LAB-SCALE DEMONSTRATION OF THE UREX+2 PROCESS USING SPENT FUEL

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ABSTRACT

The Advanced Fuel Cycle Initiative (AFCI), funded by the Department of Energy's Office of Nuclear Energy, is developing advanced technologies to greatly expand repository capacity, improve proliferation resistance, and recover valuable energy that would otherwise be discarded; thus assuring a stable energy supply for the future. 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, the AFCI is developing advanced fuel reprocessing systems that separate key radionuclides from spent fuel. One of these systems is the UREX+2 process.

The UREX+2 process is a series of three solvent-extraction flowsheets and one ion exchange process that perform the following operations: (1) recovery of Pu, Np, Tc and U (co-extraction and ion exchange), (2) recovery of Cs and Sr (CCD-PEG), and (3) recovery of Am and Cm (TALSPEAK). This paper discusses the results of the demonstration of the co-extraction, ion exchange, and CCD-PEG processes using spent nuclear fuel, as well as future development needs and plans.

INTRODUCTION

The UREX+2 process is being developed at Argonne National Laboratory (ANL) and other national laboratories under the Advanced Fuel Cycle Initiative (AFCI), funded by the Department of Energy's Office of Nuclear Energy [1]. At the end of FY 2004, three segments of the UREX+2 process that incorporates both solvent extraction and ion exchange were demonstrated using multistage, countercurrent centrifugal contactors in the Chemical Engineering Division of Argonne National Laboratory.

Processing Goals

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

- 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.

- 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 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 reduction.

- A 97% recovery is required for Cs and Sr to make their contribution 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 must be 100 nCi/g TRU content to allow its ultimate disposal as low-level waste.

- Based on a 100-fold reduction of heat load to the repository, a recovery of [z1].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 raffinate from the UREX+2 process contains all of the soluble fission products but Cs, Sr, Tc, and I. The raffinate will be converted to a solid for disposal in the repository. The recovery criteria for the components given above limit the quantity that will reside 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+2 process was demonstrated with dissolved irradiated fuel from the Big Rock Point Reactor in Michigan. The fuel pin was the same as that for the UREX+ demonstration of FY 2003 with a burnup of 29,600 MWD/MT. The UREX+2 process is a cascade of three solvent separate extraction processes, referred to here as "process segments," and one ion exchange process (Figure 1). The process steps demonstrated included: (1) recovery of Pu and Np (Co-extraction followed by selective stripping), (2) recovery of Tc and U (co-extraction followed by selective stripping), (3) separation of U from Tc (ion exchange), and (4) recovery of Cs and Sr (CCD-PEG). Demonstration of the recovery of Am and Cm was deferred. Composition adjustments are required for the dissolved fuel from the UREX+ demonstration and the CCD-PEG feeds to attain the appropriate nitric acid concentrations for each.

Three multistage 2-cm centrifugal contactors were used for this demonstration—one unit located in a shielded cell, a second unit in a glovebox, and a third unit in a vacuum-frame hood. Because of the presence of ^{137}Cs, ^{90}Sr, and ^{154}Eu in the dissolved fuel, the co-extraction and CCD-PEG segments of the UREX+2 process were run in the shielded cell. 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. Stripping of Pu and Np from the loaded co-extraction solvent was conducted in a glovebox, while Tc and U were stripped from the loaded solvent in a hood. Ion exchange to remove the Tc from the U/Tc strip product was also conducted in a hood.

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+2 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.
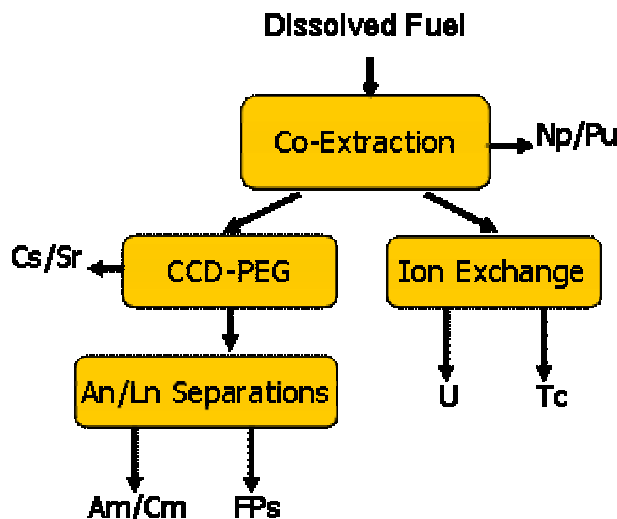
Fig. 1. Schematic of the UREX+2 Process.

