ADVANCED TECHNOLOGIES FOR THE SIMULTANEOUS SEPARATION OF CESIUM AND STRONTIUM FROM SPENT NUCLEAR FUEL

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ABSTRACT

Two new solvent extraction technologies have been recently developed to simultaneously separate cesium and strontium from spent nuclear fuel, following dissolution in nitric acid. The first process utilizes a solvent consisting of chlorinated cobalt dicarbollide and polyethylene glycol extractants in a phenyltrifluoromethyl sulfone diluent. Recent improvements to the process include development of a new, non-nitroaromatic diluent and development of new stripping reagents, including a regenerable strip reagent that can be recovered and recycled. This new strip reagent reduces product volume by a factor of 20, over the baseline process. Countercurrent flowsheet tests on simulated spent nuclear fuel feed streams have been performed with both cesium and strontium removal efficiencies of greater than 99 %. The second process developed to simultaneously separate cesium and strontium from spent nuclear fuel is based on two highly-specific extractants: 4′,4′,(5′)-Di-(t-butyldicyclo-hexano)-18-crown-6 (DtBuCH18C6) and Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6). The DtBuCH18C6 extractant is selective for strontium and the BOBCalixC6 extractant is selective for cesium. A solvent composition has been developed that enables both elements to be removed together and, in fact, a synergistic effect was observed with strontium distributions in the combined solvent that are much higher that in the strontium extraction (SREX) process. Initial laboratory test results of the new combined cesium and strontium extraction process indicate good extraction and stripping performance.

INTRODUCTION

The Advanced Fuel Cycle Initiative is developing advanced separation technologies for spent nuclear fuel treatment for potential implementation of a nuclear fuel cycle in the United States (1). One of the primary goals of the program is to develop technologies to reduce the environmental impact and the cost of spent nuclear fuel disposal. Near-term benefits of chemical separations include more effective use of repository space due to the reduction of volume (and mass) as well as reduction of the thermal load from the waste (2). Subsequent transmutation of the recovered actinide elements, along with continued reprocessing, provides for the destruction of plutonium and minor actinides, resulting in reduced long-term radiotoxicity of the waste materials in the repository. Further separation of cesium and strontium would allow a substantial increase in the utilization of repository space (up to a factor of 50, when combined with separation of Pu and Am), opening up more options for solving the issue of long-term waste disposal. Implementation of such strategies will allow the eventual transition from the current once-through use of nuclear materials to a sustainable Generation IV nuclear energy system.

The technologies for reducing the volume (and mass) of the spent fuel, as well as managing the heat generating isotopes, are chemical separation processes. These processes include both aqueous-based processes and electrochemical-based processes; however, the current focus of the AFCI program for processing the existing stockpile of spent light water reactor fuel is on aqueous-based technologies. Spent light water reactor fuel is approximately 95% uranium (by mass); therefore, initial separation of the uranium from the spent nuclear fuel can greatly reduce the size and complexity of subsequent processes. If the uranium separation process produces a uranium product that is non-transuranic (TRU), the uranium could likely meet low-level waste disposal criteria. The separated uranium could also be utilized in the production of new nuclear fuel, if desired. At this time, the AFCI program has successfully developed and demonstrated the Uranium Extraction (UREX) solvent extraction process, which effectively removes uranium and technetium (in separate streams) from spent nuclear fuel dissolved in nitric acid. The UREX process was specifically designed to not extract plutonium, leaving it mixed with the other actinide and fission products for proliferation resistance.

Simultaneous separation of the primary short-term heat generators, cesium and strontium (and consequently, their very short-lived decay products barium and yttrium), can be achieved utilizing another solvent extraction technology. Simultaneous extraction of cesium and strontium reduces overall process complexity and allows for a single product form to be produced that facilitates separate storage. The AFCI program has developed and is testing two different processes for the separation of cesium and strontium.

The first Cs/Sr separation process utilizes chlorinated cobalt dicarbollide (CCD) and polyethylene glycol (PEG) in a phenyltrifluoromethyl sulfone diluent (3). The CCD/PEG process is most efficient when the feed is < 1M nitric acid; therefore, it can be used directly on the UREX process raffinate or on the UREX co-decontamination process raffinate, after an acid recovery process. Cesium and strontium, along with any barium or rubidium present, are extracted into the solvent. A three molar nitric acid scrub is used to remove any trace actinides present in the solvent. Cesium and strontium are effectively stripped using a guanidine carbonate/ diethylenetriamine pentaacetic acid (DTPA) strip solution. Recent results indicate that a new, regenerable strip reagent, based on methylamine carbonate would significantly reduce the amount of organics in the cesium/strontium strip product and greatly simplify subsequent solidification operations (4). The cesium and strontium strip product may be solidified in a number of ways, namely sorption onto a zeolite-type matrix, mineralization by steam reforming, calcination, etc.

