LAB-SCALE DEMONSTRATION OF THE UREX+1a PROCESS USING SPENT FUEL

Candido Pereira, George F. Vandegrift, Monica C. Regalbuto, Allen Bakel,
Delbert Bowers, Artem V. Gelis, Andrew S. Hebden, Laura E. Maggos,
Dominique Stepinski, Yifen Tsai, and James J. Laidler
Argonne National Laboratory

ABSTRACT

Through the Advanced Fuel Cycle Initiative (AFCI) and the Global Nuclear Energy Partnership, the Department of Energy's Office of Nuclear Energy is developing advanced technologies for treating spent nuclear fuel to greatly expand repository capacity, improve proliferation resistance, and recover valuable energy that would otherwise be discarded; thus, a stable energy supply for the future is assured. An important element of this initiative is the separation of key radionuclides followed by either superior waste-disposal forms and/or transmutation of long-lived isotopes. To that end, advanced fuel reprocessing systems that separate key radionuclides from spent fuel are being developed. One of these systems is the UREX+1a process.

UREX+1a consists of a sequence of four solvent-extraction processes and one ion exchange operation that achieve the following objectives: (1) recovery of U and Tc (UREX followed by ion exchange), (2) recovery of Cs and Sr (CCD-PEG), and (3) group recovery of all transuranic elements, predominantly Pu, Np, Am and Cm (TRUEX followed by TALSPEAK). This paper discusses the results of the demonstration of the entire UREX+1a process using spent nuclear fuel, as well as future development needs and plans.

INTRODUCTION

The UREX+1a process is being developed at Argonne National Laboratory (Argonne) and other national laboratories under the Advanced Fuel Cycle Initiative (AFCI) and the Global Nuclear Energy Partnership (GNEP), funded by the Department of Energy's Office of Nuclear Energy [1]. At the end of FY 06, all four segments of the UREX+1a process, incorporating both solvent extraction and ion exchange, were demonstrated in the Chemical Engineering Division of Argonne.

Processing Goals

The recovery and purification goals of the UREX+1a process as set by the AFCI program are similar to those set for the other UREX+ processes demonstrated in 2003, 2004, and 2005 [2-4]:

- Recovery of transuranic elements (TRU) must be >99.9% to make possible a >100-fold reduction in heat load to the repository. To enable TRU recycle, the lanthanide content of this stream must meet fast reactor fuel specifications, which have not yet been defined. The requirements for MOX fuel as described in ASTM C833-01, <3mg/g heavy metal, were set as an initial target.

- Uranium recovery must be >95%. Its purity requirement would allow its disposal as low-level waste according to 10CFR61.55. The criterion to contain less than 100 nCi/g of TRU is the most difficult to meet, requiring a decontamination factor from plutonium of $>10^5$. If the uranium is destined for recycle in reactor fuel, its purity requirements are more severe and would be governed by ASTM C 788-98.

- Technetium recovery must be >95% to provide a 20-fold decrease in off-site dose. This effect is only expected when the Tc is encapsulated in a high integrity waste form compared to spent fuel.

- To achieve a 100-fold reduction in heat load to the repository, a recovery of 99% for Cs and Sr is required. The purity requirement for the Cs/Sr decay-storage form must be less than 100 nCi/g TRU to allow its ultimate disposal as low-level waste.

- The raffinate from the UREX+1a process contains all of the soluble fission products but Cs, Sr, Ba, Rb, Tc, and I. It will be converted to a solid for disposal in the repository. The recovery criteria for each component given above limits the quantity that will reside in this solid, e.g., only 0.1% of Pu and 1% of Cs and Sr can be left in these raffinates.