The flowsheets for the UREX+2 solvent extraction process segments were developed at ANL (co-extraction) and Idaho National Engineering and Environmental Laboratory (CCD-PEG) 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 co-extraction process segment has three parts (extraction/scrub, Np/Pu-strip, and U/Tc-strip); each part was run in a different contactor. The three parts are shown in Figure 1. The solvent for the UREX process is the typical PUREX solvent, tributyl phosphate (TBP), dissolved in n-dodecane. In the first process segment plutonium, neptunium, uranium and technetium are extracted from the bulk of the dissolved fuel. Plutonium and neptunium are then stripped by a complexant/reductant in dilute acid in the Np/Pu-strip segment. The Np/Pu product stream is then scrubbed of uranium in the U/Tc-Re-extraction section. The combined solvent is 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 and technetium 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.
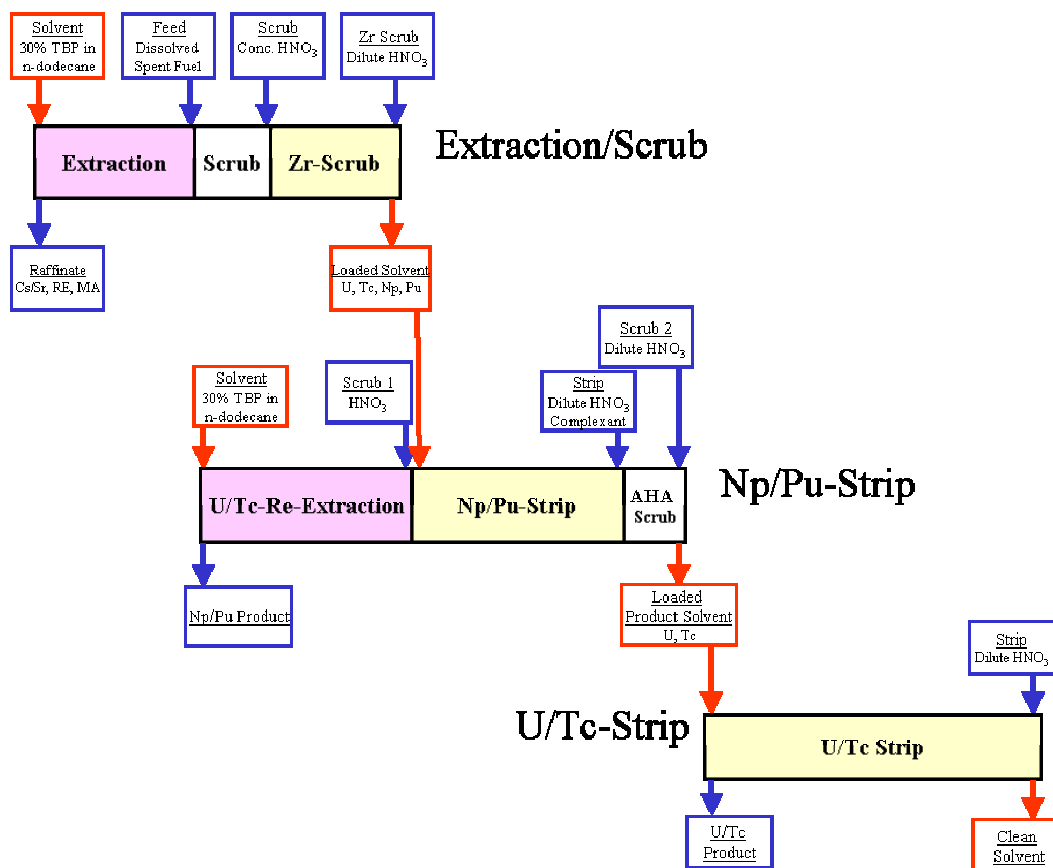
Fig. 2. Co-Extraction Process Segment Flowsheet.

The raffinate from the co-extraction segment is treated to reduce the nitric acid concentration and then becomes the feed to the CCD-PEG process segment. The CCD-PEG process and the flowsheet run during the demonstration were developed by Todd, Law et al. at INEEL [8]. 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.

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 nitrated Reillex® HPQ resin. The anion exchange resin recovers Tc as pertechnetate under process conditions developed in consultation with workers at Oak Ridge National Laboratory based on earlier work conducted at Los Alamos National Laboratory [9].

RESULTS

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

Np/Pu and U/Tc –Products

Table I shows the composition of the uranium/technetium and neptunium/plutonium product streams from the UREX process segment. Impurities in the Np/Pu product are primarily zirconium uranium, and rare earths. Table II shows that U/Tc product met all specifications for disposal of the uranium as a low level waste. Technetium was effectively separated from uranium by the Reillex HPQ column. The Tc concentration in the effluent from the column was below detection limits in all of the effluent samples indicating that the column was effective in removing Tc from the U/Tc product.

