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DEVELOPMENT AND TESTING OF SREX FLOWSHEETS FOR TREATMENT OF IDAHO CHEMICAL PROCESSING PLANT SODIUM-BEARING WASTE USING CENTRIFUGAL CONTACTORS

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ABSTRACT

Laboratory experimentation has indicated that the SREX process is effective for partitioning ^{90}Sr from acidic radioactive waste solutions located at the Idaho Chemical Processing Plant. A baseline flowsheet has been proposed for the treatment of sodium-bearing waste (SBW) which includes extraction of strontium from liquid SBW into the SREX solvent (0.15 M 4',4' (5')-di-(tert-butyldicyclohexo)-18-crown-6 and 1.2 M TBP in Isopar L®), a 0.01 M nitric acid strip section to back-extract components from the loaded solvent, and a 2.0 M HNO_3 solvent acidification section to equilibrate the solvent with HNO_3 prior to recycle to the extraction section. The flowsheet was designed to provide a decontamination factor (DF) of $>10^3$ which will reduce the ^{90}Sr activity in the waste solution to below the NRC Class A LLW limit of 0.04 Ci $^{90}Sr/m^3$. SREX flowsheet testing was performed using sixteen stages of 5.5-cm diameter centrifugal contactors. The behavior of stable Sr and other components which are potentially extracted by the SREX solvent were evaluated. Specifically, the behavior of the matrix components including Pb, K, Hg, Na, Ca, Zr, and Fe was studied. The described flowsheet achieved 99.98% Sr removal (DF=4250) with one cycle of SREX. Potassium and Zr were partially extracted into the SREX solvent with 35% and 21%, respectively, exiting in the strip product. Sodium, Ca, and Fe were essentially inextractable. Lead was determined to extract and accumulate in the SREX solvent and in the strip section. As a result, a Pb precipitate formed in the strip stages of the contactors. Mercury was also determined to extract and accumulate in the SREX solvent.

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 PUREX/REDOX type uranium recovery processes were converted to granular solids (calcine) in a high temperature fluidized bed. During the course of reprocessing, a secondary waste stream, liquid sodium-bearing waste (SBW), was also generated primarily from equipment decontamination between campaigns and solvent wash activities. This SBW can not be directly calcined due to the high sodium content and has historically been blended with reprocessing raffinates or non-radioactive aluminum nitrate prior to calcination (1). As of November 1993, all raffinate solutions were calcined, thereby eliminating the option of waste blending to deplete the SBW inventory. Currently, approximately 1.5 million gallons of liquid SBW are stored at the ICPP in large stainless steel tanks.

A Notice of Noncompliance 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 secondary containment requirements. The Department of Energy has agreed with the EPA and IDHW to remove the SBW from some of the underground storage tanks by 2009 and from the remaining tanks by 2015.

Several technologies are currently being evaluated to treat SBW. These include: 1) numerous pretreatment options to concentrate the liquid or remove sodium nitrate, followed by calcination, and 2) partitioning of transuranics (TRUs), cesium, and strontium, and immobilizing the resulting high- and low-activity segregated streams for final disposition. The StRontium EXtraction (SREX) process, developed at Argonne National Laboratory (ANL), is a potential ^{90}Sr partitioning process for the SBW (2).

The SREX process uses 4',4'(5')-di-(tert-butyldicyclohexo)-18-crown-6 (DtBuCH18C6) as a selective extractant for Sr^{2+}. Tributylphosphate (TBP) is used in the SREX solvent to prevent third phase formation (second organic phase) and Isopar L® is used as the diluent. The typical SREX solvent is 0.15 M DtBuCH18C6 and 1.2 M TBP in Isopar L®. Initial batch laboratory experiments with simulated and actual SBW solutions indicate that the ^{90}Sr concentration can be reduced to below the 0.04 Ci/m^3 NRC Class A LLW requirement using the SREX process. Herein described are continuous countercurrent studies of the SREX flowsheet with simulated SBW in centrifugal contactors.

SCOPE AND PURPOSE

The purpose of these studies was to develop and test potential SREX 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 setup 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. The behavior of Sr and the non-radioactive components was evaluated for the potential flowsheets. Specifically, reduction of the ^{90}Sr activity to below the NRC Class A LLW limit of 0.04 Ci $^{90}Sr/m^3$ with one cycle of SREX (>99.9% ^{90}Sr removal) was evaluated. 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 SREX flowsheets developed with non-radioactive SBW simulant will be used for future countercurrent flowsheet development and testing with actual SBW.

