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### SOLVENT EXTRACTION STUDIES OF COPROCESSING FLOWSHEETS — RESULTS FROM CAMPAIGN 5 OF THE SOLVENT EXTRACTION TEST FACILITY (SETF)

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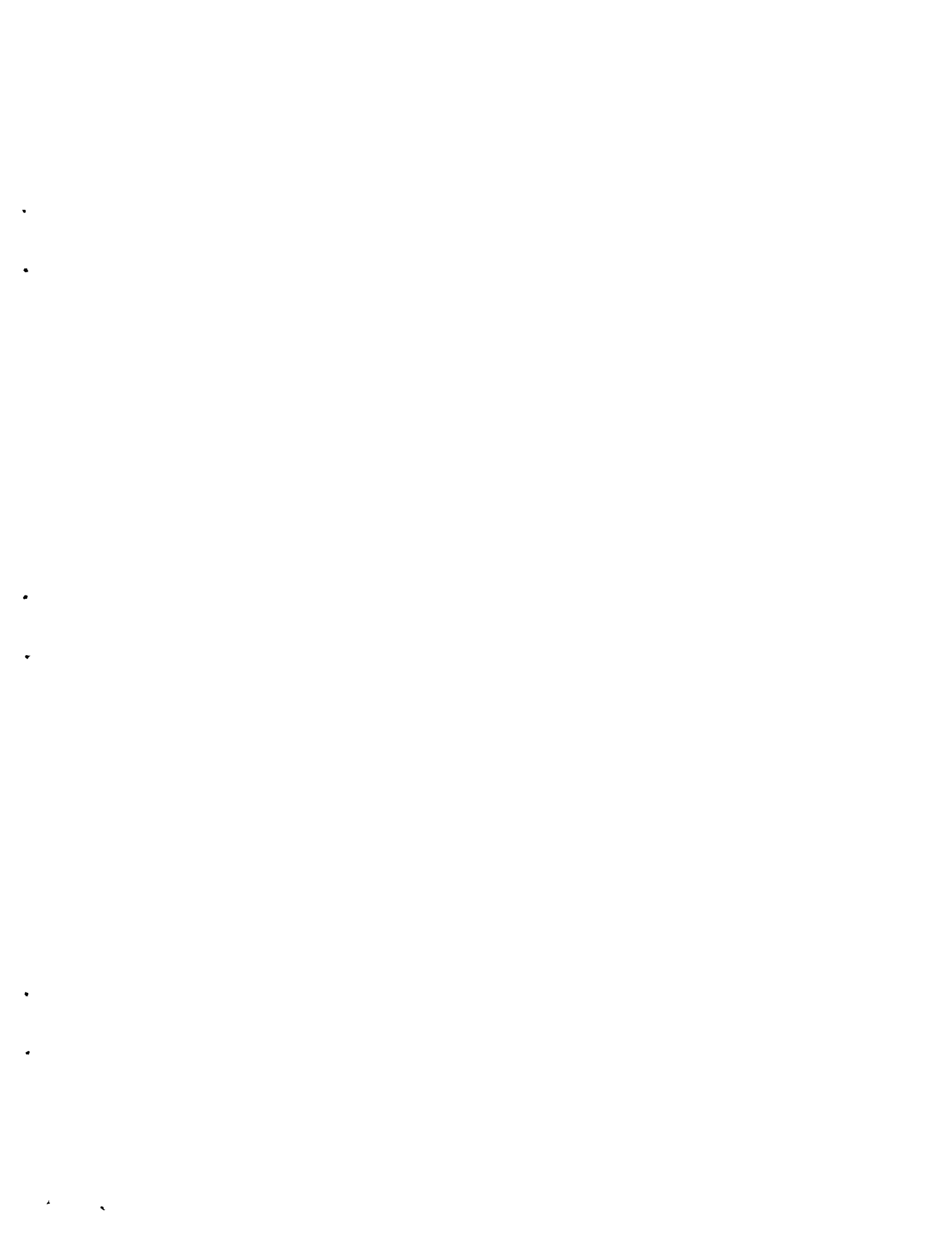
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ABSTRACT