Table I. Purity of the Np/Pu and U/Tc-strip products

Element	Np/Pu Product	U/Tc Product
Pu	89.5	1.0×10^{-4}
Np	5.5	5.3×10^{-6}
Tc	0.046	0.02
U	0.1	99.98
Zr	3.2	5.9×10^{-5}
Cs	<0.004	4.2×10^{-6}
Sr	<0.03	1.0×10^{-5}
RE	0.5	5.8×10^{-5}
Am	<0.1	$<9.9\times10^{-6}$

Table II. Isotopic purity of U product and specifications for Class C Low-level waste

Isotope	Specifications, nCi/g	Measured, nCi/g
^{90}Sr	$<1.60\times10^{6}$	<5650
^{137}Cs	$<1.10\times10^{6}$	<758
TRU	<120	<1.8
^{241}Pu	<4130	<214
^{242}Cm	$<2.40\times10^{6}$	<9

[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.

Plutonium and neptunium recovery in the Np/Pu product was 99.8 and 87.2%, respectively. The balance of Np remained in the raffinate. The lanthanide content of the Np/Pu product was slightly above the mixed-oxide fuel specifications shown in Table III. However. the specification is likely met to within the analytical uncertainty of the measurement of the lanthanide concentration.

Table III. Purity of the Np/Pu Strip Product

Purity	mg-Ln/g-HM
Specification	<3
Measured	<5*

*Lanthanide content was determined from the total gadolinium content measured by
ICP-MS and ratio-ed to the total lanthanide concentration calculated by ORIGEN2 code.

The zirconium content listed in Table I for the Np/Pu product is high, suggesting that Zr was not effectively scrubbed from the solvent in the Zr-scrub section. This poor scrubbing appears to be related to poor hydraulic performance in the contactor rather than poor chemical behavior. During process operations, and shortly after starting the dissolved-fuel feed, the flow rate of the organic effluent dropped precipitously. Apparently, loading the solvent with uranium to improve the product purity increased the density of the solvent phase to the point that the O/A density ratio was outside the design envelope for the weir dimensions of the contactor in the shielded cell. This resulted in a buildup of the organic phase in the scrub sections of the contactor. The organic phase partially reversed its flow to the same direction as the aqueous phase, which reduced the effectiveness of the scrub sections. Factors consistent with this analysis are (1) the contactor operated smoothly with cold feeds, i.e., unloaded low-density solvent, and (2) solvent was observed to leak from the stand-pipe consistent with flooded stages.

The hydraulic problem was alleviated to the point that the flowsheet could be run without over-flooding by increasing the organic to aqueous ratio, O/A, to reduce U loading and adjusting the scrub compositions and flows to attain the appropriate nitric acid concentrations. However, the lower solvent loading and poor hydraulic performance in the scrub sections degraded performance of the process, especially with respect to zirconium decontamination. The liquid volume drained from the scrub stages after the test was much higher than expected for normal steady-state operation. Figure 3 shows the effect of the flow reversal or "other-phase carryover" in the two scrub sections on the extraction of zirconium as calculated using AMUSE. Adjusting the diameter of the upper weir in the rotors will prevent the problem in future tests.
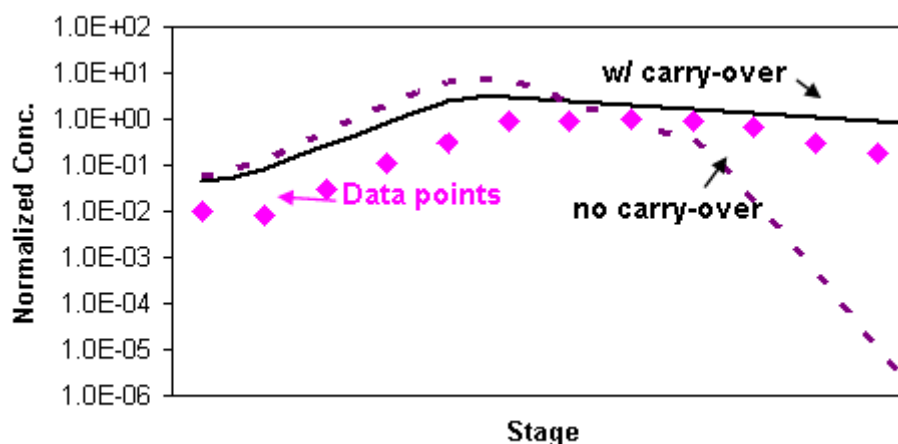
Fig. 3. Aqueous-Phase Zr Profile in Extraction/Scrub Section with Profiles Calculated by AMUSE with No Other Phase Carryover and Accounting for Carryover

