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Consolidated Fuel Reprocessing Program

COPROCESSING SOLVENT-EXTRACTION FLOWSHEET STUDIES FOR LWR AND FBR FUELS

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The Solvent Extraction Test Facility (SETF), located within a hot cell in the Transuranium Processing Plant (TRU) at Oak Ridge National Laboratory, has been used during the past several years for evaluation and demonstration of recently developed or improved Purex flowsheet modifications for reprocessing nuclear power reactor fuels. Coprocessing solvent extraction flowsheets for LWR and LMFBR fuels have been studied in mixer-settler contactors using feed solutions prepared by dissolving fully irradiated fuels. The fuels processed during these studies were obtained from the H. B. Robinson-2 PWR, the Dresden-1 BWR, and the EBR-II FBR. The plutonium content in these fuels ranged from 0.8 to 23% of the heavy metals. The studies emphasized uranium-plutonium costripping and partial partitioning using either nonreductive stripping of plutonium or reductive stripping that employed chemical reagents such as hydrazine-stabilized hydroxylamine nitrate (HAN), unstabilized HAN, or nitrous acid. Other areas of study included (1) prevention of crud formation, (2) fission product decontamination, and (3) waste solvent degradation measurements.

Three solvent extraction contactors are used in the SETF — each is a 16-stage mixer-settler that has a liquid holdup of ~80 mL/stage. Associated hot-cell equipment includes several effluent catch tanks (one of which is an evaporator), feed preparation equipment, and product purification equipment.

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The feed preparation equipment includes a batch dissolver, a feed adjustment tank, a variety of filters that are used to clarify the feed solutions, and a feed metering and flow rate control system. The product purification equipment includes two ion exchange columns. In addition, a precipitator tank, filter, and calcination furnace for conversion of plutonium product to the oxide form are available in nearby hot cells at TRU. The out-of-cell SETF equipment includes several solution makeup tanks and calibrated head tanks. Each of the latter is equipped with an automatic flow control system.

The processing rate in the SETF is in the range 0.5 to 1.5 mL/s of total solution flow, which is equivalent to 2 to 4 kg of heavy metals per day. The solvent, either 15 or 30% tri-n-butylphosphate (TBP) in a normal paraffin hydrocarbon diluent, is used on a once-through basis. In the coprocessing experiments, the uranium and plutonium are coextracted and coscrubbed in the first contactor, and the plutonium (together with either all or part of the uranium) is stripped in the second contactor. The third contactor can be used to strip uranium, although this is not done in every experiment.

Feed solutions for the experiments have been prepared by leaching the heavy metals from 2.5- to 5-cm-long pieces of irradiated fuel rods with 3 to 4 M HNO_3 in the batch dissolver tank. Typically, batches containing 2 to 3 kg of heavy metal are dissolved in 6 to 9 L of acid. The dissolver solutions are filtered to remove insoluble materials and then are adjusted to the desired acidity, metal concentration, and plutonium valence state before being fed into the mixer-settlers.

Crud formation has occurred in the extraction bank, particularly at and near the feed stage, in nearly every experiment. These cruds are suspected to be emulsions that are stabilized by the presence of colloids of the insoluble fission products, especially ruthenium. A significant reduction in the formation of these cruds has been obtained by using more efficient feed clarification filters. A filter consisting of a deep bed of diatomaceous earth has been particularly effective.

The efficiency of feed clarification also has appeared to affect the degree of decontamination obtained from fission product ruthenium. Other process parameters shown to have an effect on decontamination are the degree of solvent saturation and the temperature and residence time in the extraction/scrub bank. The decontamination factors (DFs) for ruthenium have been in the range 10^3 to 10^5. The DFs for cesium and the rare earths have ranged from 10^4 to 10^6; those for ^{95}Zr-Nb have ranged from 10^2 to 10^3. Since all of the fuels processed had been discharged from the reactors for 5 years or more, all of the ^{95}Zr-Nb had decayed; thus a ^{95}Zr-Nb spike was added to the feed solutions in some of the experiments to enable the DF measurements.

One objective of the SETF tests was an evaluation of the reductive stripping of plutonium while using a chemical reductant that did not form by-product salts or create a corrosive environment. One of the reductants evaluated was hydrazine-stabilized HAN. The explosive hazards of the hydrazine decomposition products, hydrazoic acid and metal azides, were recognized during early considerations. Thus tests were made to determine conditions necessary for the satisfactory use of HAN without hydrazine. This determination was accomplished by means of a statistically designed set of experiments which examined the effects of stripping temperature, aqueous-phase acidity, and additions of nitrous acid. The key variable was found to be the maximum acidity in the aqueous phase in the strip contactor.

Further tests were made to examine the use of nitrous acid as the reducing agent for Pu(IV), as proposed first by Bathellier[1] and later others.[2] This usage is based on the principle that the redox potential of Pu(III)/Pu(IV) in the HNO_3-HNO_2 system is such that HNO_2 reduces Pu(IV) to Pu(III) at acidities below ~0.5 M HNO_3. It is well known that, at higher acidities, HNO_2 oxidizes Pu(III) to Pu(IV). The use of HNO_2 as the reductant for plutonium stripping offers several advantages. Probably, the most attractive feature is that the HNO_2 introduces no new chemicals into the HNO_3/TBP/Pu system; it only supplements the HNO_2 already generated by radiolysis of the HNO_3. The SETF tests showed that, by adding HNO_2 into the strip bank, >99.9% of the plutonium could be stripped and a partial separation from uranium could be made. During the SETF tests, an organic backscrub was used to regulate the portion of the uranium stripped along with the plutonium. The plutonium contents in the uranium-plutonium mixtures were enriched by factors of up to 5 to 10.

The use of either HAN or HNO_2 as the reductant for Pu(IV) requires operation of the stripping contactor at a relatively low acidity; therefore, strip solutions containing acidities as low as 0.10 M HNO_3 have been used. The possibility of plutonium polymer formation at these relatively low acidities was recognized, but no evidence of polymer formation was found during the SETF operations.

The solvent used in SETF tests is not recycled, and thus a study of the buildup of nonremovable impurities cannot be made. However, samples of the waste solvent have been used in laboratory tests of alternative purification methods. Also, samples have been treated to measure the concentration of the TBP degradation product, dibutylphosphate (DBP), produced during a variety of solvent extraction conditions. The results indicated that DBP was present in the solvent but did not interfere with plutonium stripping, apparently because the DBP was complexed preferentially by uranium.

In summary, coprocessing solvent extraction studies using irradiated LWR and FBR fuels have indicated the need for an efficient feed clarification. A potentially useful filtration method for fulfilling this need has been demonstrated. Conditions necessary for the satisfactory use of unstabilized HAN or nitrous acid as the reducing agent for Pu(IV) during reductive stripping operations have been defined. Both partial partitioning and total costripping operations have been demonstrated. In addition, solvent degradation product measurements have been made, and the effect of the presence of DBP during uranium-plutonium stripping operations has been determined.

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