Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Development Of The Universal Extraction (Unex) Process For The Simultaneous Recovery Of Cs, Sr, And Actinides From Acidic Radioactive Wastes

R. Scott Herbst[a]; Jack D. Law[a]; Terry A. Todd[a]; V. N. Romanovskiy[b]; I. V. Smirnov[b]; V. A. Babain[b]; V. N. Esimantovskiy[b]; B. N. Zaitsev[b]
[a] Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho, USA [b] Khlopin Radium Institute, St. Petersburg, Russia

Online publication date: 07 September 2003

To cite this Article Herbst, R. Scott , Law, Jack D. , Todd, Terry A. , Romanovskiy, V. N. , Smirnov, I. V. , Babain, V. A. , Esimantovskiy, V. N. and Zaitsev, B. N.(2003) 'Development Of The Universal Extraction (Unex) Process For The Simultaneous Recovery Of Cs, Sr, And Actinides From Acidic Radioactive Wastes', Separation Science and Technology, 38: 12, 2685 — 2708
To link to this Article: DOI: 10.1081/SS-120022567
URL: http://dx.doi.org/10.1081/SS-120022567

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 2685–2708, 2003

Development of the Universal Extraction (UNEX) Process for the Simultaneous Recovery of Cs, Sr, and Actinides from Acidic Radioactive Wastes[#]

R. Scott Herbst,[1,*] Jack D. Law,[1] Terry A. Todd,[1] V. N. Romanovskiy,[2] I. V. Smirnov,[2] V. A. Babain,[2] V. N. Esimantovskiy,[2] and B. N. Zaitsev[2]

[1]Bechtel BWXT Idaho, LLC, Idaho Falls, Idaho, USA
[2]Khlopin Radium Institute, St. Petersburg, Russia

ABSTRACT

A synergistic extraction mixture containing chlorinated cobalt dicarbollide (CCD), polyethylene glycol (PEG), and diphenyl-*N,N*-dibutylcarbamoyl phosphine oxide (CMPO) in a suitable polar diluent is being developed for the simultaneous recovery of Cs, Sr, and the actinides from highly acidic radioactive wastes. Development of this UNEX process was by a successful

[#]The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC09-96SR18500. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

[*]Correspondence: R. Scott Herbst, Bechtel BWXT Idaho, LLC, P.O. Box 1625, Idaho Falls, ID 83415-5218, USA; E-mail: herbrs@inel.gov.

DOI: 10.1081/SS-120022567 0149-6395 (Print); 1520-5754 (Online)
Published by Marcel Dekker, Inc. www.dekker.com

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

collaboration between scientists from the Idaho National Engineering and Environmental Laboratory (INEEL) and the Khlopin Radium Institute (KRI) in St. Petersburg, Russia. Development efforts focused on the treatment of radioactive waste currently stored at the INEEL. The development of the UNEX process has and continues to be an evolutionary process. Numerous countercurrent flowsheet demonstrations have been conducted to date, including two tests with several liters of actual radioactive tank waste, one test with dissolved radioactive calcine, and several tests with surrogate INEEL tank and dissolved calcine wastes. All countercurrent flowsheet tests have been performed in banks of centrifugal contactors. Removal efficiencies of 99.95% for ^{137}Cs, 99.995% for ^{90}Sr, and 99.96% for total α (predominately ^{241}Am, ^{238}Pu, and ^{239}Pu) were observed in countercurrent tests with samples of actual INEEL tank waste. The evolutionary concepts included in the development of the UNEX process are discussed, including development of the current diluent, phenyltrifluoromethyl sulfone, to replace nitroaromatic diluents used in earlier studies. Results from the most recent countercurrent flowsheet testing with 1.2 L of actual dissolved INEEL calcine are also presented, which represents the current state of UNEX development. Finally, future research directions in the development and understanding of the UNEX process are discussed.

Key Words: Solvent extraction; Cesium removal; Strontium removal; Actinide removal; High-level radioactive waste.

INTRODUCTION

Two distinct radioactive waste streams are currently stored at the Idaho National Engineering and Environmental Laboratory (INEEL) located near Idaho Falls, ID. Final clean up and disposition of these legacy radioactive wastes from reprocessing spent nuclear fuel at the Idaho Nuclear Technology and Environmental Center (INTEC) is ultimately the charge of the United States Department of Energy. The liquid radioactive raffinates from reprocessing campaigns were stored and subsequently solidified at 500°C in a fluidized bed calciner. Calcination converted the liquid wastes into a granular, free-flowing solid (calcine). The INTEC currently has approximately 4400 cubic meters of radioactive calcine stored on site in above-ground stainless steel bins enclosed in concrete vaults. Note that aqueous based separation technologies, such as solvent extraction and ion exchange, require headend dissolution of the solid calcine in nitric acid with filtration to remove any undissolved solids from the dissolution process. Additionally, secondary, acidic, aqueous wastes were generated during equipment decontamination between reprocessing campaigns and from solvent cleanup activities. Currently,

approximately 4.8 million L of this liquid tank waste are stored in underground, concrete enclosed stainless steel tanks at the INTEC. This liquid waste is not directly amenable to calcination due to its high sodium content, which causes agglomeration of the fluidized calcination bed. Historically, the high sodium secondary wastes were blended with reprocessing raffinates; however, blending is no longer possible since all raffinate solutions have been calcined.

For nearly a decade, numerous separations operations have been evaluated at the INEEL to segregate the minor mass fraction (containing the radioactive species) from the bulk of the inert matrix components. The overarching goal of performing the radionuclide separations is to economically isolate the small mass of the radioactive species into a minimum volume, high activity waste (HAW) fraction. The HAW stream would be subsequently immobilized in a suitably inert matrix (e.g., borosilicate glass) for final disposal to a federal repository. The processing and disposal costs associated with the HAW fraction represents a substantial economic expense, in terms of both operating and life-cycle costs. The bulk, inert fraction of the waste could then be suitably packaged (e.g., grouted) and disposed of in a near-surface repository as a contact handled, low activity waste (LAW) stream. The processing, life cycle, and disposal costs for the substantial volume of contact handled LAW is perceived to be orders of magnitude lower than for remote handled HAW.

The separations technologies evaluated and demonstrated at the INEEL for treatment of these radioactive wastes include the transuranic extraction (TRUEX) process, which has been demonstrated to efficiently remove the transuranic (TRU) elements from samples of actual waste in a 2-cm centrifugal contactor pilot plant.[1,2] Likewise, strontium removal has been demonstrated in the 2-cm centrifugal contactor pilot plant using the strontium extraction (SREX) process.[3,4] Cesium removal was demonstrated in small ion-exchange columns (1 to 1.5 cm^3) loaded with either potassium hexacyanoferrate, crystalline silicotitanates, or ammonium molybdophosphate.[5,6]

Collaborative testing efforts between scientists from the INEEL and scientists from the V. G. Khlopin Radium Institute (KRI) in St. Petersburg, Russia, initiated in 1994. The initial goal of the collaboration was to evaluate separation technologies developed and demonstrated in Russia for applicability to the treatment of INEEL acidic wastes. The early collaborative efforts resulted in the successful demonstration of the chlorinated cobalt dicarbollide (CCD) process with and without polyethylene glycol (PEG) for the removal of cesium and strontium (with PEG) from samples of INTEC tank waste.[7,8] These collaborative efforts also resulted in the successful demonstration of a phosphine oxide (POR) process for removing TRUs from tank waste samples.[8]