A typical SREX process flowsheet concentrates the ^{90}Sr from an acidic aqueous feed stream, such as SBW, producing an aqueous ^{90}Sr-containing high-activity waste (HAW) product stream and a reduced ^{90}Sr 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 for ^{90}Sr.

A dilute nitric acid scrub section can be used to scrub extracted K from the SREX solvent. The K would then remain in the LAW raffinate. However, a scrub section would also result in decreased ^{90}Sr separation due to the partial scrubbing of ^{90}Sr from the SREX solvent. With SBW, two cycles of SREX or an increased number of extraction stages would likely be required in order to obtain the required ^{90}Sr separation of > 99.9%. A scrub section was not incorporated into the flowsheets tested because it was desired to demonstrate the removal of ^{90}Sr with one cycle of SREX.

Dilute nitric acid will effectively strip Sr from the SREX solvent. In addition, with ICPP SBW a second stripping section may be necessary to strip extracted metals such as Pb and/or Hg.

During processing, the SREX solvent can be degraded due to hydrolysis or radiolysis. Furthermore, trace quantities of extracted species often remain in the solvent 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 solvent degradation products.

With SBW feed, an HNO_3 equilibration section is required in order to equilibrate the SREX solvent with HNO_3 prior to recycling the solvent to the extraction section. Nitric acid equilibration is necessary in order to prevent the extraction of HNO_3 from the aqueous feed, which will result in decreased Sr distribution coefficients due to low nitrate concentration in the aqueous solution. Previous flowsheet testing in the Centrifugal Contactor Mockup without an HNO_3 equilibration section resulted in decreased Sr distribution coefficients in the extraction section.

EQUIPMENT DESCRIPTION

All testing was performed in the Centrifugal Contactor Mockup located at the ICPP. The Centrifugal Contactor Mockup consists of sixteen stages of 5.5-cm centrifugal contactors, feed and receiving vessels, feed pumps, flowmeters, filters, AC and DC motor drives, and a sample system. The centrifugal contactors were procured from Oak Ridge National Laboratory and were fabricated in blocks of four contactors.

Solution was 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 were adjusted by changing the pump speed using a ten-turn potentiometer.

The Centrifugal Contactor Mockup has provisions for sampling the aqueous and organic solutions exiting each stage during operation. In addition, aqueous and organic solution can be drained and sampled for each stage after shutdown.

METHODOLOGY/EXPERIMENTAL PROCEDURE

SBW Simulant

For the purposes of this study, the behavior of non-radioactive components in simulated SBW was evaluated. Using the analytical results obtained from characterization of SBW waste solution, a non-radioactive simulant was prepared to represent the average chemical composition of the major non-radioactive matrix components in the SBW tanks. Stable Sr was added to simulate radioactive Sr. The chemical composition of the SBW simulant is shown in Table 1. Additional Sr was added to the SBW simulant to increase the Sr concentration by one order of magnitude. This was necessary in order to obtain analytical results which are above the detection limit for Sr with the methods used for analysis.

The specific components evaluated in this study include those species potentially extracted by the SREX solvent: acid, strontium, lead, potassium, sodium, iron, calcium, zirconium, and mercury. Barium was not evaluated with this study because it is not present in the SBW. In the case that barium is present in the waste stream being evaluated, barium would compete with strontium for extraction by the crown ether.

SREX Solvent

The SREX solvent composition used in all SREX flowsheet studies reported herein was 0.15 M 4',4'(5')-di-(tert-butyldicyclohexo)-18-crown-6 and 1.2 M TBP in Isopar L® and was prepared by the ICPP Quality Control Laboratory. The extractant was obtained from Eichrom Industries, Darien, Il. The performance of this extractant is extremely sensitive to the purity of the product. The extractant used in these tests was reported to yield a D_{Sr} value of 3.8 according to Eichrom Industries quality assurance procedures. The SREX process was originally developed using 1-octanol as the diluent. This selection was made because the flash point and flammability of this diluent were determined to present minimal risk in a process operation. However, octanol is known to form degradation products when placed in contact with nitric acid. The degradation products present unknown potential safety problems in the operation of the SREX process. In addition, it has been determined that the residual presence of 1-octanol in the aqueous phase decreases the performance of CMPO in actinide removal in the TRUEX process during sequential waste treatment processes. An alternative diluent, therefore, has been studied to replace 1-octanol. The

