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DEVELOPMENT AND TESTING OF A COBALT DICARBOLLIDE BASED SOLVENT EXTRACTION PROCESS FOR THE SEPARATION OF CESIUM AND STRONTIUM FROM ACIDIC TANK WASTE

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ABSTRACT

A fission product solvent extraction technology for the simultaneous extraction of Cs and Sr from acidic tank waste has been developed as a collaborative effort of the Idaho National Engineering and Environmental Laboratory (INEEL) and the Khlopin Radium Institute in St. Petersburg, Russia. The process is being developed as a potential method for treating the current five million liter inventory of acidic tank waste stored at the INEEL. The fission product extraction process is based on an immiscible organic phase comprised of chlorinated cobalt dicarbollide (CCD, Cs extractant) and polyethylene glycol (PEG, Sr extractant)

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dissolved in a poly-fluorinated sulfone diluent. Batch contact experiments and preliminary flowsheet testing were used to define potential solvent composition and flowsheet configuration. This information was used to specify an initial flowsheet for countercurrent testing with simulated tank waste using a 3.3-cm diameter centrifugal contactor pilot plant at the INEEL. The initial extractant composition was 0.08 *M* CCD, 0.6 vol% PEG-400 in a phenyl trifluoromethyl sulfone (FS-13) diluent. Approximately 1.5 L of solvent was used (with continuous recycle) to treat 43 L of simulated tank waste during 75 hr of continuous operation. Greater than 99.992% of the Sr and 97.45% of the Cs were extracted from the simulated tank waste and recovered in the strip product. The matrix components Ba (>99.6%), Pb (99.8%), and Ca (10.6%) were also extracted from the simulated tank waste and recovered in the strip product. Less than 1% of the K, Na, Fe, Zr, and Mo were extracted from the tank waste simulant. Finally, none of the analytically determined waste components were observed to build up in the organic solvent.

INTRODUCTION

A cobalt dicarbollide based fission product solvent extraction process is being developed as a collaborative effort of the Idaho National Engineering and Environmental Laboratory (INEEL) and the Khlopin Radium Institute (KRI) in St. Petersburg, Russia for the simultaneous extraction, concentration, and recovery of Cs and Sr from acidic radioactive wastes. There are currently approximately 5 million L of acidic radioactive waste requiring treatment at the INEEL. The fission product extraction process is being developed as a potential treatment method for this waste since the predominant fission products contributing to the radioactivity of INEEL wastes are ^{137}Cs and ^{90}Sr.

Cobalt dicarbollide was first synthesized and characterized by Hawthorne and co-workers at the University of California in 1965 (1,2). Rais et al. first reported the applicability of cobalt dicarbollide in solvent extraction processes (3). The chlorinated cobalt dicarbollide (CCD) anion is a large hydrophobic species that exhibits the properties of a strong acid.

Chlorinated cobalt dicarbollide selectively extracts cesium through an uncommon cation-exchange mechanism with dissociation of the solvated species in the organic phase. Dipicrylamine, tetraphenylborate, polyiodide, and heteropolyacids extract cesium by the same mechanism, but only CCD is simultaneously a strong acid, like heteropolyacids, and extremely hydrophobic, like tetraphenylborate. This combination of properties enables CCD to extract cesium from acidic media and provides low solubility of CCD in aqueous solutions. Aliphatic and aromatic nitro-compounds, such as nitrobenzene, are the best diluents for CCD (3). However, nitrobenzene and nitroaromatic compounds are unacceptable diluents in the United States due to technical, environmental, health, and safety considerations.

The unsubstituted cobalt dicarbollide has a high resistance to acid hydrolysis, reductants, and radiation, as well as having excellent thermal stability (4). Halogenated derivatives of cobalt dicarbollide, especially CCD, exhibit even greater stability (5,6). Therefore, the hexachloro-derivative of cobalt dicarbollide has been used historically in development efforts associated with radioactive waste treatment.

Many mixtures incorporating CCD are of particular interest for the synergistic extraction of other components. Rais et al. observed a large synergistic effect on the extraction of micro-quantities of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} in the presence of polyethylene glycols (PEG) and CCD (4,7). Polyethylene glycol remains a neutral molecule when associated with ionic strontium, disrupting the hydration sphere of Sr^{2+} and creating a hydrophobic species that is transferred from the aqueous phase into a nitrobenzene phase containing the CCD anion (4). Experimentally derived data were used to validate theoretical results, which indicated the charged species PEG: Sr^{2+} and protonated polyethylene glycol (PEG: H^+) were competing counter-ions of the CCD anion in the organic phase (4).

The unique extraction properties of CCD/PEG mixtures allow the separation of Cs and Sr from acidic high activity wastes (HAW). However, the industrial use of this process was not feasible due to the lack of an appropriate diluent for CCD. Acceptable diluents for use in radioactive waste treatment must have high chemical and radiation stability, low aqueous solubility, low viscosity, and a density substantially different from the aqueous process solutions. Further, the extractants (CCD and PEG), and their solvated metal complexes, must be readily soluble in the diluent to prevent formation of an immiscible third phase or solid precipitates. Finally, the diluent should be nontoxic, inexpensive, and readily available or produced.

Identification of an optimal CCD diluent is complicated by the fact that CCD and its salts are highly polar compounds and are essentially insoluble in low-polar solvents like saturated and aromatic hydrocarbons. Consequently, nitrobenzene and its mixtures with carbon tetrachloride and saturated hydrocarbons were initially proposed as diluents (3). The high solubility of nitrobenzene in water and acidic solutions renders its use technically impractical under industrial conditions. Commercial scale processing of high level waste (HLW) in Russia was initiated after the development of *m*-nitro trifluoromethyl benzene (MNTFB), a diluent technically amenable to large-scale use (8). Approximately 800 m^3 of acidic HLW were processed using the

CCD/PEG/MNBTF system at the Mayak Production Association (Ozyorsk, Russia), and approximately 12 million Ci of Cs and Sr were recovered (9).

Collaborative efforts of the INEEL and KRI were initiated in 1994 to evaluate the applicability of the CCD/PEG process as applied to INEEL tank and dissolved calcine wastes. This early testing used nitroaromatic diluents and hydrazine as a strip reagent, both unacceptable in the United States for commercial use. Ongoing efforts have focused on development and demonstration of the Universal Extraction (UNEX) process to extract all the major radionuclides (^{137}Cs, ^{90}Sr, and the actinides) from INEEL wastes (10–13) simultaneously. The UNEX process incorporates CCD, PEG, and diphenylcarbamoylmethylphosphine oxide (CMPO) in an appropriate diluent to simultaneously extract the radioisotopes. The UNEX development efforts have recently culminated with the identification of phenyl trifluoromethyl sulfone (FS-13) as a suitable diluent for the UNEX process solvent. The FS-13 diluent, which exhibits excellent radiolytic and chemical stability, is innocuous, and provides ample solubility of CCD, PEG, and CMPO and their respective metal complexes. Finally, the physical properties of density and viscosity are suitable for countercurrent processing applications. With these properties, FS-13 is also a candidate as a diluent for a CCD/PEG fission product extraction process.