The initial collaborative efforts and previous KRI experience in the development of CCD and POR for treatment of Russian nuclear wastes formed

the basis for development of a single solvent extraction process for removal of all major radionuclides in one unit operation: the rudimentary concept of the universal extraction (UNEX) process. The possibility of combining CCD, PEG, and a carbamoylmethyl phosphine oxide into a single solvent for simultaneous recovery of Cs, Sr, actinides, and lanthanides was discussed in early 1995. A single process based on a universal solvent would provide a simplified and cost-effective method for waste treatment compared to processes utilizing two or three separate processes to achieve the same results. Proof of the UNEX concept was demonstrated in 1997 during batch contact testing of the universal solvent with samples of radioactive INTEC tank waste.[9]

A lot of the initial development work was based on the treatment of the INEEL tank waste, with limited development activities evaluating relevance to the dissolved calcine waste. The decision was made to treat the remaining INEEL tank waste by direct vitrification of the liquid in FY 2000. This decision mitigated any further development efforts for separations and the use of the UNEX for treatment of the residual INEEL tank wastes. However, a decision as to the treatment alternative and final disposal of the solid calcine waste stored at the INEEL has not currently been declared. Separation via the UNEX process is still a viable option for calcine treatment. Ongoing development efforts associated with UNEX focused on INEEL dissolved calcine. The transition in UNEX development relied heavily on the information that had been obtained in the process as applied to tank waste; virtually all of the process enhancements were relevant to the calcine.

Since the initial concept of a UNEX process in 1995, it has evolved and changed as the result of data generated during numerous experimental tests with simulated and actual INTEC wastes. The results and data from these tests have been individually reported in numerous references over the past several years. The intent of this article is to chronologically describe the experimental efforts and results in a manner consistent with the evolution of the UNEX process to the current state of development.[9–20]

EXPERIMENTAL

Waste Compositions

Numerous nonradioactive surrogate and actual radioactive waste samples were used in the development efforts of the UNEX process; these samples span a wide compositional range. The different INTEC wastes represent a large compositional variation depending on the type of waste studied (dissolved calcine vs liquid tank waste) and the source of the waste samples used in the specific tests.

For example, tank waste samples have compositional variations relative to the tank from which actual samples were taken or the particular tank simulated, in the case of tests with surrogate wastes. Furthermore, calcine compositions are very diverse depending on the type of calcine [as defined by the type(s) of waste from which it was produced] examined. In general, the only consistencies in the wastes used for UNEX process developments were the following: the presence of 1–3 *M* HNO_3, and the specific components (but NOT the relative amounts) are reasonably typical. The compositional ranges used in the development efforts for

Table 1. Compositional ranges for the wastes used in development of the UNEX process.

Component	Tank waste composition range	Dissolved calcine composition range
Acid (*M*)	1.45–2.0	0.86–1.14
Al (*M*)	0.51–0.68	0.29–0.89
Ba (*M*)	3.4E-05–2.1E-04	2.8E-05–1.1E-04
Ca (*M*)	0.049–0.054	0.052–0.49
Cr (*M*)	0.01–0.005	~4.0E-03
F (*M*)	0.13–0.47	0.023–0.74
Fe (*M*)	0.021–0.038	≤9.1E-03
Pb (*M*)	0.001–0.002	1.1E-04–2.5E-04
Hg (*M*)	0.0016–0.0041	2.1E-05
Mo (*M*)	0.0002–0.012	3.4E-06–1.5E-04
K (*M*)	0.14–0.2	6.7E-04–0.038
Na (*M*)	1.06–1.53	0.01–0.24
NO_3 (*M*)	4.38–5.13	~5.0
Zr (*M*)	0.0054–0.013	0.004–0.12
Eu (M)[a]	5.1E-04–5.6E-04	—[b]
Cs (M)[a]	8.1E-04–9.1E-04	—[b]
Sr (M)[a]	8.7E-04–1.1E-03	—[b]
Alpha (nCi/g)[c]	473–525	9.97E + 01–3.02E + 03
^{241}Am (nCi/g)[c]	50–54	10–51
^{137}Cs (Ci/m^3)[c]	88–185	24.6–200
^{238}Pu (nCi/g)[c]	343–435	7.9E + 01–1.17E + 03
^{239}Pu (nCi/g)[c]	53–71	>80
^{99}Tc (Ci/m^3)[c]	0.031–0.034	—[b]
^{90}Sr (Ci/m^3)[c]	75–181	17.6–168

[a] Stable Eu, Cs, Sr were added to simulated wastes to establish their behavior in the extraction flowsheets.
[b] No analysis for this component (as opposed to not analytically detectable).
[c] These radionuclides were present only in the actual radioactive waste solutions.

tank and calcine wastes are indicated in Table 1. Note that the radionuclide load is pertinent only in the case of actual waste samples and was not present during testing with simulated wastes.

2.0-cm Centrifugal Contactor Pilot Plant

The flowsheet demonstrations with actual wastes were performed using 2-cm diameter centrifugal contactors installed in a shielded cell at the INEEL. This equipment consists of 24 stages of 2-cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, and an air purge system for the contactor bearings. The aqueous and organic feed pumps and feed vessels were located inside the shielded cell. The remaining feed pumps and feed vessels were located outside the cell. All of the feed pump controllers were located outside the cell. Nonradioactive solutions used for the flowsheet tests were pumped to the centrifugal contactors through penetrations in the cell wall.

The centrifugal contactors were designed and fabricated by Argonne National Laboratory (ANL) specifically for operation of the TRUEX process with INTEC tank waste. It is particularly noteworthy that the ANL contactors have been successfully used at the INEEL to test a variety of technologies spanning a wide range of organic phase physical properties, from light phase diluents (TRUEX and SREX in Isopar L) to heavy phase organics (CCD and UNEX in sulfone). This point emphasizes the versatility of the ANL contactors. The contactors were modified at the INTEC for remote installation and operation in the cell. Solutions were fed to the contactors using valveless metering pumps. Flowrates were adjusted by controlling the pump speed or by manually adjusting the piston stroke length. Clear, flexible Teflon or Teflon-lined Tygon tubing was used for routing solutions to the feed and receiving vessels.

3.3-cm Centrifugal Contactor Pilot Plant

Flowsheet testing with simulated wastes was performed using 3.3-cm diameter centrifugal contactors installed in a nonradioactive area at the INEEL. The contactor setup consists of 26 independent 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). The NIKIMT contactors incorporate a variable length weir system that allows adjustments to compensate for density differences between the organic and aqueous phases. This capability allows for enhanced phase separation at

the individual stages but is only practical for hands-on operation (as opposed to remote operation in a hot cell).

Solutions were fed to the contactors using valveless metering pumps with controllers. Flow rates were adjusted by controlling pump speed or by manual adjustment of the piston stroke length. Once entering the contactors, solutions flow through the equipment by gravity (i.e., the solutions in the contactors are not under pressure) and then drain to the product vessels. The 3.3-cm centrifugal contactors do not have provisions for sampling aqueous or organic streams exiting from individual stages. Aqueous raffinate, aqueous strip product, and solvent recycle streams were sampled by periodically routing the solution draining to the appropriate receiving vessel into a sample bottle.

