# LAB-SCALE DEMONSTRATION OF THE UREX+ PROCESS

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## ABSTRACT

The Advanced Fuel Cycle Initiative (AFCI), funded by the U.S. Department of Energy's Office of Nuclear Energy, Science and Technology, is developing advanced technologies to safely and economically reduce the volume and heat generation of material requiring geologic disposition, thereby extending the capacity of the Yucca Mountain repository and delaying or avoiding the need for a second repository. An important element of this initiative is the separation of key radionuclides followed by superior waste-disposal forms and/or transmutation of long-lived isotopes. To that end, the AFCI is developing advanced fuel reprocessing systems that separate key radionuclides from spent fuel. One of these systems is the UREX+ process.

The UREX+ process is a series of five solvent-extraction flowsheets that perform the following operations: (1) recovery of Tc and U (UREX), (2) recovery of Cs and Sr (CDC-PEG), (3) recovery of Pu and Np (NPEX), (4) recovery of Am, Cm, and rare-earth fission products (TRUEX), and finally (5) separation of Am and Cm from the rare earths (Cyanex 301). This paper discusses the results of the demonstration, lessons learned during the demonstration, and future development needs and plans.

## INTRODUCTION

The UREX+ process is being developed at Argonne National Laboratory (ANL) and other national laboratories under the Advanced Fuel Cycle Initiative (AFCI), funded by the U.S. Department of Energy's Office of Nuclear Energy, Science and Technology [1]. At the end of Fiscal Year 03, the complete UREX+ solvent extraction process was demonstrated using multistage, countercurrent centrifugal contactors in ANL's Chemical Engineering Division [2].

### Processing Goals

The recovery and purification goals of the UREX+ process as set by the AFCI program are:

- Uranium recovery must be >90%. 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 greater and would be governed by ASTM C 788-98.

- Technetium recovery must be >95% to provide a 20-fold decrease in off-site dose reduction. If transmutation of Tc is the chosen option, the Tc product must contain less than 16 μg of fissile actinides per g of Tc.
- Iodine recovery during fuel dissolution should be >95% to provide a 20-fold decrease in off-site dose reduction. If transmutation of I is the chosen option, the I product must contain less than 4 μg of fissile actinides per g of I.
- A 97% recovery is required for Cs and Sr to make their contributions to the heat load in the repository equal to that of all other fission products. The purity requirement for the Cs/Sr decay-storage form is 100 nCi/g TRU content to allow its ultimate disposal as low-level waste.
- Plutonium/neptunium recovery must be >99%. The purity of this product stream is required to meet mixed-oxide (MOX) fuel specifications as described in ASTM C833-01.
- Based on a 100-fold reduction of heat load to the repository, a recovery of 99.5% is required for americium and curium. Based on fast-reactor recycle of all TRU, the lanthanide content of the Am/Cm product must be <20mg/g uranium plus TRU.
- The two raffinates from the UREX+ process—TRUEX, containing all soluble fission products but Cs, Sr, Tc, I, and the rare earth elements, and Cyanex 301, containing the rare earth elements—will be converted to a solid for disposal in the repository. The recovery for each component listed above means that 100% minus that per cent recovery does not show up in this solid, e.g., only 1% of Pu and 3% of Cs and Sr can be left in these raffinates.

**Process Demonstration**

The UREX+ process demonstration was run twice, initially with a simulated dissolved spent fuel derived from ORIGEN2 code data, and subsequently with a feed consisting of actual spent fuel that had been dissolved in nitric acid. For the actual-dissolved-fuel demonstration, a pin of irradiated Big Rock Point uranium oxide fuel was dissolved in nitric acid at temperature and pressure. The volume and concentration of the initial nitric acid solution was adjusted to provide a uranium solution appropriate to the low-acid requirements of the UREX process. The composition of the fuel pin was calculated by John Stillman (ANL Nuclear Engineering Division) using the ORIGEN2 code with the following input: (1) burn-up of 29,600 MWd/MT, (2) initial enrichment of 4.6% $^{235}U$, (3) 1% gadolinium burnable poison, and (4) cooling time of 21 years. Additional input was derived from the known and assumed operating parameters of the Big Rock Point boiling water reactor. In preparation for dissolution, the fuel pin was chopped into 3- to 5-cm segments.

