

INL/CON-07-13096
PREPRINT

Advances in Development of the Fission Product Extraction Process for the Separation of Cesium and Strontium from Spent Nuclear Fuel

11th International Conference on Environmental
Remediation and Radioactive Waste Management
(ICEM 2007)

Jack Law
Dean Peterman
Cathy Riddle
David Meikrantz
Terry Todd

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

September 2007

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may 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.



ICEM07-7077

ADVANCES IN DEVELOPMENT OF THE FISSION PRODUCT EXTRACTION PROCESS FOR THE SEPARATION OF CESIUM AND STRONTIUM FROM SPENT NUCLEAR FUEL

Jack Law/Idaho National Laboratory

Dean Peterman/INL

Cathy Riddle/INL

David Meikrantz/INL

Terry Todd/INL

ABSTRACT

The Fission Product Extraction (FPEX) Process is being developed as part of the United States Department of Energy Advanced Fuel Cycle Initiative for the simultaneous separation of cesium (Cs) and strontium (Sr) from spent light water reactor (LWR) fuel. Separation of the Cs and Sr will reduce the short-term heat load in a geological repository, and when combined with the separation of americium (Am) and curium (Cm), could increase the capacity of the geological repository by a factor of approximately 100. The FPEX process is based on two highly specific extractants: 4,4', (5')-Di-(t-butylidicyclo-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. Results of flowsheet testing of the FPEX process with a simulated feed solution in 3.3-cm centrifugal contactors are detailed. Removal efficiencies, distribution coefficient data, coextraction of metals, and process hydrodynamic performance are discussed along with recommendations for future flowsheet testing with actual spent nuclear fuel.

INTRODUCTION

As part of the Advanced Fuel Cycle Initiative (AFCI), the reduction in volume and heat generation of spent nuclear fuel requiring geologic disposal is currently being addressed [1]. The goal is to optimize utilization of the nation's first repository and potentially reduce or eliminate the need for additional repositories. This goal can be achieved through

separating long-lived, highly toxic elements; reducing high-level waste volumes and the toxicity of spent nuclear fuel; and reducing the heat generation of spent nuclear fuel. The Idaho National Laboratory (INL) is working closely with a team of national laboratories and other organizations to support development of these separations processes.

Key to the reduction of short-term heat load in a geological repository is the separation of ¹³⁷Cs and ⁹⁰Sr. Removing these highly radioactive fission products reduces the short-term (~100 yr) heat-generation source of the spent nuclear fuel. Once separated, the Cs and Sr would be placed in storage until the activity has decayed to low-level waste (LLW) levels, at which time it could potentially be disposed of as a non-transuranic (TRU) LLW.

To support development of this separations process, technologies for simultaneously separating Cs and Sr from dissolved spent nuclear fuel are being developed. In previous work, Cs and Sr have been removed from acidic nuclear waste solutions and related alkaline wastes using separate solvent-extraction processes designed specifically for these elements. In general, crown ethers have been selected to remove strontium, [2 – 4], and calixarenes [5 – 10] have been selected for separating cesium. A novel process is being developed at INL that combines these two types of extractants to constitute a solvent that will extract both cesium and strontium from acidic media, simultaneously. This technology, the Fission Product Extraction (FPEX) Process, utilizes 4,4', (5')-di-(t-butylidicyclohexano)-18-crown-6 (DtBuCH18C6) for the extraction of Sr, calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) for the extraction of Cs, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) as a modifier, TOA (trioctylamine) and an Isopar[®] L diluent. Initial development of the FPEX process at INL began

in FY-04 [11]. Results from this initial testing were promising. Further testing was performed in FY-05 and FY-06.

Process goals for separating Cs and Sr from the spent LWR fuel require $\geq 99.9\%$ removal. Additionally, the TRU content of the Cs/Sr product must be less than 100 nCi/g so that this waste stream will be classified as a non-TRU LLW once the ^{137}Cs and ^{90}Sr decay. This requires a decontamination factor of approximately $1\text{E}+05$ to $1\text{E}+06$, depending on the fuel composition and preceding separation processes, for the TRU from the Cs/Sr product. Laboratory testing indicates that the FPEX process can effectively separate Cs and Sr from acidic solutions containing large quantities of actinides and lanthanides, such as spent LWR fuel [11]. It should be noted that there are issues relative to the stability of the BOBCalixC6. Due to the alkyl substituent on the benzyl moiety of the BOBCalixC6, the benzyl ring is activated towards nitration. While nitration of the BOBCalixC6 does not severely impact the measured Cs distribution ratios, the products of the nitration of BOBCalixC6 are less soluble in the organic solvent. This further exacerbates the limited BOBCalixC6 solubility in the process solvent. An effort is underway to develop a more stable calixarene for the extraction of Cs. However; the scope of this flowsheet testing was to evaluate the performance of the FPEX process with the BOBCalixC6 Cs extractant.