In Campaign 5, fast breeder reactor (FBR) fuel [average burnup  $\sim 2.6$  TJ/kg ( $\sim 30,000$  Mwd/t)] was processed for the first time. Operations in a single extraction cycle with 30% TBP-NPH were satisfactory with low heavy-metal losses ( $<0.02\%$ ) and high decontamination factors (DFs  $>1000$ ) for all fission products except  $^{95}\text{Zr}$ , which exhibited moderate DFs (180 and 750, respectively, in two runs). The use of a split scrub stream (0.5 M and 3 M  $\text{HNO}_3$ ) vs a single scrub stream (3 M  $\text{HNO}_3$ ) resulted in the higher DF. An extractant backscrubbing stream was not needed to produce partially partitioned uranium-plutonium products containing 30-35% plutonium when processing the core FBR fuel (22% Pu). The necessary enrichment factor ( $\sim 1.5$ ) was attained by maintaining the temperature at 25-30°C in partial partitioning and adjusting the relative flow rates of the aqueous and organic phases. The plutonium recovered in the two runs ( $\sim 400$  g) was purified by anion exchange and converted to  $\text{PuO}_2$  for fuel refabrication studies.

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1. INTRODUCTION

The Solvent Extraction Test Facility (SETF), which is located in a hot cell at the Transuranium Processing Plant (TRU), utilizes mixer-settler contactors to test solvent extraction flowsheet options for reprocessing irradiated commercial nuclear power reactor fuels.<sup>1</sup> Emphasis is placed on FBR fuels. Tests at this facility provide comparisons of flowsheet options in regard to uranium and plutonium recoveries, their decontamination from fission products, and general operability of the system.

The broad objectives of studying uranium-plutonium coprocessing flowsheets carried out in Campaigns 1-4<sup>1,2</sup> were continued in Campaign 5, using

irradiated FBR fuel [average burnup  $\sim 2.6$  TJ/kg ( $\sim 30,000$  MWd/t)] for the first time in the SETF. Two solvent extraction flowsheet tests were made to: (1) determine the general solvent extraction behavior of FBR fuel solutions, and (2) evaluate options for scrubbing in the extraction step and stripping in the partial partitioning step. In addition to providing information on coprocessing flowsheet options for FBR fuels, Campaign 5 recovered the plutonium from the irradiated (U-Pu) $O_2$  fuel for use in fuel fabrication studies. Also, sufficient quantities of acid-insoluble fission product residues were provided for characterization studies<sup>3</sup> (composition, particle size distribution, etc.), and high-level raffinate solutions were provided for waste concentration studies being conducted in other research and development areas of the Consolidated Fuel Reprocessing Program (CFRP).

The irradiated FBR fuel (2 kg of uranium plus plutonium) processed was from two different sources and included 16 intact fuel pins plus pieces of three other fuel pins. Before irradiation, the composition of the fuel was  $\sim 25\%$  plutonium and  $\sim 75\%$  natural uranium. Nine pins (PNL-3 and PNL-15) had been irradiated in the EBR-II and seven (PNL-59) in the GE Test Reactor (GETR) and had been discharged from these reactors for at least six years. Fuel burnups ranged from 70 GJ/kg to 5.7 TJ/kg (810 to 66,000 MWd/t). The pins were sheared into 2.5-cm-long pieces at the High Radiation Level Examination Laboratory (HRLEL), blended, and packaged into two batches. Average burnups for the two batches were  $\sim 2.3$  TJ/kg ( $\sim 27,000$  MWd/t) and  $\sim 3.0$  TJ/kg ( $\sim 35,000$  MWd/t). Since this fuel had been discharged more than six years ago, it was necessary to add  $^{95}\text{Zr}$  tracer to dissolver solutions to obtain DF values of zirconium in solvent extraction.

Following each solvent extraction test, the plutonium was first separated from the uranium and purified using one cycle of anion exchange, and then converted to  $\text{PuO}_2$  by precipitation and calcination of plutonium oxalate. A total of  $\sim 400$  g of plutonium was shipped to the Hanford Engineering Development Laboratory (HEDL) for use in fuel fabrication studies.

## 2. EQUIPMENT AND OPERATIONAL PROCEDURES

The SETF equipment items and most operational procedures used during Campaign 5 for fuel dissolution, feed clarification and adjustment, and solvent extraction were the same as those described for previous campaigns.<sup>1,2</sup> However, because of the differences between the fuel dissolution characteristics of FBR and LWR fuels and because it was desired that the insoluble fuel residues be recovered for characterization studies,<sup>3</sup> different conditions were required for fuel dissolution and the operating procedure for feed clarification was modified.