Process Demonstration

The UREX+1a process is a cascade of four solvent separate extraction processes, referred here as "process segments" and one ion exchange process. The process steps demonstrated included: (1) recovery of U and Tc and (UREX), (3) separation of U from Tc (ion exchange) (3) recovery of Cs and Sr (CCD-PEG), (4) separation of transition metal fission products from lanthanide fission products and TRU elements (TRUEX), and (5) recovery of lanthanide fission products (TALSPEAK) and (6) recovery of Pu, Np, Am, and Cm (TALSPEAK).

The process was demonstrated with dissolved irradiated fuel that consisted of a mixture of two fuels: 461 g of ATM-105 and 8 g of H.B. Robinson fuel. The ATM-105 fuel (Cooper Nuclear Power Plant, Nebraska) was declad fuel with an average burn-up of 33 GWD/MTIHM. The Robinson fuel had an average burn-up of approximately 76 GWd/MTU. The high burnup fuel was added to increase the amount of Cm in the dissolved fuel to improve its detection. The dissolution was done in the modified glass vessel equipped with a condenser at the boiling point of the acid (~100ºC).

Two multistage 2-cm centrifugal contactors were used for this demonstration—one unit located in a shielded cell and a second unit in a vacuum-frame hood. Because of the presence of ^{137}Cs, ^{90}Sr, and ^{154}Eu in the dissolved fuel, all of the extraction processes sections were run in the shielded cell except the UREX strip. Ion exchange to remove the Tc from the UREX strip product was also conducted in a hood. Because the organic phase is the heavy phase in the CCD-PEG process, extensive decontamination and refitting of feed and effluent stages and lines were required between these two process segments.

The process flowsheets were designed for the number of stages available for use and, therefore, not optimized for plant-scale processes. On a production scale, the UREX+1a process would be

run continuously, with all of solvent extraction processes run sequentially and the ion exchange process in parallel. Because of space constraints, the number of stages available in the shielded cell facility was limited which necessitated that each process segment be run individually, independent of the other segments.

All of the flowsheets for the UREX+1a solvent extraction process segments were developed at Argonne with the exception of CCD-PEG which was designed by Idaho National Laboratory (INL)[8] using the Argonne Model for Universal Solvent Extraction (AMUSE) code. AMUSE is an updated version of the Generic TRUEX Model (GTM) that was developed during the 1980s to design multistage countercurrent flowsheets for the TRUEX solvent extraction process [5, 6]. AMUSE has been developed to give highly accurate predictions of chemical behavior in a solvent extraction process by calculating component distribution ratios using (1) chemically correct equilibria and (2) thermodynamic activities for major components hydrogen ion, nitrate, and water [7]. Further, the countercurrent mass balance algorithm contains terms for stage efficiency and other-phase-carryover for both the aqueous and organic phases.

The UREX process segment has three sections (extraction, scrub, and strip). The three parts are shown in Fig. 1. The solvent for the UREX process is the typical PUREX solvent, tributyl phosphate (TBP) dissolved in n-dodecane. In the first process segment, uranium and technetium are extracted from the bulk of the dissolved fuel. Co-extraction of Pu and Np is prevented by introduction of a complexant/reductant in scrub section. The loaded solvent is stripped of U and Tc by dilute nitric acid. In this demonstration, the solvent was not recycled; in an actual plant

