DEVELOPMENT OF PROCESS SIMPLIFICATIONS AND COST REDUCTIONS FOR SPENT FUEL PROCESSING

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ABSTRACT

A project is in progress within the AFCI program, including collaborative process design through the U.S. Department of Energy–Commissariat a'l Energie Atomique (France) technical exchange, to develop the UREX+ 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) contained in spent fuel from light water reactors. Development of optimum flowsheet conditions is based on experimental tests, technical literature studies, calculations using computer models, and confirming demonstration tests**.**

INTRODUCTION

Near-term deployment of the closed fuel cycle will be needed to enable more efficient use of the Yucca Mountain Repository if a growth in nuclear power is expected and the need for additional repositories is to be minimized. At the current level of nuclear power generation in the United States (~100 GWe), approximately 2000 metric tons of spent fuel is produced annually. Even with no growth, the licensed capacity will be reached by ~2010, and the estimated physical capacity limit could be reached within a few decades.

Closing the fuel cycle by treating spent fuel to separate long-lived, heat-generating actinides for use in mixed-oxide (MOX) fuels and burnable poison rods can extend the lifetime of the repository to 100 years or more. However, costs of the closed fuel cycle also must be minimized by practical means such as process simplification.

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 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.

UREX+ CO-DECONTAMINATION FLOWSHEET TESTS

A project is in progress within the AFCI program―including collaborative process design through the U.S. Department of Energy (DOE)–Commissariat a'l Energie Atomique (CEA) (France) technical exchange―to develop a simplified process, 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) contained in LWR spent fuel. (Fig. 1) 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. Initial DOE-CEA collaborations concerned flowsheet optimization of the UREX process during hot demonstration tests conducted at the Savannah River Technology Center (SRTC). [1]

Fig. 1 UREX+ co-decontamination solvent extraction flowsheet

Experimental tests have been conducted at Oak Ridge National Laboratory in the Solvent Extraction Test Facility (SETF), located in the high-level cells of the Radiochemical Engineering Development Center. 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 (PWR) spent fuel from the H. B. Robinson-2 reactor and boiling-water-reactor (BWR) spent fuel from the Dresden-1 reactor. [2] These spent fuels had been irradiated to ~30 GWd/MT and cooled for ~5 years.

Extraction/Scrubbing Operations

The areas of concern in the extraction/scrubbing operations included (1) the formation of crud in the extraction bank; (2) losses of uranium, plutonium, neptunium, and technetium in the extraction bank raffinate stream (AW); and (3) fission product contamination.

Crud Formation

In all first-cycle tests, black interfacial crud formed and accumulated in the settling chambers of the extraction stages near the feed inlet. The sticky crud had to be removed periodically by agitation, vacuuming, and flushing.

The crud appeared to be an emulsion, believed to be stabilized by minute particles of insoluble fission product metals. Significant amounts of noble metal fission products, which were not soluble in the nitric-acid feed solutions, had been removed by means of filtration. However, some of the insoluble particles were apparently small enough to pass through the feed clarification filter, which had 1-Φm pores. During second-cycle tests, in which the feed solutions did not contain insoluble fission products, crud did not form.

In related work, crud formation was prevented during small-scale mixer-settler runs made at SRTC by using feed solutions that had been clarified with the aid of a flocculating agent. Either manganese dioxide or an organic polyamine, Primafloc C-3 (manufactured by the Rohm and Haas Company), was successfully utilized. [3]

Also, approximately 2.5 metric tons of spent fuel from the Point Beach-1 BWR were processed in small-scale (4.5-cm-diam) pulsed columns at the Pacific Northwest Laboratory. [4] The dissolver solutions were clarified by means of a sintered-metal filter rated at 100 Φm. A filter of that size would not be expected to retain the insoluble metal particles, but even so, no crud accumulation sufficient to cause a shutdown was observed during the several months of operation. This experience appeared to confirm that crud formations similar to those observed in mixer-settlers do not represent a significant problem in pulsed column contactors.

Extraction Losses

Uranium and plutonium losses to the extraction raffinate stream have been measured during numerous tests and have been within the range of 0.0002 to 0.09%, with median values of 0.004% for uranium and 0.007% for plutonium. These values are somewhat higher than those predicted by SEPHIS code calculations, probably because of the presence of different ionic or non-ionic species. Plutonium, neptunium, and technetium are minor components in comparison to the uranium and are multivalent and susceptible to complexing with other constituents. Previous studies have 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. [5] Recent tests of the UREX+ co-decontamination flowsheet appeared to confirm the previous studies. The technetium concentration profile in the extraction contactors was similar to that of plutonium, and the measured loss of technetium to the raffinate was 0.9%. With regard to neptunium, it is well known that Np(V) is inextractable in the solvent, and 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 [6] or (2) the addition of a small amount of NO_2 to the extraction contactors to minimize the presence of Np(V). Recent tests of the UREX+ co-decontamination flowsheet confirmed the positive effect of leaving ~35% Pu(VI) in the feed. The neptunium concentration profile in the extraction contactors was similar to that of plutonium, and the measured loss of neptunium to the raffinate was <2.5%.

