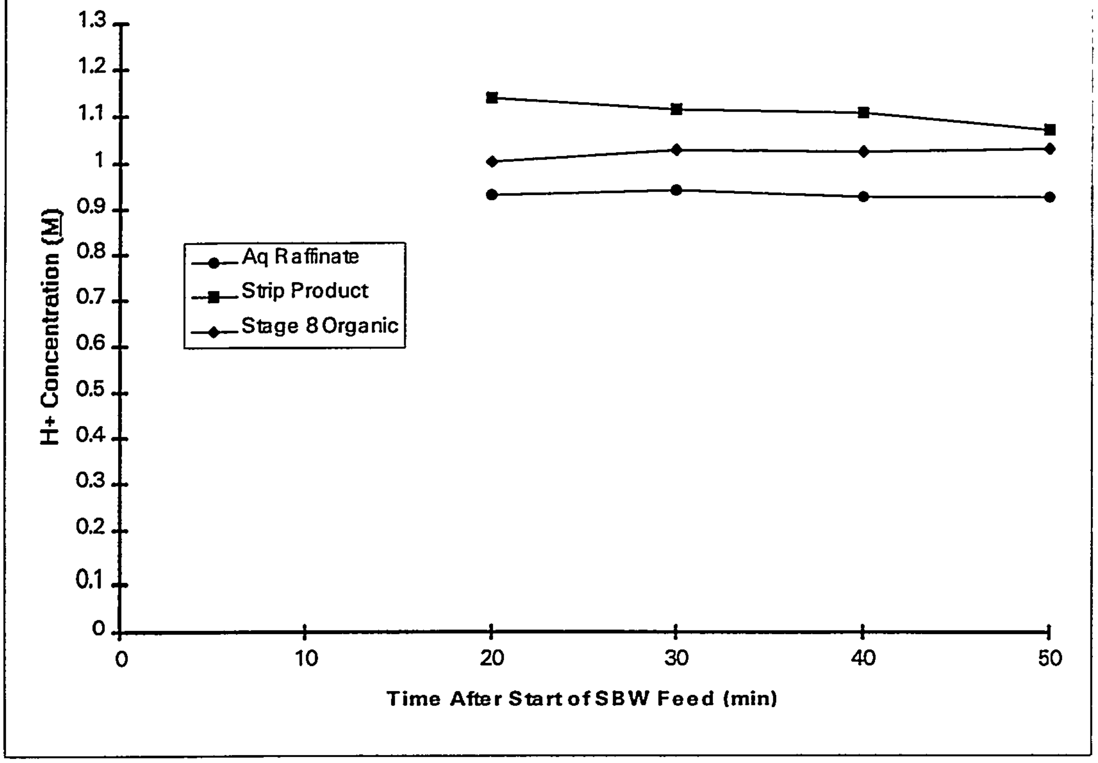


Figure 9. Nd Concentration Vs. Time

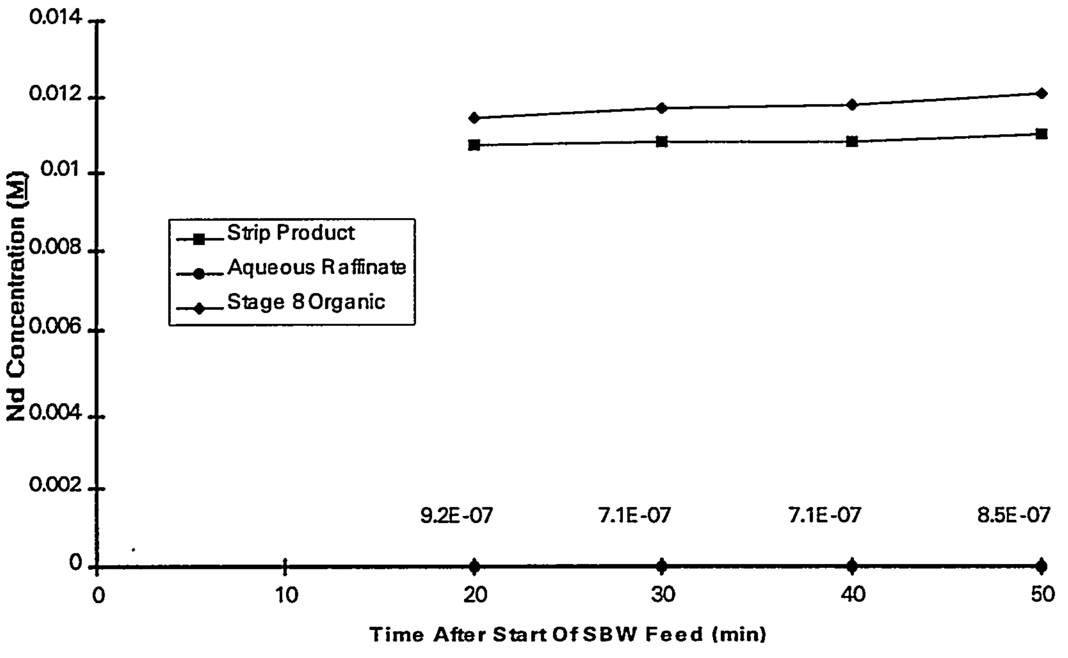


Figure 10. Zr Concentration Vs. Time

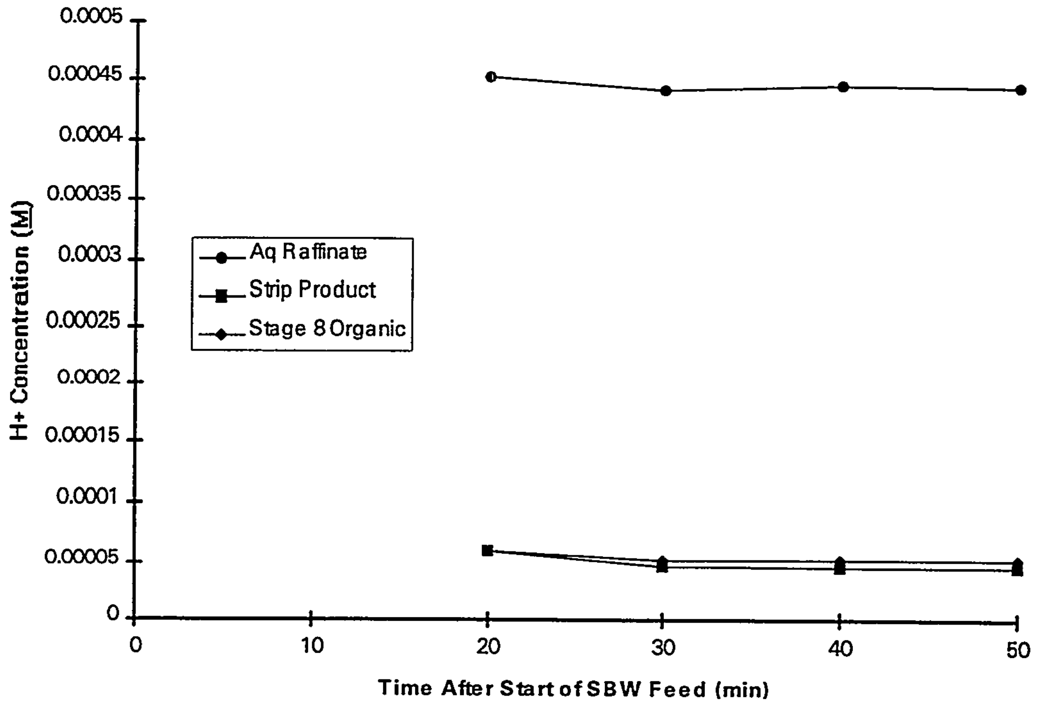


Figure 11. Fe Concentration Vs. Time

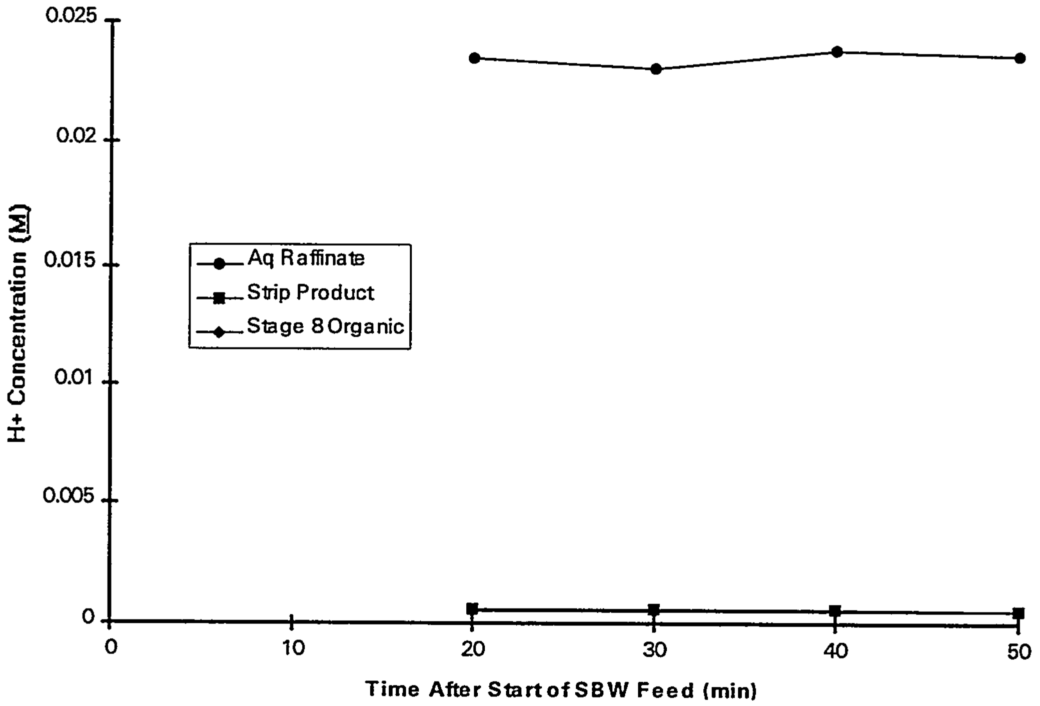


Figure 12. Hg Concentration Vs. Time

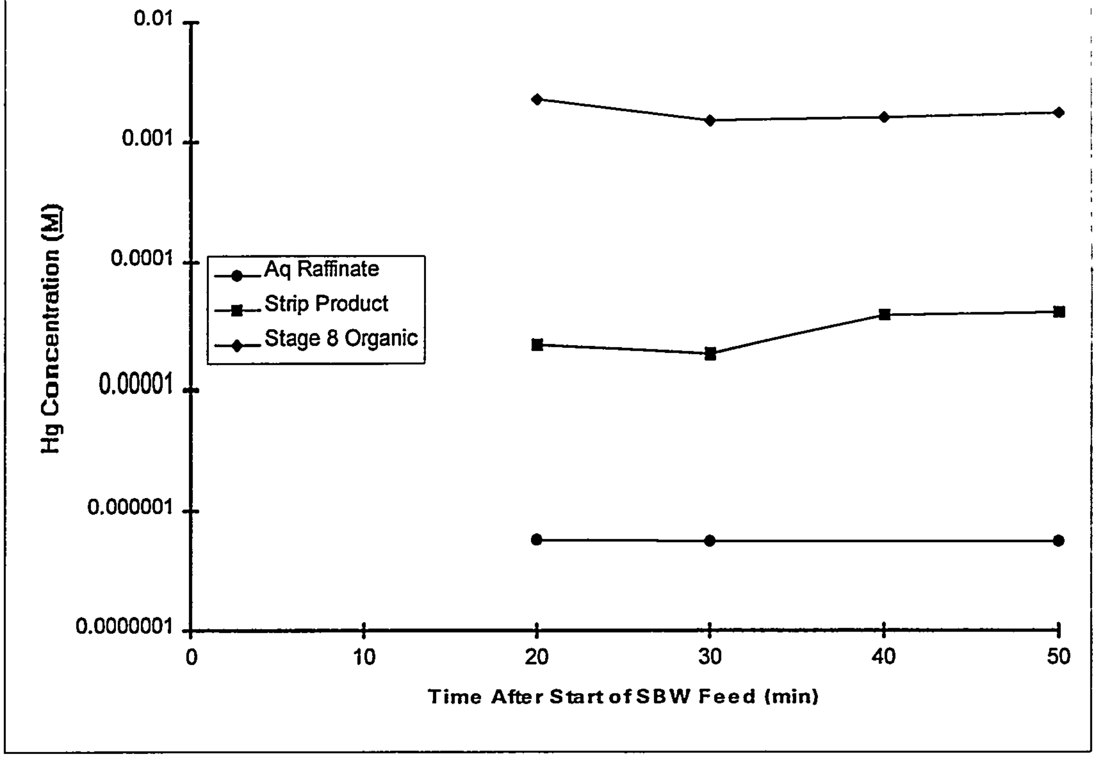
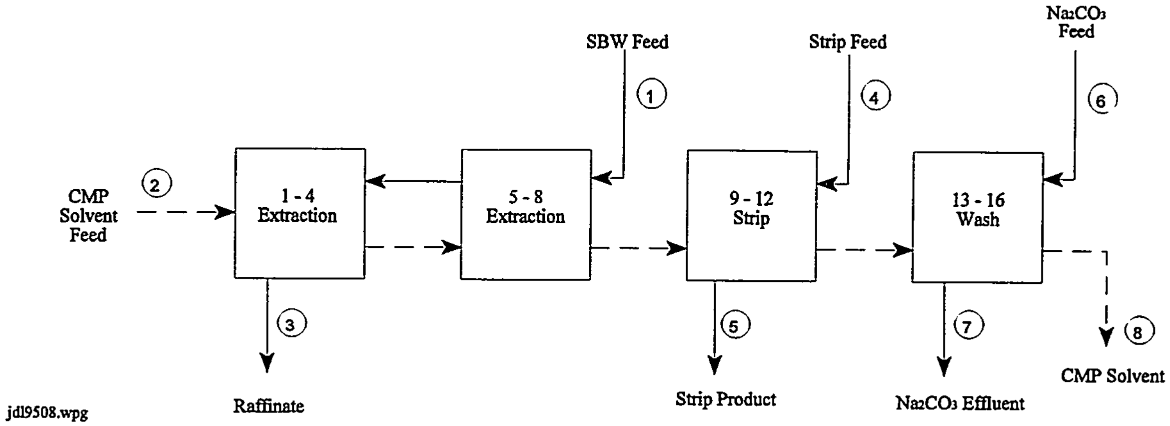


Figure 13. CMP Flowsheet Test Steady-State Concentrations



