

Development of Technologies for the Simultaneous Separation of Cesium and Strontium from Spent Nuclear Fuel as Part of an Advanced Fuel Cycle

2005 AIChE Spring National Meeting

J. D. Law
R. S. Herbst
D. H. Meikrantz
D. R. Peterman
C. L. Riddle
R. D. Tillotson
T. A. Todd

April 2005

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may not be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



Development of Technologies for the Simultaneous Separation of Cesium and Strontium from Spent Nuclear Fuel as Part of an Advanced Fuel Cycle

J. D. Law, R. S. Herbst, D. H. Meikrantz, D. R. Peterman, C. L. Riddle, R. D. Tillotson, and T. A. Todd, Idaho National Laboratory, Idaho Falls, ID 83415

Abstract

As part of the Advanced Fuel Cycle Initiative, two solvent extraction technologies are being developed to simultaneously separate cesium and strontium from dissolved spent nuclear fuel. 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. Countercurrent flowsheets have been designed and tested on simulated and actual spent nuclear fuel feed streams 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-butyl)dicyclo-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 than 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. A flowsheet for treatment of spent nuclear fuel is currently being developed.

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.

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 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-butyl)dicyclo-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.

EXPERIMENTAL

All diluents were reagent grade and were used as received. Deionized water was used to prepare all aqueous acid solutions. 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 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.

Nitric acid dependency tests for Cs and Sr were performed in varying concentrations of HNO₃ 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.

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 for the flowsheet testing was 0.13 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 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 concentration.

Results of cesium and strontium nitric acid dependency tests for the CCD/PEG process with the CCD/PEG solvent at temperatures of 15°C, 25°C, and 35°C are presented in Figure 1. 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 HNO₃ to 6.5 in 10 M HNO₃. 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 HNO₃, with the optimum nitric acid concentration below approximately 1.0 M.

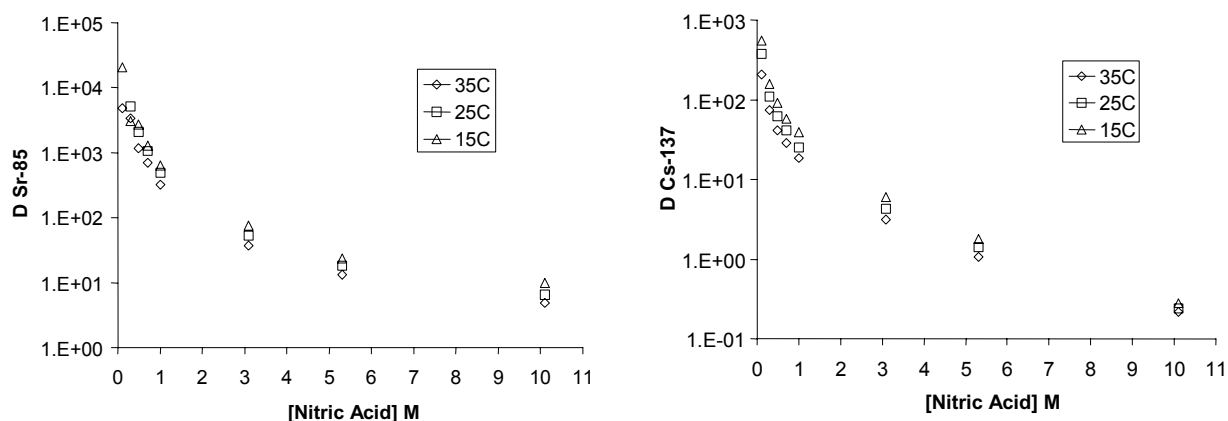


Figure 1. Nitric Acid Dependencies of Sr and Cs in CCD/PEG solvent

Results of cesium and strontium nitric acid dependency tests for the FPEX process are shown in Figure 2. 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.

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 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, 9). 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 3.