The most serious potential for large extraction losses occurs when the heavy metal concentration in the organic solvent is maintained at a high level (e.g., ≥75% of saturation) in an effort to obtain high decontamination factors from the fission products. Under these conditions, the system is susceptible to upset as a result of slight changes in flow rates or concentrations of the inlet streams that might cause internal refluxing of the heavy metals. A series of SEPHIS code calculations was performed to illustrate this problem. The results are plotted in Fig. 2.

These calculations were made for different feed flow rates with all other conditions held constant; however, the same effects would result from small reductions in the extractant flow rate. These assumed changes are quite small: a variation of only 3.4% in the intended flow rate (or perhaps only 1.7% each in the feed and extractant flow rates in the "wrong" direction) could cause a serious upset in the concentration profile in the system. In plant-scale equipment, it is very difficult to establish and maintain a flow rate with such a high degree of accuracy and precision for an extended period of time without the use of automated control. Thus, it appears imperative to monitor the heavy metal concentrations within the extraction contactor continuously and to control the flow rates as required to keep the concentration "wave front" far enough from the raffinate outlet to maintain acceptably low losses.

Fission Product Decontamination

Fission product behavior in the process is generally well known. However, to re-illustrate this behavior, a typical graph of fission product concentration profiles in the extraction/scrub bank is shown in Fig. 3. Cesium extraction was at least two orders of magnitude lower than the rate for other contaminants. Ruthenium and the rare earths were extracted to the same degree, but the rare earths were more effectively removed in the scrub section of the bank. A recent test showed that the concentration profile of zirconium was similar to that of ruthenium.
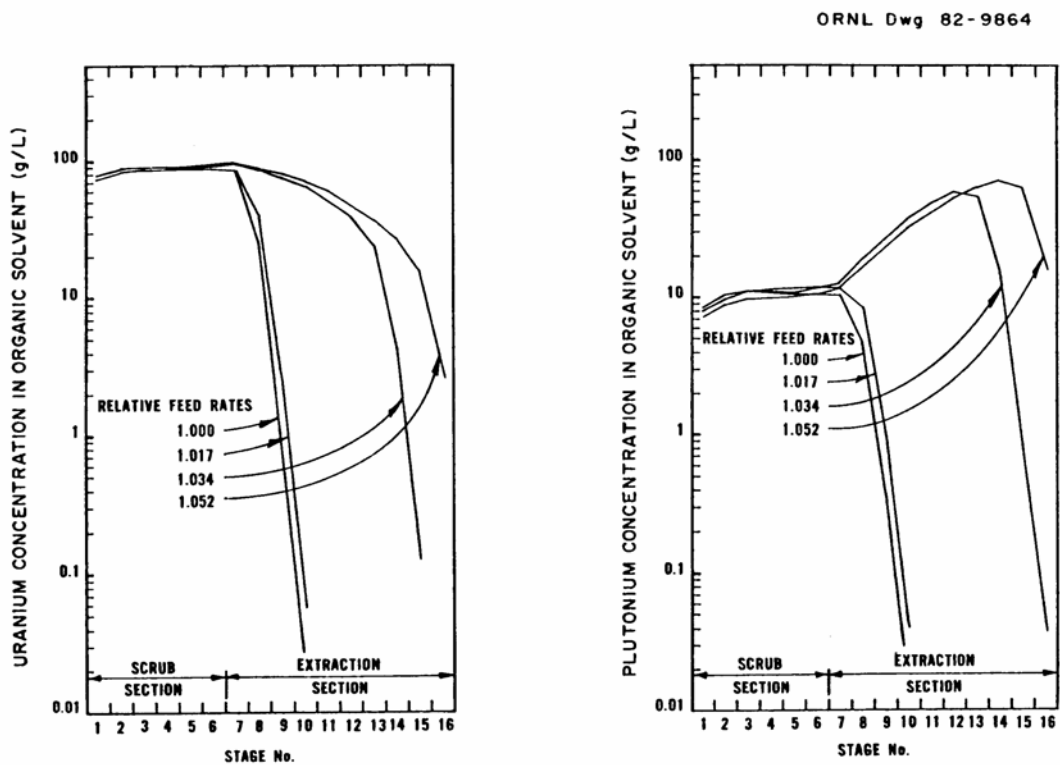
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Fig. 2 SEPHIS calculations showing the effect of slight changes in feed flow rate during operations with heavy-metal concentrations in the solvent.
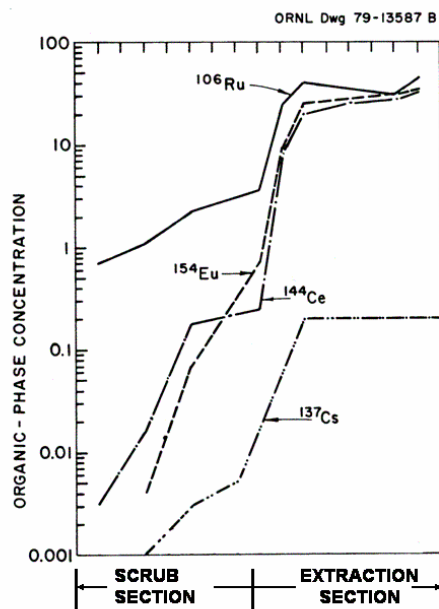
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Fig. 3   Typical fission product concentration profiles in the extraction/scrub bank.