TABLE 1. COMPOSITION OF SIMULATED SODIUM-BEARING WASTE

Component	M	Component	M
Acid (H^+)	1.26	K	1.38E-01
Al	5.63E-01	Mn	1.42E-02
B	1.40E-02	Mo	1.49E-03
Cd	2.05E-06	Na	1.17
Ca	3.41E-02	NO_3	4.46
Ce	3.63E-04	Ni	1.63E-03
Cl	3.52E-02	Pb	9.51E-04
Cs	7.52E-05	PO_4	<9.18E-03
Cr	5.63E-03	Sr	5.15E-03
F	9.66E-02	SO_4	3.86E-02
Fe	2.40E-02	Zr	3.86E-04
Hg	1.80E-03		

alternative solvent is composed of an isoparaffinic hydrocarbon diluent (Isopar L® from Exxon Corp.) and 1.2 M TBP as a phase modifier. This solvent is less likely to form explosive acid degradation products and is compatible with the TRUEX solvents currently being studied at the ICPP.

The purity and composition of the SREX solvent were established prior to use in the centrifugal contactors by determining D_{Sr} using the SREX solvent and 3.0 M HNO_3 solution. This method of determining the strontium distribution coefficient was established as a quality control procedure for testing the initial SREX solvent and the SREX solvent product from each flowsheet test. The solvent was considered suitable for extraction studies if the results were within the acceptable range ($D_{Sr} > 2.5$).

Only six liters of SREX solvent was prepared due to the limited availability and high cost associated with the DtBuCH18C6. This limited quantity of solvent made it necessary

to recycle the solvent during each flowsheet test. The SREX solvent was fed to the contactors out of a carboy and the solvent product leaving the contactors drained back into the feed carboy.

Analytical

Preliminary batch contacts with SBW simulant indicate 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) is extremely effective at quantitatively back-extracting all metals, except mercury, from the SREX solvent. Consequently, the organic samples were contacted with 0.25 M HEDPA in 0.05 M HNO_3. An O/A ratio of 0.4 was used to insure quantitative metal recovery in a single contact. The HEDPA was assumed to strip all of the Sr, Pb, K, Na, Fe, Ca, and Zr, but not the Hg, out of the SREX solvent. The aqueous phase from the HEDPA strip was separated from the solvent and submitted for Sr, Pb, K, Na, Fe, Ca, and Zr analysis. The solvent was then contacted with 0.05 M ethylene diamine tetraacetic acid (EDTA) at an O/A of 0.4 to strip the Hg out of the solvent. The aqueous phase from the EDTA strip was separated from the solvent and submitted for Hg analysis. These procedures provided an indirect measure of organic phase compositions and allowed the use of material balances to validate experimental results. All aqueous sample analyses were performed by the ICPP Analytical Section. Mercury analyses were performed using Cold Vapor Atomic Absorption Spectrophotometry. All other analyses were performed using Inductively Coupled Plasma Atomic Absorption Spectroscopy (ICP-AES). When detection of an analyte required increased sensitivity, inductively coupled plasma with mass spectrometric detection (ICP-MS) was employed for analytical determination.

SREX Flowsheet Testing

Based on the results of SREX testing performed with radioactive tracers and simulated SBW, a potential SREX flowsheet was developed for the separation of ^{90}Sr from SBW. This flowsheet, shown in Figure 1, consists of eight stages of extraction, four stages of 0.01 M HNO_3 strip, and four stages of 2.0 M HNO_3 solvent equilibration. The O/A ratio was 1.0 in the extraction and strip sections, and 2.0 in the HNO_3 equilibration section. The high O/A ratio and number of stages in the extraction section is required in order to obtain >99.9% removal of ^{90}Sr which is necessary to meet NRC Class A LLW limits with only one cycle of SREX. This flowsheet was used as a basis for SREX flowsheet testing.