Three multistage 2-cm centrifugal contactors were used for this demonstration—one unit located in a shielded cell, a second in a glovebox, and a third in a vacuum-frame hood. Because of the presence of $^{137}Cs$, $^{90}Sr$, and $^{154}Eu$ in the dissolved fuel, most of the UREX+ process had to be run in the shielded cell. Uranium and technetium were extracted from the dissolved fuel in the shielded cell; however, stripping of Tc and then U from the loaded UREX solvent was conducted in a glovebox and a hood, respectively. The entire flowsheets for CCD-PEG (Cs and Sr removal), NPEX (Pu and Np removal), TRUEX (Am, Cm, and rare-earth-fission-product removal), and Cyanex-301 (separation of Am and Cm from the heavy rare earths) were run sequentially in the same shielded-cell contactor. Extensive decontamination and refitting of feed and effluent stages and lines were required between each process demonstration. Because the solvent for the CCD-PEG process is denser than water, refitting and decontamination were a far greater effort before and after this process. The process flowsheets were designed for the number of stages available for use and therefore were not optimized for plant-scale processes. In addition, a plant would use continuous banks of contactor and would not require refitting and decontamination.

The flowsheets for the process segment were developed using the AMUSE (Argonne Model for Universal Solvent Extraction) 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 [3, 4]. GTM and AMUSE are developed to give highly accurate predictions of chemical behavior in a solvent extraction process by calculating component distribution ratios using chemically correct equilibria and thermodynamic activities for major components hydrogen ion, nitrate, and water. Further, the countercurrent mass balance algorithm contains terms for stage efficiency and other-phase-carryover for both the aqueous and organic phases. The five process segments of the UREX+ process were all designed using the AMUSE code.

The first segment of the demonstration was the UREX process flowsheet (see Fig.1). The solvent for the UREX process is the typical PUREX solvent, tributyl phosphate (TBP) dissolved in n-dodecane. In this process, a reductant/complexant is added to the process through the scrub to limit the extractability of plutonium and neptunium. The feed and the scrub contain low concentrations of nitric acid to enhance the complexation of Pu and Np and increase the extractability of pertechnetate ion. As seen in Figure1, uranium and technetium in the feed are extracted into the solvent in the extraction section; other extractible species are scrubbed from the solvent in the scrub section. The solvent, now loaded with uranium and technetium, is stripped of technetium in the Tc-Strip section using a high concentration of nitric acid. The Tc product stream is scrubbed of uranium in the U-Re-Extraction section. The combined solvent is then scrubbed of excess nitric acid with a feed of dilute nitric acid before entering the U-Strip section, where a dilute nitric acid feed removes uranium from the solvent. In this demonstration, the solvent was not recycled; in an actual plant application, a solvent wash section would be added to the process before recycling the solvent to the front end of the process.

The raffinate from the UREX segment is fed directly to the feed stage of the CCD-PEG segment. (The flowsheet run during the demonstration and the CCD-PEG process itself were developed by Law et al., Idaho Engineering and Environmental Laboratory [5].) A summary CCD-PEG flowsheet is shown in Figure 2. The solvent for this process is a mixture of chlorinated cobalt dicarbollide (CCD) for cesium extraction and polyethylene glycol (PEG) for strontium extraction diluted by phenyltrifluoromethyl sulfone. This process segment has four sections. In the extraction section, Cs and Sr (with a significant fraction of 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 elements (TRU) from the solvent. In the strip section, the alkali and alkaline-earth cations are stripped by a combination of a carbonate salt and complexing agent. Because this solvent was recycled, a solvent wash section was added to prepare the solvent for addition to the extraction section.