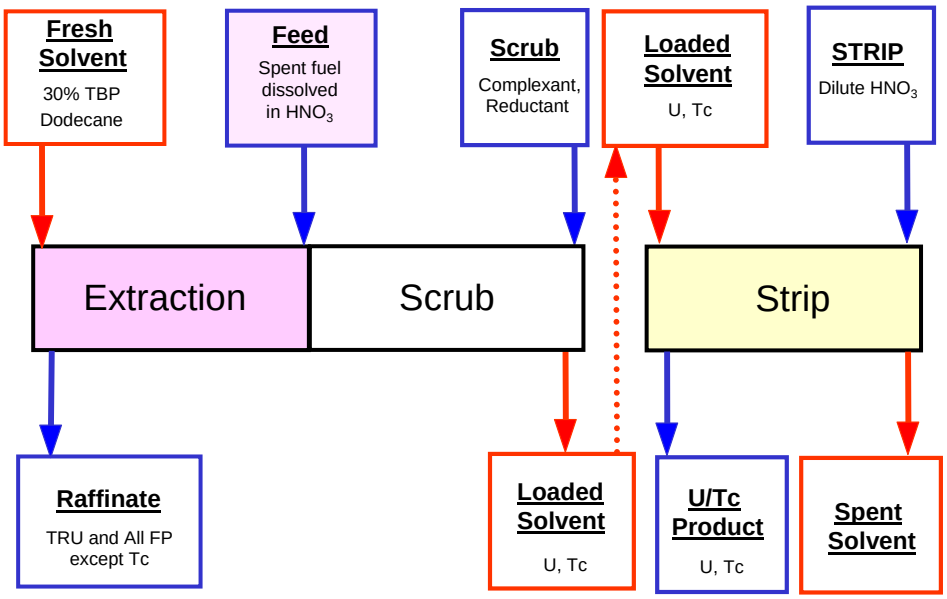

Fig. 1. UREX Process Segment Flowsheet

application, a solvent wash section would be added to the process, before recycling the solvent to the front end of the process.

Technetium is removed from the U/Tc-strip product by an ion exchange process. The U/Tc product is fed directly to a column loaded with Reillex^{TM} HPQ resin. The anion exchange resin recovers Tc as pertechnetate under process conditions developed in consultation with workers at Oak Ridge National Lab based on earlier work conducted at Los Alamos National Lab [9]. The experiment was run with three columns in series.

The raffinate from the UREX segment is the feed to the CCD-PEG process segment shown in Fig. 2. The solvent for this process is a mixture of chlorinated cobalt dicarbollide (CCD) for cesium extraction and polyethylene glycol (PEG) for strontium extraction; the diluent is phenyltrifluoromethyl sulfone (FS-13). This process segment was run with four sections. In the extraction section, Cs and Sr (with Rb and Ba) are extracted into the solvent. In the scrub section, a solution of nitric acid at moderate concentration, scrubs other species, primarily transuranic and rare earth elements (TRU), from the solvent. In the strip section, the alkali and alkaline-earth cations are stripped by a combination of an organic ammonium carbonate salt and a complexing agent. This solvent was recycled due to a limited supply; a solvent wash section was added to reprotonate the CCD extractant in the solvent.

To serve as the TRUEX feed, the CCD-PEG raffinate composition was adjusted by addition of concentrated nitric acid. Just prior to introduction of the feed, a reductant was added to reduce Np(V) to extractable Np(IV). The TRUEX process separates the rare earth and transuranic actinides from the other components in the CCD-PEG raffinate, notably zirconium and noble metals. The process flowsheet is given in Fig. 2. The process consists of five sections: extraction, three scrubs, and a strip. Trivalent, tetravalent, and hexavalent ions are extracted. In the first scrub section, impurities are removed from the solvent using oxalic acid. Moderately concentrated nitric acid scrubs oxalic acid from the solvent in the second scrub section. In the third scrub section, addition of dilute nitric acid lowers the acid concentration in the solvent to allow effective stripping. The actinides and rare earth elements are stripped from the solvent using a lactate buffer containing a complexant which becomes the feed to TALSPEAK.

Since the TRUEX strip is a buffered lactic acid feed similar to the TALSPEAK feed, only a minor pH adjustment was required. The TALSPEAK process segment has three sections: extraction, scrub, and strip, as shown in Fig. 3. The actinide:lanthanide separation achieved by TALSPEAK is based on the preferential complexation of actinides by aminopolyacetic acids and effective extraction of trivalent lanthinides by bis(2-ethylhexyl)phosphoric acid (HDEHP). In the extraction section, the more weakly complexed lanthanides are extracted, while the stronger actinide complexes remain predominantly in the aqueous phase. The scrub removes the small fraction of Am and Cm that are extracted by HDEHP. The lanthanides are stripped from the solvent with moderately concentrated nitric acid.