SCOPE AND OBJECTIVES

Currently, there are 5 million L of radioactive acidic waste stored at the INEEL. The residual tank wastes were a result of solvent wash and equipment decontamination activities associated with previous reprocessing activities. One of the current, economically appealing methodologies for the disposal of INEEL tank waste involves chemically separating and concentrating the radionuclide fraction into a relatively small volume for disposal as a remote handled waste at the Hanford Reservation or the Nevada Test Site. The residual bulk of the separated waste would be grouted and disposed of as contact-handled Transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP). This disposal alternative is contingent on obtaining a Waste Incidental to Reprocessing (WIR) determination for these tank wastes currently stored in the INEEL.

The scope of this project was to demonstrate the applicability of the fission product extraction process for Cs and Sr removal from simulated INEEL tank wastes. The significance of this effort is the initial development of a robust process, and the associated data, supporting the development of a treatment facility for the INEEL tank waste.

The purpose of the effort was to evaluate a viable process flowsheet based on CCD/PEG for the simultaneous removal of Cs and Sr from simulated INTEC tank waste during extended countercurrent flowsheet testing. To this end, the objectives of this program included:

Identify a precursory diluent and solvent composition (CCD and PEG) for testing,
Define a potential flowsheet and perform dynamic countercurrent testing,
Evaluate the ability to control PEG losses by addition to PEG to the strip feed solution,
Verify the potential to eliminate the solvent wash section used in previous flowsheets,
Evaluate the solvent loading and compositional changes with multiple solvent turnovers in the countercurrent flowsheet.

EXPERIMENTAL

Flowsheet testing at the INEEL was performed using 3.3-cm diameter centrifugal contactors. The contactor pilot plant consists of 26 available stages, reagent feed and receiving vessels, and feed pumps with associated controllers.

The 3.3-cm contactors were designed and fabricated in Moscow, Russia by the Research and Development Institute of Construction Technology (NIKIMT). Table 1 lists the operating specifications of the contactors. A total of 26 contactors were obtained from NIKIMT for testing purposes. Each stage can be operated independently allowing numerous combinations for changing flowsheet configurations.

Table 1. Operating Specifications for the 3.3 cm Contactors

Size	3.3-cm rotor diameter
Mixing chamber volume	22 mL
Separating chamber volume	32 mL
Overall dimensions	
Length	105 mm (4.13 in)
Width	132 mm (5.2 in)
Height	286 mm (11.26 in)
Volumetric capacity	25 L/hr (for the system TBP-kerosene/2 M HNO_3)
Mass	5 kg per stage (includes electric motor)
Motor	160–180 V, 50–60 Hz, 0.04 kW (Russian design)
RPM	2700 rpm (slightly adjustable)
Material of construction	12X18H10T stainless steel (Russian designation)
Inlet and outlet ports	3/8 in. o.d. tubing
Configuration	Single stage units, which can be configured as desired. Stages connected using U-tubes.

Solutions are fed into the contactors using valveless metering pumps with controllers. Surge suppression tubes, 4 in. long and 1 in. in diameter, were placed on the pump outlets to dampen solution flow fluctuations. Flow rates were adjusted by controlling pump speed using a 10-turn potentiometer or by manual adjustment of the piston stroke length and/or a combination of the two. Once the solutions enter the contactors, flow through the equipment is by gravity, i.e., the solutions in the contactors are not under pressure. The product solutions from the contactors drain by gravity to the product vessels. Solvent exiting the strip section was cooled prior to recycle to the extraction section by pumping the solvent through a cooling coil submerged in an ice water bath.

The tank waste stored at the INEEL will be concentrated from the current inventory of ~5 million L to ~4.2 million L using the High-Level Liquid Waste Evaporator. The expected composition of select constituents in the evaporated waste is indicated in Table 2. The simulated waste used in this project was prepared with the appropriate chemicals to approximate the anticipated composition of the actual waste (less the radionuclides) indicated in Table 2. Approximately 40 L of the simulated waste were prepared for the development efforts at the INEEL, including the countercurrent flowsheet testing. Approximately 39 L of simulated waste was diluted by 20 vol% with water to a final volume of 48.75 L for use as feed in the flowsheet test. The aqueous feed was diluted to reduce the acid and metals concentration, thus enhancing the extraction of Cs and Sr (vide infra). The concentration of stable Cs, Sr, and Eu (actinide surrogate) in the simulated waste was several orders of magnitude higher than that in the actual waste. The increased composition of these elements was

Table 2. Tank Waste and Simulant Composition

Component (*M*)	Composition	Component	Composition
Acid	1.96[a]	Na (*M*)	1.59
Al	0.61	NO_3 (*M*)	5.64
Ba	6.5×10^{-5}	Zr (*M*)	0.014
Ca	0.060	Radionuclides	
Cs	8.9×10^{-6}	^{137}Cs (Ci/m^3)	42
F	0.099	^{90}Sr (Ci/m^3)	38
Fe	0.023	Alpha (nCi/g)	576
Pb	1.1×10^{-3}	^{241}Am (nCi/g)	65
Hg	2.9×10^{-3}	^{238}Pu (nCi/g)	454
Mo	9.8×10^{-4}	^{239}Pu (nCi/g)	57
K	0.18	^{99}Tc (Ci/m^3)	0.016

[a] Acid concentration may be up to 50% higher depending on the tank farm management scenario.

necessary to facilitate inductively coupled plasma emission spectroscopy (ICP) and atomic absorption (AA) analyses of the process samples.

RESULTS AND DISCUSSION

Preliminary Experimental Efforts

Specialists at the KRI have many years of experience with the development and industrial application of the fission product extraction process based on earlier diluents such as nitrobenzene and *m*-nitro trifluoromethyl benzene (MNTFB, $m\text{-}CF_3C_6H_4NO_2$). A goal of this project was to evaluate a new class of diluents, polyfluoro-substituted sulfones, as applied to the fission product extraction process. The significant advantages of these compounds include their low toxicity and high radiation and chemical stability relative to previous diluents; however, these types of compounds are at present not available from commercial sources. The KRI expertise also includes the synthesis and purification of numerous sulfone derivatives. Consequently, KRI collaborated to perform an initial experimental work of comparing properties of several different diluents and propose potential flowsheets based on batch contact information. Ultimately, KRI also provided the necessary quantity of the selected diluent for experimental work at the INEEL.