Between the CCD-PEG and the NPEX process (for recovery of a pure Pu/Np product) is a significant feed adjustment step. Feed adjust is required to (1) thermally destroy the reductant/complexant added in the UREX process to suppress extraction of plutonium and neptunium, (2) increase the concentration of nitric acid, and (3) convert and maintain plutonium and neptunium in the (IV) extractible oxidation state. In the demonstration, this procedure increased the volume of solution. However, in an operating plant this process would be done with extensive evaporation, and, therefore, volume reduction.

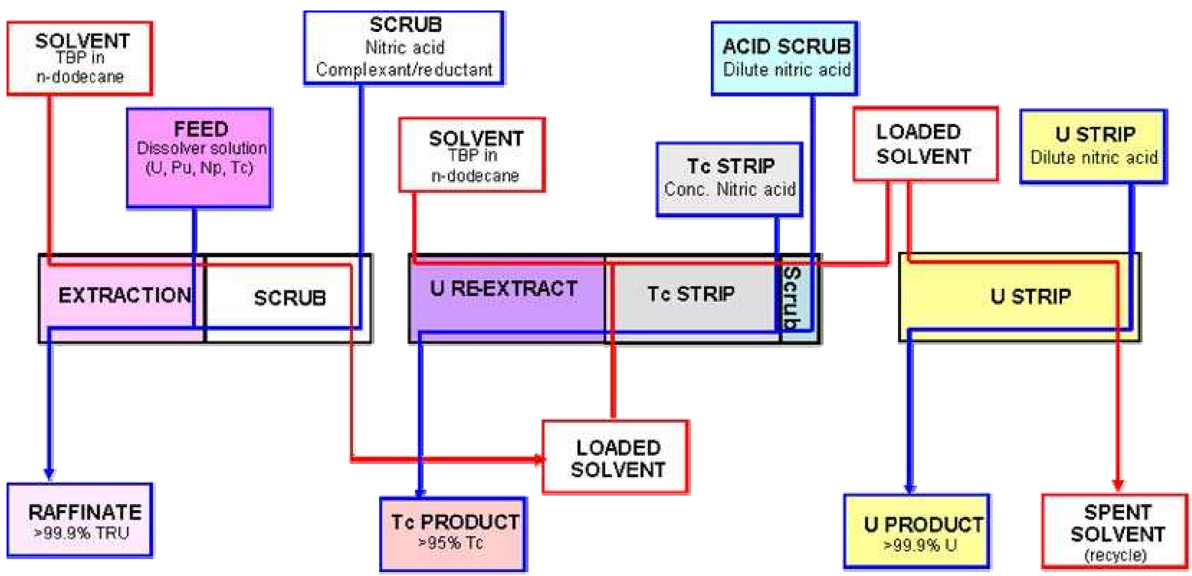


Fig.1. Summary flowsheet for the UREX process segment.

Following feed adjustment, the CCD-PEG raffinate was fed to the NPEX process (Fig. 2). The NPEX solvent composition is the same as for UREX, typical PUREX solvent. Impurities are removed from the solvent in the scrub section, and plutonium and neptunium are stripped using the same reductant/complexant that was fed to the scrub section of the UREX process. Because of the limited number of stages available to us in the shielded cell, there was no solvent wash or recycle of the solvent.

The raffinate of the NPEX process was fed directly to the extraction section of the TRUEX segment with no feed adjustment. The TRUEX process flowsheet is shown in Figure 3. Americium, curium, the rare elements, and residual plutonium and neptunium are extracted by the TRUEX solvent, which is 0.2 M CMPO [octyl(phenyl)-N,N-diisobutylcarboylmethyl-phosphine oxide] and 1.4 M TBP diluted by n-dodecane. Lesser amounts of other fission products are also extracted and must be scrubbed from the solvent. The TRUEX flowsheet is unique to the UREX+ process by having three scrub sections. In the first scrub section the impurities are removed from the solvent using oxalic acid. The second scrub uses moderately concentrated nitric acid to scrub oxalic acid from the solvent. The third scrub section uses relatively dilute nitric to lower the nitric acid concentration in the solvent to allow effective stripping. The strip section uses a weak complexant salt to strip the actinides and rare earth elements from the solvent and to maintain a pH of 3-4, which allows extraction of actinides by the Cyanex 301 solvent.