The second technology for the separation of cesium and strontium, referred to as the fission product extraction (FPEX) process, is based on a combined solvent containing two extractants - 4′,4′,(5′)-Di-(t-butyldicyclo-hexano)-18-crown-6 (DtBu18C6) and Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) combined with a phase modifier- 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) in a branched aliphatic hydrocarbon diluent (Isopar® L). This solvent composition was based on the Strontium Extraction (SREX) process developed at Argonne National Laboratory and the Caustic Side Solvent Extraction (CSSX) process developed at Oak Ridge National Laboratory (for alkaline waste) (5,6). A simple combination of the two solvents produced unacceptable extraction results; however, it was found that the Cs-7SB modifier used in the CSSX process had a synergistic

effect on the extraction of strontium. Therefore, the modifier used in the SREX process (TBP) was not needed in the new combined solvent. Preliminary batch contact testing of the combined Cs/Sr extraction process has been completed and results indicate that the process is effective at selectively removing cesium and strontium from simulated UREX raffinates and that the cesium and strontium can be stripped from the solvent using dilute nitric acid.

EXTRACTION MECHANISMS

CCD/PEG

Cesium extraction in the CCD/PEG solvent occurs by an uncommon liquid-liquid phase cation-exchange mechanism with complete dissociation of the solvated species in the organic phase. The CCD anion does not directly participate in the extraction process, but serves as the counter ion to stabilize the charge of the metal cation in the organic phase, as shown in the following equation.
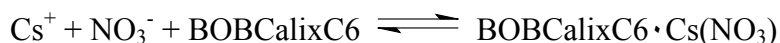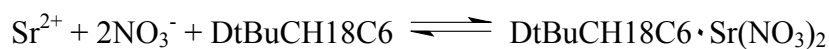
$$[M^{n+}]_{aq} + n[H^+ \cdot bH_2O]_{org} + n[CCD^-]_{org} \leftrightarrow [M^{n+}]_{org} + n[H^+]_{aq} + n[CCD^-]_{org} + bH_2O$$
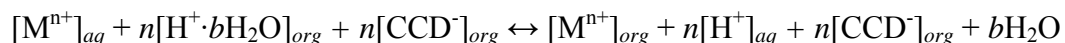
It is of interest to note that the number of water molecules, b, associated with the hydrated proton in the organic phase is reported as 5.5 in the literature for CCD in nitrobenzene (7). dipicrylamine, tetraphenylborate, polyiodide, and heteropolyacids extract cesium by the same mechanism, but only HCCD is simultaneously a strong acid and extremely hydrophobic. 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, have been the most widely used diluents for CCD. Technical, environmental, health, and safety considerations of nitrobenzene-based diluents have stimulated significant research, with excellent progress in the identification of alternative diluents for use in cobalt dicarbollide extraction.

Polyethylene glycol remains as a neutral molecule when associated with ionic strontium by disrupting the hydration sphere of Sr^{+2}. The result is an ionic, yet hydrophobic, species with a 2+ charge. This species is transferred from the aqueous phase into a polar organic phase containing the CCD anion. Experimental studies indicated that the charged species PEG:Sr^{2+} and protonated polyethylene glycol (PEG:H^+) were competing counter-ions of the CCD$^-$ anion in the organic phase (8).

FPEX

Both the DtBu18C6 and BOBCalixC6 extractants in the FPEX solvent are neutral extractants that extract $CsNO_3$ and $Sr(NO_3)_2$, as neutral ion pairs, as shown in the following equations.

$$Sr^{2+} + 2NO_3^- + DtBuCH18C6 \rightleftharpoons DtBuCH18C6 \cdot Sr(NO_3)_2$$

$$Cs^+ + NO_3^- + BOBCalixC6 \rightleftharpoons BOBCalixC6 \cdot Cs(NO_3)$$

The crown ether or calixarene extractants complex with the metal ion to form a large, hydrophobic cation. Nitrate ion is typically the predominate anion in spent nuclear fuel that has been dissolved in nitric acid, and therefore an excess of nitrate ion drives the reaction to the right. Therefore, extraction of cesium and strontium in the FPEX solvent are a function primarily of the nitrate ion concentration, rather than acidity.

