

DEVELOPMENT OF THE UREX+ CO-DECONTAMINATION SOLVENT EXTRACTION PROCESS

E. D. Collins, D. E. Benker, W. D. Bond, D. O. Campbell, and B. B. Spencer

*Oak Ridge National Laboratory, 1 Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831-6176
(collinsed@ornl.gov)*

INTRODUCTION

The initial reference process of the U.S. Advanced Fuel Cycle Initiative (AFCI) program was designed to treat light-water-reactor (LWR) spent fuel by means of a hybrid flowsheet that would separate uranium in an aqueous-based solvent extraction process (UREX), followed by a pyroprocessing-based electrorefining process to recover the transuranium (TRU) actinides (Np, Pu, Am, Cm) in a metallic form. The TRU metal would then be irradiated in a fast spectrum reactor and/or accelerator to transmute the actinides and to recover the contained energy resource as electrical power. Subsequently, the program has recognized that the United States currently has only thermal spectrum reactors (103 LWRs) and is not likely to have a fast spectrum reactor or accelerator for several decades. Thus, the near-term goal evolved into separation of a plutonium-neptunium product for irradiation in a uranium matrix as mixed oxide (MOX) fuel. The minor actinides would also be separated and stored for eventual irradiation in a fast spectrum reactor or subjected to one or more initial cycles of transmutation in existing LWRs.

WORK DESCRIPTION

A project is in progress within the AFCI program to develop UREX+, a co-decontamination solvent extraction process that will simultaneously separate a uranium product, a plutonium-neptunium product, and a technetium product from the minor actinides and fission products [high-level waste (HLW)] contained in LWR spent fuel. The process will utilize tributyl phosphate as the extractant and normal paraffin

hydrocarbon as the diluent. Development of the optimum flowsheet and operating conditions is based on experimental tests, technical literature studies, calculations using computer models, and confirming demonstration tests.

The experimental tests were made at Oak Ridge National Laboratory in the Solvent Extraction Test Facility (SETF), located in the high-level cells of the Radiochemical Engineering Development Center (REDC). The SETF is a small engineering-scale facility containing a spent fuel dissolver, feed adjustment and feed metering tanks, and three 16-stage mixer-settler, continuous countercurrent solvent extraction contactors. The SETF also contains a variety of reagent metering tanks and product/waste stream collection tanks.

RESULTS

Numerous test runs were made in the SETF using pressurized-water-reactor spent fuel from the H. B. Robinson-2 reactor and boiling-water-reactor spent fuel from the Dresden-1 reactor. [1] These spent fuels had been irradiated to ~30 GWd/MT and cooled for ~5 years. During these tests, typical uranium and plutonium extraction losses to the HLW stream were ~0.005% while operating with the solvent nearly saturated with uranium and plutonium to maximize decontamination from the fission products. Computer code calculations showed the necessity of using in-line instrumentation to measure and control the solvent-phase uranium/plutonium concentration to prevent large losses to the HLW as a result of slight changes in flow ratios.

Studies of the accumulation of interfacial solids in the extraction-scrubbing

contactors were made and compared with experience using other types of contactors. The studies indicated that pulsed column contactors were able to operate with less difficulty than mixer-settlers (and likely with less difficulty than centrifugal contactors).

Moreover, optimum conditions were studied for the use of hydroxylamine nitrate (HAN) as the reducing agent for Pu(IV) to Pu(III) in the partitioning contactors. The results indicated that optimum performance was obtained when the aqueous-phase acidity in the stripping contactors is kept low.

Previous tests did not consider the behavior of either neptunium or technetium. As is the case with plutonium, these two elements are multivalent and subject to complex formation with other constituents. The use of added oxidants and reductants, as well as adjustments to nitric acid concentration, temperature, etc., may be chosen to enhance either extraction or rejection.

A study of the literature indicated that technetium, in the form of pertechnetate, is complexed with fission product zirconium and then with uranium in the solvent phase, leading to enhanced extraction. [2] Partitioning from uranium is possible with a relatively large volume of $>5 M HNO_3$, as was shown in previous tests of the UREX process. [3] However, this creates a technetium product of large volume and high acidity, which is difficult to process in subsequent steps. Two alternatives were identified for further testing: (1) co-stripping with the uranium, followed by separation via anion exchange and (2) reductive partitioning, using either hydrazine-U(IV) or hydrazine alone.

Although it is well known that neptunium in the form of Np(V) is inextractable in the solvent, both Np(VI) and Np(IV) are extractable. Literature studies showed that extraction may be enhanced by either (1) the presence of part of the plutonium in the Pu(VI) state or (2) the addition of a small amount of NO_2 to the extraction contactor. Stripping is enhanced

by the use of reductive stripping using HAN or reduction/complexation via the addition of acetohydroxamic acid (AHA). Tests to evaluate these methods are in progress, and results of the tests will be presented.

REFERENCES

- [1] E. D. COLLINS et al. "Solvent Extraction Studies of Co-Processing Flowsheets," *Summary of Proceedings Fuel Cycles for the 80's*, CONF-800943, pp. 33–34, American Nuclear Society, La Grange Park, Illinois (1980).
- [2] P. BARON et al. "Extraction Cycles for LaHague Plants," *Proceedings of the Global '93 Conference*, pp. 63–70, American Nuclear Society, La Grange Park, Illinois (1993).
- [3] T. S. RUDISILL et al. "Demonstration of the UREX Solvent Extraction Process with Dresden BWR Spent Fuel Solution," to be published in *Transactions of the American Nuclear Society*, Vol. 88 (2003).