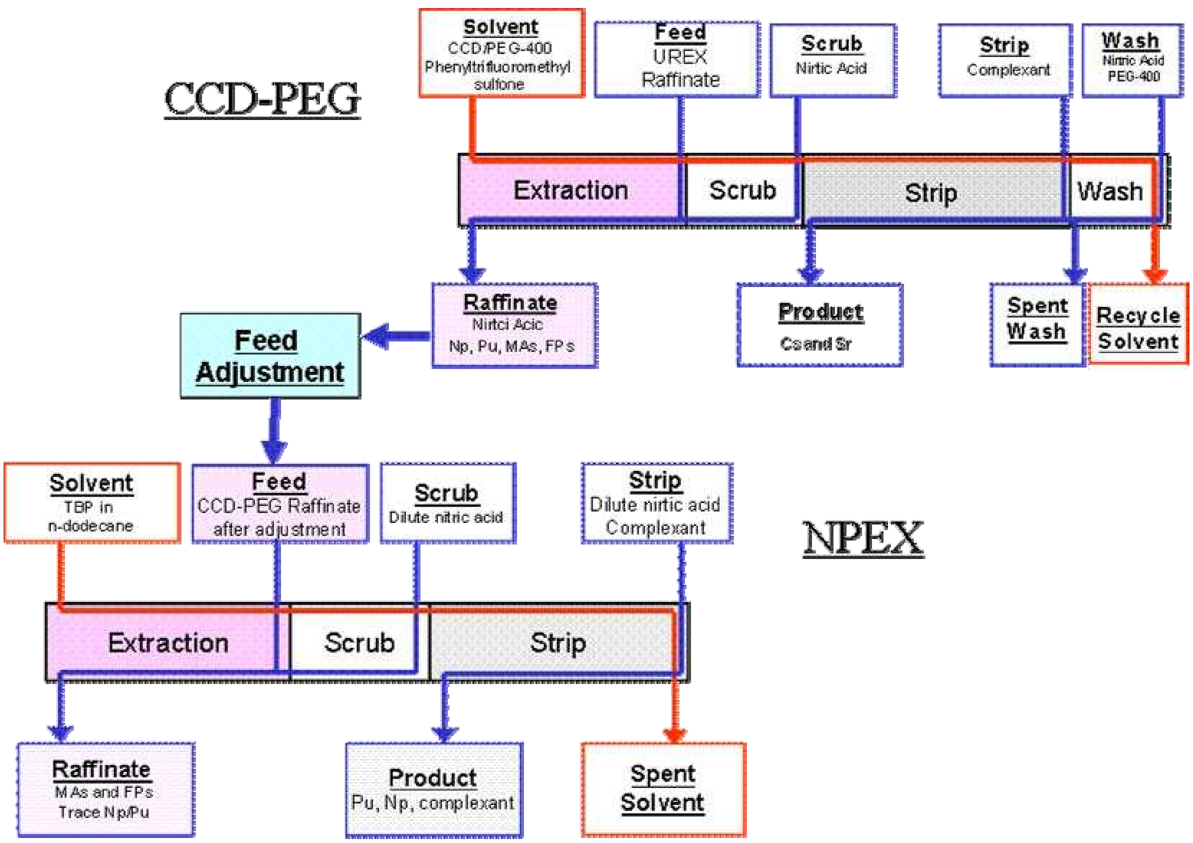


Fig 2. Summary flowsheets for the CCD-PEG and NPEX process segments.