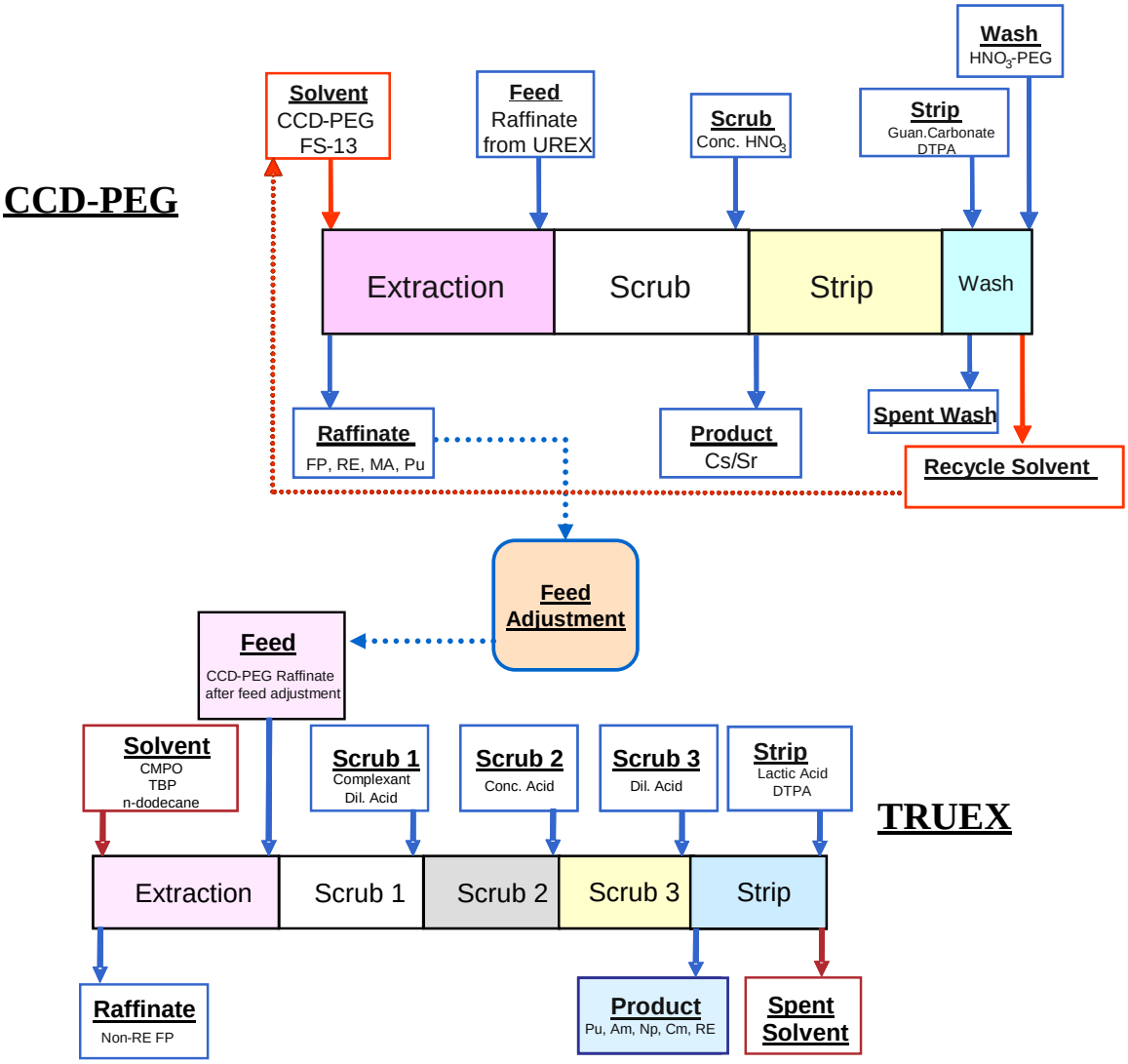

Fig. 2. CCD-PEG and TRUEX Process Segment Flowsheets

RESULTS

Overall, the demonstration was a success. The goals for the product recoveries and purity specifications were met based on preliminary analysis of all of the effluents. The isotopic