Component (M)	SBW Feed 1	CMP Solvent Feed 2	LAW Raff. 3	Strip Feed 4	Strip Product 5	Na_2CO_3 Feed 6	Na_2CO_3 Effluent 7	CMP Solvent 8
H^+	1.31	0.0168	0.094	0.01	1.11			
HEDPA				0.04	0.04			
Na_2CO_3						0.25	0.25	
Nd	3.75E-03		<6.9E-07		1.05E-02		<6.9E-07	<6.9E-07
Hg	1.20E-03		1.04E-05		2.49E-05		2.87E-03	9.22E-04
Fe	0.0226		0.0218		7.25E-04		2.81E-06	6.94E-06
Zr	5.12E-04		4.63E-04		6.07E-05		6.11E-06	<1.9E-06
Flowrate (LPH)	0.819	0.264	0.819	0.27	0.27	0.253	0.253	0.264

Table V. Percentage of Component in Each of the Effluent Streams for CMP Flowsheet Testing

Stream	HNO_3	Nd	Fe	Hg	Zr	Al	B	Ca	Ce
Aq. Raffinate	69.3% (72.1%)	<0.018% (<0.02%)	96.8% (98.9%)	0.86%	90.4% (95.5%)	100.7% (99.9%)	104.1% (99.1%)	96.2% (96.1%)	<0.79% (<0.81%)
Strip Product	26.9% (27.9%)	99.6% (99.97%)	1.06% (1.08%)	0.68%	3.9% (4.1%)	0.10% (0.10%)	0.90% (0.86%)	3.9% (3.9%)	97.5% (99.2%)
Na_2CO_3 Product	nd	<0.006% (<.006%)	0.004% (0.004%)	73.7%	0.37% (0.39%)	nd	nd	nd	nd
Organic Product	nd	<0.015% (<.016%)	0.01% (0.01%)	24.75%[1]	0.12% (0.13%)	nd	nd	nd	nd
Percent[2] Recovery	96.1%	92.6%	97.9%	nd	94.6%	100.8%	105.0%	100.1%	98.3%