Two different sulfone diluents were evaluated: phenyl trifluoromethyl sulfone (FS-13, $C_6H_5SO_2CF_3$) and phenyl-1,1,2,2-tetrafluoroethyl sulfone (FS-24, $C_6H_5SO_2CF_2CF_2H$). Several properties of these two diluents are indicated in Table 3. The properties of MNTFB, a diluent used in Russia on the industrial scale, are also indicated in Table 3 for comparison. Note that FS-24 exhibits a slightly higher Cs distribution coefficient ($D_{Cs} \equiv [Cs]_{Organic}/[Cs]_{Aqueous}$ at equilibrium) and lower solubility in 3 *M* HNO_3, but also has a correspondingly higher viscosity than FS-13.

Table 3. Experimentally Determined Physical Properties of Several Diluents

Diluent	Density (20°C)	Viscosity (mPa sec)	Solubility in 3 *M* HNO_3 (g/L)	D_{Cs} (from 3 *M* HNO_3 with 0.06 *M* CCD Solution)
$m\text{-}CF_3C_6H_4NO_2$ (MNTFB)	1.44	3.0	1.23	16
$C_6H_5SO_2CF_3$ (FS-13)	1.41	3.6	0.6	3.8
$C_6H_5SO_2CF_2CF_2H$ (FS-24)	1.47	9	<0.5	4.9

Table 4. Cs and Sr Distributions from Simulated INEEL Tank Waste

Extractant Composition	D_{Sr}	D_{Cs}
0.08 *M* CCD, 0.6 vol% PEG-400 in FS-13	2.3	1.5
0.08 *M* CCD, 0.6 vol% PEG-400 in FS-24	1.7	2.3

The distribution coefficients of Cs and Sr were determined by performing batch contacts with simulated INEEL tank waste solution using CCD and PEG-400 to further elucidate the selection of an appropriate sulfone diluent. The results of these experiments are indicated in Table 4. The measured distribution coefficients are high enough for the acceptable recovery of Cs and Sr in the extraction section of a countercurrent flowsheet. The recovery of Sr from the tank waste is considered to be more difficult (relative to Cs), and the higher Sr distribution along with the dramatically lower viscosity associated with the FS-13 diluent is desirable. For these reasons, the extractant based on CCD and PEG-400 in the FS-13 diluent was that of choice.

Several potential stripping reagents were also evaluated by measurement of Cs and Sr batch distribution coefficients. The stripping reagents evaluated were ammonium nitrate (NH_4NO_3), methylamine (CH_3NH_2), guanidine nitrate ($CH_5N_3 \cdot HNO_3$), and dimethylformamide ($HCON(CH_3)_2$), each in a nitric acid matrix. The experimentally measured stripping distribution coefficients are indicated in Table 5. Ammonium nitrate is the least favored stripping reagent due to the rather high distribution coefficients obtained (strip distributions should be as small as possible), particularly for Sr. Guanidine nitrate and dimethylformamide are both very effective at stripping Sr and Cs from the organic phase; however, these compounds may be difficult to wash out of the organic phase. Methylamine in nitric acid is the most interesting of the strip reagents studied

Table 5. Cs and Sr Stripping Distributions from 0.1 *M* CCD and 1 vol% PEG in FS-13

Strip Reagent	Concentration (*M*)	HNO_3 Concentration (*M*)	D_{Cs}	D_{Sr}
NH_4NO_3	1.0	4.0	0.24	0.18
	2.0	6.0	0.037	0.034
CH_3NH_2	3.0	4.5	0.053	0.033
	3.5	3.5	0.048	0.019
$CH_5N_3 \cdot HNO_3$	1.0	1.0	0.22	0.064
$HCON(CH_3)_2$	1.5	2.0	0.037	0.049
	1.5	4.0	0.012	0.018

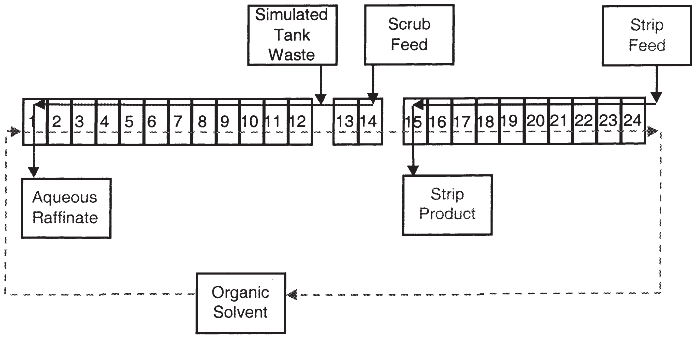
since it allows a high degree of concentration of Sr and Cs in the strip solution, based on the low distribution coefficients for both these elements. Further, methylamine should be easily washed from the organic phase with nitric acid solutions. On the basis of this data, methylamine in nitric acid was chosen as the stripping reagent for use in countercurrent flowsheet tests at KRI. It should be noted that methylamine, as well as dimethylformamide, have a serious drawback due to the safety concern that hydrazine nitrate is formed from the compounds in the presence of nitric acid in the aqueous strip solution.

Dynamic Flowsheet Testing at KRI

On the basis of the results of the laboratory experiments and modeling calculations, a conceptual flowsheet was developed for countercurrent testing. The developed flowsheet fundamentally differs from predecessors in that the solvent wash section for extractant regeneration could be completely eliminated. Such a dramatic change would substantially simplify the flowsheet and eliminate the solvent wash secondary waste stream. The ramifications of this change include alteration of the organic extractant composition and an increase in the necessary number of stages in the extraction section to compensate for carryover of entrained or dissolved strip reagent recycled to the extraction section in the organic phase. The proposed flowsheet developed in accord with these considerations was tested at KRI's Gatchina Facility near St. Petersburg, Russia in June 2000. The countercurrent flowsheet tested at Gatchina is schematically shown in Fig. 1.

The flowsheet shown in Fig. 1 used 0.13 *M* CCD as the Cs extractant and 0.3 vol% Slovafol-909 (Czech product, which is an analog of PEG-400) in FS-13 diluent. The increased concentration of CCD and Slovafol (relative to the previous development efforts) was thought necessary to enhance the Cs and Sr extraction in the absence of a solvent wash section for the removal of methylamine from the organic phase prior to recycle of the solvent to the extraction section. Slovafol-909 was substituted for PEG-400 in the organic extractant due to the lower solubility of Slovafol in the aqueous process streams. Additionally, 3 g/L oxalic acid was added to the simulated feed and scrub solutions in an attempt to reduce the amount of co-extracted Fe and Zr that would be carried over into the strip product phase. The analytical results of this flowsheet test are summarized in Table 6.