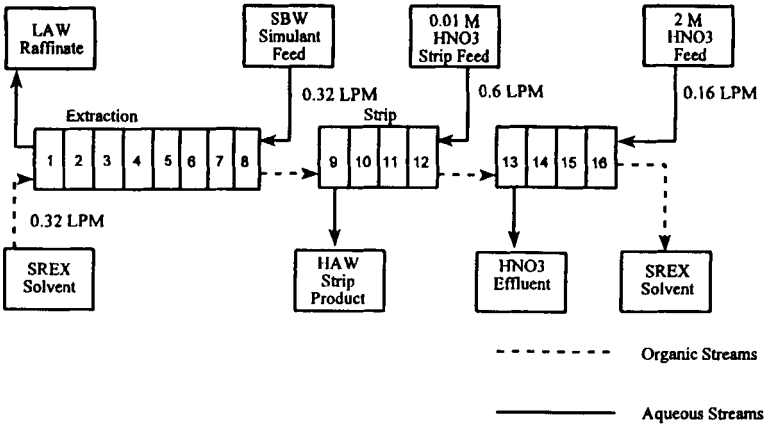


FIGURE 1. SREX Flowsheet for the Separation of Sr from SBW

The operating parameters for the solvent equilibration section were determined using the Generic TRUEX Model (GTM) for the modelling of the distribution of HNO_3 in the SREX flowsheets (3). Nitric acid distributions have been determined to be comparable for the TRUEX and SREX solvents. The SREX HNO_3 distributions in the extraction and strip sections from previous flowsheet testing were 0.69 and 0.30, respectively. The HNO_3 distributions obtained from TRUEX flowsheet testing in the Centrifugal Contactor Mockup were 0.64 and 0.28 in the extraction and strip sections, respectively (4). Therefore, GTM results, using the TRUEX solvent with 1.2 M TBP, can be expected to accurately model the distribution of HNO_3 in the SREX solvent. Several runs were performed using the GTM in which the HNO_3 concentration and O/A ratio of the equilibration section were varied. Results of this modelling indicated that four stages of 2.0 M HNO_3 wash at an O/A of 2.0 would increase the HNO_3 concentration of the solvent to approximately 0.6 M HNO_3 and would result in less HNO_3 extracting from the SBW feed. As a result, the acid and nitrate concentrations in the aqueous raffinate should remain above 1.0 M and 4.0 M, respectively. With the aqueous phase nitrate concentration above 4.0 M, Sr distribution coefficients of 3.7 are expected, which should result in > 99.99% Sr removal.

Prior to testing, the solvent was equilibrated with HNO_3 by performing two contacts with 2.0 M HNO_3 at an O/A of 1.0. The solvent was equilibrated in order to be consistent with recycled solvent in the SREX process.

The goals of the SREX flowsheet testing were to determine 1) if equilibration of the SREX solvent with HNO_3 reduces the amount of HNO_3 extracted from the aqueous feed, resulting in Sr extraction distribution coefficients of approximately 3.7, 2) the concentrations and distribution coefficients of H^+, Sr, K, Pb, Na, Ca, Fe, Zr, and Hg at steady state for SBW feed, 3) if greater than 99.9% of the Sr is removed by one cycle of SREX, and 4) if precipitation or third phase formation problems exist with this flowsheet.

SREX flowsheet testing was performed as follows. The contactors were started at 3000 rpm based on previous results of hydraulic performance of the centrifugal contactors with SREX solvent. The aqueous feed, strip feed, and HNO_3 equilibration feed flows were then established. An aqueous feed solution of 2.0 M HNO_3 was used in order to establish aqueous flow in the extraction section during startup. Once aqueous solution was observed exiting from each section, solvent flow was started. When organic solution was observed exiting the last stage of the HNO_3 equilibration section, SBW feed solution flow was started and the 2.0 M HNO_3 feed was stopped. The contactors were operated for 50 minutes after the start of SBW simulant feed to ensure steady-state conditions were reached. Sightglass readings on each of the feed tanks were taken in order to determine actual solution flowrates based on tank depletion rates. Aqueous raffinate and strip product samples were taken and the contactor mockup was shutdown by simultaneously stopping the contactor motors and feed pumps. Each of the stages remain at approximately the steady-state operating conditions with this type of shutdown. This allowed aqueous and organic samples to be taken from each stage and distribution coefficients to be determined for each of the sixteen stages.

RESULTS AND DISCUSSION

Contactor Operation

No problems were encountered while performing the SREX flowsheet test. Flooding, third phase formation, and/or precipitation problems were not observed. However, while draining the contactors to pull samples after shutdown, a small amount of white precipitate was observed suspended in the stage 10 and 11 organic. A significant amount of precipitate

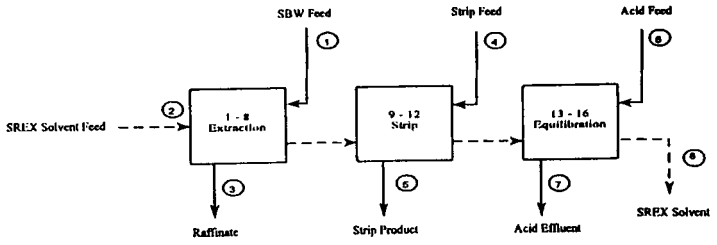
was observed in the stage 9, 10, 11, and 12 organic samples after the samples were allowed to stand for several days. A small amount of precipitate was also observed in the stage 13 and 14 organic samples. The precipitate was collected and submitted for analysis by x-ray fluorescence. Results indicate that the precipitate was primarily Pb. It is believed that this precipitate consists of a Pb:crown complex which is insoluble in both phases.