Equipment and procedures used in the recovery of plutonium as PuO<sub>2</sub> from the aqueous U-Pu streams generated by the solvent extraction flow-sheet tests are described in Sects. 2.4 and 2.5. The recovery is accomplished by using one cycle of anion exchange to purify and concentrate the plutonium and then converting it to PuO<sub>2</sub> by batch precipitation and calcination of plutonium oxalate. These operations and the associated equipment have not been described prior to this time because they are primarily support activities to the mainline effort of solvent extraction processing of fully irradiated fuels. However, the PuO<sub>2</sub> product was shipped to HEDL where it will be used in fuel fabrication studies, and therefore, these operations and associated equipment items are described in this report to document the processing history and purity of the PuO<sub>2</sub> product.

### 2.1 Fuel Dissolution

The dissolution of the first batch of fuel was attempted using the same conditions and procedure that have been routinely used in the SETF for dissolving LWR fuel. This procedure includes: (1) adding the fuel to 3 M HNO<sub>3</sub>, (2) heating to 50°C while adding 11 M HNO<sub>3</sub>, and (3) heating to 90°C for a 2-h digest. Only ~87% of the heavy metals in the first batch of fuel was dissolved with this procedure. A second dissolution of the fuel residues using 7 M HNO<sub>3</sub> at 90°C for 4 h dissolved the rest of the heavy metals. A third dissolution recovered very little additional material.

To improve the recovery from the second batch of fuel, the digestion time was increased from 2 to 5 h, and the digestion temperature was



increased from 90 to 95°C. Again, the fuel was only partially dissolved in the first dissolution (~81%), and a second dissolution, with 7 M HNO<sub>3</sub>, was required. The nitric acid concentration was lower in the first dissolver product solution for the second batch (~1.9 M) than in the first dissolver product solution for the first batch (~2.6 M). This accounts for the poorer recovery in the second run and may have been the result of a suspected leak in the nitric acid metering line. Use of a higher acid concentration and possibly an increase in the dissolution time is indicated for future runs with FBR fuel.

## 2.2 Addition of <sup>95</sup>Zr Tracer to the Aqueous Feed Solution

A <sup>95</sup>Zr tracer was used in these runs to permit comparisons of decontamination factors (DF) at different flowsheet conditions and determine the most important variables affecting zirconium decontamination. These zirconium DF values will, of course, have to be confirmed using short-cooled fuels, when available.

The <sup>95</sup>Zr tracer was added to the dissolver product solution. This procedure was adopted because the subsequent feed adjustment step provided a possible pathway for the enhancement of chemical exchange with the various hydrolytic species of the dissolved fission product zirconium in the fuel solution. In addition, the feed filtration steps afforded a potential for removing any colloidal zirconium that might be present in filterable or sorbable forms. Achievement of equilibrium among the various species of zirconium in solution is a slow process that is dependent on the nature of the initial stock solutions or compounds.<sup>4</sup> Our tracer technique may only approximate the quantitative solvent extraction behavior of the bulk fission product zirconium dissolved from the fuel. Zirconium solutions can contain both moderately extractable and inextractable species<sup>5</sup> and we cannot be certain that complete equilibrium distribution of the <sup>95</sup>Zr tracer among the various species from the fuel was achieved.

### 2.3 Feed Clarification and Recovery of Acid-Insoluble Residues

Feed clarification was performed in a way that would permit the collection of a sample of dissolver solids for subsequent characterization studies.<sup>3</sup> Clarification was accomplished in two filtration steps. First, the bulk of the acid insoluble residue was removed in a primary filtration, using an etched-disc filter (1- $\mu$ m openings) without precoat. Then, after feed adjustment, the feed was given a polishing filtration by passing it through a deep-bed filter<sup>2</sup> of diatomaceous earth as it was metered from the feed tank to the extraction-scrubbing, mixer-settler bank. The polishing filtration was used to remove any solids that might have passed through the etched-disc filter in primary filtration or that were perhaps precipitated during feed adjustment and aging. Feed adjustment consisted of the usual procedure<sup>1,2</sup> which includes: (1) H<sub>2</sub>O<sub>2</sub> addition and digestion over a 4-h period at 90°C to enhance the dissolution of any unfilterable colloids, (2) adjustment of the plutonium valence to Pu(IV) by N<sub>2</sub>O<sub>3</sub> sparging at ambient conditions, and (3) adjustment of feed concentration to  $\sim 3$  M HNO<sub>3</sub> -150 g/L U+Pu by nitric acid addition. This is the first campaign where a deep-bed filter was used for feed polishing. The polishing filter was made with a smaller diameter glass housing ( $\sim 5$  cm) than the original deep-bed filter ( $\sim 8$  cm) in order to reduce the inventory of adjusted feed solution in the filter.