The product stream from the TRUEX product was fed directly to the extraction section of the Cyanex 301 flowsheet (Fig. 3). Cyanex 301 is a commercial product supplied in an impure form by Cytec Industries, Canada. The chemical name of the predominant ingredient is bis(2,4,4-trimethylpentyl)dithiophosphinic acid. Before it can be used for actinide/lanthanide separations, it must be purified. We used a method that was developed by Zhu et al. and detailed by Modolo and Odoj [6] based on a private communication with Zhu. The purified Cyanex 301 was diluted by TBP and n-dodecane based on the results of Hill et al. [7]. Because of the tendency of the Cyanex 301 to decompose both as a solid and in solution, after purification the solid was kept in a freezer under vacuum and the solution was prepared immediately before use. To further slow decomposition by hydrolysis and oxidation, none of the aqueous streams has a pH below 3. The scrub feed is the acid form of the weak complexant in the feed and the strip feed is an ammonium salt of a powerful complexant.

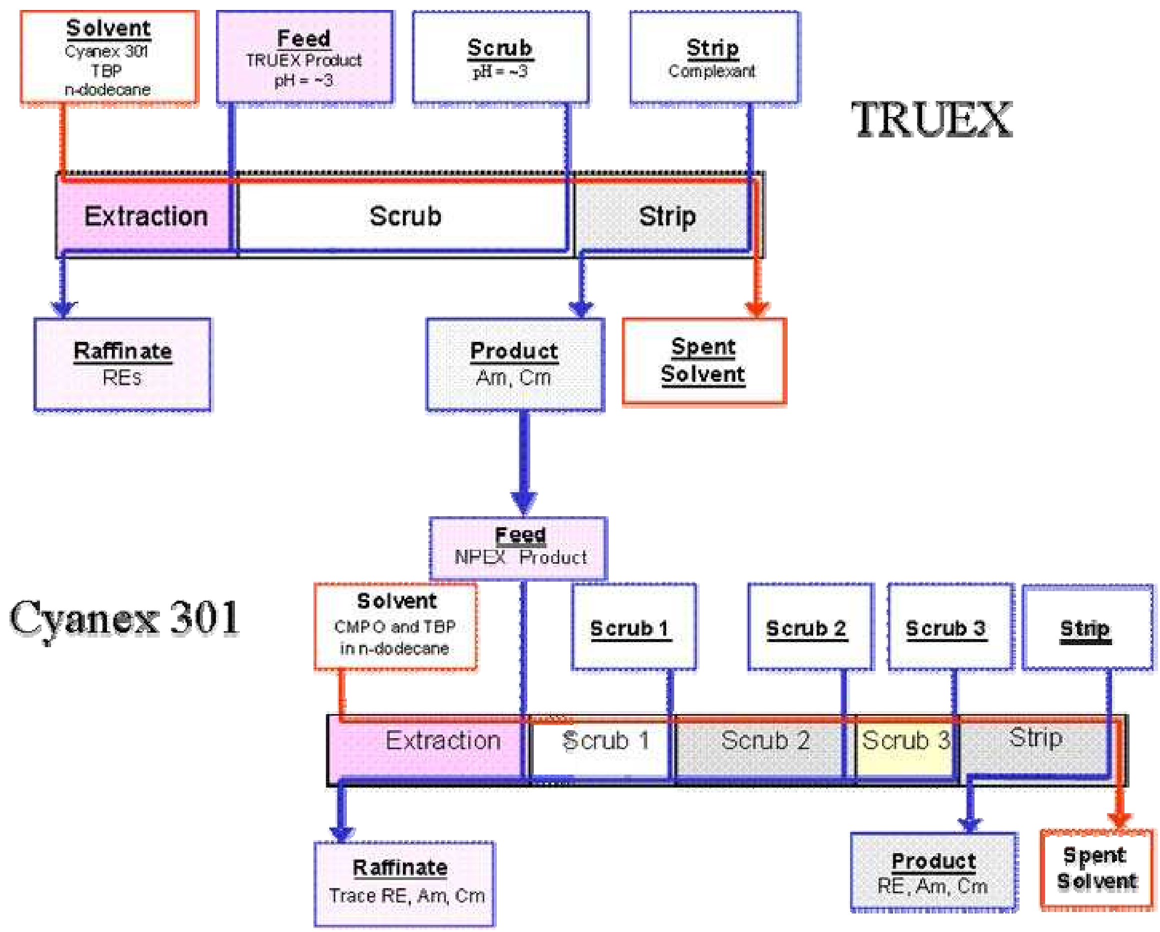


Fig. 3. Summary flowsheets for TRUEX and Cyanex 301 process segments.