() = Normalized percentage

[1] = A material balance was used to calculate solvent Hg concentrations

[2] = The percent recovery is the amount of a component accounted for by a mass balance of the sample analysis results.

nd = not determined

Table V. Percentage of Component in Each of the Effluent Streams for CMP Flowsheet Testing (Continued)

Stream	Cr	Cs	Pb	Ni	Na	K	Sr	Cl	F	SO_4
Aq. Raffinate	103.1% (99.9%)	92.3% (99.8%)	84.9% (84.4%)	109.8% (99.9%)	107.7% (99.8%)	94.8% (99.8%)	100.9% (98.5%)	86.3% (98.6%)	96.8% (99.4%)	99.3% (99.95%)
Strip Product	0.11% (0.11%)	0.18% (0.19%)	10.1% (10.6%)	0.15% (0.13%)	0.19% (0.17%)	0.15% (0.16%)	1.60% (1.50%)	1.22% (1.39%)	<0.58% (<0.6%)	<0.05% (<0.05%)
Na_2CO_3 Product	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Organic Product	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Percent[1] Recovery	103.2%	92.5%	95.0%	110.0%	107.9%	95.0%	102.5%	87.5%	97.4%	99.4%

() = Normalized percentage

[1] = The percent recovery is the amount of a component accounted for by a mass balance of the sample analysis results.

nd = not determined

Table VI. Component Distribution Coefficients for CMP Flowsheet Testing

Comp.	Stage	Aqueous Conc. (M)	Organic Conc. (M)	D	Comp.	Stage	Aqueous Conc. (M)	Organic Conc. (M)	D
Nd	Extr. 1	<6.93E-07	<1.73E-06	nd	Fe	Extr. 1	0.022	8.68E-04	0.040
	2	<6.93E-07	<1.73E-06	nd		2	0.023	7.83E-04	0.034
	3	<6.93E-07	<1.73E-06	nd		3	0.023	8.33E-04	0.036
	4	<6.93E-07	6.57E-06	>9.5		4	0.024	8.01E-04	0.034
	5	1.55E-06	3.03E-05	19.6		5	0.023	7.12E-04	0.030
	6	1.12E-05	2.69E-04	23.9		6	0.023	7.25E-04	0.032
	7	7.97E-05	2.06E-03	25.9		7	0.023	7.12E-04	0.031
	8	5.50E-04	1.18E-02	21.4		8	0.023	6.45E-04	0.028
	Strip 9	1.05E-02	9.15E-03	0.87		Strip 9	7.25E-04	1.40E-05	0.019
	10	7.35E-03	8.04E-04	0.11		10	4.37E-05	6.40E-06	0.15
	11	6.23E-04	3.45E-06	0.006		11	6.36E-06	7.48E-06	1.18
	12	2.48E-06	<1.73E-06	<0.7		12	1.14E-05	6.98E-06	0.62
	Carb. 13	<6.93E-07	<1.73E-06	nd		Carb. 13	2.81E-06	6.94E-06	2.5
	14	<6.93E-07	<1.73E-06	nd		14	1.84E-06	6.67E-06	3.6
	15	<6.93E-07	<1.73E-06	nd		15	1.48E-06	7.83E-06	5.3
	16	<6.93E-07	<1.73E-06	nd		16	1.54E-06	6.94E-06	4.5
Zr	Extr. 1	4.63E-04	7.78E-05	0.17	Hg	Extr. 1	1.04E-05	nd	nd
	2	4.72E-04	5.07E-05	0.11		2	9.57E-06	5.44E-05	5.7
	3	4.65E-04	5.40E-05	0.12		3	2.79E-05	3.46E-05	1.2
	4	4.75E-04	5.51E-05	0.12		4	2.15E-05	6.56E-05	3.0
	5	4.88E-04	5.97E-05	0.12		5	3.15E-05	2.59E-04	8.2
	6	4.86E-04	5.95E-05	0.12		6	9.37E-05	5.38E-04	5.7
	7	4.88E-04	6.06E-05	0.12		7	1.84E-04	1.22E-03	6.7
	8	4.57E-04	6.06E-05	0.13		8	4.05E-04	3.70E-03	9.1
	Strip 9	6.07E-05	2.37E-06	0.04		Strip 9	2.49E-05	3.68E-03	148
	10	3.51E-06	<1.92E-06	<0.55		10	1.27E-05	3.68E-03	290
	11	1.66E-06	<1.92E-06	<1.16		11	8.23E-06	3.68E-03	447
	12	3.60E-06	4.66E-06	1.3		12	7.88E-06	3.67E-03	466
	Carb. 13	6.11E-06	<1.92E-06	<0.31		Carb. 13	2.87E-03	9.34E-04	0.33
	14	4.00E-06	1.92E-06	<0.48		14	1.23E-05	9.24E-04	75
	15	2.36E-06	1.92E-06	<0.81		15	1.14E-06	9.24E-04	810
	16	1.49E-06	1.92E-06	<1.29		16	2.00E-06	9.22E-04	461

Table VI. Component Distribution Coefficients for CMP Flowsheet Testing (Continued)