Previously,<sup>1,2</sup> we have employed a precoated etched-disc filter for primary clarification. To avoid contamination of the solids that were recovered for characterization studies, the precoat was not used in Campaign 5. The solids were recovered from the filter as a dilute slurry by backflushing with nitric acid (3 M) and subsequently concentrated by settling and decantation.

The nitric acid insoluble residues in FBR dissolver solutions are easier to filter than those in LWR dissolver solutions as was indicated in earlier work by Savage.<sup>6</sup> Rapid and near complete plugging of the etched-disc filter occurred in filtrations of LWR dissolver solutions unless the filter was precoated. The dissolver solutions from the first FBR fuel batch filtered quite well using the uncoated filter. However, the filtration of the solution from the second fuel batch was noticeably slower.

Since the filter was only given the normal backflushing for a coated filter after the first filtration, a more thorough backflushing might have improved filtration rates of the second filtration. The effectiveness of a more thorough backflushing would, of course, depend on the tenaciousness of the solids plugging the pores of the filter and could only be evaluated by experiment.

#### 2.4 Anion Exchange Purification of Plutonium

The well-known, nitrate-based anion exchange process<sup>7</sup> is used to recover and purify the plutonium. A photograph of the anion exchange column and equipment rack is shown in Fig. 1. The ion exchange equipment is located in the upper portion of the rack. The lower portion of the rack contains equipment for sampling the tanks that are located in the tank pit portion of Cell 5. The column (0.108 m diam and 0.710 m high) is constructed of 304 stainless steel. The anion exchange column holds ~6 L of 0.3-mm- to 1-mm-diam (16-50 mesh) Ionac A-580 resin and has a plutonium capacity of ~300 g. A replaceable glass pot, attached to the top of the column, is equipped with a valve to permit gas to be vented so that the column can be filled with liquid. The glass permits visual verification that the column is filled with liquid, which is necessary to avoid channeling during operation. For safety reasons, the nitrate-form anion exchange resin is kept immersed in liquid, and the column is vented when not in use. The glass pot permits continual surveillance of this condition. Temperature control during operation is provided by recirculating water from a thermostated bath through the jacket surrounding the column. Loading, washing, and elution of the column are carried out in the down-flow mode while the column temperature is maintained at 55-60°C.

Feed solutions are prepared by mixing the plutonium-bearing aqueous product solutions together, adjusting to 7.5 M HNO<sub>3</sub> using concentrated nitric acid (15.8 M) addition, and when necessary, sparging with N<sub>2</sub>O<sub>3</sub> until all of the plutonium is adjusted to the tetravalent state. The feed is then filtered through a stainless steel etched-disc filter (3-μm-diam opening).