EXPERIMENTAL

Deionized water was used to prepare all aqueous acid solutions. The nitric acid was reagent grade from Aldrich Chemical Co. (Milwaukee, WI). Isopar[®] L isoparaffinic diluent was obtained from Exxon Chemical Company (Houston, TX). The ^{85}Sr and ^{137}Cs radiotracers used for spiking the simulants were obtained as $^{85}\text{SrCl}_2$ in 1 M HCl and $^{137}\text{CsCl}$ in 1 M HCl from Isotope Products (Burbank, CA). The DtBuCH18C6 crown ether was purchased from Eichrom Industries, Inc. (Darien, IL). The BOBCalixC6 calixarene crown ether was received from Marshallton Research Laboratories (King, NC). The FPEX solvent used in these studies consisted of 0.075 M DtBuCH18C6, 0.007 M BOBCalixC6, 0.75 M Cs-7SB modifier, and 0.003 M trioctylamine (TOA) in Isopar[®] L.

The simulant compositions used in this testing are based on a typical composition expected for leaching of spent LWR fuel with nitric acid. It was also assumed that the UREX process for the separation of uranium (U) and technetium (Tc) from the spent LWR would precede this process; therefore, the simulant used did not contain U.

Analytical measurement of the radioactive tracers used in this testing (^{241}Am , ^{154}Eu , ^{137}Cs , and ^{85}Sr) was performed using gamma spectroscopy. Concentrations of stable (non-radioactive) metals were determined by inductively coupled plasma mass spectrometry (ICP-MS). Stable metals in the organic phase were analyzed by destruction of the organic, followed by ICP-MS analysis.

RESULTS AND DISCUSSION

Flowsheet testing of the FPEX process for separating Cs and Sr from dissolved LWR fuel was performed using a series of 3.3-cm diameter centrifugal contactors and simulated feed solution (see Fig. 1). The FPEX solvent used for the flowsheet testing contained BOBCalixC6 (Cs extractant), DtBuCH18C6 (Sr extractant), Cs-7SB Modifier and TOA in Isopar-L. The flowsheet shown in Fig. 2 was used for testing and was designed to meet the requirements of removing $>99.9\%$ Cs and Sr and leaving < 100 nCi/g TRU contamination in the Cs/Sr strip product solution.



Fig. 1. This figure shows the configuration for the centrifugal contactor experiment.

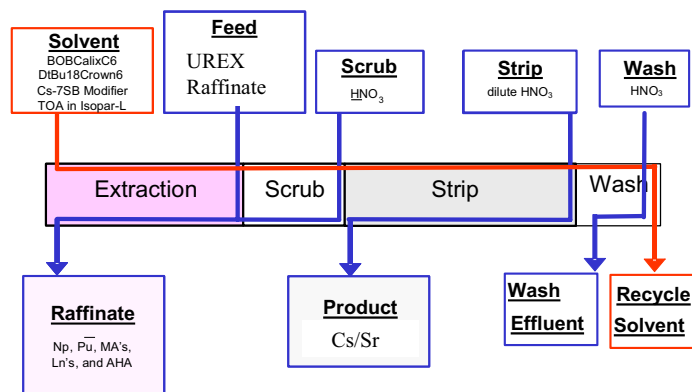


Fig. 2. This flowsheet shows the FPEX process.

The flowsheet testing consisted of approximately two hours of startup, including the initiation of feed flows and filling of contactor stages, followed by 270 minutes of operation with feed simulant. The solvent was recycled during testing for a total of 2.6 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. After shutdown, liquid phases from the stages were drained into individual bottles and the two phases sampled.

The percentages of Cs, Sr, and the lanthanides in the effluent streams at the time of shutdown are shown in Table I. The removal efficiencies were $>99.99\%$ and $>99.98\%$ for Cs

and Sr, respectively. Greater than 99.98% of the barium (Ba) and

Table I. Percentages of each component in effluents.

Effluent Stream	Cs	Sr	Ba	La	Ce
Raffinate	<3E-5%	< 2E-4%	<1E-4%	89.7%	90.6%
Strip Product	98.9%	101%	101%	0.03%	9E-4%
Wash Effluent	2E-04%	<3E-4%	<1E-4%	3E-4%	3E-4%
Effluent Stream	Nd	Sm	Zr	Rb	
Raffinate	96.6%	96.4 %	96.1%	<2E-04%	
Strip Product	1E-03%	2E-3%	<1E-3%	101%	
Wash Effluent	2E-4%	2E-4%	2E-3%	<2E-4%	

99.99% of the rubidium (Rb) were also extracted. Distribution coefficients for Cs, Sr, Ba, and Rb were calculated on each stage. ¹³⁷Cs and ⁹⁰Sr were also spiked into the stage samples, re-equilibrated, sampled and analyzed. Extraction distribution coefficients for Sr generally ranged from 5 to 10. The variability in results is attributed to the difficulty in analyzing the organic phase samples by ICP. For the stage samples spiked with ⁸⁵Sr, distribution coefficients ranged from 2.9 to 4.6. Stable Cs distribution coefficients were not determined due to difficulties analyzing the organic phase samples. However, ¹³⁷Cs results in the extraction section ranged from 6.7 to 9.3. Extraction distribution coefficients ranged from 2.9 to 4.4 for Ba and from 3.5 to 4.9 for Rb. Strip distribution coefficients for Cs and Sr were as expected; approximately 0.25 for Cs and 0.007 for Sr.