Comp.	Stage		Aqueous Conc. (M)	Organic Conc. (M)	D
HNO_3	**Extr.**	**1**	**0.941**	**0.974**	**1.04**
		2	**1.212**	**1.068**	**0.88**
		3	**1.246**	**1.134**	**0.91**
		4	**1.272**	**1.178**	**0.93**
		5	**1.273**	**1.155**	**0.91**
		6	**1.288**	**1.146**	**0.89**
		7	**1.284**	**1.144**	**0.89**
		8	**1.266**	**1.137**	**0.90**
	Strip	**9**	**1.107**	**0.536**	**0.48**
		10	**0.537**	**0.214**	**0.40**
		11	**0.297**	**0.071**	**0.24**
		12	**0.173**	**0.021**	**0.12**
	Carb.	**13**	**nd**	**0.0062**	**nd**
		14	**nd**	**nd**	**nd**
		15	**nd**	**nd**	**nd**
		16	**nd**	**nd**	**nd**

nd = not determined

Table VII. Comparison of Distribution Coefficients to Laboratory Data

Section	D_{Am}		D_{Fe}	
	Contactor Mockup (Nd)	Spiked Simulant (^{241}Am)	Contactor Mockup	SBW Simulant
Extraction	20-26	23	0.03-0.04	0.06
0.04M HEDPA Strip	0.006-0.11	0.01-0.31	0.02-1.2	nd
0.25 M Carb. wash	nd	nd	2.5-5.3	nd

Section	D_{Zr}		D_{Hg}	
	Contactor Mockup	Spiked Simulant (^{95}Zr)	Contactor Mockup	Spiked Simulant (^{203}Hg)
Extraction	0.11-0.17	1.0	1.2-9.1	7.5-9.3
0.04M HEDPA Strip	0.04	<<1	148-466	52-137
0.25 M Carb. wash	nd	nd	0.33	0.83

The four stages of HEDPA strip at an O/A of 1.0 removed greater than 99.98% of the Nd from the CMP solvent. Again, the lower detection limit for Nd was reached.

As shown in Table VII, the distribution coefficients obtained for Nd compare well with Am distribution coefficients obtained from batch contacts with SBW simulant spiked with ^{241}Am. Similar results were obtained when comparing the Nd distribution coefficients from TRUEX flowsheet tests with batch contact data [13]. This indicates that Nd is an appropriate surrogate for ^{241}Am.

Iron

The distribution coefficients obtained for Fe in the extraction section ranged from 0.028 to 0.040. As a result, 99% of the Fe in the SBW feed remained in the aqueous raffinate and 1% exited in the strip product. The HEDPA strip was very effective in back-extracting the small amount of Fe that was extracted into the CMP solvent. Essentially all of the Fe in the solvent was removed with the first stage of the 0.04 M HEDPA strip section (D_{Fe}= 0.02).

Extraction distribution coefficients obtained for Fe compare well with Fe distribution coefficients obtained from batch contacts with SBW. Strip and Na_2CO_3 wash laboratory data have not been obtained.

Zirconium

The distribution coefficients obtained for Zr in the extraction section ranged from 0.11 to 0.17. As a result, 95.5% of the Zr in the SBW feed remained in the aqueous raffinate and 4.1% exited in the strip product. The HEDPA strip was very effective in back-extracting the small amount of Zr that was extracted into the CMP solvent. Essentially all of the Zr in the solvent was removed with the first stage of the 0.04 M HEDPA strip section (D_{Zr} = 0.039).

The Zr extraction distribution coefficients (D_{Zr} = 0.1) are considerably lower than those obtained from batch contacts with ^{95}Zr spiked SBW simulant (D_{Zr} = 1.0). Strip distribution coefficients are comparable to batch contact data.

Mercury

Organic phase Hg distribution coefficients were calculated by performing a material balance around each stage. The resulting organic phase concentrations were used to calculate distribution coefficients. The distribution coefficients obtained for Hg in the extraction section ranged from 1.2 to 9.1. As a result, 99.1% of the Hg was extracted from the SBW simulant. Very little Hg was back-extracted in the strip section (D_{Hg} = 148 to 466). The Na_2CO_3 wash removed 74% of the Hg in the first contact (D_{Hg} = 0.33). On the remaining Na_2CO_3 wash stages D_{Hg} was greater than 75, resulting in no additional Hg removal. As a result, 26% of the Hg in the SBW simulant exited with the CMP solvent. On a process scale, Hg would be recycled back to the extraction section resulting in Hg building up in the CMP solvent until steady-state conditions are reached. Distribution coefficients obtained from this flowsheet test were used in conjunction with the GTM to model the CMP flowsheet. Results indicate the Hg concentration in the CMP solvent will build up to 1.2E-03 M. Testing needs to be performed to determine if this concentration of Hg in the solvent will have any adverse effects on the CMP flowsheet.

Another option available for the removal of Hg from the CMP solvent is an 8 M HNO_3 strip section. Distribution coefficients of 0.6 were obtained for ^{203}Hg in batch contacts of the CMP solvent with 8 M HNO_3. Results of solvent wash testing with 8 M HNO_3 are presented later in this report.

Extraction and strip distribution coefficients obtained for Hg compare well with Hg distribution coefficients obtained from batch contacts with SBW spiked with ^{203}Hg. The Hg distribution coefficient of 0.33 obtained in the Na_2CO_3 wash section was lower than the distribution coefficient of 0.83 obtained from batch contacts. However, the data obtained from flowsheet testing and the laboratory data indicate that Hg is stripped in the first Na_2CO_3 wash stage ($D_{Hg} < 1$) and no further removal is obtained from additional contacts ($D_{Hg} >> 1$).