The results in Table 6 indicate 99.7% of the Cs and 99.98% of the Sr in the simulated waste feed were extracted and quantitatively recovered in the strip product. Virtually all of the Ba and Pb were also extracted from the feed and recovered in the strip product. The extraction of Ba and Pb was anticipated since these elements typically compete with and follow the Sr in the process. The



Stream	Composition	Flowrate (mL/min)
Simulated INEEL Tank Waste	Refer to Table 2 (undiluted) 3 g/L $H_2C_2O_4$ added	2.1
Organic Solvent	0.13 M CCD, 3 vol. % Slovafol-909 in FS-13	3.2
Scrub Feed	0.1 M HNO_3, 3 g/L $H_2C_2O_4$	0.80
Strip Feed	3 M methylamine nitrate, 3 M HNO_3	0.45
Raffinate	- - -	2.9
Strip Product	- - -	0.45

Figure 1. Fission product extraction process flowsheet tested by KRI at Gatchina, Russia.

extraction and recovery of the other reported elements is less clear due to the rather poor material balances obtained, i.e., the material balance for Na is ~132% (% in raffinate + % in strip). Due to the dynamic nature of the test and the use of ICP and AA analytical methods, acceptable material balances are typically in the ±10% range. The data in Table 6 indicate that up to 13.4% of the Ca, 6.6% of the Na, 2.6% of the Ni, and 1.9% of the Cd (relative to their concentration in feed) were extracted and exited in the strip product. Less than 1% of the other metals examined were extracted. The CCD potentially extracts Na and K as competing ions with Cs in the process. Considering the bulk concentration of Na relative to Cs in the simulated waste, the selectivity from Cs was quite high. Data were not available regarding the behavior of K in this particular test. The KRI scientists also indicated, based on this testing, that the addition of oxalic acid to the tank waste and scrub feed solutions would be unnecessary in future flowsheet tests.

Dynamic Flowsheet Testing at INEEL

Recently, flowsheet testing of the related UNEX process was performed and results from these tests provided valuable insight for an INEEL dynamic test

Table 6. Distribution of Feed Components in the KRI Dynamic Test (% of Content in Feed)

	Component							
Stream	Cs	Sr	Ba	Pb	Ca	Na	Al	Cr
Raffinate	0.3	0.02	<0.1	<0.001	111	127	115	115
Strip product	104	107	103	127	13.4	6.6	0.03	0.4
	Cd	Fe	Mo	Mn	Ni	Pd	Zr	
Raffinate	123	121	111	121	117	114	110	
Strip product	1.9	1.0	0.2	0.8	2.6	1.1	0.03	

of the fission product extraction process (14). In collaboration with the KRI specialists, several necessary flowsheet parameters were defined and tested, largely due to the preliminary results of the UNEX testing. A joint decision was made to evaluate an extractant composition of 0.08 *M* CCD and 0.6 vol% PEG-400 in FS-13 for the INEEL dynamic test. Computer modeling for the number of available contactor stages indicated that distribution coefficients of $D_{\mathrm{Cs}} \geq 1.5$ and $D_{\mathrm{Sr}} \geq 2.2$ in the extraction section were necessary for high recovery (>99.9%) of cesium and strontium. Additionally, distribution coefficients of D_{Cs} and $D_{\mathrm{Sr}} \leq 0.2$ in the strip section were required for effective stripping of these elements. Much of the previous data, including that from the UNEX testing, indicated that the above-prescribed solvent composition would likely be capable of achieving the necessary distribution coefficients. The other conditions discussed included use of a 0.3 *M* HNO_3 solution in the scrub section, and a strip solution consisting of 100 g/L (0.56 *M*) guanidine carbonate (GC, $CH_5N_3 \cdot HCO_3$) and 20 g/L (0.05 *M*) diethylenetriaminepentaacetic acid (DTPA, $C_{14}H_{23}N_3O_{10}$). The DTPA was deemed necessary in the strip solution to prevent the formation of insoluble carbonates. Several of these changes, particularly in the choice of suitable strip reagents, were a substantial departure from the KRI flowsheet tested previously, and were predicated on the technical data from the more recent UNEX testing at the INEEL.

Several batch contact experiments were performed using ^{137}Cs and ^{85}Sr traced feeds to determine the batch distribution coefficients under the proposed conditions of extraction and stripping for the INEEL dynamic flowsheet. These batch contact tests were performed with two different feed solutions. The first feed solution was the simulated waste + 20 vol% of 0.3 *M* HNO_3 (scrub solution) to emulate the scrub dilution of the feed in the extraction section. The second feed solution was simulated waste +20 vol% of 0.3 *M* HNO_3 (scrub solution) + 20 vol% H_2O (total dilution of 40 vol%); the water dilution in this feed was intended to observe the effect of decreasing (diluting) the acid and metals concentration on Cs and Sr distribution coefficients. The feed solutions were spiked with trace quantities of the radionuclides ^{137}Cs and ^{85}Sr to facilitate analysis by gamma spectroscopy. The organic extractant (0.08 *M* CCD, 0.6 vol% PEG-400 in FS-13) was contacted three consecutive times with fresh aliquots of the respective feed solutions (contacts E1, E2, E3) and the extraction distribution coefficients of Cs and Sr were measured after each contact. The organic from the contacts with the feed solutions (loaded with the extracted species) were subsequently contacted two consecutive times with fresh strip solution (contacts St1 and St2) and the strip distribution measured for each contact. The results of these laboratory tests are indicated in Table 7.

The data in Table 7 indicate that the 20 vol% scrub dilution of the simulated waste does not provide sufficiently high Cs and Sr distribution coefficients for effective removal of the these components in the extraction section. The additional 20 vol% water dilution (for a total feed dilution of 40 vol%) does produce marginally acceptable distribution coefficients for Cs and Sr recovery. In all cases, the distribution coefficients in the strip contacts were very low and therefore acceptable. The St2 stripping distributions are indicated to be much less than one since all detectable quantities of Cs and Sr were removed from the organic phase in the second strip contact.

There was a concern that the reported extraction distributions were artificially high for the feed solutions used to generate the data shown in Table 7. Millimolar quantities of stable Cs and Sr had not been added to the simulated waste solution prior to performing the batch contacts (~0.001 *M* concentration of stable Cs and Sr were to be added to the feed to facilitate analysis by ICP for Sr and AA for Cs). The small volume of extractant used in the batch contact tests had been washed with K_2CO_3 and HNO_3 solutions (to remove impurities from

Table 7. Batch Distribution Coefficients with 0.08 *M* CCD, 0.6 vol% PEG-400 in FS-13

Contact	E1	E2	E3	St1	St2
Feed #1: simulated INEEL tank waste + 20 vol% HNO_3					
D_{Cs}	0.66	0.93	0.63	0.22	$\ll 1$
D_{Sr}	1.47	1.42	1.05	0.02	$\ll 1$
Feed # 2: simulated INEEL tank waste + 20 vol% HNO_3 + 20 vol% H_2O					
D_{Cs}	1.36	1.19	1.18	0.20	$\ll 1$
D_{Sr}	2.73	2.17	1.81	$\ll 1$	$\ll 1$

the CCD) after the PEG-400 had been added. These washes should have been performed prior to preparing the solvent for the batch contacts to prevent washing PEG out of the extractant. Consequently, there was also some concern that the PEG-400 concentration in the organic extract used in the batch contacts was lower than the required 0.6 vol% due to the wash procedures used to prepare the solvent for the batch contacts. Due to the uncertainties in the batch distribution data arising from these concerns, the batch contact experiments were partially repeated. The required 0.001 *M* Cs and 0.001 *M* Sr were added to the simulated tank waste prior to dilution with scrub and/or water for the repeat experiments. A small aliquot of stock (0.16 *M*) CCD solution was washed with K_2CO_3 and HNO_3 prior to preparing the final extractant used in the batch contacts. In these experiments, a single extraction contact was performed with the freshly prepared extractant and each waste feed solution. The results of these experiments are presented in Table 8.