One of the objectives of the most recent UREX+ co-decontamination flowsheet tests was to determine if the plutonium-neptunium product would be decontaminated sufficiently from europium and cesium fission products to meet the specifications for use of the plutonium-neptunium in light-water-reactor MOX fuel. Measurements taken throughout the tests varied somewhat, but in all cases, the specification limits were met. The decontamination factors for europium ranged from 10^4 to 10^6, and those for cesium ranged from 10^5 to 10^7.

Co-Partition of Plutonium and Neptunium

The major gamma emitter in most of the product solutions was not a fission product but ^{239}Np, the decay daughter of ^{243}Am (Table I). This result was an effect of choosing the operating conditions to co-strip neptunium and plutonium. Although the ^{239}Np decays rapidly (half-life of 2.35 days) after being separated from the ^{243}Am, it emits a relatively strong gamma (0.28 MeV). Thus, the presence of ^{239}Np in fresh plutonium-neptunium product solutions should be considered in the design of shielding for the stripping contactor and product tanks.

Table I Gamma-emitting Components in Typical Plutonium–Neptunium Product Solutions

Component	Activity Level (ΦCi/g Pu)
^{106}Ru	141
^{110m}Ag	<0.3
^{125}Sb	<1.4
^{134}Cs	4.6
^{137}Cs	16
^{144}Cd	<14
^{154}Eu	<0.7
^{239}Np	1873

Use of Reducing Agents and Complexants

One of the initial objectives was to establish the necessary operating conditions for the effective use of hydroxylamine nitrate (HAN) and to determine whether stabilization with hydrazine is necessary. Hydrazine is typically used as a holding reductant, protecting the reduced species by reacting with any nitrous acid that may be generated within the system and thus preventing reoxidation by the nitrous acid. Elimination of the need for hydrazine in a reprocessing plant is desirable because of a potential safety hazard—the formation of highly explosive compounds, such as hydrazoic acid and metal azides. Two solvent extraction tests were conducted using unstabilized HAN as the reductant. In one of the test runs, a significant amount of nitrous acid was added to the system via the back scrub solvent to adjust the nitrous acid/plutonium mole ratio to ~1.0. The results indicated that the plutonium stripping effectiveness was not decreased by the presence of the nitrous acid. The plutonium concentration profiles were nearly identical, and >99.99% of the plutonium was stripped in each run.

The maximum aqueous-phase acidity is probably the key variable in determining whether HAN is a satisfactory holding reductant for Pu(III). Kinetic studies have shown that the rate of reduction of plutonium by HAN is inversely proportional to the fourth power of the aqueous acidity. [7] Empirical data from laboratory experiments associated with SETF operations were in agreement. Based on the

stripping coefficients measured and the low aqueous-phase/organic-phase ratio normally used in partitioning, a relatively large number of stages would be required to strip the plutonium at acidities greater than $\sim 1.5\,M$ HNO$_3$. This is probably because the rate of reduction is slower than the rate of reoxidation at these acidities. Thus, in a countercurrent partitioning contactor, plutonium will be stripped in the region where the aqueous acidity is low enough for HAN to be effective; however, if the aqueous strip solution containing Pu(III) subsequently passes into a region of the contactor where the acidity is high enough to make HAN ineffective, the rate of reoxidation and reextraction may exceed the rate of reductive stripping and cause the reflux to occur. Furthermore, at acidities below $\sim 0.5\,M$ HNO$_3$, the redox potential of the plutonium- HNO$_3$-HNO$_2$ system has been reported to be such that nitrous acid causes reduction of Pu(IV) to Pu(III). [8, 9] Thus, when HAN is being used at low acidity, the plutonium reduction would be enhanced by the presence of nitrous acid. However, the nitrous acid would destroy an equivalent amount of HAN.