The major technological differences between the two cesium and strontium separation processes are: 1) the CCD/PEG process is most effective if nitric acid concentrations in the feed are less than 1 M, while the crown ether/calixarene solvent effectively extracts cesium and strontium at nitric acid concentrations between 0.5 and 2.5 M and 2) the stripping of cesium and strontium in the crown ether/calixarene solvent can be accomplished in dilute nitric acid rather than a concentrated carbonate/complexant solution for CCD/PEG. It should be noted, however, that the development state of the CCD/PEG process is significantly more advanced than for the crown ether/calixarene solvent extraction process.   No countercurrent flowsheet testing has been performed to date on the crown ether/calixarene solvent extraction process, while the CCD/PEG process has been successfully tested with UREX raffinates from simulated and actual spent nuclear fuel.

EXPERIMENTAL

All diluents were reagent grade and were used as received. Deionized water was used to prepare all aqueous acid solutions. The nitric acid was reagent grade from Aldrich Chemical Co. (Milwaukee, WI).). The ^{85}Sr and ^{137}Cs radiotracers used for spiking the simulants were obtained as ^{85}SrCl$_2$ in 1 M HCl and ^{137}CsCl in 1 M HCl from Isotope Products (Burbank, CA).   The tracers were diluted and carriers were added that consisted of 0.001 M Sr(NO$_3$)$_2$ for strontium and 0.0001 M CsNO$_3$ for cesium, which was consistent with previous work. The mixture was heated to incipient dryness and concentrated HNO$_3$ was added to finish the conversion of the tracers to the nitrate salts. After three such cycles, 10mL of varying concentrations from 0.01 M to 10 M of HNO$_3$ were added to the tracers and carriers to re-dissolve the salts in preparation for the extraction studies.

The CCD/PEG solvent consists of 0.08 – 0.13 M CCD for the extraction of Cs, 0.016 – 0.027 M PEG-400 for the extraction of Sr, and a phenyltrifluoromethyl sulfone (FS-13) diluent. The cesium salt of hexachlorocobalt dicarbollide was obtained from Katchem (Czech Republic) and used as received without additional purification. Phenyltrifluoromethyl sulfone, synthesized and purified by the Khlopin Radium Institute (Russia), was used as received. The PEG-400, obtained from Fisher Scientific (USA), was used as received.

For the Fission Product Extraction (FPEX) solvent, Isopar® L isoparaffinic diluent was obtained from Exxon Chemical Company (Houston, TX). The DtBuCH18C6 crown ether was purchased from Eichrom Industries, Inc. (Darien, IL). The BOBCalixC6 calixarene crown ether and Cs-7SB modifier, obtained from Oak Ridge National Laboratory, were originally received from IBC Advanced Technologies, Inc. (American Fork, UT) and Boulder Scientific Company (Mead, CO), respectively, and were used as received (9,10). Figure 1 shows the structures of the individual components. The FPEX process solvent was a mixture of 0.15 M DtBuCH18C6,

0.007 M BOBCalixC6 and 0.75 M Cs-7SB modifier in Isopar® L. The solvent was prepared by adding neat DtBuCH18C6, BOBCalixC6, and Cs-7SB modifier to a mixing vessel. Approximately 10% of the required final Isopar® L volume was added to lower the viscosity and the mixture was left to stir overnight. The remainder of the Isopar® L was then added the next morning. Ambient temperature throughout the experiments was $23^{\circ}C \pm 2^{\circ}C$ unless otherwise specified.