Aluminum, Boron, Calcium, Cerium, Cesium, Chromium, Lead, Nickel, Potassium, Sodium, Strontium, and Sulfate

Concentrations of Al, B, Ca, Ce, Cr, Cs, K, Na, Ni, Pb, SO_4, and Sr were obtained for the aqueous raffinate and strip product streams. Of these species, only Pb and Ce were extracted significantly. Essentially all of the Ce and 10% of the Pb were extracted by the CMP solvent. The Ce and Pb were effectively back-extracted from the solvent in the strip section. The extraction of Pb is not completely understood and further testing needs to be performed to verify the results obtained.

Solvent Wash Testing

The CMP solvent from the flowsheet testing was contacted with nitric acid to re-acidify the solvent after the Na_2CO_3 wash. After this re-acidification was performed, analytical results were obtained from the CMP flowsheet test which indicated 26% of the Hg remained in the CMP solvent. A second wash was performed in which 8 M HNO_3 was used to strip the Hg from the solvent. This strip was followed by a Na_2CO_3 wash and a dilute nitric acid rinse.

Solvent Re-acidification

The CMP solvent product from the flowsheet tested would typically be contacted with 0.1 M HNO_3 in order to re-acidify the solvent prior to recycling it to the extraction section. Dispersion numbers were calculated using the Na_2CO_3 washed solvent product from the flowsheet testing and various concentrations of aqueous nitric acid solutions in order to determine the required HNO_3 concentration to enhance phase disengagement and prevent the

Table VIII. Dispersion Numbers of CMP with Various Nitric Acid Solutions

Aqueous	Organic	Contact	O/A	N_{Di}
0.1 M HNO_3	Solvent from flowsheet test	1	3.0	2.8E-04
0.5 M HNO_3	Solvent from flowsheet test	2	3.0	3.2E-04
1.0 M HNO_3	Solvent from flowsheet test	3	3.0	5.0E-04
1.0 M HNO_3	Solvent from contact #3	4	3.0	6.1E-04
1.5 M HNO_3	Solvent from flowsheet test	5	3.0	4.5E-04
1.5 M HNO_3	Solvent from contact #5	6	3.0	4.4E-04
2.0 M HNO_3	Solvent from flowsheet test	7	3.0	7.4E-04
2.0 M HNO_3	Solvent from contact #7	8	3.0	8.9E-04

flooding problems encountered when the CMP solvent was initially washed. The results of these dispersion number tests are given in Table VIII. The dispersion numbers were very low at HNO_3 concentrations of 0.1 M to 1.5 M. With 2.0 M HNO_3, the dispersion numbers were close to 8E-04. As a result, the acid rinse was performed using 2.0 M HNO_3.

The solvent re-acidification was performed using four stages of acid rinse at an O/A of 3.0. Under these condition, the aqueous product was approximately 20% flooded. No flooding occurred in the solvent product. The O/A was decreased until no flooding was observed (O/A=1.0, <1% flooding). Re-acidification of the solvent then continued at these flowrates. Precipitation problems were not encountered with the solvent re-acidification test.

8M HNO_3 Solvent Wash Testing

Results from the CMP flowsheet test indicated that Hg is extracted by the CMP solvent and the 0.25 M Na_2CO_3 wash is only partially effective in stripping the Hg from the solvent. A second solvent wash test, consisting of four stages of 8 M HNO_3 wash, four stages of 0.25 M

Na_2CO_3 wash, and four stages of 0.1 M HNO_3 acid rinse, was performed to evaluate the removal of Hg. This flowsheet was previously described in conjunction with Figure 6.

Previous solvent wash tests resulted in flooding problems due to poor dispersion numbers when using a dilute nitric acid rinse. Also, dispersion number tests with the CMP solvent and potential flowsheets for the separation of actinides from dissolved calcine solutions indicated that flooding problems may occur in the scrub section of the flowsheet (0.05 M oxalic acid in 3 M nitric acid scrub solution). Maximum throughput for the centrifugal contactors (aqueous plus organic flowrates) is proportional to the dispersion number. With solutions that result in low dispersion numbers, reducing the solution flowrates will result in longer residence time in the contactors which may prevent flooding. However, the flowrates at which flooding was encountered were already at the low end of operability of the contactors. Since further reduction in flowrate was not possible, other methods were evaluated to solve the flooding problem. The solvent used for all previous testing was 0.75 M CMP and 1.0 M TBP in Isopar-L®. No attempt had been made to optimize the solvent composition. Laboratory testing was performed to evaluate alternative solvent compositions and it was determined that 0.50 M CMP and 1.0 M TBP in Isopar-L® will adequately separate the actinides from SBW and dissolved calcine solutions [8]. In addition, with this solvent composition there were no problems with low dispersion numbers in the dilute acid rinse section or in the scrub section of the dissolved calcine flowsheet.

As a result of the CMP solvent optimization tests, the CMP solvent used in the Centrifugal Contactor Mockup was diluted to 0.5 M CMP and 1.0 M TBP in Isopar-L®. The 8 M HNO_3 solvent wash test was then performed using this diluted solvent. No attempt was made to repeat the previous flowsheet testing with the altered CMP solvent.

Contactor Operation

Actual solution flowrates for the solvent wash test were calculated from tank depletion rates and are compared to the desired flowrates in Table IX. The flowrates and O/A ratios compare very well with the desired values. Flooding, precipitation, and/or third phase problems were not encountered with this test.