During the most recent tests of the UREX+ co-decontamination flowsheet, the plutonium-neptunium product was collected in high yield and with excellent decontamination from lanthanide and other fission products. When either HAN or a complexing agent was used, about 10% of the technetium (apparently a reduced species) was collected in the plutonium-neptunium product. This is not considered to be a significant problem, because the technetium will be either (1) separated for recycle in subsequent processing steps or (2) included in the MOX fuel. Other alternatives are also possible.
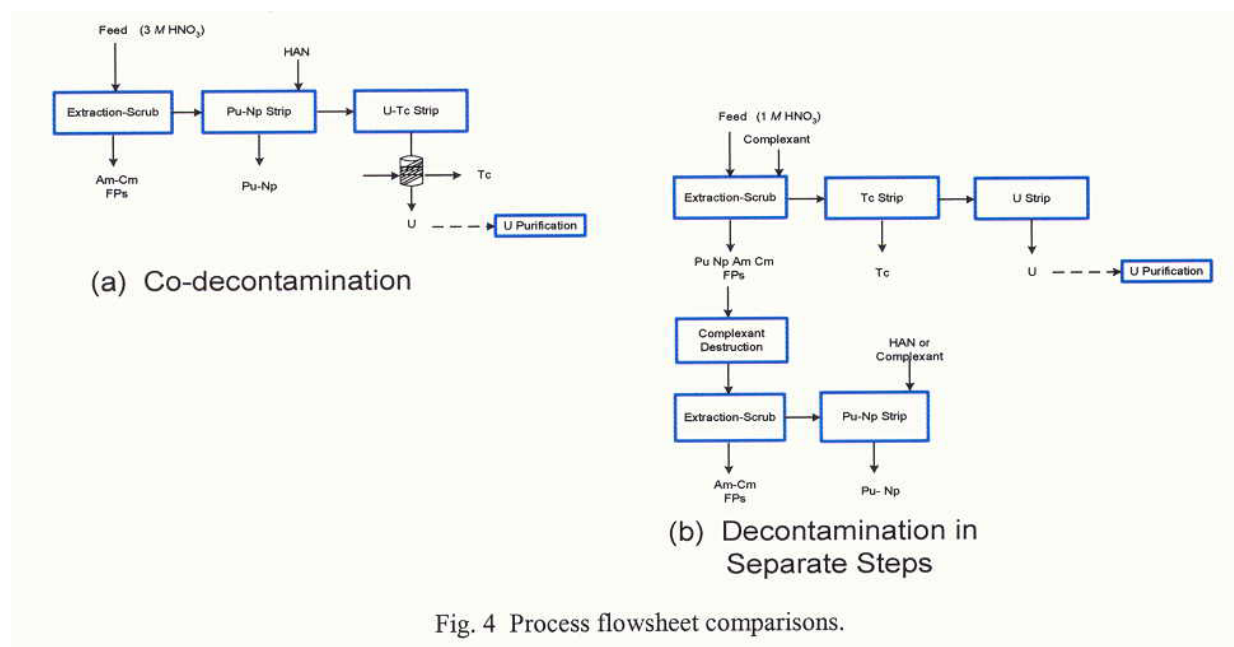
Process Simplification

Fig. 4 Process flowsheet comparisons.

The flowsheet for the UREX+ co-decontamination solvent extraction process is compared in Fig. 4 with the multi-step process that starts with the UREX process. The multi-step process (4b) is complicated by several factors: (1) a requirement for more process contactors and stages; (2) difficult spent fuel dissolution, requiring the use of a pressurized dissolver, because of the low acidity ($\leq 1\,M$ HNO$_3$) feed requirement; (3) less efficient decontamination from fission products; and (4) a requirement for a difficult complexant destruction step prior to recovery of the plutonium-neptunium product. The UREX+ co-decontamination process (4a) appears to be more efficient, less complicated, and less costly than the multi-step process. Therefore, the UREX+ co-decontamination process represents a significant process simplification and improvement and thus is recommended to become the reference process.

SUMMARY

Numerous solvent extraction test runs have been made using both PWR and BWR spent fuels to determine both physical and chemical characteristics of the process solutions. These characteristics included (1) crud formation in the extraction stages, (2) losses to the extraction raffinate, (3) fission product decontamination, and (4) partitioning of a plutonium-neptunium product from co-extracted uranium and technetium. Recently, the simplified UREX+ co-decontamination flowsheet was tested, and the plutonium-neptunium product was collected in high yield and with excellent decontamination from lanthanide and other fission products. About 10% of the co-extracted technetium was collected in the plutonium-neptunium product. Further testing and refinement of the process are planned.

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