RESULTS AND DISCUSSION

Flowsheets Tested

The UNEX development program has been an iterative process and progressed by first evaluating process chemistry, using primarily batch contact experiments, to determine distribution coefficients and evaluate physical behavior of the organic and aqueous phases. The batch contact data were used to postulate potential flowsheets to develop and demonstrate process behavior under conditions of true countercurrent, continuous operation. Information obtained in the countercurrent experiments was then used to design additional batch contact experiments to obtain data for use in refinement of the next generation of countercurrent flowsheet testing. Thus, the history of UNEX development is most easily portrayed by examination of the countercurrent flowsheets that have been tested; these flowsheet tests propagate the relevant data from the laboratory studies. Since the UNEX concept was first introduced in 1995, six countercurrent flowsheet tests have been completed at the INEEL with actual and simulated wastes. The different flowsheets tested are shown chronologically in Figs. 1 through 6. Comparison of the flowsheets indicates that the process has been greatly simplified. The important modifications and data from these tests are summarized in Table 2. The major modifications are discussed individually in the following sections.

UNEX Extractant Composition

Table 2 indicates that the concentrations of the active extractants were reasonably consistent in each of the flowsheets tested. This was based on

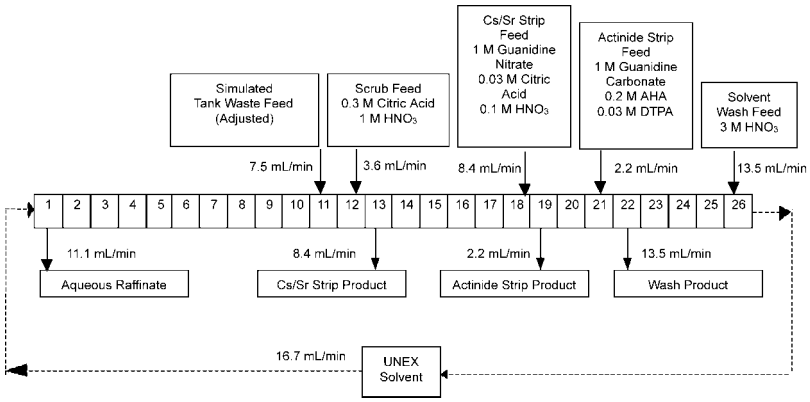

Figure 1. Flowsheet configuration with the light phase UNEX process and simulated INEEL tank waste (Test 1).

detailed laboratory work performed early during the development process.[12] This early work demonstrated that the extraction properties of the UNEX mixture depend on the concentration ratio of the active extractants. These data indicated that CCD, PEG-400, and diphenyl-*N*,*N*-dibutylcarbamoylmethyl phosphine oxide (CMPO) in the approximate, optimal molar ratios of [CCD]:[PEG]:[CMPO] ≈ 5:1:1 provided efficient recovery of cesium, strontium, lanthanides, and actinides, respectively. Note that 0.4 vol % PEG-400 corresponds to an 0.01 *M* solution. The slight variations in the PEG-400 concentration was associated with the fact that given a constant CCD

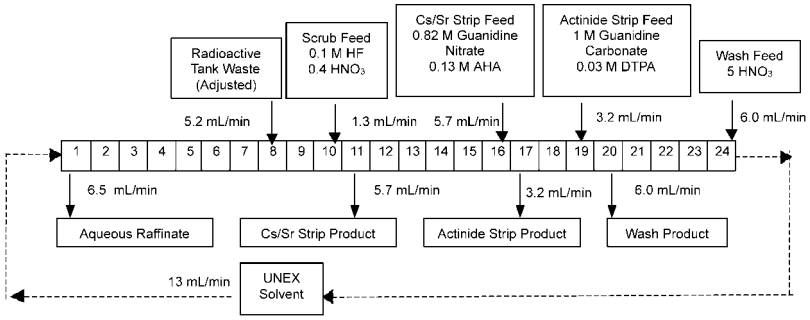

Figure 2. Flowsheet tested with heavy phase (FS-24 diluent) UNEX solvent and actual tank waste (Test 2).

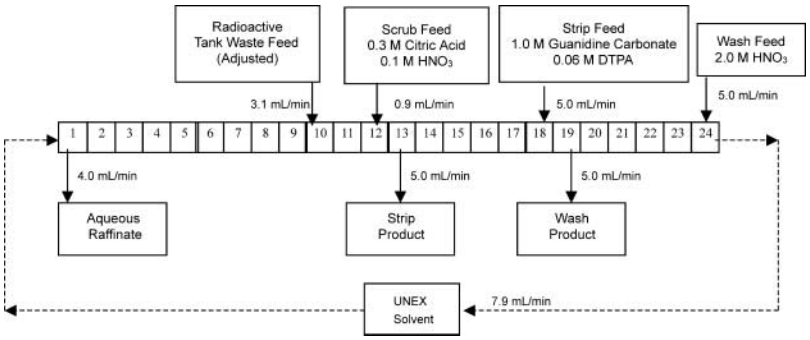

Figure 3. UNEX flowsheet tested with actual tank waste with the FS-13 diluent (Test 3).

concentration, the degree of Sr recovery increases with increasing PEG concentration and the recovery of cesium declines. Thus, adjusting the PEG concentration is a juggling act to simultaneously maximize the recovery Cs and Sr. It is also known that the simultaneous extraction of bulk matrix elements, predominately Zr, Fe, and Mo, by the CMPO tends to load the solvent, consuming all the free CMPO, resulting in decreased actinide recovery. Consequently, CMPO concentrations were varied slightly to achieve adequate actinide extraction, while minimizing extraction of stable metals.

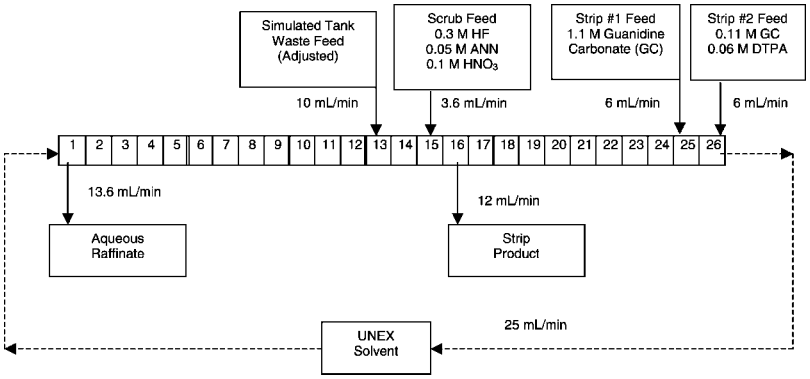

Figure 4. Flowsheet for extended testing of the UNEX process with simulated tank waste (Test 4).