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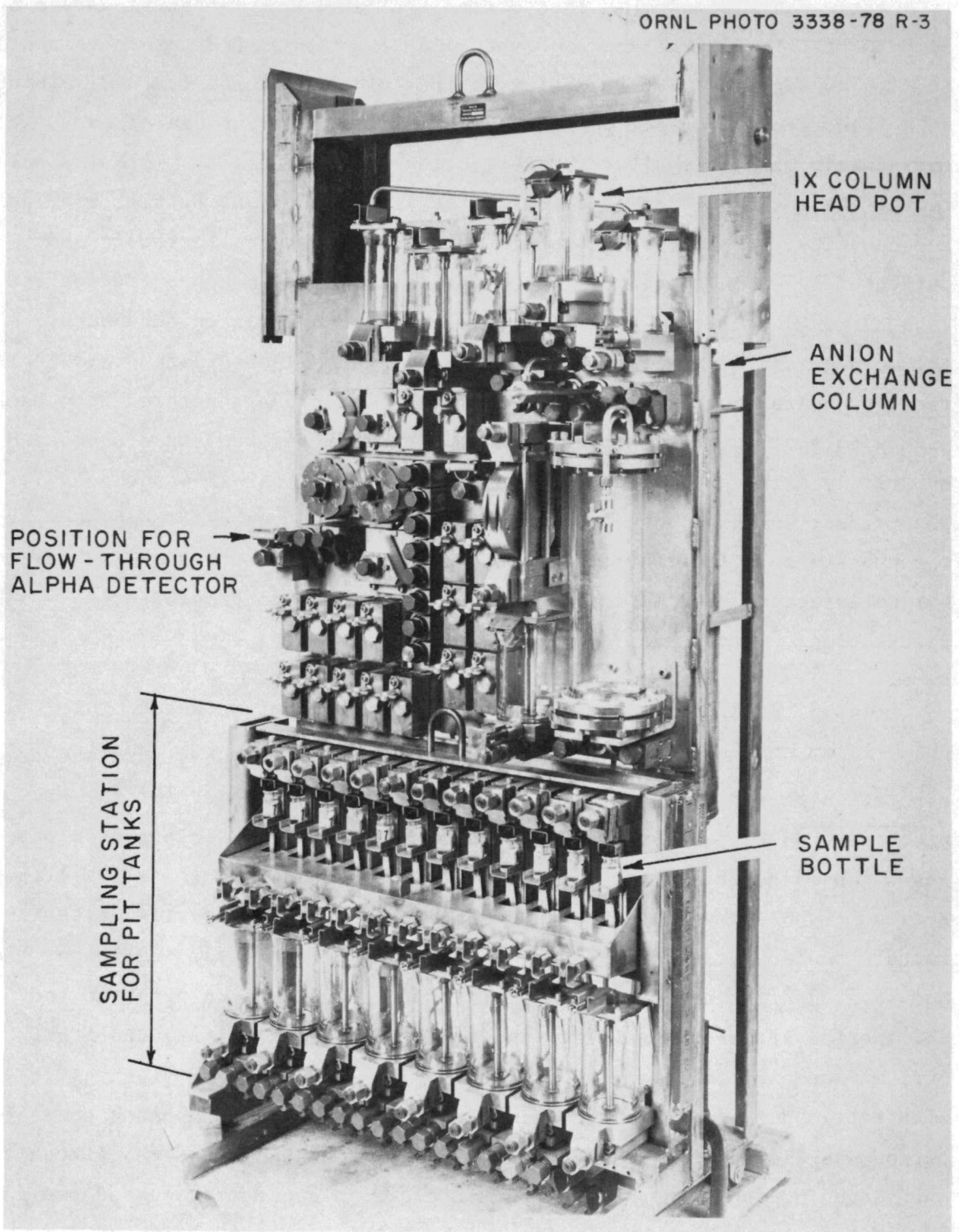


Fig. 1. SETF anion exchange, sampling, and transfer rack.

After the plutonium is loaded from the feed at a linear flow rate of  $\sim 1.8$  cm per min, the column is washed with  $7.5 \text{ M HNO}_3$  ( $\sim 3$  column volumes) at  $\sim 1.8$  cm per min. The plutonium is then eluted using  $0.7 \text{ M HNO}_3$  eluent at a flow rate of  $\sim 0.9$  cm per min. An in-line, flow-through alpha detector is used to monitor the collection of the purified plutonium solution. The purified product is collected in polyethylene bottles with a 1-L capacity. About 99% of the plutonium is usually collected in about 8 bottles ( $\sim 1.3$  column volumes) which range in plutonium concentration from about 1 to 40 g/L. Column effluents of less than 1 g/L Pu (end cuts, column regeneration raffinate, and loading wastes) are routed to recycle recovery operations. The uranium-plutonium solutions generated from each of the solvent extraction runs ( $\sim 200$  g plutonium per run) were processed separately using one cycle of anion exchange in runs 5-AX-4 and 5-AX-5. The product solution cuts from each anion exchange run were combined into a composite solution that was of the appropriate concentration and volume for satisfactory feed to the subsequent batch oxalate precipitation-calcination processing.

## 2.5 Precipitation and Calcination of Plutonium Oxalate

In previous SETF runs with LWR plutonium fuel, a Pu(IV) oxalate precipitation procedure had been used. However, the customer for the FBR plutonium, HEDL, requested a more complicated Pu(III) precipitation process which is described in this section. The method used was a Los Alamos National Laboratory procedure (FOP-PP-OP-R03) that has provided a satisfactory powder for work at HEDL. The equipment is the same equipment that has been used for several years at TRU for the batch precipitation and calcination of curium oxalate. The equipment was decontaminated from curium (where  $^{244}\text{Cm}$  is the major activity) by leaching and flushing it with nitric acid prior to operations with plutonium. Each batch precipitation was limited to  $<90$  g of plutonium by the capacity of the filter cartridge for the precipitate. The amount of plutonium processed per run varied from 50 to 90 g, depending on the initial concentration of plutonium in the purified feed solution from anion exchange operations. Six oxalate precipitation-calcination processing runs were used to convert  $\sim 400$  g of plutonium.