**RESULTS**

Overall, the demonstration was a success and AFCI goals for the product recoveries were met. However, several operational mishaps caused less than optimized process behavior. For example, during the UREX segment, a leak developed in the scrub section during the run. The raffinate flow rate dropped from the prescribed value to 86% and finally to 74% during the run. The prescribed scrub flow rate was 67% of the raffinate flow rate. Assuming the drop in raffinate flow was primarily due to loss of aqueous scrub flow as the leak increased during the run, the "steady-state" samples collected at the end of the run were taken when the most of the scrub section and the extraction section saw a greatly decreased amount of complexant/reductant, leading to less plutonium decontamination of the U and Tc product than expected. Another mishap was an inadvertent shutoff of the feeds to the scrub, strip, and acid wash sections of the CCD-PEG sections near the end of the run. Without these feeds entering the contactor, the solvent loaded with the alkali and alkaline-earth fission products was fed directly to the first extraction stage, resulting in contamination of the extraction stages. The run could not recover completely from this process upset, resulting in poor mass balance and process performance.

The bulk of the data collecting during the demonstration was measured by ICP-MS (inductively coupled plasma-mass spectroscopy) for all samples. Data were also collected by gamma and alpha-pulse measurements as appropriate, as was TIMS (thermal ionization mass spectrometry) for uranium and plutonium isotopes for the dissolved-fuel solution and feed solution for the UREX+ process. The following sections discuss how the effluent streams met the AFCI process goals.

**U- and Tc –Products**

Uranium recovery in the U-product stream was greater than 99.95%. Technetium recovery in the Tc-product was 95%. Table I shows the composition of the technetium and uranium product streams from the UREX process segment. Impurities to the technetium product are primarily ruthenium and chemically unlikely barium. Table II shows the fissile content of Tc was slightly higher than the target value. The fissile content was 65/35 U-235/Pu-239.

Table I. Purity of the U- and Tc-Strip Products

| Element | Tc Product wt% | U Product wt% |
|---|---|---|
| Tc | 85.0 | $6.5 \times 10^{-6}$ |
| U | $8.9 \times 10^{-2}$ | 99.9991 |
| Ru | 8.7 | $2.4 \times 10^{-4}$ |
| TRU | $2.6 \times 10^{-2}$ | $1.2 \times 10^{-6}$ |
| Ba[a] | 5.5 | $3.1 \times 10^{-4}$ |

[a]Barium is an unlikely contaminant in this stream, and the material balance shows a significantly greater amount of barium in the samples than predicted by the ORIGEN2 code. This may be a sampling/analysis contaminant rather than actual.

Table II. Isotopic Purity of Tc Product and Specifications

| | g fissile actinides/g Tc-99[a] |
|---|---|
| Tc-product | $1.9 \times 10^{-5}$ |
| Specifications | $<1.63 \times 10^{-5}$ |

[a]Fissile actinides included are Pu-239 and U-235.

Table III shows that the fission products in the uranium product are far below the low-level waste (LLW) Class-C limits. However, the TRU limit was missed by a factor of 5, due to plutonium contamination. The uranium product contained $2 \times 10^{-4}$ of the plutonium that was in the feed stream. Meeting the TRU limit required that $<4 \times 10^{-5}$ of the initial plutonium be in the uranium product. A factor of 5 decrease could easily be achieved under planned operation. The U product from the demonstration at the Savannah River Technology Center [8] and the ANL simulant run both easily met the TRU waste limit.