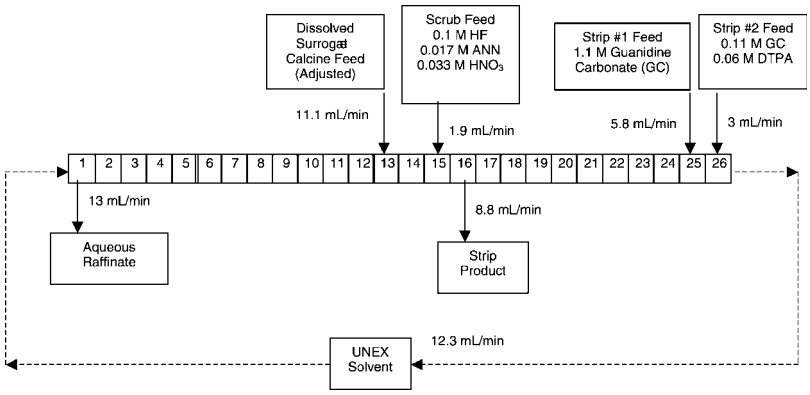

Figure 5. UNEX flowsheet used for testing dissolved INEEL calcine surrogate (Test 5).

UNEX Diluent

Initial efforts focused on moving away from nitroaromatic diluents (initially nitrobenzene and later, meta-nitrobenzotrifluoride, MNBTF). A stable replacement diluent without the technical, safety, and health concerns associated with nitroaromatic compounds was necessary for acceptance in the United States. The search for a new diluent was complicated by the fact that

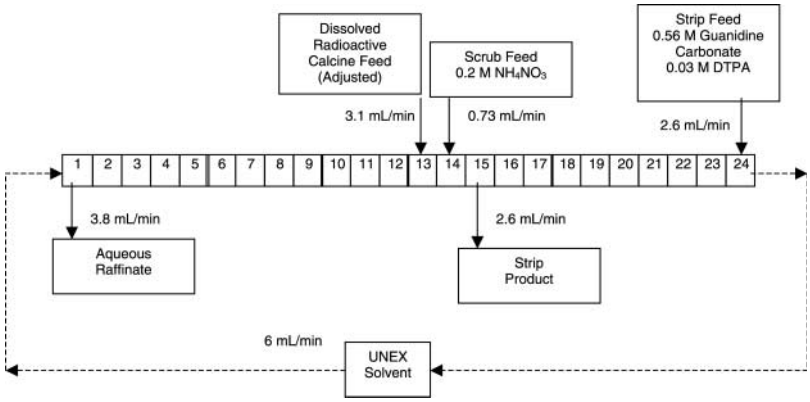

Figure 6. UNEX flowsheet used for testing radioactive dissolved INEEL calcine (Test 6).

Table 2. Summary of the flowsheet tests completed during UNEX development.

	Test 1 1997 surrogate tank	Test 2 1998 actual tank	Test 3 1999 actual tank	Test 4 2000 surrogate tank	Test 5 2000 surrogate calcine	Test 6 2001 actual calcine
UNEX solvent composition	0.08 *M* CCD 0.5 vol % PEG 0.02M CMPO	0.08 *M* CCD 0.6 vol % PEG 0.02 *M* CMPO	0.08 *M* CCD 0.5 vol % PEG 0.02 *M* CMPO	0.08 *M* CCD 0.35 vol % PEG 0.008 *M* CMPO	0.08 *M* CCD 0.35 vol % PEG 0.01 *M* CMPO	0.08 *M* CCD 0.4 vol % PEG 0.01 *M* CMPO
UNEX diluents	29 vol % octyldifluoromethyl sulfone and 71 vol % p-xylene	Phenyltetrafluoroethyl sulfone (FS-24)	Phenyltrifluoromethyl sulfone (FS-13)	Phenyltrifluoromethyl sulfone (FS-13)	Phenyltrifluoromethyl sulfone (FS-13)	Phenyltrifluoromethyl sulfone (FS-13)
Feed adjustments	Addition of solid citric acid for 0.03 *M* citrate in the feed	1.1 vol % dilution w/10 *M* HF	10 vol % dilution w/5.2 *M* HF	10 vol % dilution w/3.3 *M* HF	20 vol % dilution w/0.1 *M* HF	30 vol % dilution w/0.5 *M* HF
Scrub solutions	0.03 *M* citric acid in 1 *M* HNO_3	0.1 *M* HF in 0.4 *M* HNO_3	0.3 *M* citric acid in 0.1 *M* HNO_3	0.3 *M* HF 0.05 *M* ANN 0.1 *M* HNO_3	0.1 *M* HF 0.017 *M* ANN 0.033 *M* HNO_3	0.2 *M* NH_4NO_3
Strip solutions	2 Strip sections: Cs/Sr: 1 *M* GN 0.1 *M* HNO_3, 0.03 *M* citrate Actinide: 1 *M* GC, 0.2 *M* AHA, 0.03 *M* DTPA	2 Strip sections: Cs/Sr: 100 g/L GN 0.1 *M* AHA Actinide: 1 *M* GC 0.03 *M* DTPA	1 Strip section: 1 *M* GC 0.06 *M* DTPA	Strip section w/2 strip solutions: Strip #1: 1.1 *M* GC Strip #2: 0.11 *M* GC 0.06 *M* DTPA	1 strip section with two strip solutions: Strip #1: 1.1 *M* GC Strip #2: 0.11 *M* GC 0.06 *M* DTPA	1 strip section: 0.56 *M* GC 0.03 *M* DTPA
Solvent wash	3-*M* HNO_3	5-*M* HNO_3	2-*M* HNO_3	None	None	None
Radionuclide removal efficiencies	Cs 99.4% Sr 99.97% Eu 4.3% to >99.92%	^{137}Cs 99.95% ^{90}Sr 99.985% Alpha 95.2%	^{137}Cs 99.4% ^{90}Sr 99.995% Alpha 99.96%	Cs > 97.5% Sr > 99.993% Eu 17.2% to 34.1%	Cs > 99.95% Sr > 99.999% Nd > 98.3% Ce > 99.6%	^{137}Cs 99.99% ^{90}Sr 99.73% Alpha > 99.9%

(*continued*)

Table 2. Continued.

	Test 1 1997 surrogate tank	Test 2 1998 actual tank	Test 3 1999 actual tank	Test 4 2000 surrogate tank	Test 5 2000 surrogate calcine	Test 6 2001 actual calcine
Matrix metal removal efficiencies	Zr 52% Mo < 3.1% Fe 10% Ba 99.5% Pb 99.8% K 20%	Zr > 97.7% Mo 19% Fe 6.9% Ba > 87% Pb > 98.5% K 17%	Zr 87% Mo 32% Fe 8% Ba > 99% Pb > 98.8% Ca 10% K 28%	Zr < 6.4% Mo < 19.2% Fe < 13.2% Ba > 99.6% Pb >99.94%	Zr 3% Mo > 2% Fe 9% Ba 99.7% K 50%	Zr 0.7% Mo 12% Fe 2% Ba, Pb 100% Mn 23%
Notes	Two tests with light phase solvent; flooding and precipition observed in strip section of initial test	4-hour test with solvent recycle; flooding was observed in the actinide strip section	3-hour test with solvent recycle, no precipitation or flooding was observed	66-hour run time w/solvent recycle; no precipitation or flooding was observed	4-hour test with solvent recycle; no precipitatio or flooding was observed	3-hour test with solvent recycle; no precipitation or flooding was observed
References	16	11	13,17	18	19	20

GN = guanidine nitrate; GC = guanidine carbonate; AHA = acetohydroxamic acid; DTPA = diethylenetriamine pentaacetic acid; and ANN = aluminium nitrate.