Cs/Sr-Product

The CCD-PEG process was run using a flowsheet that was slightly modified from that run in FY 2003. The nitric acid concentration of the raffinate from the co-extraction process segment was adjusted by evaporation and acidification to attain the desired acidity while maintaining a constant volume of solution. A schematic of the process sections and feeds is given in Figure 4.
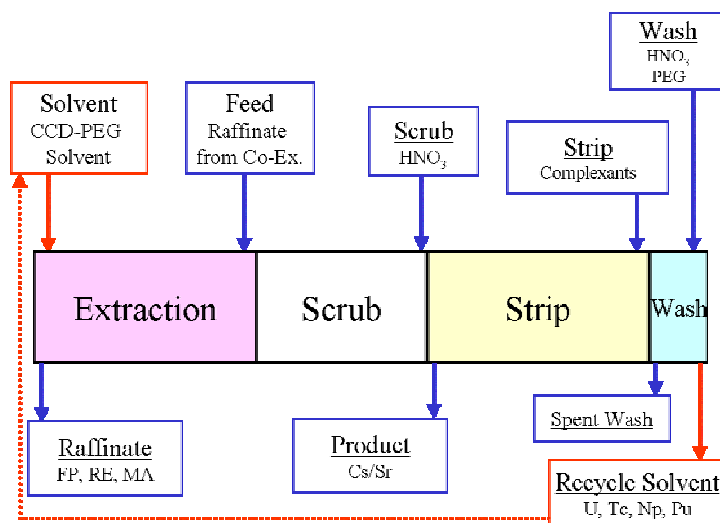

Fig. 4. CCD-PEG Process Segment Flowsheet.

The elemental distribution between the raffinate and product is given in Table IV. The major fractions of Cs and Sr are in the product stream, 99.8 and 98.6%, respectively. Rb is also predominantly in the product stream, but Ba is distributed between the two effluent streams. The rare earths and Am are predominantly in the raffinate, as desired.

Table IV. Elemental Distribution in the CCD-PEG Raffinate and Product, %

	Raffinate	Product
Sr	< 1.4	> 98.6
Cs	0.3	99.7
Am	> 99.9	< 0.1
Rb	3.3	96.7
Ba	30.9	69.1
RE	> 99.6	< 0.4

Table V lists the isotopic purity and LLW specifications for the Cs/Sr product. The concentration is given in terms of nCi/g of total oxide. The oxide was assumed to be a mixture of oxides of the fission products: Cs, Rb, Sr, and Ba. Even without addition of a matrix material, the TRU components are present at concentrations only slightly above the limits for low-level waste. The measured TRU concentrations may be lower, as these results are to a significant extent limited by counting time used for the analysis. In actual practice, fabrication of a Cs/Sr waste form will require addition of an aluminosilicate to the fission product oxides that will reduce the curie concentration well below the LLW specifications. These results demonstrate that the poor results obtained in the FY 2003 demonstration [3, 4] were due to operational upsets rather than chemical or engineering uncertainties.

Table V. Isotopic Purity of Cs/Sr Product and Waste Form Specifications for LLW

	nCi/g of total product*
Cs/Sr-Product	<168
Waste Form Specifications	<100

* The Cs/Sr product was assumed to be a mixture of Cs, Sr, Rb, and Ba oxides.

Raffinates

The raffinate from CCD-PEG process will serve as the feed to an actinide/lanthanide separation process. The raffinate from that process is bound for the repository and should contain less than 5% of the uranium and technetium. Based on the uranium and technetium distributions between the first two process segments, the feed to the An/Ln separation will contain <0.003% of the uranium in the feed but 18.6% of the Tc. The high Tc value is likely related to the poor hydraulics observed in the scrub sections, as the extraction of Tc is strongly affected by the presence of Zr.

CONCLUSIONS

The UREX+2 process was successfully demonstrated with a dissolved spent fuel feed. Product specifications were met for disposal of uranium as class C low-level waste. Separation of U from Tc by ion exchange was successful; no Tc was detected in the U stream. Preliminary data indicate that the lanthanide content of the Pu/Np product was slightly above the specification for MOX fuel, though the specification is met to within analytical uncertainty. The TRU activity in the Cs/Sr product also met the specification for disposal as low-level waste form. The required addition of aluminosilicate to the Cs/Sr stream will reduce the activity below the LLW requirements.

ACKNOWLEDGEMENTS

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