Steady-State Concentrations

The concentration of Hg was reduced from 4.54E-05 M in the solvent feed to 1.68E-05 M in the solvent product exiting the 8 M HNO_3 wash section. This corresponds to 63% removal of the Hg. Based on the batch contact ^{203}Hg distribution coefficient of 0.6 obtained with 8 M HNO_3, 96% removal of Hg from the CMP solvent was expected. A distribution coefficient of 0.93 was obtained on the third 8 M HNO_3 wash stage which corresponds to the actual removal efficiency obtained. No additional Hg was removed in the Na_2CO_3 wash or 0.1 M HNO_3 rinse section.

Table IX. Flowrates and O/A Ratios From the 8 M HNO_3 Solvent Wash Test

		Flowrate (LPM)		O/A Ratio		Total
Section	Feed	Desired	Actual	Desired	Actual	Flow
8 M Wash	Org	0.31	0.34	1.0	0.95	0.70 LPM
	Aq	0.31	0.358			
Na_2CO_3 wash	Aq	0.08	0.064	3.9	5.3	0.40 LPM
Acid Rinse	Aq	0.1	0.107	3.1	2.9	0.45 LPM

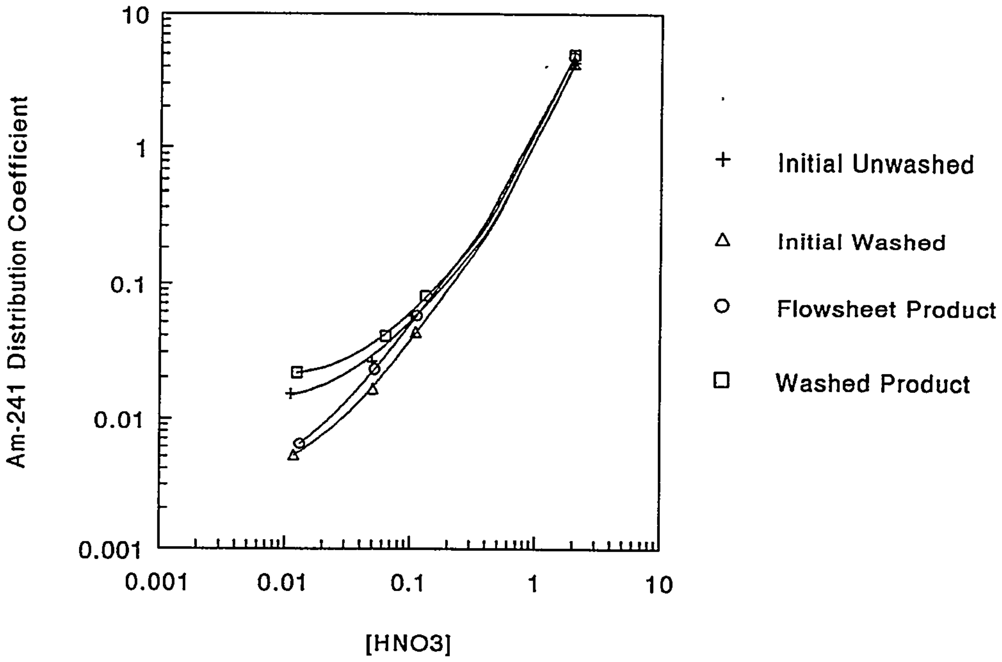
The 8 M HNO_3 wash was not as effective as the initial 0.25 M Na_2CO_3 wash in stripping Hg from the CMP solvent. Additional tests need to be performed to determine if the 74% Hg removal obtained with the 0.25 M Na_2CO_3 wash prevents the buildup of Hg to unacceptable levels.

Solvent Degradation

Impurities in the CMP solvent, resulting from acid hydrolysis, may hinder the ability to strip the actinides. The distribution coefficient of ^{241}Am is particularly sensitive to CMP impurities. D_{Am} was evaluated as a function of nitric acid concentration from HNO_3 solutions using the solvent product from the CMP flowsheet test and again using the same solvent after performing each solvent wash test. The distribution coefficients obtained for ^{241}Am were compared to results obtained with the initial CMP solvent in order to determine if any noticeable degradation of the solvent occurred during testing and to determine if the solvent wash was effective in removing any degradation products which may have formed. Results of this testing are given in Figure 14.

The distribution coefficients of ^{241}Am at HNO_3 concentrations greater than 0.1 M remained approximately constant (within analytical error) for each test. However, with 0.05 M HNO_3 and 0.01 M HNO_3 the distribution coefficients of ^{241}Am varied slightly. D_{Am} is most sensitive to degradation products at 0.01 M HNO_3. After washing the initial CMP solvent with Na_2CO_3 and HNO_3, D_{Am} decreased from 0.018 to 0.005 indicating that some manufacturing impurities or degradation products in the CMP solvent may have been removed. D_{Am} for the organic product from the CMP flowsheet testing increased only slightly to 0.006 indicating that very little CMP degradation due to acid hydrolysis occurred. After this solvent was washed, D_{Am} increased to 0.022. Although this higher value is still acceptable, it is unknown why D_{Am} increased after the solvent wash. D_{Am} will continue to be measured with future CMP flowsheet testing with dissolved pilot plant calcine in order to continue to evaluate degradation of the CMP solvent and the effectiveness of the Na_2CO_3 wash.

Figure 14. CMP Solvent Purity Results



CONCLUSIONS AND RECOMMENDATIONS

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

Conclusions

1. A CMP flowsheet has been developed which is capable of sufficiently removing the actinides from SBW to meet NRC Class A LLW criteria (see Figure 5).

2. For this CMP flowsheet, no precipitation or third phase formation problems were observed or are anticipated with actual waste.

3. Mercury was extracted into the CMP solvent. The 0.25 M Na_2CO_3 solvent wash section removed 74% of the Hg from the solvent. An 8 M HNO_3 wash section removed 63% of the Hg from the solvent.