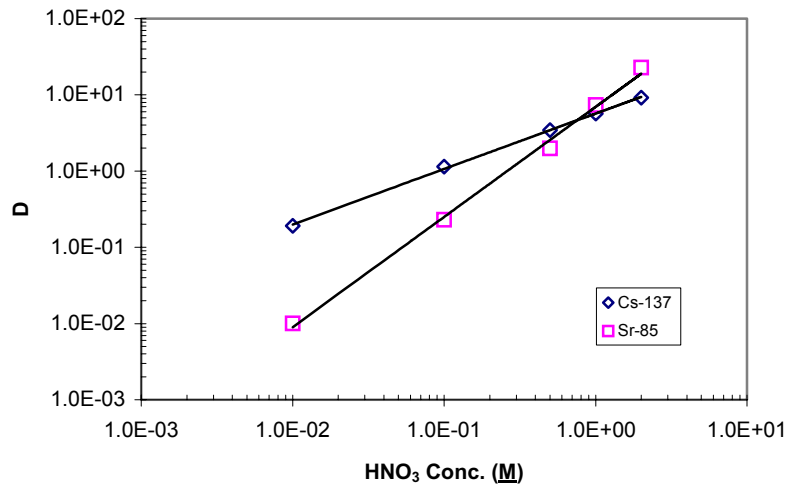


Figure 2. Nitric acid dependencies of Cs and Sr in the FPEX solvent

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.

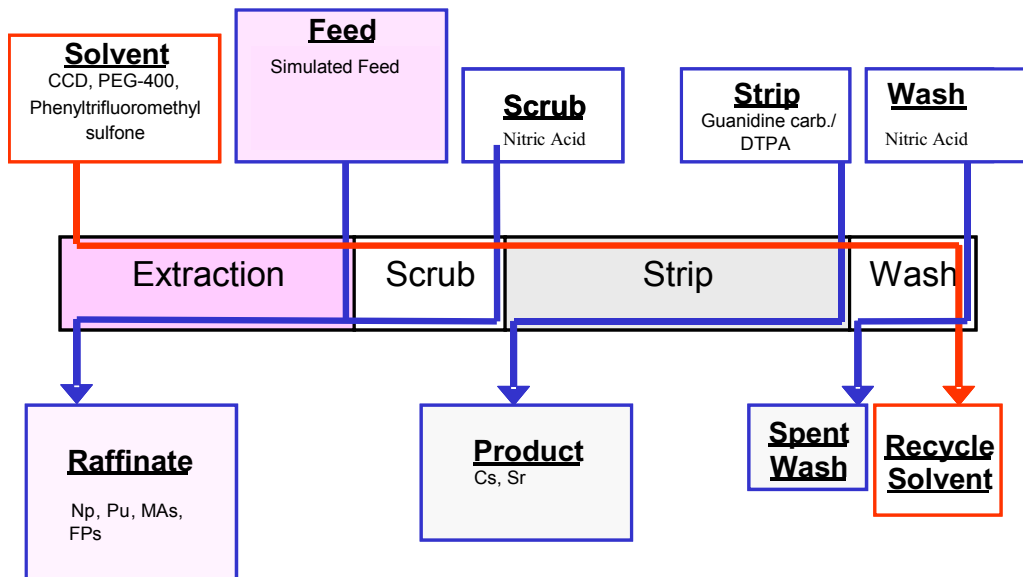


Figure 3. Schematic of flowsheet used for testing of CCD/PEG process

The percentages of Cs, Sr, and the lanthanides in the effluent streams at the time of shutdown are shown 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.

Distribution coefficients for ¹³⁷Cs 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 ⁸⁵Sr, 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 ¹³⁷Cs and ⁸⁵Sr support the overall removal efficiencies of 99.6% and >99.995%, respectively, that were achieved in this testing. For ²⁴¹Am, 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.