BOBCalixC6
Calix[4]arene-bis-(tert-octylbenzo-crown-6)

DtBuCH18C6
4,4′,(5′)-Di-(t-butyldicyclo-hexano)-18-crown-6

Cs-7SB modifier
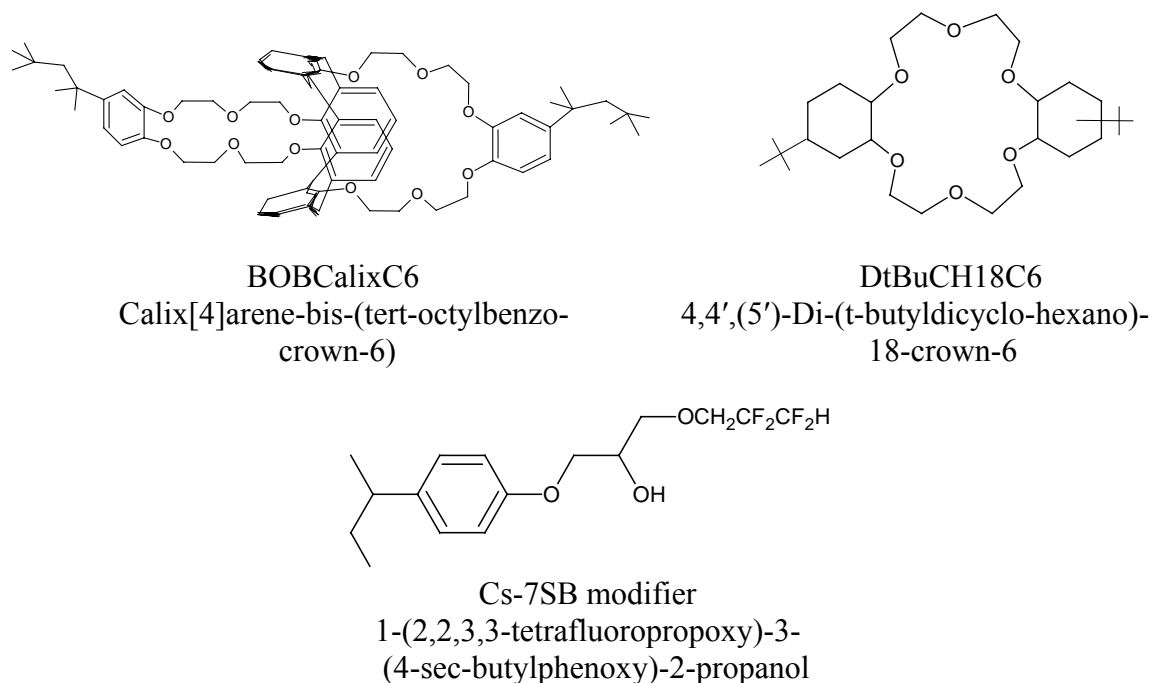1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol

Fig. 1. Molecular structures of the cesium and strontium extractants and the Cs-7SB modifier for the FPEX solvent

Nitric acid dependency tests for Cs and Sr were performed in varying concentrations of HNO_3 contacted with the appropriate solvent in equal proportions. All batch contacts were shaken by hand for 1 minute, centrifuged for 1 minute, the organic and aqueous fractions were separated and the two phases analyzed. The organic and aqueous aliquots were analyzed by gamma spectroscopy using a HPGe detector. The 661 keV line of ^{137}Cs and the 514 keV line of [85]Sr were used to measure these elements. Concentrations of stable (non-radioactive) metals were determined by ICP-MS. Stable metals in the organic phase were analyzed by first stripping the metals into an aqueous guanidine carbonate/ DTPA solution followed by ICP-MS analysis of the resulting aqueous phase.

Flowsheet testing of a chlorinated cobalt dicarbollide (CCD)/polyethylene glycol (PEG-400) based solvent extraction process for the separation of Cs and Sr from dissolved LWR fuel was performed using 24 stages of 3.3-cm diameter centrifugal contactors and simulated feed solution. The CCD/PEG solvent composition suggested for the flowsheet testing was 0.11 M CCD and 0.027 M PEG-400 in phenyltrifluoromethyl sulfone (FS-13), which was developed to minimize loading of the PEG-400 extractant with Sr and Ba. The CCD concentration in the solvent actually

used for the testing was determined to be 0.13 M based on titration of the solvent. The composition of the feed simulant used for this testing is given in Table I and is based upon a U separation process preceding the CCD/PEG process.