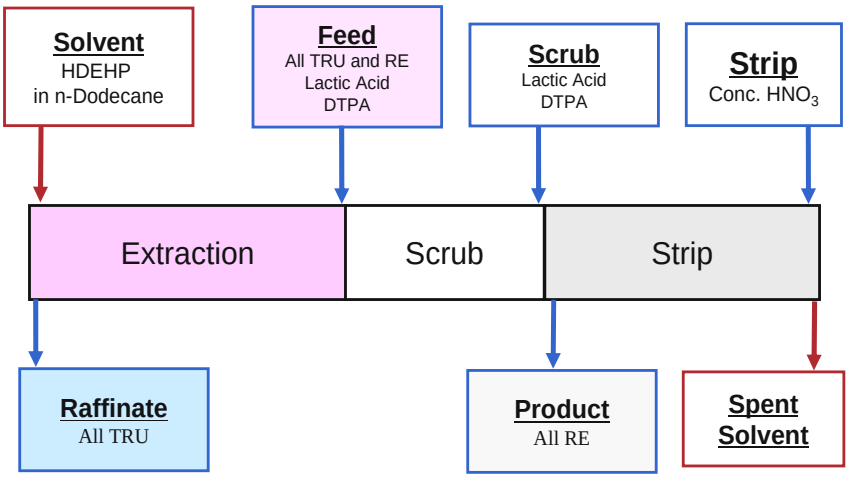

Fig. 3. TALSPEAK Process Segment Flowsheet

concentrations were obtained by: (1) gamma spectroscopy, (2) alpha spectroscopy, and (3) inductively coupled plasma-mass spectroscopy (ICP-MS). ICP-MS was used to analyze the effluents from all process segments and are the primary analyses reported here for trace elements. The following sections discuss how the effluent streams met the AFCI process goals.

U/ and Tc –Products

Table I shows the composition of the uranium/technetium product stream from the UREX process segment. The results show that the U/Tc product met all specifications for disposal of the uranium as a low level waste. The strip solution contained very little extracted Pu, while the raffinate contained very little uranium and is dominated by Pu, rare earths, Cs, and transition metal fission products.

Table I Isotopic purity of U/Tc product and specifications for Class C Low-level waste

Isotope	Spec.(nCi/g)	Calc. (nCi/g)
Sr-90	<1.60E+06	4.00E+05
Cs-137	<1.10E+06	8.1E+05
TRU[a]	<120	18.7
Pu-241[b]	<4130	130.1
Cm-242	<2.40E+04	< 5.5E+03

[*] Conversions were made to LLW (10CFR61.55) Ci/m^3 Class-C limits for fission products to nCi/g assuming the product was UO_3. The 100 nCi/g-waste limit for TRU waste was converted to g-U assuming the waste was UO_3.

[a] TRU includes ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, and ^{241}Am.

[b] ^{241}Pu based on ^{239}Pu:^{241}Pu ratio from ORIGEN

Technetium was effectively separated from uranium by the Reillex HPQ column. Fig. 4 shows breakthrough curves for the three columns in series. Breakthrough at 1% of the initial Tc content

in the effluent, occurs at 440 column volumes for the first column. For the second column, 50% breakthrough occurs at 2310 column volumes and corresponds with a 98% breakthrough on the first column. No Tc was detected in the effluent of the third column during the test.