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%	<.0036%	<0.0002%	113.3%
Wash Effluent	0.04%	< 0.30%	<0.0002%	<.0002%	0.0004%	<.00006%	<.0009%	<0.0002%	<0.004%

Process Comparison

The FPEX process has the following potential advantages as compared to the CCD/PEG process: 1) stripping with a dilute nitric acid solution results in no inert or organic components in the strip product stream and is easily treated, 2) the activity of actinides extracted with the process is minimal whereas a small amount of TRU extraction is obtained with the CCD/PEG process which makes it more difficult to achieve a non-TRU strip product, 3) the diluent in the FPEX process is Isopar-L, as compared to phenyltrifluoromethyl sulfone diluent with the CCD/PEG process, which makes it more compatible with the other likely solvent extraction processes for the separation of U, Pu, Np, and actinides, and 4) the FPEX process is effective at nitric acid concentrations up to 2 M as compared to 1.35 M with the CCD/PEG process.

The CCD/PEG process has the following potential advantages as compared to the FPEX process: 1) the CCD/PEG process is a considerably more mature process with many years of development and demonstrated effectiveness, 2) The chemical/radiation stability of the CCD/PEG solvent is demonstrated to be very good whereas this is less known with the FPEX process, and 3) the strip product with the CCD/PEG process is basic which may be more amenable to solidification via steam reforming or ion exchange.

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 HNO₃. 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.

ACKNOWLEDGMENTS

This work was carried out under the auspices and financial support of the U. S. Department of Energy, Office of Nuclear Energy, Science and Technology through contract DE-AC07-99ID13727. The authors would like to thank their colleagues at the Khlopin Radium Institute in St. Petersburg, Russia for their support and prior research in developing the Universal Solvent Extraction Process for the treatment of INEEL waste solutions, which provided the basis for the development of the CCD/PEG process. We also wish to thank Drs. Bruce A. Moyer, Laetitia H. Delmau and Peter V. Bonnesen at Oak Ridge National Laboratory for providing the calixarene crown ether, the modifier and many helpful discussions.

REFERENCES

1. Laidler, J. J.; Bresee, J. C., "The U.S. Advanced Fuel Cycle Initiative: Development of Separation Technologies," *proceedings of Advances for Nuclear Fuel Cycles (ATALANTE 2004)*, Nimes, France, June 2004.
2. Wigeland, R. A.; Bauer, T. H.; Fanning, T. H.; Morris, E. E., "Spent Nuclear Fuels Separation and Transmutation Criteria for Benefit to a Geologic Repository," *proceedings of Waste Management '04*, Tucson, AZ, March 2004 (submitted to Nuclear Technology).
3. Law, J. D.; Herbst, R. S.; Peterman, D. R.; Tillotson, R. D.; Todd, T. A. *Nuclear Technology*, **2004**, 147(2), 284-290.
4. Law, J. D.; et al., *submitted to Solvent Extraction and Ion Exchange*, 2004.

5. Horwitz, E. P.; Dietz, M. L.; Fisher, D. E. *Solvent Extraction and Ion Exchange*, **1991**, 9(1), 1-25.
6. Bonnesen, P. V.; Delmau, L. H.; Moyer, B. A.; Leonard, R. A. *Solvent Extraction and Ion Exchange*, **2000**, 18 (6), 1079–1108.
7. Sachleben, R.A.; Bonnesen, P.V.; Descazeaud, T.; Haverlock, T.J.; Urvoas, A.; Moyer, B.A. *Solvent Extr. Ion Exch.* **1999**, 17(6), 1445-1459.
8. Bonnesen, P.V.; Haverlock, T.J.; Engle, N.L.; Sachleben, R.A.; Moyer, B.A.; Development of Process Chemistry for the Removal of Cesium from Acidic Nuclear Waste by Calix[4]arene-crown-6 Ethers, ACS Symposium Series 757 (Calixarenes for Separations), American Chemical Society, Washington, D.C., 2000, 27-44.
9. Riddle, C. L.; et al. *submitted to Solvent Extraction and Ion Exchange*, 2004.