The extraction distribution coefficients shown in Table 8 indicate that a 40 vol% dilution of the simulated tank waste feed solution is required to obtain high enough Cs distribution coefficients for effective Cs recovery for the extractant composition identified for the dynamic test. Note that alteration of the extractant composition, likely increasing the CCD concentration and perhaps reducing the PEG-400 concentration, could potentially produce the necessary increase in the Cs extraction distributions. Such a study is a rather detailed effort and the necessary time and resources were unavailable to evaluate such alterations in solvent composition. Optimization of the extractant composition is recommended for future efforts. Consequently, a 40 vol% dilution of the feed was necessary for the dynamic testing at the INEEL. There are two potential methods to achieve a 40 vol% dilution of the waste. One approach is to simply increase (double) the scrub solution feed flow rate, which already accounts for a 20 vol% dilution in the proposed dynamic test, resulting in an overall dilution of 40 vol%. While this approach is operationally quite simple, it would result in a slightly different (higher) acidity than was tested in the above batch contacts. Alternatively, the feed could be diluted by 20 vol% with water and the additional 20% dilution would

Table 8. Repeated Distribution Coefficients for 0.08 *M* CCD, 0.6 vol% PEG-400 in FS-13

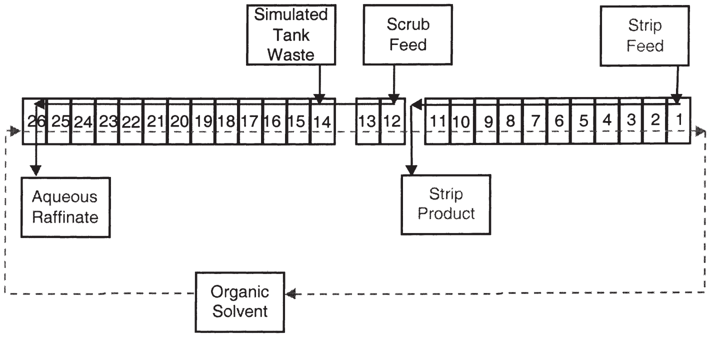
	Feed #1: Simulated INEEL Tank Waste + 20 vol% HNO_3	Feed # 2: Simulated INEEL Tank Waste + 20 vol% HNO_3 + 20 vol% H_2O
D_{Cs}	0.85	1.4
D_{Sr}	3.8	6.3

occur with the scrub solution in the flowsheet, essentially the conditions used to determine the above batch distribution coefficients. In order to prepare the necessary volume of simulated tank waste required to operate the dynamic flowsheet test for 80 hr (~50 L), the latter approach was taken.

The fundamental purpose of this effort was to validate that the CCD based fission product extraction process, with numerous modifications relative to previous tests, is a viable method to selectively partition and recover Cs and Sr from the tank waste under dynamic flowsheet conditions. To this end, experience, laboratory data and modeling results culminated in a countercurrent flowsheet proposed for testing at the INEEL as shown in Fig. 2.

The dynamic test was operated continuously for 74.9 hr and processed a total of 43 L of (20 vol% diluted) simulated tank waste using 1.57 L of organic solvent. On the basis of the 74.9 hr duration, 1.57 L of solvent, and an average organic flow rate of 1.1 L/hr, the solvent was estimated to recycle through the system 52 times.

It is of interest to note that the concentration of the organic phase could potentially vary due to solubility of the PEG-400 and sulfone in the aqueous process solutions. Solubility of the sulfone diluent is estimated to be 200 mg/L in the raffinate stream and 120 mg/L in the GC strip solution. Samples of the initial organic solvent, the solvent after 45 hr of operation, and the end of the test were



Stream	Composition	Flowrate (mL/min)
Simulated INEEL Tank Waste	Diluted 20 vol. % with water	10
Organic Solvent	0.08 M CCD, 0.6 vol. % PEG-400 in FS-13	15.5
Scrub Feed	0.3 M HNO_3	2.5
Strip Feed	100 g/L Guanidine Carbonate 20 g/L DTPA	8.7
Raffinate	- - -	12.5
Strip Product	- - -	8.7

Figure 2. Fission product extraction process flowsheet tested at the INEEL.

Table 9. CCD Analyses in the Organic Solvent from the Dynamic Test

		Organic Phase CCD Concentration (*M*)	
Method	Initial	45 hr	Conclusion
ICP	0.080	0.081	0.081
XRF	0.081	—	0.082

taken for CCD analysis. The resulting concentrations are indicated in Table 9. The CCD concentration was determined independently by: (1) X-ray fluorescence (XRF) for Co concentration, and (2) ICP analysis of Co and B following destructive digestion. The results indicate an initial concentration of 0.08 *M* CCD that remained constant during the experiment. Although there is currently no available analytical method to determine sulfone concentration, the constant CCD concentration implies sulfone losses were minimal since the CCD (virtually insoluble) concentration would increase with a corresponding decrease (loss) of diluent.

One of the objectives of this test was to determine if losses of PEG-400 from the organic solvent (due to solubility of PEG) could be controlled by the addition of PEG to the process strip solution. The solubility of PEG-400 is estimated to be 50 mg/L (0.005 vol%) in the raffinate stream and 250 mg/L (0.025 vol%) in the GC strip solution. The solubility losses can be partially controlled by the use of a different, less soluble PEG, such as Slovafol-909. Analytical methods are currently unavailable at the INEEL to accurately estimate PEG-400 concentration in the organic phase. Nuclear magnetic resonance (NMR) analysis was explored with inconclusive results. To control PEG losses from the solvent, 600 mg/L (0.06 vol%) PEG-400 was added to the strip feed solution beginning at 17 hr during the test. A material balance was used to estimate the final PEG-400 concentration in the organic phase. On the basis of the solubility in the raffinate and strip streams, the average strip and raffinate flow rates (vide infra), and the addition of 600 mg/L PEG-400 to the strip feed during the test, the final PEG-400 concentration was estimated as 1.28 vol%. Thus, the PEG-400 concentration in the organic phase was potentially double the target concentration. In retrospect, the addition of 300 g/L PEG-400 to the strip feed would have likely been sufficient to account for solubility losses and maintain the organic phase concentration of 0.6 vol% in the solvent for the duration of the test. Future efforts will be required to quantify the solubility of PEG-400 (and related PEGs) and develop standard analytical procedures to determine PEG concentrations, allowing better estimates of any necessary PEG addition to the strip feed solution for controlling PEG concentration in the solvent.