Table III. Isotopic Purity of U Product and Specifications for Class C Low-Level Waste

| Isotope | Specification (nCi/g)[a] | *Measured (nCi/g) |
|---|---|---|
| Tc-99 | <693 | 1.9 |
| Sr-90 | $<1.6x10^6$ | $1.4x10^4$ |
| Cs-137 | $<1.1x10^6$ | $1.7x10^3$ |
| TRU | <120 | 620 |
| Pu-241 | $<4.13x10^3$ | $6.9x10^3$ |
| Cm-242 | $<2.4x10^4$ | <5.1 |

[a]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 $UO_3$.

## Cs/Sr-Product

The Cs/Sr product contained 96% of the cesium and 99% of the strontium, and most of the Rb and Ba. However, mass balance calculations for the process segment showed that the flowsheet was far from steady state; more Cs and Sr were discharged from the effluents than was being fed to the process. This product contained over 50 times more TRU than allowed for non-TRU waste. The bad performance was due to an operations upset and should not be considered due to chemical or engineering uncertainties. This process will be demonstrated again in 2004 to show its efficacy.

## Pu/Np-Product

The Pu/Np product contained 99.5% of the plutonium and 71% of the neptunium. The method used to hold neptunium as Np(IV) in the NPEX was not successful; further development work is underway to better control the neptunium oxidation state. However, most of the Np lost to the raffinate in NPEX was recovered in the Cyanex 301 product, for a total recovery of 98%. The requirement for less than 3 mg lanthanides per g of Pu/Np was easily met; the product contained less than $2x10^{-2}$ mg-lanthanides/g heavy metal.

## Am/Cm Product

The Cyanex-301 product contained >98% of the Am and >79% of the Cm. Given the uncertainty in the Cm data, its recovery is equivalent to that of Am. Of major interest is the fractionation of the rare-earth elements in the Cyanex-301 process. Lanthanum, cerium, and praseodymium all reported to the Am/Cm product, while all the other rare earths acted as expected by not extracting [6, 7]. This was not expected and an explanation is not readily available. As seen in Table IV, La, Ce, and Pr are the major constituents in this product.

Table IV. Purity of the CYANEX-301 Product

| Element | Raffinate wt % | Product wt % |
|---|---|---|
| Am | 6.0E-04 | 8.6 |
| Cm | 1.2E-02 | 6.4E-02 |
| La, Pr, Ce | 1.7E-02 | 89.5 |
| Other RE | 96.6 | 0.3 |
| Np | 3.2E-04 | 1.0 |
| Pu | 2.9E-03 | 7.8E-02 |

**Combined Raffinates**

The combined raffinates from TRUEX and the Cyanex-301 processes are bound for the repository. They should contain less than 5% of the uranium and technetium and 1 % of the TRU elements. They did contain <0.0006% of the uranium, 3.4% of the Tc, 0.02% of the Pu, <2% of Np, <0.04% of the Am, and <1.2% of the Cm.

## CONCLUSIONS

Clearly, the UREX+ demonstration was not perfect, and not all process goals were met. However, it did demonstrate that these processes show promise for meeting all process goals. Because of limited funding and time constraints, not all the supporting R&D required for complete success was performed. With the knowledge gained through this demonstration and completion of the required chemistry, complete success is highly probable.

## 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-March, 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. 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.
4. 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.
5. J. D. Law, R. S. Herbst, D. R. Peterman, R. D. Tillotson, and 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 of GLOBAL 2003, New Orleans, LA, November 2003.

6. G. Modolo and R. Odoj, "Influence of the Purity and Irradiation Stability of Cyanex 301 on the Separation of trivalent Actinides from Lanthanides by Solvent Extraction," J. Rad. Nucl. Chem., vol 228 (1998), 83.
7. C. Hill, C. Madic, P. Baron, M. Ozowa, and Y. Tanaka, "Trivalent Minor Actinide/Lanthanide Separations, Using Organophosphinic Acids, J. Alloys and .Compounds, vol. 271-23 (1998), 159.
8. M. C. Thompson, M. A. Norato, G. F. Kessinger, R. A. Pierce, T. S. Rudisill, and J. D. Johnson, "Demonstration of the UREX Solvent Extraction Process with Dresden Reactor Fuel Solution," WSRC-TR-2002-00444, Revision0, September 30, 2002.