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

a very polar solvent is required for CCD solubility. The requirements of a polar diluent was also a factor in the choice of the diphenyl derivative of CMPO for the UNEX solvent since it is more polar and, therefore, more soluble in such diluents than the aliphatic derivatives, such as the octylphenyl CMPO used in the classical TRUEX process.[21] Note that the diphenyl CMPO derivative used in the UNEX solvent is also a slightly stronger, more selective actinide extractant than the octylphenyl CMPO used in the TRUEX process.[21]

It was initially believed that a light phase organic would be more acceptable based on U.S. experience with such solvent extraction processes as PUREX and TRUEX, which both rely on a light phase organic. The UNEX solvent used in the initial flowsheet (Test 1) was based on a light phase diluent system consisting of octyldifluoromethyl sulfone and p-xylene. The p-xylene was required so that all of the active extractants are miscible and meet the requirements of being the less dense phase. Flooding in the actinide strip, a Zr precipitate forming in Cs/Sr strip section, low solubility of the CMPO in the light phase components, and very low Eu (Am surrogate) extraction (4.3% of the Eu extracted from the feed) resulted in halting development efforts on a light phase UNEX solvent. Also, the use of a mixture of diluents to achieve a light organic phase was deemed undesirable from the standpoint of process control and complexity.

Development activities subsequently focused on a heavy phase organic diluent since previous batch contact data indicated that improved distribution coefficients for Cs and Sr can be obtained with the heavy diluent.[12] Phenyltrifluoromethyl sulfone (FS-13) and phenyltetrafluoroethyl sulfone (FS-24) were the most promising with respect to the properties evaluated.[12] These compounds possess high density, low viscosity, slight water solublity, and ability to readily dissolve both CCD and its mixtures with PEG and CMPO. The extraction ability of CCD in these polyfluoroalkylphenyl sulfones is somewhat lower than in MNBTF but is sufficient for the efficient extraction of the targeted elements from acidic solutions. Also, the improved solubility of CMPO in the sulfone diluents decreases the potential for precipitation of the CMPO and the metal complexes. In the countercurrent flowsheet test using the FS-24 diluent (Test 2), flooding was observed in the actinide strip section of the flowsheet. This phenomenon resulted in actinide recycle through the wash section and into the extraction section of the flowsheet, reducing the actinide removal efficiency to 95.2%. Improved hydrodynamic properties of the organic phase were necessary to alleviate the flooding problems.

Continued development efforts focused on the use of FS-13 as the UNEX diluent. The FS-13 diluent has a slightly lower viscosity and density than the FS-24 diluent used previously, which improved the hydrodynamics in the

centrifugal contactors and resulted in better phase separation and the consequent elimination of flooding in the stripping section of the flowsheet.[12] The third flowsheet (Test 3) used UNEX solvent with the FS-13 diluent. Flooding problems were not apparent during the test and excellent recovery of the major radionuclides was observed. Physical properties for a solvent composition of 0.08 *M* CCD, 0.02 *M* CMPO, and 0.5 vol % PEG-400 in FS-13 used in Test 3, include a density of 1.417 g/cm^3 and viscosity of 4.6 mPas at 20°C.[12] Furthermore, this solvent composition exhibits high chemical stability in that it does not react with 14 *M* HNO_3 at temperatures up to 120°C. At higher temperatures (about 150°C), weak uniform gas evolution is observed without any heat release. As for explosion and fire safety, the UNEX solvent greatly surpasses the typical PUREX solvent of 30 vol % TBP in n-dodecane. The flash point of the UNEX solvent is above 90°C, while that of the PUREX solvent is about 70°C. Exposure of the UNEX solvent up to an absorbed dose of 20 W h/L, has no effect on its extraction and hydrodynamic properties. For the treatment of INEEL radioactive tank waste, this dose equates to about 350 extraction cycles. The total yield of FS-13 radiolytic decomposition products is 4.5 to 5.0 molecules/100 eV. The primary radiolysis products include hexafluoroethane and benzenesulfonic acid, which do not accumulate in the organic phase. The radiolytic gas-evolution rate does not exceed 4.5 mL/h L at a dose rate of 10 kGy/h. The UNEX solvent losses due to solubility do not exceed 0.02 vol % in a 3 *M* HNO_3 aqueous phase. The FS-13 solubility in both the INEEL tank waste and the proposed stripping reagents is even lower. The results obtained in the Test 3 flowsheet, coupled with the chemical and radiolytic stability, made FS-13 the diluent of choice for all subsequent development and experimental activities.

Feed Adjustment and Scrub Solutions

The CMPO used in the UNEX solvent strongly interacts and extracts some of the bulk matrix metals present in the INEEL wastes, most notably Zr, Fe, and Mo. The ramifications of bulk matrix metal extraction include loading the CMPO by these components with a dramatic decrease in the actinide extraction and precipitation of the CMPO metal complexes in various portions of the flowsheet. In addition, the extraction and subsequent stripping of the components with the radionuclide-containing HAW fraction can substantially increase the volume of this waste stream, negating potential benefits of the separation concept. The concentrations of these metals in the tank wastes are fairly dilute (refer to Table 1); however, the calcine wastes, particularly those derived from dissolution of Zr clad fuels, contain significant quantities of Zr

(concentrations up to 0.5 *M* Zr are possible). To alleviate the extraction and subsequent stripping of Zr, Fe, and Mo in the UNEX flowsheet, two simultaneous routes were studied: selectively complexing the matrix metals by adjusting the fluoride concentration of the radioactive waste fed to the process and the traditional route of selectively re-extracting these metals in the scrub section. Feed adjustment can incorporate the additional advantage of diluting the waste and, therefore, the concentration of the metals. Selectively scrubbing the organic phase is advantageous in that the re-extracted metals are recycled to the extraction section with the scrub solution. Dilution of the waste and scrubbing both have the drawback of increasing the volume of the LAW raffinate and must, therefore, be kept to a reasonable minimum.

During initial testing (Test 1), citrate was added to the feed, scrub, and Cs/Sr strip solutions to complex Zr and prevent precipitation in the Cs/Sr strip section as indicated in Fig. 1. Table 2 indicates the early test with citrate resulted in low removal efficiency for Eu coupled with rather large recoveries of Zr, Mo, and Fe.[16] Citrate suffers from the additional complication that it adversely impacts the ability of the final grouted waste produced from the LAW raffinate to solidify or set. This complication, coupled with the poor performance of citrate in the flowsheet, resulted in the subsequent, exclusive study of dilution and fluoride addition to the waste to complex and suppress Zr and Fe extraction and enhance actinide extraction. Note that the use of fluoride is intended to complex only the Zr and Fe and is ineffective for the complexation of Mo and other matrix elements.