The only physical problem encountered during the test was slight flooding of the strip product (carryover of organic solvent in the aqueous strip product). In order to minimize losses of organic to the strip product, a 250 mL gravity settling vessel was placed between the strip product contactor and receiving vessel. Much of the organic settled out in this vessel and the accumulation could be measured over many hours of operation. On the basis of these measurements, the strip product was estimated to contain ~0.3 vol% organic, or was 0.3% flooded. The flooding is postulated to be associated with the design of the centrifugal contactors. As opposed to completely redesigning and reengineering the contactor stages, the flooding could likely be eliminated by increasing the residence time of the solutions in the separating zone of the current contactors. This could be most simply accomplished by decreasing the flow rates of the organic and aqueous phases. Alternatively, it may be possible to use a single contactor stage (placed as the final or product stage in the strip section) as a centrifugal separator by diverting the organic flow around that stage and allowing only the (flooded) aqueous phase to enter. These methodologies to eliminate flooding should be explored in continued development efforts.

Analysis of the process samples taken early in the run indicted Cs removals (relative to the feed) of 98.4% and 99.3% at 15 and 25 hr, respectively. The Sr removal was >99.99% for both of these samples. Since the Cs removal efficiency was lower than anticipated, the flow rate of the organic solvent was increased approximately to 50% (from 14.8 to 22.3 mL/min) in an attempt to increase the Cs removal efficiency. To ensure Cs stripping remained acceptable due to the increased organic flow, the strip feed flow rates were increased by ~40% (from 8.5 to 14.1 mL/min). These flow rates were increased at approximately 39 hr into the run, and were maintained for the duration of the test. The target flow rates, actual flow rates, and O/A phase ratios during the dynamic test are indicated in Table 10. Note that the actual flow rates of the organic solvent and the strip feed

Table 10. Target and Actual Flow Rates in the INEEL Dynamic Tests

	Flow Rate (mL/min)			O/A Ratio		
Section	Phase	Target	Actual	Target	Actual	Total Flow (mL/min)
All	Organic	15.5	18.3	—	—	—
Extraction	Aqueous	12.5	11.6	1.24	1.58	29.9
Scrub	Aqueous	2.5	2.4	6.20	7.56	20.7
Strip	Aqueous	8.7	11.1	1.78	1.65	28.4

are time weighted average for the entire test and reflect the increased flows mentioned earlier, while the target values are those for the initial startup of the test. Despite the increased solvent and strip flow rates during the test, the actual and target flow rates and O/A ratios indicate reasonable agreement. The flow rates in Table 10 were used to calculate the overall removal efficiencies and material balances based on the composite product samples.

The key data used to evaluate the overall flowsheet performance are from the composite product streams. Samples of the composite raffinate and the strip product were collected at the conclusion of the test and represent the cumulative, average behavior of the key components for the duration of the test. The composition in the various streams, removal efficiencies, material balance data, and other pertinent information is summarized in Table 11.

The data in Table 11 reflect the rather poor removal efficiency of 97.45% for Cs from the simulated waste solution. It was anticipated that >99.9% of the Cs would be extracted from the simulated waste during the dynamic test. The reason for the low Cs recovery is unclear at this point and warrants future study. The most plausible explanation for the low Cs removal efficiency is a low CCD concentration relative to the amount of PEG in the organic solvent. Due to competition between the Cs and K with the PEG complexes of Sr, Ba, Pb, and Ca for the available CCD extractant, the PEG complexes consume much of the extractant and result in suppressed Cs extraction.

While the Cs extraction efficiency was somewhat lower than expected, Table 11 indicates that the extracted Cs was stripped quantitatively by the GC solution. The overall Cs material balance is marginal at 108.2%, with much of the discrepancy likely associated with the analysis of the strip product sample. Analysis of the organic phase indicated Cs was not present, further indicating excellent Cs stripping was achieved.

The removal and stripping efficiency of Sr was excellent with >99.992% of the strontium extracted and recovered in the strip product stream. Detectable quantities of Sr were not found in the organic phase, supporting the excellent stripping efficiency. The overall material balance was very good at 101.3%.

Barium and Pb were also efficiently extracted by the solvent and recovered in the strip product. This is not surprising, since these matrix components tend to behave very similar to Sr in the process flowsheet. Calcium is chemically similar to Sr and could potentially follow Sr through the flowsheet, some of the Ca, 10.1%, was also extracted and recovered in the strip product.

Approximately 28% of the K was extracted and recovered in the process flowsheet. A small amount of Na, 2.8%, was also extracted and recovered. Due to their chemical similarities, these two matrix components would tend to follow Cs in the flowsheet. On the basis of relative concentrations of Na, K, and Cs in the feed, the excellent selectivity of the process solvent for Cs over Na and K is apparent.

Table 11. Components and Parameters in the Composite Product Samples

Component	Simulated Tank Waste	Aqueous Raffinate	Strip Product	Organic Solvent[a]	Material Balance[b]
Cs (mg/L)	105	2.20	95.5	<0.05	—
% per stream	—	2.55	105.7	<0.09	108.2
Sr (mg/L)	67.9	<0.004	59.2	<0.06	—
% per stream	—	<0.008	101.3	<0.2	101.3
Ba (mg/L)	6.74	<0.02	5.96	0.25	—
% per stream	—	<0.38	102.8	7.01	103.1
Pb (mg/L)	186	0.26	164	<1	—
% per stream	—	0.23	102.1	<1	102.3
K (mg/L)	6140	3650	1500	107	—
% per stream	—	72.4	28.4	3.35	100.8
Na (mg/L)	33,400	25,400	800	174	—
% per stream	—	92.7	2.78	v	95.4
Ca (mg/L)	1760	1220	152	174	—
% per stream	—	84.8	10.1	0.72	94.9
Fe (mg/L)	1050	831	6.18	7.73	—
% per stream	—	96.3	0.68	1.41	97.0
Zr (mg/L)	1040	819	3.24	1.48	—
% per stream	—	95.8	0.36	0.27	96.1
Mo (mg/L)	50.0	41.4	<0.03	<0.1	—
% per stream	—	100.8	<0.06	<0.5	100.9
Eu (mg/L)	784	609	0.09	<0.2	—
% per stream	—	94.6	0.014	<0.04	94.6
Final volume (L)	—	52.9	50.2	—	—
Flow rate (mL/min)	9.5	11.6	11.1	18.3	—

[a] Organic composition was not used in the material balance due to recycle.