Table I. Feed simulant composition

Component	Concentration (M)	Component	Concentration (M)
HNO$_3$	0.6	Nd	5.20E-03
Sr	1.60E-03	Sm	1.00E-03
Cs	2.33E-03	Gd	9.33E-03
Zr	1.27E-03	Eu	1.27E-04
Ba	5.53E-03	Y	8.67E-04
La	1.53E-03	Pr	1.53E-03
Ce	2.60E-03	Rb	6.67E-04

RESULTS AND DISCUSSION

Nitric Acid Dependencies

Nitric acid dependency tests were performed with both processes. The CCD/PEG solvent functions as an acidic extractant, and distribution coefficients typically decrease with increasing nitric acid concentration. Crown ether and calixarene extractants are neutral extractants, extracting neutral ion pairs (typically nitrate is the anion associated with either cesium or strontium extraction). Neutral extractants typically exhibit higher distribution coefficients with increasing nitric acid (i.e. nitrate) concentration.

Results of cesium and strontium nitric acid dependency tests for the CCD/PEG process are shown in Figure 2. The decreasing distribution coefficient with increasing nitric acid concentration trend was observed. Acid dependency data for the extraction of Cs and Sr with the CCD/PEG solvent at temperatures of 15°C, 25°C, and 35°C are presented in Figure 2. The distribution coefficient of Cs decreases with increasing nitric acid concentration, ranging from 379 in 0.1 M HNO3 to 0.24 in 10 M HNO3. Also, the distribution coefficients drop as temperature is increased from 15°C to 35°C. The distribution coefficient of Sr decreases with increasing nitric acid concentration, ranging from 5,100 in 0.1 M HNO$_3$ to 6.5 in 10 M HNO$_3$. Also, the distribution coefficients drop slightly as temperature is increased from 15°C to 35°C.

These data indicate that the simultaneous extraction of Cs and Sr, using the CCD/PEG solvent, is viable from aqueous solutions with acid concentrations below approximately 5 M HNO$_3$, with the optimum nitric acid concentration below approximately 1.0 M.
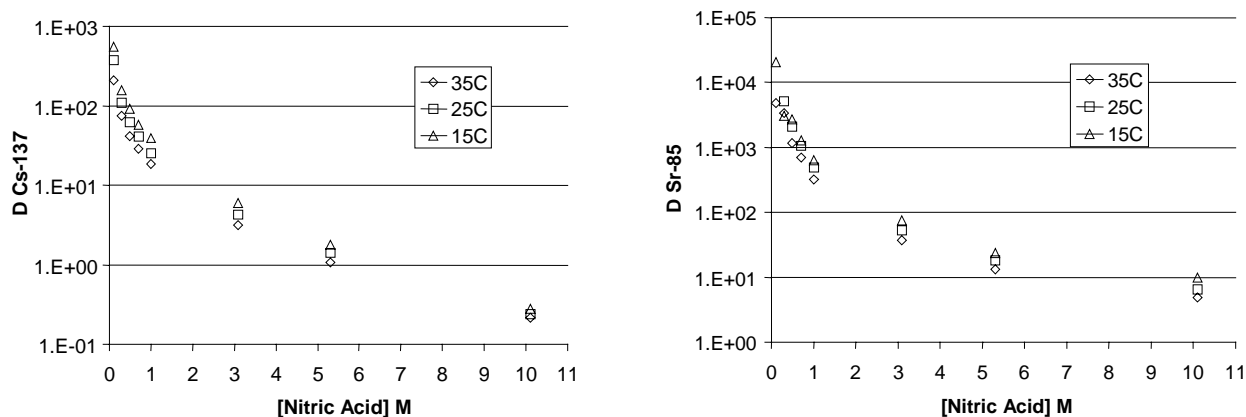
Fig. 2. Nitric Acid Dependencies of Cs and Sr in CCD/PEG solvent

Results of cesium and strontium nitric acid dependency tests for the FPEX process are shown in Figure 3. The increasing distribution coefficient with increasing nitric acid concentration trend was observed, as expected from previous work with the individual extractants. The FPEX solvent requires nitric acid concentrations of about 0.5 M or higher to effectively separate cesium and strontium. At nitric acid concentrations above 2.5 M, coloration of the solvent was observed; therefore, use of this process is not recommended in this nitric acid regime. The results for the FPEX process solvent show the nitric acid slope for Sr = 1.4 ±0.1 and the nitrate slope for Cs = 0.70 ±0.03 were approximately the same as previous tests using the individual solvents containing the same extractants from the SREX and CSSX processes. This suggests that reaction stoichiometry has not changed in the FPEX solvent mixture.