4. Very little Fe or Zr were extracted with the CMP flowsheet. Only 1% of the Fe and 4% of the Zr exited with the HAW strip product.

5. Al, B, Ca, Cr, Cs, K, Na, Ni, SO_4, and Sr were not extracted by the CMP solvent. Essentially all of the Ce and 10% of the Pb were extracted by the CMP solvent.

6. A 0.04 M HEDPA strip solution is very effective in stripping Nd, Fe, and Zr from the CMP solvent.

7. Nd, Fe, and Hg distribution coefficients obtained compared favorably with laboratory distribution coefficients obtained with spiked SBW simulant. Zr extraction distribution coefficients were considerably lower than those obtained in the laboratory.

8. Significant degradation of the CMP solvent does not appear to be occurring. However, additional data must be obtained from further centrifugal contactor operation in order to thoroughly evaluate any solvent degradation and the effectiveness of the Na_2CO_3 wash.

9. Steady state was reached in the Centrifugal Contactor Mockup for Nd, Fe, Zr, and H^+ within 40 minutes.

10. With the centrifugal contactor design being utilized in the Centrifugal Contactor Mockup flooding problems occur when contacting the 0.75 M CMP solvent with nitric acid solutions in the solvent wash section of the flowsheet. This flooding is due to poor phase separation of the two solutions (low dispersion numbers).

11. No operational problems were noted with the centrifugal contactors.

Recommendations

1. A flowsheet similar to the one tested in this CMP flowsheet testing should be used as a baseline flowsheet for future TRUEX testing with actual SBW (see Figure 15).

2. This flowsheet testing should be repeated using 0.5 M CMP and 1.0 M TBP in Isopar L® in order to determine if flooding problems can be alleviated and acceptable Nd removal obtained.

3. Waste form studies should be performed to determine if the phosphorus in the 0.04 M HEDPA strip will adversely impact the development of a suitable waste form or produce excessive waste volumes. Also, flowsheet tests should be performed to evaluate the use of lower HEDPA concentrations in order to minimize the amount of phosphorus in the waste form.

4. Distribution coefficients of ^{241}Am in the CMP solvent used for these tests should continue to be evaluated as future testing is performed in order to further evaluate the degradation of the CMP solvent and the effectiveness of the Na_2CO_3 wash.

5. Additional testing should be performed to verify and further understand the results obtained for Pb (10 % extraction by the CMP solvent).

6. For future CMP flowsheet testing at similar flowrates, the Centrifugal Contactor Mockup should be operated a minimum of 40 minutes prior to sampling to ensure steady state has been reached.

REFERENCES

1. Newby, B.J., "Calcination Of Sodium-Bearing Waste Using Aluminum Nitrate," WINCO-1026, March 1988.

2. Rapko, B. M., Lumetta, G.L., *Sol. Extr. & Ion Exchange*, **12**(5), 967-986 (1994).

3. Marsh, S. F., Yarbo, S. L., "Comparative Evaluation of DHDECMP and CMPO as Extractants for Recovering Actinides from Nitric Acid," Report LANL-11191, Los Alamos National Laboratory, Los Alamos, New Mexico, 1988.

4. McIsaac, L. D., Baker, J. D., and Tkachyk, J. W., "Actinide Removal From ICPP Waste," ICP-1080, August 1975.

5. Baker, J. D., McIsaac, L. D., Krupa, J. F., Meikrantz, D. H., and Schroeder, N. C., "Experimental Mixer Settler Actinide Partitioning From ICPP Acidic Waste," ICP-1182, August 1979.

6. Maxey, H. R., Chamberlain, D. B., McManus, G. J., Colton, E. L., and Nebeker, R. L., "Removal of Actinides From ICPP Fuel Reprocessing Wastes Engineering Studies Terminal Report," ENICO-1057, September 1980.

7. Olson, A.L., Schulz, W.W., Burchfield, L.A., Carlson, C.D., Swanson, J.L., Thompson, M.C., "Evaluation And Selection Of Aqueous Based Technology For Partitioning Radionuclides From ICPP Calcine," WINCO-1071, February 1993.

8. R. S. Herbst, Unpublished data.

9. Brewer, K. N., Herbst, R. S., Tranter, T. J., Todd, T. A., "CMPO Purity Tests in the TRUEX Solvent Using Americium-241," WINCO-1177, December 1993.

10. Vandegrift, G.F., *et. al.*, "The Generic TRUEX Model: Operating Manual for the IBM-PC Compatible and Macintosh Computers," ANL-92/41, 1992.

11. Vandegrift, G.F., *et. al.*, "The Generic TRUEX Model Volume Two: Description of the Chemistry and Engineering Principles Used in the Model," ANL-89/18, 1989.

12. Vandegrift, G.F., *et. al.*, "The Generic TRUEX Model Volume Three: Experimental Database Generated in Support of the Model," ANL-89/19, 1989.

13. Law, J. D. and Herbst, R. S., "TRUEX Flowsheet Development as Applied to ICPP Sodium-Bearing Waste Using Centrifugal Contactors," INEL-95/0130, February 1995.

REFERENCES (Continued)

14. Leonard, R. A. and Steindler, M. J., "Summary Report on the Development of Annular Centrifugal Contactors," ANL-82-21, June 1982.

15. Murphy, J. A., Pincock, L. F., Christiansen, I. N., "ICPP Radioactive Liquid and Calcine Waste Technologies Evaluation Final Report and Recommendation," INEL-94/0119, April 1995.