Steady-State Concentrations

The concentrations of H^+, Sr, Pb, K, Na, Ca, Fe, Zr, and Hg at steady state are listed in Figure 2. A material balance for each component is given in Table 2. Distribution coefficients were calculated for each of the sixteen stages. The aqueous phase concentrations, along with the resulting distribution coefficients, are given in Table 3. A discussion of the behavior of each of the components follows.

Acid. The distribution coefficients obtained for H^+ were approximately 0.7 in the extraction section and 0.3 in the strip section. The 2.0 M HNO_3 solvent equilibration section was very effective at reducing the extraction of nitric acid from the SBW feed in the extraction section. The acid concentration in the raffinate was 1.0 M as compared to 0.19 M in previous SREX flowsheet testing which did not incorporate an acidification section. With little acid and, therefore, nitrate extracted from the SBW feed, suppressed strontium distribution coefficients in the extraction section are not expected.

Strontium. The Sr concentration was reduced from 5.15E-03 M in the feed to 1.21E-06 M in the raffinate. This corresponds to a removal efficiency of 99.98%. Assuming a SBW feed ^{90}Sr activity of 39.7 Ci/m^3 and that 1.0 m^3 of LAW grout would be formed per m^3 of SBW (5), the ^{90}Sr concentration in the grout would be 0.0093 Ci/m^3 which is well below the NRC Class A LLW limit of 0.04 Ci/m^3. Distribution coefficients obtained for stages 1 through 8 of the extraction section ranged from 2.4 to 3.2 which is lower than the distribution coefficients of approximately 3.7 obtained from batch contacts with SBW. The aqueous and organic samples obtained from stages 1, 5, and 8 were re-equilibrated in the laboratory with ^{85}Sr spiked in the aqueous phase. Distribution coefficients of 4.4, 3.7, and 3.2 were obtained for stages 1, 5, and 8, respectively. The total throughput in the extraction section (aqueous plus organic flowrate) was 640 ml/min which is in the lower range of operability of the centrifugal contactor design. As a result, it is believed that the lower distribution coefficients obtained for Sr during SREX flowsheet testing may be attributed



	SBW Feed 1	SREX Solvent 2	LAW Raff. 3	Strip Feed 4	Strip Product 5	Acid Feed 6	Acid Effluent 7	SREX Solvent 8
H+ M	1.26	0.554	1.00	0.01	0.432	1.93	0.87	0.554
Sr M	5.15E-03	4.74E-07	1.21E-06		2.89E-03		3.42E-08	4.74E-07
Pb M[a]	9.51E-04	1.14E-03	2.58E-06		1.17E-05		1.08E-05	1.14E-03
K M	0.138	5.43E-05	0.0921		0.0281		3.58E-07	5.43E-05
Na M	1.17	4.46E-04	1.22		0.0165		6.09E-06	4.46E-04
Ca M	0.0341	2.08E-04	0.0337		3.49E-04		<2.0E-05	2.08E-04
Fe M	0.024	7.16E-06	0.0242		4.08E-05		4.37E-06	7.16E-06
Zr M	3.86E-04	1.98E-05	3.00E-04		4.78E-05		3.51E-06	1.98E-05
Hg M[a]	1.80E-03	4.24E-03	2.84E-05		6.13E-06		9.87E-06	4.24E-03
Flow (ml/min)	320	320	320	540	540	160	160	320

[a]Pb and Hg did not reach steady state

FIGURE 2. Steady-State Concentrations for SREX Flowsheet Test

to low stage efficiency resulting from the low total throughput in the contactors. The lower distribution coefficients correspond to 57% to 75% stage efficiency. Another possible explanation for the low stage efficiencies is that the residence time in the mixing zone of the centrifugal contactors was not long enough to allow the Sr to be completely extracted by the SREX solvent. This problem was encountered at ANL when performing SREX flowsheet tests (0.1 M DtBuCH18C6 in 1-octanol) using 2-cm diameter centrifugal contactors (6).