Nitrate dependency tests were performed using $Al(NO_3)_3$, with constant HNO_3 and the expected solvation numbers required for charge balance were found. The relationship between Log D and Log $[NO_3^-]$ indicate a slope for strontium of 2.2 ±0.3 and a slope for cesium of 1.0 ±0.4. The slopes are similar to previous work (11), and indicate that 2 NO_3^- anions participate in the extraction of Sr and one NO_3^- anion participates in the extraction of Cs as shown in the previous equations.
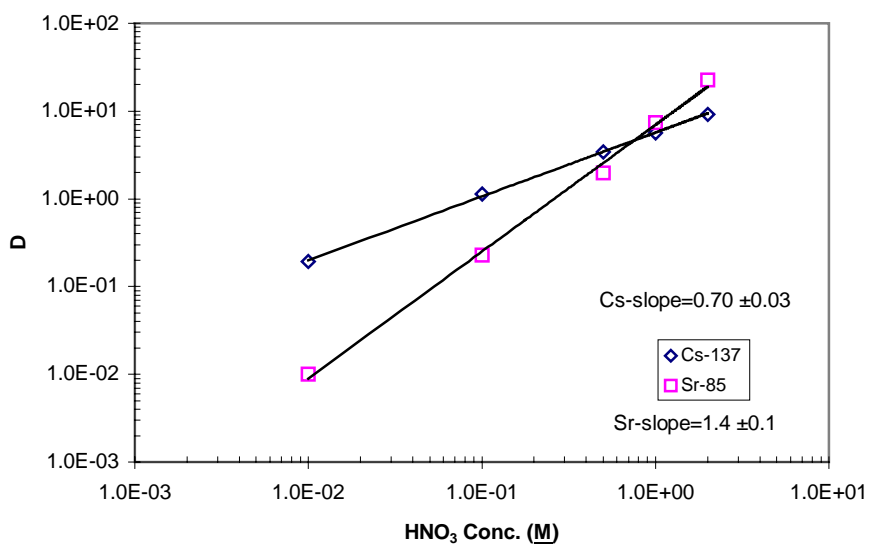
Fig. 3. Nitric acid dependencies of Cs and Sr in the FPEX solvent

Flowsheet Testing of CCD/PEG Process

Significantly more work has been performed in the development of the CCD/PEG process over the FPEX process, resulting in a different level of technical maturity. Nitric acid and nitrate dependencies are important to determine process feasibility, but significantly more work is needed to develop a process flowsheet. Significant amounts of research have been performed on both the CCD/PEG and FPEX process, which cannot be reported here (3, 12). The FPEX solvent has been shown to be effective in equilibrium batch contacts, but has not been tested in a countercurrent flowsheet. This work is planned in the near future. The CCD/PEG process was tested in a countercurrent flowsheet test, as described previously. The flowsheet for the CCD/PEG process is shown in Figure 4.
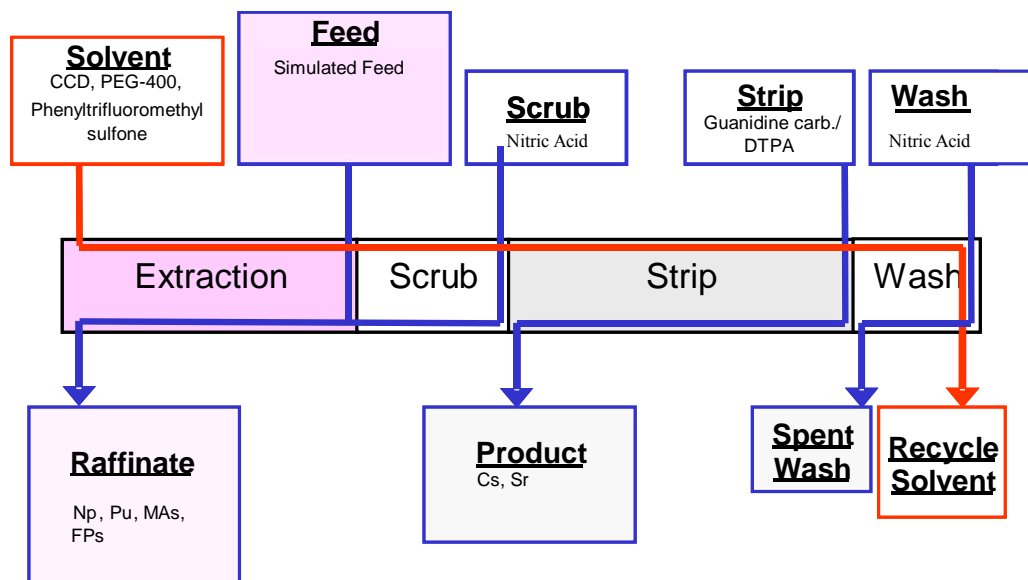
Fig. 4. Schematic of flowsheet used for testing of CCD/PEG process