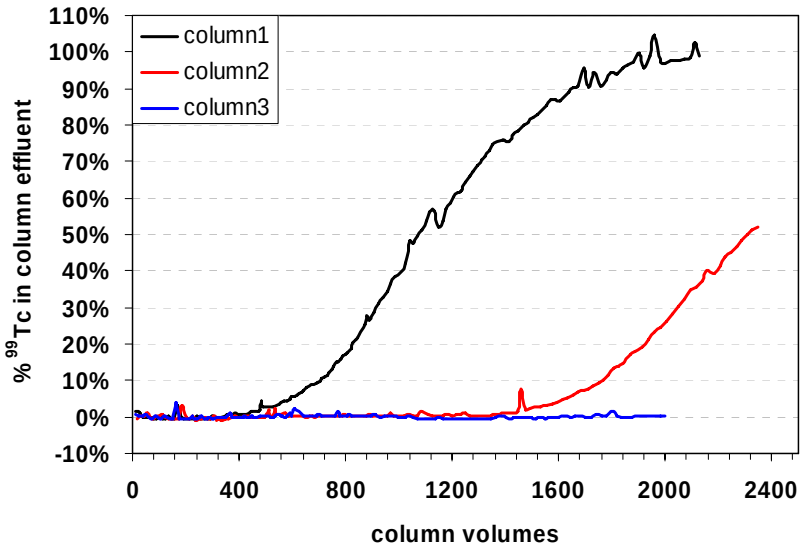

Fig. 4. Breakthrough curves for Tc anion exchange columns

Cs/Sr-Product

The elemental distribution between the raffinate and product is given in Table II. Essentially all of the cesium (it was not detected in the raffinate) and >99% of the strontium in the effluents is in the product. Rb and Ba are similarly distributed between the raffinate and product. The Cs and Rb background levels were high and which reduced their detectability in the raffinate. The rare earths and Am are predominantly in the raffinate as desired.

TRUEX--Product

The elemental distribution between the raffinate and product streams is given in Table III. Essentially all of the Pu, Np, and Am, and >99.9% of the rare earth elements report to the product. The major fraction of non-rare earth fission products end up in the raffinate as desired.

Table II: Elemental Distribution in the CCD-PEG Raffinate and Product, %

Element	*Raffinate*	*Product*
Cs	< 0.15%	> 99.85%
Sr	0.86%	99.14%
Rb	BDL	(100%)
Ba	0.4%	99.6%
Am	(100%)	BDL
RE	99.93%	0.07%

BDL = Below detection limits of ICP-MS
Values in parenthesis indicate amounts of the element in other streams were not measurable.

Table III. Elemental distribution in the TRUEX effluents

Element	*Raffinate*	*Product*
Ru	94.6%	5.4%
Rh	99.8%	0.2%
Mo	96.4%	3.6%
Pd	77.2%	22.8%
Pu	< 0.005%	> 99.995%
Np	< 0.001%	> 99.999%
Am	BDL	(100%)
RE	< 0.09%	> 99.91%
Zr	99.6%	0.4%

BDL = Below detection limits of ICP-MS

TALSPEAK—Product

Pu, Np, and Am are the major components in the raffinate. Rare earths and transition metal fission products are the primary elements in the product. Table IV shows the elemental distribution between the raffinate and product streams. TRU recovery is very high with the process as >99.99% of the Pu, Np and Cm remain in the raffinate. The Am is slightly lower at 99.97%. Essentially all of the lanthanides end up in the product. The measured lanthanide concentration in the raffinate was <0.02 mg/g HM. These results show that TALSPEAK performed as desired.