TABLE 2. PERCENTAGE OF COMPONENTS IN EACH OF THE EFFLUENT STREAMS FOR THE SREX FLOWSHEET TEST

Stream	Hg	Sr	Pb	K	Na	Fe	Ca	Zr
Aqueous Raffinate	1.6 % (65.0%)[a]	0.024% (0.025%)	0.27% (9.31%)	64.8% (65.4%)	103.7% (97.8%)	100.7% (99.7%)	98.5% (98.3%)	77.8% (78.5%)
Strip Product	0.587% (23.7%)	94.66% (99.97%)	2.07% (71.2%)	34.4% (34.7%)	2.38% (2.24%)	0.29% (0.28%)	1.72% (1.72%)	20.9% (21.1%)
SREX[b] Solvent	236%	0.009%	119.7%	0.039%	0.038%	0.030%	0.61%	5.1%
Acid Effluent	0.28% (11.3%)	3.3E-04% (4E-04%)	0.57% (19.5%)	1E-04% (1E-04%)	3E-04% (2E-04%)	0.01% (0.01%)	<0.03% (<0.03%)	0.45% (0.46%)
Percent[c] Recovery	70.5%	94.7%	55.8%	99.2%	106.1%	101.0%	100.3%	99.2%

[a]The percentages were normalized to yield a recovery of 100% by maintaining the ratio of the concentration of the component in each product stream.

[b]The SREX solvent effluent was recycled and is not a part of the percent recovery.

[c]Percent recovery is the amount of a component accounted for by performing a mass balance of sample analysis results.

TABLE 3. COMPONENT DISTRIBUTION COEFFICIENTS FOR SREX FLOWSHEET TESTING

Stage		Aqueous Conc. (M)	D	Stage		Aqueous Conc. (M)	D	Stage		Aqueous Conc. (M)	D
		Strontium				**Potassium**				**Nitric Acid**	
Extr.	1	1.77E-06	2.5	Extr.	1	0.0921	0.41	Extr.	1	1.00	0.75
	2	5.22E-06	2.8		2	0.128	0.37		2	1.19	0.69
	3	1.50E-05	3.1		3	0.136	0.37		3	1.24	0.67
	4	3.61E-05	2.5		4	0.133	0.39		4	1.22	0.70
	5	8.35E-05	2.4		5	0.146	0.34		5	1.25	0.68
	6	2.53E-04	2.7		6	0.143	0.35		6	1.25	0.66
	7	6.64E-04	3.2		7	0.161	0.31		7	1.25	0.65
	8	2.24E-03	2.4		8	0.166	0.30		8	1.23	0.66
Strip	9	2.89E-03	0.28	Strip	9	0.0281	0.41	Strip	9	0.43	0.52
	10	7.42E-04	0.016		10	1.38E-03	0.083		10	0.074	0.18
	11	1.13E-05	0.037		11	1.84E-05	3.47		11	0.016	0.45
	12	8.33E-08	4.0		12	5.63E-07	100.0		12	0.018	0.90
Equil.	13	3.42E-08	11.1	Equil.	13	3.58E-07	153.6	Equil.	13	0.87	0.28
	14	3.20E-08	12.7		14	<3.1E-07	>179.2		14	1.39	0.27
	15	3.31E-08	15.3		15	<3.1E-07	>179.2		15	1.65	0.30
	16	3.65E-08	13.0		16	<3.1E-07	>177.1		16	1.86	0.30
		Lead				**Sodium**				**Mercury**	
Extr.	1	2.58E-06	249.5	Extr.	1	1.22	0.024	Extr.	1	2.84E-05	nd
	2	6.37E-06	90.3		2	1.22	0.023		2	6.43E-04	3.9
	3	7.43E-06	73.7		3	1.22	0.023		3	7.18E-04	nd
	4	7.24E-06	66.3		4	1.30	0.022		4	7.48E-04	3.4
	5	7.63E-06	68.4		5	1.30	0.021		5	2.54E-05	nd
	6	5.55E-06	92.2		6	1.44	0.019		6	3.94E-05	89.6
	7	7.48E-06	72.3		7	1.39	0.019		7	1.10E-04	29.5
	8	2.06E-05	37.5		8	1.44	0.018		8	2.89E-04	nd
Strip	9	1.17E-05	84.3	Strip	9	0.0165	0.020	Strip	9	6.13E-06	477
	10	4.02E-04	3.3		10	1.52E-03	0.30		10	1.12E-06	2969
	11	2.34E-03	0.64		11	2.39E-05	20		11	1.64E-06	2294
	12	1.41E-03	0.85		12	4.05E-06	112.9		12	2.07E-06	2012
Equil.	13	1.08E-05	113.8	Equil.	13	6.09E-06	71.4	Equil.	13	9.87E-06	404
	14	1.75E-05	73.2		14	8.26E-06	52.6		14	1.83E-05	196
	15	1.68E-05	76.1		15	1.91E-06	244.3		15	2.42E-05	175
	16	1.76E-05	64.8		16	1.48E-06	301.5		16	2.33E-05	nd