The flowsheet testing consisted of approximately 2 hours of startup, including the initiation of feed flows and filling of contactor stages, followed by 255 minutes of operation with feed simulant. The solvent was recycled during testing for a total of 4.1 solvent turnovers within the 24 stages of contactors. Samples of each of the effluent streams were taken every 30 minutes and immediately prior to shutdown. Shutdown was performed by simultaneously stopping the feed flow and centrifugal contactors. With this type of shutdown, the stages remain approximately at the steady state conditions achieved during operation. Liquid phases from the stages were drained into individual bottles, re-equilibrated, and the two phases sampled.

The percentages of Cs, Sr, and the lanthanides in the effluent streams at the time of shutdown are show in Table II. The removal efficiencies for Cs and Sr were 99.6% and >99.995%, respectively. Also, an average decontamination factor of 2.6E+05 was obtained for the lanthanides.

Table II. Percentage of each component in each of the effluent streams for CCD/PEG flowsheet test

Effluent Stream	Cs	Sr	Ba	La	Ce	Nd	Sm	Pr	Rb
Raffinate	0.42%	< 0.27%	< 0.025%	109.8%	90.6%	97.8%	90. %	102.3%	0.02%
Strip Product	113.4%	106.6%	109.4%	0.004%	0.0007%	0.0004%	<0.0036%	<0.0002%	113.3%
Wash Effluent	0.04%	< 0.30%	<0.0002%	< 0.0002%	0.0004%	<0.00006%	<0.0009%	<0.0002%	<0.004%

Distribution coefficients for ^{137}Cs ranged from 18 to 25 in the extraction section, 3.6 to 4.3 in the scrub section, and 0.49 to 0.51 in the strip section. For ^{85}Sr, distribution coefficients ranged from 325 to 939 in the extraction section, 39 to 46 in the scrub section, and were <1E-04 on all strip stage. These distribution coefficients for ^{137}Cs and ^{85}Sr support the overall removal efficiencies of 99.6% and >99.995%, respectively, that were achieved in this testing. For ^{241}Am, which would be the primary contributor to the TRU activity when the preceding process is the co-decontamination process (which separates Pu), the extraction distribution coefficients ranged from 0.06 to 0.12, the scrub distribution coefficients ranged from 0.0025 to 0.0032, and the strip distribution coefficients were <1E-04 on all strip stages. When these distribution coefficients are used in conjunction with the AMUSE code, the predicted decontamination factor for Am in the strip product is 2E+05, assuming a stage efficiency of 80%. This is in good agreement with the actual average lanthanide decontamination factor of 2.6E+05 obtained with this testing.

Several other components of the spent fuel were also studied, including Ba, Rb, Y, and Zr. As expected, Ba and Rb were nearly completely extracted with the Cs and Sr. Only 0.02% of the Y and 0.14% of the Zr were extracted and exited with the strip product.

CONCLUSIONS

The results of this study demonstrate that the CCD/PEG and FPEX process solvents efficiently extract cesium and strontium from acidic nitrate media. The CCD/PEG solvent is most effective at nitric acid concentrations of approximately 1 M and lower. The FPEX solvent effectively extracts cesium and strontium in the range of >0.5 M to <2.5 M HNO$_3$. Organic complexants (such as guanidine carbonate or methylamine carbonate and DTPA) are required to strip cesium and strontium from the CCD/PEG solvent. Dilute nitric acid effectively strips both cesium and strontium from the FPEX solvent.

A flowsheet test of the CCD/PEG process was successfully completed using 24 stages of 3.3-cm diameter centrifugal contactors and simulated feed solution. With this test, 99.6% Cs separation and >99.995% Sr separation were obtained. Additionally, a decontamination factor of 2.6E+05 was obtained for the lanthanides (Am surrogate) from the Cs and Sr strip product, which indicates the Cs/Sr strip product would be non-TRU. Based upon these results, a flowsheet was recommended for testing at ANL-E with actual spent LWR fuel.

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