Several different scrub solutions were tested in conjunction with dilution and HF feed adjustment of the waste, as indicated in Table 2. Citrate was added to the scrub solution in Test 3 to provide substantial suppression and scrubbing of bulk matrix metals while achieving a high removal efficiency of the radionuclides. The actinide removal efficiency was substantially improved in Test 3, and was attributed to reduced loading of the CMPO by stable matrix elements (Zr, Mo, Fe). Based on an assumed 3 moles of CMPO consumed per mole of metal, it was estimated that approximately 52% of the CMPO in Test 3 was tied up by Fe, Mo, and Zr; in previous tests, virtually all of the CMPO was consumed by these species. The scrub solution was altered in flowsheet Test 4 to provide an *added* fluoride concentration in the raffinate of 0.1 *M* F^-.[18] The increased concentrations of F^- was deemed necessary to adequately scrub Zr and Fe from the organic; however, dilute HF/HNO_3 solutions are very corrosive to typical steels used in the process equipment. Consequently, dilute ANN was added to the scrub to mitigate corrosion associated with the higher HF concentration. Note that once the scrub solution is combined with the waste in the extraction section, enough complexing metals are present (Al, B, Ca, etc.) that the additional fluoride introduced by the scrub is complexed and

corrosion concerns mitigated. The early tests with actual and simulated tank wastes indicate a progressive improvement in actinide recovery with a concomitant decrease in Zr, Mo, and Fe extraction as a result of different scrub solutions, feed dilution, and fluoride addition to the waste.

The most recent tests with dissolved calcine (referring to Tests 5 and 6 in Table 2), indicated substantial increases in actinide recovery with a dramatic decrease in the extraction of Zr, Mo, and Fe, relative to the earlier tests with tank wastes. Test 5 with surrogate calcine utilized fluoride adjustment of the feed (20 vol % dilution with 0.1 *M* HF) and a scrub solution containing 1.0 *M* HF and 0.017 *M* ANN in 0.033 *M* HNO_3; the results indicate high Nd and Ce (actinide surrogates) extraction efficiencies ($>98.3\%$) and the lowest Zr (3%), Mo ($>2\%$), and Fe (9%) removal was observed relative to all previous tests. The most recent test with actual calcine (Test 6) included fluoride addition to the feed (30 vol % dilution with 0.5 *M* HF) and simple 0.2 *M* NH_4NO_3 scrub solution. The Test 6 results with radioactive calcine were the most promising to date from the standpoint that high actinide recovery was observed ($>99.9\%$ gross α removal) with low recovery of Zr (0.7%) and Fe (2%) and moderate recovery of Mo (12%). Based on the results in Test 6, the use of sufficient fluoride in the feed, coupled with a simplified dilute NH_4NO_3 scrub solution, is the current recommended method for effectively reducing Zr, Fe, and Mo extraction by the current UNEX process. Continued development efforts will also focus on improvements in the scrub composition and feed complexation methodologies.

Strip Sections and Strip Solutions

Cesium and Sr can be stripped with nitric acid of moderate concentrations (5- to 8-*M* HNO_3) but require a complexant for effective re-extraction in dilute acid solutions. Dilute nitric acid solutions containing soluble amines, amides, or alcohols are the only known means for stripping Cs and Sr from the organic phase, as these types of aqueous soluble complexants promote proton transfer into the organic phase, with the subsequent displacement of Cs and Sr to the aqueous phase.[12] Re-extraction of the lanthanides and transplutonium elements is accomplished by means of complexing agents, such as acetohydroxamic acid (AHA) or diethylenetriamine pentaacetic acid (DTPA), in the presence of buffer additives, maintaining the $pH > 3$.[12] Additionally, solutions of sodium or ammonium carbonate are effective and U can be stripped only by means of carbonate solutions.[12] The use of strong complexants, such as DTPA and AHA, is required with the UNEX solvent due to the strong affinity of the organic phase for the radioactive species. The requirements of both acid and basic strip solutions are, of course, chemically incompatible and it was initially believed that

two separate strip sections were necessary to recover the Cs/Sr and actinide fractions independently.

The dual strip section concept was successfully used in the initial flowsheet tests (Tests 1 and 2) with excellent recoveries of the extracted metals in the strip sections. Continued laboratory efforts indicated that DTPA was capable of efficiently recovering the extracted metals from the organic phase and the addition of AHA was not necessary. It was also determined that the basic solution of guanidine carbonate would adequately strip Cs and Sr, although not as effectively as a guanidine nitrate (GN)–dilute HNO_3 system. These developments resulted in a dramatic simplification of the Test 3 flowsheet, where a single strip section was used with re-extraction accomplished by a solution of 1 *M* guanidine carbonate and 0.06 *M* DTPA. The results from flowsheet Test 3 indicated efficient recovery of the extracted species in a single strip product.[13,17] Consequently, the concept of a single strip section and strip product using a solution of guanidine carbonate and DTPA was successfully used in all subsequent tests. Note that in Tests 4 and 5, an additional strip stage was incorporated at the end of the re-extraction section. The main strip section used a 100-g/L guanidine carbonate solution to back extract primarily Cs and Sr, the more difficult components to re-extract from the organic phase (based on stripping distribution coefficients slightly greater than unity). A solution of 20-g/L guanidine carbonate and 40-g/L DTPA was introduced in the final strip stage and served two purposes. First, the reduction in guanidine carbonate concentration at the final strip stage substantially reduces the concentration of guanidine carbonate in the organic phase, facilitating the use of the first few extraction stages to remove the remaining traces of guanidine carbonate from the solvent (*vide infra*). Secondly, the DTPA effectively re-extracts the actinide, lanthanide, and transition metals, which requires only a few strip stages. Using this stripping methodology, the efficiency of the strip section is enhanced and there is no net increase in the volume of the HAW strip product since the two strip solutions are combined.

Solvent Wash Section

A solvent wash section using 1- to 5 *M* HNO_3 was included in the first three countercurrent flowsheet tests (Tests 1 through 3). The solvent wash section was designed to remove trace quantities of the stripping reagents (primarily guanidine carbonate and GN) from the organic phase and re-acidify the solvent prior to recycle of the organic to the extraction section. It was realized early in the development process that the nitric acid wash product

generated a significant volume of secondary waste, which would have to be dispositioned or recycled to the process. A unique concept to significantly simplify the process flowsheet was propagated: eliminate the solvent wash section and use acid present in the waste solutions to function as the solvent wash in the later extraction stages. Although this modification would require additional extraction stages, this is a small price to pay for the benefits of completely eliminating the secondary waste stream from solvent washing. Laboratory measurements indicated that the concept was feasible and the solvent wash section was first eliminated in the Test 4 flowsheet.[18] To compensate for the lack of solvent wash, additional stages of extraction were added to the flowsheet. In addition, a second strip solution with dilute guanidine carbonate and the DTPA were added in the final stage of the strip section. Although the two strip solutions were combined in the next strip stage, the lower concentration of guanidine carbonate used on the final stage was designed to limit the amount of guanidine carbonate in the organic phase and minimize the impact of guanidine washing necessary in the extraction section. The results of Test 4 indicated elimination of the solvent wash section was practical; the Cs distribution coefficients gradually increased from <0.08 on the first extraction stage (stage 1 in Fig. 4) and leveled to approximately $D_{Cs} = 0.5$ on the sixth extraction stage (stage 6 in Fig. 4). The gradual increase in the Cs distribution was an excellent indication that the entrained guanidine carbonate in the organic was being removed. The effects of eliminating the wash section were optimized by adjustment of flowrates and O/A ratios in subsequent tests; in the next flowsheet tested with calcine (Test 5), entrained guanidine carbonate in the solvent was removed after eight stages of extraction. The most recent improvement and simplification in this area occurred in the last flowsheet performed to date (Test 6). Refinement of flowrates to adjust strip and extraction section organic-to-aqueous (O/A) phase ratios resulted in the elimination of the second, lower concentration guanidine, strip solution. The results in the Test 6 flowsheet with dissolved calcine indicated the guanidine carbonate was efficiently scrubbed from the solvent in the first four extraction stages (stages 1 through 4, Fig. 6).