nd = not determined

The strip section was very effective in back-extracting the Sr from the SREX solvent. With four stages of 0.01 M HNO_3 strip at an O/A of 0.58, 99.994% of the Sr was stripped from the SREX solvent.

Lead. Results obtained for Pb in the SREX flowsheet test were similar to those obtained with previous flowsheet testing. The Pb is extracted into the solvent and is not back-extracted in the strip section. Distribution coefficients for stages 1 through 8 of the extraction section ranged from 38 to 250. For stages 11 and 12 of the strip section, distribution coefficients of 0.6 and 0.8, respectively, were obtained. However, for stages 9 and 10 of the strip section, distribution coefficients of 84 and 3.3, respectively, were obtained. These higher distribution coefficients are a result of the higher acid concentrations for stages 9 and 10 due to the high acid concentrations in the SREX solvent leaving the extraction section (0.82 M). With high distribution coefficients for stages 9 and 10 and low distribution coefficients for stages 11 and 12, a buildup of Pb in the aqueous phase occurs. Because of this pinching action the aqueous Pb concentration in stage 11 was 2.34E-03 M, 2.5 times greater than the feed Pb concentration. Also, the poor stripping of Pb from the SREX solvent resulted in Pb building up in the solvent product stream to 120% of the feed Pb concentration. Continued operation would likely have resulted in a continued build-up and precipitation of Pb.

A poor overall material balance (56%) was obtained for Pb. A considerable amount of Pb precipitate was noted in the stage 9, 10, 11, and 12 organic samples. This precipitate is attributed to the buildup of Pb in the strip section and would result in a poor overall recovery for Pb.

The results obtained for Pb in the SREX flowsheet testing indicate the need for development of a method to scrub or strip Pb from the SREX solvent. Laboratory testing has identified ammonium citrate as a potential Pb stripping agent. Additional testing is being performed to evaluate various other solutions for scrubbing or stripping Pb. As a result, flowsheet testing which incorporates a Pb scrub or strip has not been performed at this time.

Potassium. Potassium was partially extracted from the SBW feed. Distribution coefficients ranged from 0.30 to 0.41 in the extraction section. As a result, 35% of the K was extracted from the SBW feed. The strip section was very effective in back-extracting the K from the SREX solvent. Only 0.04 % of the K remained in the solvent. If desired, the amount of K exiting in the strip product could be reduced by including a scrub section.

Sodium, iron, and calcium. Very little Na, Fe, or Ca was extracted from the SBW feed. Analytical results indicate that 97.8% of the Na, 99.7% of the Fe, and 98.3% of the calcium exited in the aqueous raffinate.

Zirconium. Results from the SREX flowsheet testing indicate that Zr was extracted with the SREX solvent. Twenty-one percent of the Zr in the SBW feed exited in the strip product and 78% remained in the aqueous raffinate. If desired, the amount of Zr exiting in the strip product could be reduced by including a scrub section.

Results obtained for Zr are inconsistent with those obtained from laboratory batch contacts. Batch contacts indicate that Zr is inextractable from SBW with the SREX solvent ($D<0.01$). However, results obtained from SREX flowsheet testing indicate that Zr was partially extracted. Distribution coefficients obtained from batch contacts using 1.2 M TBP in Isopar L® and 2.0 M HNO_3 solutions spiked with ^{95}Zr were approximately D=0.1, indicating Zr is partially extracted by TBP. Additional testing needs to be performed to verify the results obtained for Zr and explain the discrepancies with laboratory data.

Mercury. Hg was extracted into the SREX solvent and was not back-extracted in the strip section. Distribution coefficients ranging from 3 to 90 were obtained in the extraction section, 478 to 2969 in the strip section, and 175 to 404 in the 2.0 M HNO_3 equilibration section. As a result, the concentration of Hg in the SREX solvent built up to 236% of the feed concentration. Continued operation would likely have resulted in a continued build-up of Hg in the solvent.