[b] Material balance calculated as a percentage of material in/material out.

Other key data pertinent to the evaluation of the overall process performance are the stagewise distribution coefficients obtained for the extracted species. At the conclusion of the test, the contactors and feed pumps are shut down simultaneously; leaving the two phases in each stage at their respective equilibrium concentrations. The stages can then be drained, and the phases separated and sampled to determine stagewise distribution coefficients and evaluate concentration profiles through the system. Additionally, equal volume samples of the organic and aqueous phases from each stage can be spiked with trace quantities of radionuclides (in this case, ^{137}Cs and ^{85}Sr). Thus, the distribution coefficients can be determined radiometrically for those stages where the concentrations of stable Cs and Sr are below the analytical detection limits for ICP or AA analyses. The measured stagewise distribution coefficients, including the distributions determined radiometrically from ^{137}Cs and ^{85}Sr, are listed in Table 12.

The Cs distributions in the strip section (Stages 1–11) were very consistent at 0.3 to 0.4 for both stable and radioactive Cs. The distribution data in the strip section are consistent with those obtained in the batch contacts (Table 7) and are sufficiently low for the number of stages and flow rates to insure complete Cs stripping from the organic phase. The distribution coefficients for stable Cs on Stages 1–5 are meaningless since the Cs concentration in one or both of the phases were below analytical detection limits; this trend is observed for many of the analyzed species in the different stages. The Cs distributions measured on the scrub stages (12 and 13) were sufficiently high to insure that the Cs was not scrubbed from the organic phase and recycled to the extraction section. The unanticipated low Cs removal efficiency during the test is related to the low Cs distribution coefficients measured in the extraction section. The Cs extraction distribution coefficients were consistently lower than the anticipated value of ~1.4 obtained in the batch contacts (refer to Tables 7 and 8). The Cs distribution on the raffinate stage was ~0.2, and continuously increased toward the feed stage to a value of ~1. The measured extraction stage distributions are consistent with overall Cs removal efficiency of ~97%.

The Sr distributions in the strip section (stages 1–11) for both the stable and radioactive Sr indicate very effective Sr stripping. The distributions based on stable Sr were meaningless for Stages 1–9 since the Sr concentration in the organic phase was at or below the analytical detection limits, indicating Sr stripping occurred on the first two strip stages (11 and 10). The strip distributions based on the ^{85}Sr spiked samples exemplify effective Sr removal; the less than values reflect the fact that ^{85}Sr was consistently below detection limits in the organic phase. The stripping distribution data are consistent with those obtained in the batch contacts (Table 7) and indicate an excessive number of strip stages to insure that Sr was removed from the organic phase. The Sr distributions measured on the scrub stages (12 and 13) were extremely high and ensure that the Sr was

Table 12. Stagewise Distribution Coefficients at Shutdown of the INEEL Dynamic Test

		Component							
Flowsheet Section	Stage #	Cs	^{137}Cs	Sr	^{85}Sr	Pb	K	Fe	Zr
Strip	1	—	0.38	—	<0.0003	—	7.9	27	>6.1
	2	—	0.36	—	<0.0002	—	18	17	4.98
	3	<0.25	0.36	—	<0.0003	—	4.1	27	>5.2
	4	<0.11	0.37	—	<0.0003	—	2.7	27	5.0
	5	0.07	0.40	—	<0.0003	—	1.7	24	>5.1
	6	0.21	0.35	—	<0.0002	<4.2	1.1	29	>5.1
	7	0.28	0.35	—	<0.0003	—	0.76	26	<4.6
	8	0.30	0.38	—	<0.0003	—	0.61	13	—
	9	0.29	0.31	—	<0.0003	—	0.46	15	<2.4
	10	0.30	0.36	0.33	<0.0003	<0.36	0.38	3.4	<0.7
	11	0.30	0.33	0.005	<0.0003	<0.008	0.33	1.6	0.20
Scrub	12	36	14	2200	1000	>870	7.2	30	1.7
	13	21	8.6	700	460	>880	4.4	5.6	0.24
Extraction	14	1.2	0.81	6.0	6.0	54	0.18	0.02	0.003
	15	0.64	0.67	5.9	5.5	8.7	0.18	0.02	0.003
	16	0.60	0.71	7.6	5.6	<4.7	0.15	0.02	0.003
	17	0.59	0.67	24	5.8	<3.8	0.16	0.02	0.002
	18	0.56	0.73	—	6.0	<4.3	0.17	0.02	0.003
	19	0.54	0.65	—	5.8	<4.6	0.15	0.02	0.003
	20	0.49	0.66	—	5.6	<3.2	0.15	0.02	0.003
	21	0.49	0.56	—	5.5	<3.4	0.15	0.02	0.003
	22	0.44	0.61	—	5.4	<3.9	0.15	0.02	0.004
	23	0.41	0.35	—	5.0	<4.7	0.16	0.02	0.004
	24	0.39	0.50	—	5.2	<4.0	0.16	0.02	0.004
	25	0.28	0.34	—	4.9	<4.0	0.16	0.02	0.006
	26	0.15	0.20	—	3.8	<3.8	0.14	0.02	0.008

not scrubbed from the organic phase and recycled to the extraction section. The excellent Sr removal efficiency observed in the test is consistent with the large Sr distribution coefficients measured in the extraction section. All of the Sr removal occurred on the first four extraction stages (14–17) and the ^{85}Sr distributions are consistent with the batch data (Table 7).

The distribution data measured for the other elements show consistent trends with their respective extraction and stripping, and parallels the Cs and Sr distributions. It is interesting to note that the scrub distribution coefficients for Pb, K, and Fe indicate that these bulk matrix components were not effectively removed from the organic phase in the scrub section. The Zr distribution coefficient of 0.24 on Stage 13 indicates the occurrence of some scrubbing of Zr. The only other species potentially removed in the scrub section were Na and Ca; the distribution data were not requested for these components. The only utility of the scrub section may be the removal of acid from the solvent (to prevent foaming from carbonate neutralization in the strip solution) and/or the dilution of the waste to enhance Sr and Cs recoveries. This observation suggests it may be possible to modify or eliminate the scrub section, further simplifying the flowsheet and waste volumes. Such an assumption must be validated in future experiments.