Other Considerations

The Ba and Pb present in the waste streams is quantitatively extracted and recovered with the HAW fraction in the UNEX process. This recovery is attributed to extraction by the PEG, due to chemical similarity of Ba and Pb relative to Sr. Efforts have not been directed at scrubbing or masking the extraction of these elements for several reasons. First, the concentration of

Ba and Pb in the wastes are fairly dilute, typically on the order of $10^{-4}\,M$ (refer to Table 1), and recovery of these minor components with the HAW fraction has a minimal effect on the HAW volume or the efficiency of Sr extraction. Second, Ba and Pb are both considered RCRA hazardous constituents; consequently, their immobilization and disposal with the final HAW is viewed as a positive attribute of the UNEX process.

Small quantities of other minor matrix constituents in the wastes are also extracted and recovered with the HAW fraction, most notably K and, to a lesser extent, Ca. Efforts to prevent these components from partitioning to the HAW fraction have not been evaluated. The minor quantities of these and other constituents that report to the HAW fraction is considered inconsequential from the standpoint of the final waste volume. Increasing the selectively of the UNEX process to eliminate the minor quantities of these components reporting to the HAW fraction has thus far been not been considered because of other possible impacts on the flowsheet (*inter alia*).

A development question was raised regarding the ability to control the concentration of PEG-400 in the UNEX solvent. The PEG-400 has the greatest solubility in the aqueous process solutions relative to the other components in the UNEX solvent. A 0.6 vol % PEG-400 solution has a solubility of ~250 mg/L in the guanidine carbonate/DTPA strip product and ~50 mg/L in the acidic waste.[18] One of the key issues associated with operating Test 5 for an extended time period was to evaluate the losses and control of PEG-400 from the UNEX solvent. During that test, 500-mg/L PEG-400 was added to the guanidine carbonate (strip #1) solution. The results (based on Sr distributions and recovery for the course of the test) indicated that this was an effective means of controlling PEG concentration in the organic phase.

The development efforts to date have also indicated the UNEX process is more effective if the extraction section can be operated at lower temperatures, in the range of 18 to 20°C. The Cs extraction has been shown to improve (i.e., higher Cs extraction distribution coefficients) with lower temperatures. Additionally, operating the strip section of the flowsheet at higher temperatures, preferably in the region of 50 to 60°C, enhances the re-extraction efficiency (lower Cs stripping distribution coefficients) of the process. These temperatures are easily maintained from an engineering perspective by cooling the organic solvent prior to recycle to the extraction section, and preheating the strip reagent before introduction to the process. It is also possible to selectively heat or cool individual contactor stages by jacketing and insulating the exterior housing. These engineering controls have been successfully used in many of flowsheet demonstrations at the INEEL and Savannah River Site.[22]

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

CONCLUSION

The UNEX process was successfully developed and demonstrated on acidic INEEL waste streams since the concept was initially introduced in 1995. Improvements in process efficiency include optimization of both the solvent composition and diluent. Efficiency of the process has also been increased by the use of fluoride to adjust the waste and scrub the loaded organic in the process flowsheet. The use of fluoride increases the removal of the actinide and lanthanide species while minimizing the extraction of bulk matrix components such as Zr and Fe. The process has also been greatly simplified by elimination of a solvent wash section and the secondary waste stream emanating from solvent washing. The stripping section of the flowsheet was consolidated to a single section. Process simplifications resulted in a flowsheet that produces only two product streams, the LAW and HAW fractions. The most recent flowsheet demonstration with radioactive calcine resulted in the removal and recovery of 99.99%, 99.73%, and $>99.9\%$ of the ^{137}Cs, ^{90}Sr, and alpha emitters, respectively. Barium and Pb were quantitatively recovered with only 0.7% of the Zr, 2% of the Fe, and 12% of the Mo transferred to the strip product.

CONTINUED DEVELOPMENT EFFORTS

Ongoing efforts to improve the UNEX process are currently planned. One of the major concerns associated with the current process is the use of an organic (guanidine carbonate) and the fate of this material in the subsequent vitrification step. A new class of stripping reagents is currently being evaluated to mitigate this concern. The nature of the reagents is currently proprietary. These reagents can be regenerated from the UNEX strip product solution and reused in the strip section of the flowsheet. Preliminary results are promising and indicate an additional benefit of reducing the volume of the HAW stream by an order of magnitude. Laboratory tests are currently being conducted to design a flowsheet demonstration of this concept with dissolved surrogate calcine solutions in FY 2002.

The development of the UNEX process has, to date, been an applied development effort, with little understanding of the fundamental chemistry behind the process. The Environmental Management Science Program (EMSP) funded a joint effort between the INEEL, KRI, and Washington State University to examine the fundamental extraction mechanisms occurring in the UNEX process. This is a 3-year grant, commencing in FY 2002, to examine the mechanisms and coordination geometries of extracted metal

species. This project will combine classical chemical techniques (wet chemistry), advanced instrumental methods (NMR and IR), and subsequent verification by extended x-ray absorption fine structure (EXAFS) to develop a fundamental understanding of the complicated extraction chemistry associated with the multicomponent UNEX solvent. It is anticipated that such knowledge will be instrumental to enhancing process efficiency by facilitating methods to reduce the volumes of primary and secondary wastes and enhance the compatibility of the product streams with the final waste forms.

REFERENCES

1. Law, J.D.; Brewer, K.N.; Herbst, R.S.; Todd, T.A. *Demonstration of the TRUEX Process for Partitioning of Actinides from Actual ICPP Tank Waste Using Centrifugal Contactors in a Shielded Cell Facility*, Idaho National Engineering and Environmental Laboratory Report INEL-96/0353; INEL: Idaho Falls, ID, 1996.
2. Law, J.D.; Brewer, K.N.; Herbst, R.S.; Todd, T.A.; Olson, L.G. *Demonstration of an Optimized TRUEX Flowsheet for Partitioning of Actinides from Actual ICPP Sodium-Bearing Waste Using Centrifugal Contactors in a Shielded Cell Facility*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-98-00004; INEEL: Idaho Falls, ID, 1998.
3. Law, J.D.; Wood, D.J.; Olson, L.G.; Todd, T.A. *Demonstration of a SREX Flowsheet for the Partitioning of Strontium and Lead from Actual ICPP Sodium-Bearing Waste*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-97-00832; INEEL: Idaho Falls, ID, 1997.
4. Law, J.D.; Wood, D.J.; Todd, T.A.; Olson, L.G. In *Demonstration of the SREX Process for the Removal of ^{90}Sr from Actual Highly Radioactive Solutions in Centrifugal Contactors*, Proceedings from the International Conference on Future Nuclear Systems (GLOBAL '97), Yokohama, Japan, Oct 5–10, 1997; p. 1412.
5. Brewer, K.N.; Todd, T.A.; Tullock, P.A.; Gelis, V.M.; Kozlitin, E.A.; Milyutin, V.V. *The Use of a Russian Manufactured Potassium Copper Hexacyanoferrate to Remove Cesium from Idaho Nuclear Technology and Engineering Center Radioactive Wastes*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-99-00663; INEEL: Idaho Falls, ID, 1999.