Table IV Element distribution in TALSPEAK Effluents

Element	*Raffinate*	*Product*
Pu	> 99.998%	< 0.002
Np	> 99.9992	< 0.0008
Am	99.97	0.03
Cm	99.9993	0.0007
RE	< 0.03%	> 99.97%

CONCLUSIONS

The UREX+1a process was successfully demonstrated with a dissolved spent fuel feed. Product specifications were met for disposal of Uranium as class C LLW. Breakthrough curves showed that separation of U from Tc by ion exchange was successful. The product distributions for CCD-PEG and TRUEX indicated successful separation. TALSPEAK showed excellent recovery of TRU elements and separation from the lanthanide elements; the lanthanide content of the TRU product was very low, well-below 1%.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under Contract DE-AC0Z-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

REFERENCES

1. J. J. Laidler and J. C. Bresee, "The Advanced Fuel Cycle Initiative of the U.S. Department of Energy: Development of Separations Technologies," Proceedings of WM-04, Tucson, AZ February 27-March 4, 2004.
2. S. Aase, A. Bakel, et al., "Demonstration of the UREX+ Process on Irradiated Nuclear Fuel," 13th Annual Separations Science and Technology Conference, Gatlinburg, TN, October 2003.
3. George F. Vandegrift, Monica C. Regalbuto, Scott Aase, Allen Bakel, Terry J. Battisti, Delbert Bowers, James P. Byrnes, Mark A. Clark, Jeff W. Emery, John R. Falkenberg, Artem V. Gelis, Candido Pereira, Lohman Hafenrichter, Yifen Tsai, Kevin J. Quigley, and Mark H. Vander Pol, "Designing and Demonstration of the UREX+ Process Using Spent Nuclear Fuel," Proceedings of Atalante 2004, Nimes, France, June 21-24, 2004.
4. George F. Vandegrift, Monica C. Regalbuto, Scott Aase, Hassan Arafat, Allen Bakel, Delbert Bowers, James P. Byrnes, Mark A. Clark, Jeff W. Emery, John R. Falkenberg, Artem V. Gelis, Lohman Hafenrichter, Ralph Leonard, Candido Pereira, , Kevin J Quigley, Yifen Tsai, Mark H. Vander Pol, and James J. Laidler, "Lab-Scale Demonstration of The Urex+ Process," Proceedings of WM-04, Tucson, AZ February 27-March 4, 2004.
5. G.F. Vandegrift, D. B. Chamberlain, C. Conner, J. M. Copple, J. A. Dow, L. Everson, J. C. Hutter, R. A. Leonard, L. Nuñez, M. C. Regalbuto, J. Sedlet, B. Srinivasan, S. Weber, and D. G. Wygmans, "Development and Demonstration of the TRUEX Solvent Extraction Process," Proceedings of WM-93, vol 2, 1045.

6. G. F. Vandegrift and M.C. Regalbuto, "Validation of the Generic TRUEX Model Using Data from TRUEX Demonstrations with Actual High-Level Waste," Proceedings of the Fifth International Conference on Radioactive Waste Management and Environmental Remediation (ICEM'95) vol 1, Cross-Cutting Issues and Management of High-Level Waste and Spent Fuel, Berlin, Germany, September 3-7, 1995, 457.
7. Monica C. Regalbuto, Jacqueline M. Copple, Ralph Leonard, Candido Pereira, and George F. Vandegrift, "Solvent Extraction Process Development for Partitioning And Transmutation of Spent Fuel," presented at the 8th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, November 9-11, 2004, Las Vegas, Nevada, USA.
8. J. D. Law, R. S. Herbst, D. R. Peterman, R. D. Tillotson, T. A. Todd, "Development of a Cobalt Dicarbollide/Polyethylene Glycol Solvent Extraction Process for Separation of Cesium and Strontium to Support Advanced Aqueous Reprocessing," Proceedings from GLOBAL 2003, New Orleans, LA, November 2003.
9. K.R. Ashley, J. Ball, A. Pinkerton, K.D. Abney, and N.C. Schroeder, "Sorption Behavior of Pertechnetate on Reillex^{TM}-HPQ Anion Exchange Resin from Nitric Acid Solution," Solvent Extraction and Ion Exchange, 12(2), 1994, 239.