The results obtained for Hg indicate the need to develop a method for stripping Hg from the SREX solvent. Laboratory testing of alternative stripping solutions, including dilute nitric acid, sodium carbonate, HEDPA, and EDTA, were performed. Of these potential stripping solutions only EDTA was effective in back-extracting Hg from the SREX solvent (D_{Hg} = 0.1). Further laboratory testing is planned to evaluate other potential stripping solutions such as concentrated HNO_3 (>5 M). As a result, flowsheet testing which incorporates a Hg strip has not been performed at this time. It should be noted that the SREX process might follow the TRUEX process. Since Hg is extracted with the TRUEX process, little Hg would remain in the feed to the SREX process (4). If this is the case, development of a method for stripping Hg from the SREX solvent would not be required.

Comparison of Distribution Coefficients to Laboratory Data

A comparison of the distribution coefficients obtained from the SREX flowsheet

TABLE 4. COMPARISON OF DISTRIBUTION COEFFICIENTS TO LABORATORY DATA

Section	D_{Sr}			D_{Pb}		
	Contactor Mockup	Spiked Simulant	Actual SBW	Contactor Mockup	Non-Radioactive Simulant	Actual SBW
Extraction	2.4 to 3.2	4.05	3.2[a]	37 to 90	53	na
0.01 M HNO_3 Strip	0.016 to 0.28	0.02[a]	0.01[a]	0.64 to 85	1.3	na

Section	D_K			D_{Na}		
	Contactor Mockup	Non-Radioactive Simulant	Actual SBW	Contactor Mockup	Non-Radioactive Simulant	Actual SBW
Extraction	0.3 to 0.41	0.4	0.2[a]	0.02	0.14[a]	0.15[a]
0.01 M HNO_3 Strip	0.08	na	<0.1[a]	0.02	Na	0.1[a]

Section	D_{Hg}		
	Contactor Mockup	Non-Radioactive Simulant	Actual SBW
Extraction	3 to 90	22	na
0.01 M HNO_3 Strip	478 to 2969	6000	na

[a] Octanol diluent

testing with distribution coefficients obtained from laboratory testing with non-radioactive simulant, spiked SBW simulant, and/or actual SBW waste is given in Table 4. The experimental distribution coefficients for Sr, Pb, K, Na, and Hg are all in agreement with laboratory data. However, the Sr distribution coefficients obtained from the SREX flowsheet testing were slightly lower than obtained with the batch contacts.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A potential SREX flowsheet has been developed which will reduce the ^{90}Sr concentration of ICPP SBW to below the NRC Class A LLW limit of 0.04 Ci/m^3 with

only one cycle of SREX (see Figure 1). With this SREX flowsheet, Pb and Hg are extracted into the SREX solvent. The Pb builds up in the SREX solvent and in the aqueous phase of the strip section, resulting in a Pb precipitate. Mercury also builds up in the SREX solvent. Potassium and Zr were partially extracted by the SREX solvent and back-extracted into the HAW strip product resulting in 21% of the Zr and 35% of the K exiting in the strip product. The addition of a scrub section is expected to reduce the quantity of K and Zr exiting in the strip product. The 0.01 M HNO_3 strip section was effective in stripping all components from the SREX solvent with the exception of Pb and Hg.

Strontium, Pb, K, Na, and Hg distribution coefficients obtained compared favorably with laboratory distribution coefficients obtained with non-radioactive SBW simulant, spiked SBW simulant, and actual SBW. The Generic TRUEX model is accurate in predicting H^+ concentrations for the SREX flowsheets using 0.15 M DtBuCH18C6 and 1.2 M TBP in Isopar L®.

Equilibration of the SREX solvent with HNO_3 prior to feeding the extraction section is required in order to reduce the extraction of acid and nitrate from the SBW or TRUEX raffinate feed, which results in suppressed Sr distribution coefficients.

No flooding problems were observed during SREX flowsheet testing. Also, no operational problems were noted with the centrifugal contactors.

Recommendations

Laboratory testing should be performed to evaluate potential methods for scrubbing and/or stripping Pb, Hg, and Zr from the SREX solvent. Also, laboratory batch contacts should be performed to verify the Zr distribution coefficients obtained. Future flowsheet testing, which incorporate these scrub and/or strip sections, should be performed in the Centrifugal Contactor Mockup. Ultimately, the flowsheet must be validated using samples of actual SBW. Future testing with actual SBW is planned using 24 stages of ANL designed 2-cm centrifugal contactors which have been procured and are being installed in the Remote Analytical Laboratory shielded sample cell.

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