6. Todd, T.A.; Brewer, K.N.; Wood, D.J.; Tullock, P.A.; Mann, N.R.; Olson, L.G. Evaluation and testing of inorganic ion exchange sorbents for the removal of ^{137}Cs from Idaho chemical processing plant acidic tank waste. Sep. Sci. Technol. **2001**, *36* (5&6), 999–1016.
7. Law, J.D.; Herbst, R.S.; Todd, T.A.; Brewer, K.N.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. *Flowsheet Testing of the Cobalt Dicarbollide Solvent Extraction Process for the Partitioning of ^{137}Cs and ^{90}Sr from Actual ICPP Sodium-Bearing Waste Using Centrifugal Contactors in a Shielded Cell Facility*, Idaho National Engineering and Environmental Laboratory Report INEL-96/0192; INEL: Idaho Falls, ID, 1996.
8. Law, J.D.; Brewer, K.N.; Todd, T.A.; Wade, E.L.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. *Flowsheet Testing of the Cobalt Dicarbollide and Phosphine Oxide Solvent Extraction Processes for the Partitioning of Radionuclides from Actual ICPP Tank Waste Using Centrifugal Contactors in a Shielded Cell Facility*, Idaho National Engineering and Environmental Laboratory Report INEL/EXT-97-00064; INEL: Idaho Falls, ID, 1997.
9. Brewer, K.N.; Todd, T.A.; Law, J.D.; Wood, D.J.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. *The Removal of TRUs and Fission Products from Actual Radioactive Waste Using a Universal Solvent Process*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-98-00094; INEEL: Idaho Falls, ID, 1998.
10. Law, J.D.; Herbst, R.S.; Todd, T.A.; Brewer, K.N.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N.; Dzekun, E.G. In *Collaborative Flowsheet Development Studies Using Cobalt Dicarbollide and Phosphine Oxide for the Partitioning of Radionuclides from Idaho Chemical Processing Plant High-Activity Liquid Waste with Centrifugal Contactors*, Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, SPECTRUM '96, Seattle, WA, Aug 18–23, 1996; American Nuclear Society: LaGrange Park, IL, 1996; Vol. 3. 2308–2313.
11. Law, J.D.; Herbst, R.S.; Brewer, K.N.; Todd, T.A.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. *Demonstration of a Universal Solvent Extraction Process for the Separation of Radionuclides from Actual INEEL Sodium-Bearing Waste and Dissolved Calcine*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-98-01065; INEEL: Idaho Falls, ID, 1998.

12. Romanovskiy, V.N.; Smirnov, I.V.; Babain, V.A.; Todd, T.A.; Herbst, R.S.; Law, J.D.; Brewer, K.N. The universal solvent extraction process. I. Development of the UNEX process solvent for the separation of cesium, strontium, and the actinides from acidic radioactive waste. Solvent Extr. Ion Exch. **2001**, *19* (1), 1–21.
13. Law, J.D.; Herbst, R.S.; Todd, T.A.; Romanovskiy, V.N.; Babain, V.A.; Esimantovskiy, V.M.; Smirnov, I.V.; Zaitsev, B.N. The universal solvent extraction (UNEX) process. II. Flowsheet development and demonstration of the UNEX process for the separation of cesium, strontium, and actinides from actual acidic radioactive waste. Solvent Extr. Ion Exch. **2001**, *19* (1), 23–36.
14. Law, J.D.; Herbst, R.S.; Todd, T.A.; Wood, D.J.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. In *Development and Demonstration of the Universal Solvent Extraction Process for the Simultaneous Separation of Cesium, Strontium, and the Actinides from Actual Highly Radioactive Waste*, Proceedings of Waste Management 2000, Tucson, AZ, Feb 2000.
15. Todd, T.A.; Brewer, K.N.; Law, J.D.; Wood, D.J.; Herbst, R.S.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A. Development of a universal solvent for the Decontamination of acidic liquid radioactive wastes. Czech. J. Phys. **1999**, *49* (Suppl. S1), 931–936.
16. Law, J.D.; Herbst, R.S.; Brewer, K.N.; Todd, T.A.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N.; Kuznetsov, G.I.; Shklyar, L.I. *Testing of a Universal Solvent for the Removal of the Radionuclides from INEEL Simulated Tank Waste Using Centrifugal Contactors*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-98-00544; INEEL: Idaho Falls, ID, 1998.
17. Law, J.D.; Herbst, R.S.; Todd, T.A.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. *Demonstration of the UNEX Process for the Simultaneous Separation of Cesium, Strontium, and the Actinides from Actual INEEL Tank Waste*, Idaho National Engineering and Environmental Laboratory Report INEEL/EXT-99-00954; INEEL: Idaho Falls, ID, 1999.
18. Law, J.D.; Herbst, R.S.; Todd, T.A.; Peterman, D.R.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N.; Podoynitsyn, S.V. *Extended Flowsheet Testing of the UNEX Process for the Simultaneous Separation of Cesium, Strontium, and the Actinides from Simulated INEEL Tank Waste*, Idaho National Engineering and

Environmental Laboratory Report INEEL/EXT-2000-01328; INEEL: Idaho Falls, ID, 2000.

19. Law, J.D.; Herbst, R.S.; Todd, T.A.; Peterman, D.R.; Romanovskiy, V.N.; Esimantovskiy, V.M.; Smirnov, I.V.; Babain, V.A.; Zaitsev, B.N. In *Flowsheet Testing of the Universal Extraction Solvent Process for the Simultaneous Recovery of Cesium, Strontium, and the Actinides from Dissolved INEEL Calcine*, Proceedings of Waste Management, 2001, Tucson, AZ, Feb 25–Mar 1, 2001.
20. Herbst, R.S.; Law, J.D.; Todd, T.A.; Romanovskiy, V.N.; Babain, V.A.; Esimantovskiy, V.M.; Smirnov, I.V.; Zaitsev, B.N. Universal solvent extraction (UNEX) flowsheet testing of the removal of cesium, strontium, and actinides from radioactive, acidic dissolved calcine waste. Solvent Extr. Ion Exch. **2002**.
21. Horwitz, E.P.; Martin, K.A.; Diamond, H.; Kaplan, L. Extraction of Am from nitric acid by carbamoyl-phosphoryl extractants: the influence of substituents on the selectivity of Am over Fe and selected fission products. Solvent Extr. Ion Exch. **1986**, *4* (3), 449–494.
22. Campbell, S.G.; Geeting, M.W.; Kennell, C.W.; Law, J.D.; Leonard, R.A.; Norato, M.A.; Pierce, R.A.; Todd, T.A.; Walker, D.D.; Wilmarth, W.R. *Demonstration of Caustic-Side Solvent Extraction with Savannah River Site High Level Waste*, Westinghouse Savannah River Company Report WSRC-TR-2001-00223; 2001.