To get an idea of how much TRU would be extracted with this flowsheet, ²⁴¹Am and ¹⁵⁴Eu were spiked into the stage samples, re-equilibrated, sampled and analyzed. Extraction distribution coefficients for Am ranged from <0.009 to <0.04 and for Eu ranged from <0.001 to <0.004. In all cases, activities in the organic phase were below analytical detection limits so actual distribution coefficients are not known. These low distribution coefficients indicate that the amount of TRU extracted with this flowsheet would be very small; however, testing with actual spent nuclear fuel will be required to verify that the Cs/Sr strip product is non-TRU.

CONCLUSIONS

An FPEX flowsheet has been successfully demonstrated with spent LWR fuel simulant. Hydraulic performance of the process was excellent. Removal efficiencies of >99.99 and >99.98% were obtained for Cs and Sr, respectively. These results exceeded the process goals of 99.9% separation. Additionally, distribution coefficients for Am and Eu were very low indicating little of the TRU should be extracted with this

flowsheet. Flowsheet testing with actual spent fuel is recommended to verify these results. Development of alternative calixarenes for the extraction of Cs are also recommended to increase the solubility and stability of the calixarene during long-term operation.

ACKNOWLEDGMENTS

This work was performed under the auspices and financial support of the United States Department of Energy, Office of Nuclear Energy, Science and Technology through contract DE-AC07-05ID14517. The authors would also like to acknowledge Byron White for the analytical support provided.

REFERENCES

1. J. Laidler, "Chemical Separation Schemes for Partitioning and Transmutation Systems," ANL/CMT/CP-107557, Proc. ANS 2002 Annual Meeting, Hollywood, FL, June 9-13, (2002).
2. Horwitz, E.P.; Dietz, M.L.; Fisher, D.E. SREX: a new process for the extraction and recovery of strontium from acidic nuclear waste streams. *Solvent Extr. Ion Exch.* 1991, **9** (1), 1–25.
3. Wood, D.J.; Tranter, T.J.; Todd, T.A. Effect of the interference of alkali and earth metal ions on the extraction of ⁹⁰Sr from acidic nuclear waste solutions by 18-crown-6 derivative. *Solvent Extr. Ion Exch.* 1995, **13** (5), 829–44.
4. McDowell, W.J. Crown ethers as solvent extraction reagents: where do we stand? *Ep. Sci. and Technol.* 1988, **23**, 1251–68.
5. Dozol, J.F.; Simon, N.; Lamare, V.; Roquette, H.; Eymard, S.; Tournois, B.; DeMarc, D.; Macias, R.M. Solution for Cs removal from high-salinity acidic or alkaline liquid waste: the crown calix[4]arenes. *Sep. Sci. and Technol.* 1999, **34** (6&7), 877–909.
6. Bonnesen, P.V.; Delmau, L.H.; Haverlock, T.J.; Moyer, B.A. Alkaline-Side Extraction of Cesium from Savannah River Tank Waste Using a Calixarene Crown Ether Extractant; Oak Ridge National Laboratory: Oak Ridge, TN December 1998; Report ORNL/TM-13704.
7. Dozol, J.F.; Asfari, Z.; Hill, C.; Vicens, J. Bis-crown calix[4]arenes, their preparation process and their use for the selective extraction of cesium and actinides. French Patent n892 14245 B11385.3/MDT, Nov. 26, 1992.
8. Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.J.; Egberink, R.J.M.; DeJong, F.; Rienhoudt, D.N. Synthesis, complexation and membrane transport studies of 1,3-alternate calix[4]arene crown-6 conformers: a new class of cesium selective ionophores. *J. Am. Chem. Soc.* 1995, **117**, 2767–77.
9. Sachleben, R.A.; Bonnesen, P.V.; Descazeaud, T.; Haverlock, T.J.; Urvoas, A.; Moyer, B.A. Surveying

- the extraction of cesium nitrate by 1,3-alternate calix[4]-arene crown-6 ethers in 1,2-dichloroethane. *Solvent Extr. Ion Exch.* 1999, **17** (6), 1445–59.
10. 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, 26–44.
 11. Riddle, C. L., Baker, J. D., Law, J. D., McGrath, C. A., Meikrantz, D. H., Mincher, B. J., Peterman, D. R., and Todd, T. A. Fission Product Extraction (FPEX): Development of a Novel Solvent for the Simultaneous Separation of Strontium and Cesium from Acidic Solutions. *Solvent Extr. Ion Exch.* 2005, **23** (3), 449-461.