The increase in Cs and Sr distributions from the product end of the cascade to the feed point is of particular interest. The primary purpose of a solvent wash section, following the strip section, in the process flowsheet would be to remove entrained or soluble strip solution (GC/DTPA) from the organic prior to solvent recycle to the extraction section. The carryover of residual strip solution with the recycled organic could potentially impede the extraction of target species in the extraction section and reduce the overall extraction efficiency of target components. Unfortunately, a solvent wash section also requires input of additional wash solutions (HNO_3 in this process), which increases secondary waste volumes generated and adds additional complexity to the process. The fundamental concept used in eliminating solvent washing in the flowsheet tested was to perform solvent wash in the first few extraction stages. Thus, the Cs and Sr distribution coefficients would be suppressed in the early stages (the raffinate end of the cascade where the organic is introduced) due to the recycle of guanidine, then approach an equilibrium value after several of the extraction stages. The data for the first two extraction stages (Stages 25 and 26) indicate suppressed Cs distribution coefficients, which then approach an equilibrium value of 0.4–0.6 in the remainder of the extraction section. Thus, two extraction stages appear to provide sufficient washing of residual strip components from the organic phase. The ^{137}Cs and ^{85}Sr distribution data also strongly support this conclusion.

Samples of the product solutions (strip and raffinate) and the organic solvent were taken every hour for the first six hours, and at 10-hr intervals thereafter until the conclusion of the test. These time-wise samples were all

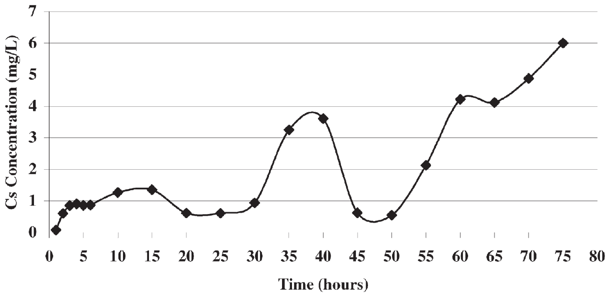


Figure 3. Time-wise concentration of Cs in the raffinate.

analyzed for Cs and Sr. The Cs concentration in the raffinate as a function of time is of particular interest, and is as shown in Fig. 3. Note that the rapid increase in Cs concentration to approximately 1 mg/L early in the test indicate steady state operation was achieved by approximately 3 hr into the test. The interesting features of the data are the cyclic behavior observed during the course of the run and the general increase in the Cs concentration toward the end of the test. Cesium extraction (the Cs distribution coefficient) is temperature dependent, increasing as the temperature decreases. Thus, at higher temperatures, the extraction efficiency would tend to decrease. The cyclic behavior tends to follow ambient temperature in the lab, which ranged from ~18 to 32°C, during the course of the experiment. Consequently, the Cs concentration in the raffinate samples tends to be higher during the hotter parts of the day. Time zero corresponds to 7 a.m., and the higher Cs concentrations observed at 15, 40, and 65 hr coincide with warmer ambient temperature during afternoon and early evenings. Note that the flow rate of the organic solvent was increased immediately after the 40 hr sample was taken and that the Cs concentration generally increased with the duration of the test. Operationally, temperature

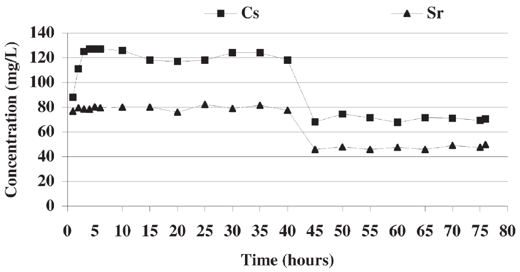


Figure 4. Time-wise concentration of Cs and Sr in the strip product.

dependence poses no serious problem, provided the temperature dependence is understood, since the process solutions or even the individual contactors can be temperature controlled. The information in Fig. 3 tends to indicate that the increased organic flow was actually detrimental to Cs extraction efficiency. However, the data are inconclusive and it is uncertain whether the increase in Cs concentration would have continued or would have cycled to a lower value due to a reduction in ambient temperature. Further experimental work is required to quantify the temperature dependence of the Cs distribution coefficient and allow accurate predictions of extraction efficiency.

The Cs and Sr concentration in the strip product are shown as a function of time in Fig. 4. The rapid increase in initial Cs and Sr concentrations indicate that the strip section reached steady-state operation after less than 3 hr of operation. The concentration decrease after 40 hr reflects the increase in the strip feed and organic solvent flow rates immediately after taking the samples at 40 hr. Following the adjustment in flow rates, the strip section returned to steady state operation, which remained constant for the duration of the test.

CONCLUSIONS

The results of this testing indicates this CDC/PEG based fission product extraction process to be viable for the treatment of INEEL acidic tank waste. Laboratory data and preliminary dynamic testing at KRI were used to formulate a potential, preliminary flowsheet for time-wise extended dynamic testing at the INEEL in a 3.3-cm centrifugal contactor pilot plant with simulated tank waste. In the flowsheet tested, 97.5% of the Cs, $>$99.992% of the Sr, $>$99.6% of the Ba, and 99.8% of the Pb were extracted from the simulated tank waste and recovered in the strip product. Lesser amounts of the major, bulk species of Na, K, and Ca were also extracted and recovered in the dynamic test. Minor ($<$1%) of the Fe, Zr, Mo, and Hg followed the fission product surrogates to the final strip product solution. Extraction of Eu, used as an actinide surrogate, was negligible, indicating the process efficiently fractionates Cs and Sr (predominate fission products) from the TRU fraction in INEEL tank waste. The dynamic flowsheet tested indicates process viability while incorporating significant changes and recent developments with regard to previously established and tested separation flowsheets. A new, less toxic organic phase diluent (FS-13) was evaluated as an alternative to MNTFB used in previous flowsheets. Guanidine carbonate was used as a substitute for hydrazine, concentrated nitric acid, and ammonium nitrate solutions, previously used as stripping and scrubbing reagents. Finally, the solvent wash and regeneration section of the previous flowsheets was completely eliminated with positive results, thereby minimizing the quantity of secondary waste generated during the process.

While these process-alterations resulted in a net, positive effect on the extraction process, the flowsheet developed and tested during this project still has substantial potential for improvement and optimization, and ultimately must be demonstrated on samples of actual INEEL tank waste. Future work should emphasize refinement of the organic phase composition for a substantial increase in Cs removal efficiency, while maintaining a high Sr extraction efficiency. Methods to minimize waste (raffinate and strip) volumes should be explored. Potential strategies to reduce waste volumes include reducing or eliminating the initial 20 vol% dilution of the waste used in this test, decreasing the flow rate of scrub solution, and/or reducing the flow rate of the aqueous strip solution. An evaluation regarding the necessity of the scrub section or using different scrub solutions may provide an alternative means to reduce the raffinate volume. The temperature dependence of the Cs extraction distribution coefficient must be elucidated. The required analytical methods to accurately establish the PEG concentration in the organic phase must be developed. Finally, additional testing on samples of actual tank waste is necessary to validate flowsheet characteristics and process improvements.

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