The oxalate precipitation was carried out in a 4.5-L glass vessel in which process solutions were mixed using a motor-driven, variable-speed, Zircaloy-2 stirrer. Temperature was controlled by means of a water-heated immersion coil located within the vessel. The oxalate precipitate was collected from the pumped slurry in a filter cartridge consisting of an Inconel outer body and a removable, fritted-bottomed, platinum liner which also served as the container for batch calcination. The fritted openings are 10 to 15  $\mu\text{m}$  in diameter and the liner capacity is 0.25 L. Calcination was accomplished by removing the platinum liner containing the oxalate precipitate and placing it in an electrically heated furnace where it was calcined at 500°C for 2 h.

The Pu(III) oxalate precipitation was effected by the following sequence of operations after the feed had been charged to the precipitation vessel: (1) adjustment of acid concentration in the feed; (2) batch addition of urea to scavenge nitrite; (3) slow, metered addition of hydroxylamine nitrate (HAN), and digestion to adjust the plutonium valence; and (4) precipitation of plutonium oxalate by a fast addition of oxalic acid. Ambient temperature of  $\sim 30^\circ\text{C}$  was maintained throughout this sequence, except during the HAN addition and digestion period where the solution was maintained at  $\sim 40^\circ\text{C}$ . The oxalate precipitate was then collected on the filter, and the filter cake was washed with 0.1 M oxalic acid - 0.7 M  $\text{HNO}_3$  - 0.1 M HAN. The acidity of the product solutions from anion exchange purification varied from 0.7 to 7 M. The acidity of the feed for oxalate precipitation was adjusted to a 0.7 to 1.5 M range by the appropriate combination of these purified solutions plus dilution with 0.7 M  $\text{HNO}_3$ .

Although the plutonium contents of composite feeds prepared from the anion column product cuts varied from 50 to 90 g of plutonium in the six oxalate precipitation-calcination runs, the runs were not carried out using a fixed excess of process reagents. To simplify operating procedures, the quantities of reductant and precipitant were the same in all runs and were based on the amounts necessary to ensure a satisfactory excess for the feed of highest plutonium content. Quantities added in each run were 0.075 L of  $\sim 2$  M urea and 0.50 L of  $\sim 1.7$  M HAN for valence adjustment, and 0.75 L of 0.8 M oxalic acid for precipitation.

### 3. EXPERIMENTAL CONDITIONS, RESULTS, AND DISCUSSIONS OF SOLVENT EXTRACTION TESTS

Two experimental solvent extraction runs (5-1 and 5-3\*) were carried out with irradiated FBR fuel solutions using coprocessing flowsheets in which partial partitioning was accomplished by selective stripping (Figs. 2 and 3). It was not necessary to use an extractant backscrubbing stream to obtain a uranium-plutonium product containing ~35% plutonium because a concentration factor of only about 1.6 was needed for the FBR fuel (22% Pu). For this slight degree of separation, the portion of uranium stripped along with the plutonium was controlled by using a temperature of 25–30°C and adjusting the BX/AP flow ratio. A test of a CFRP reference coprocessing flowsheet in which two aqueous nitric acid solutions of different concentrations are used both in the scrubbing step and in the partial partitioning step was made in the first run (Fig. 2). In the second run (Fig. 3), however, only a single nitric acid stream was used for the scrubbing and stripping tests, which permitted a comparison of the effects of different conditions to those of the reference case. The extractant used in both tests was tri-n-butyl phosphate (TBP) at a concentration of 30 vol % in normal paraffin hydrocarbon (NPH) diluent. Operating conditions and detailed stream analyses for each test are tabulated in the Appendix.

The CFRP reference coprocessing flowsheet utilizes two aqueous nitric acid streams in both scrubbing and stripping to generate stagewise nitric acid profiles that have potential advantages. For example, in the extraction-scrubbing contactor (Fig. 2), the use of a 3 M HNO<sub>3</sub> intermediate acid scrub (AIS) and a 0.5 M HNO<sub>3</sub> final scrub (AS) allows effective zirconium scrubbing. The more dilute acid scrub at the end of the contactor decreases nitric acid transfer to the stripping contactor and improves the stripping efficiency. Similarly, an optimization of desired effects can be accomplished in costripping by using a BIX stream of 3 M HNO<sub>3</sub> and a BX stream of 0.01 M HNO<sub>3</sub> as depicted in Fig. 2. This input configuration

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\*Runs 5-2 and 5-4 were made to recover plutonium from the second-stage dissolutions from the two fuel batches. There was insufficient feed material in these runs to allow any meaningful experimental data to be collected.

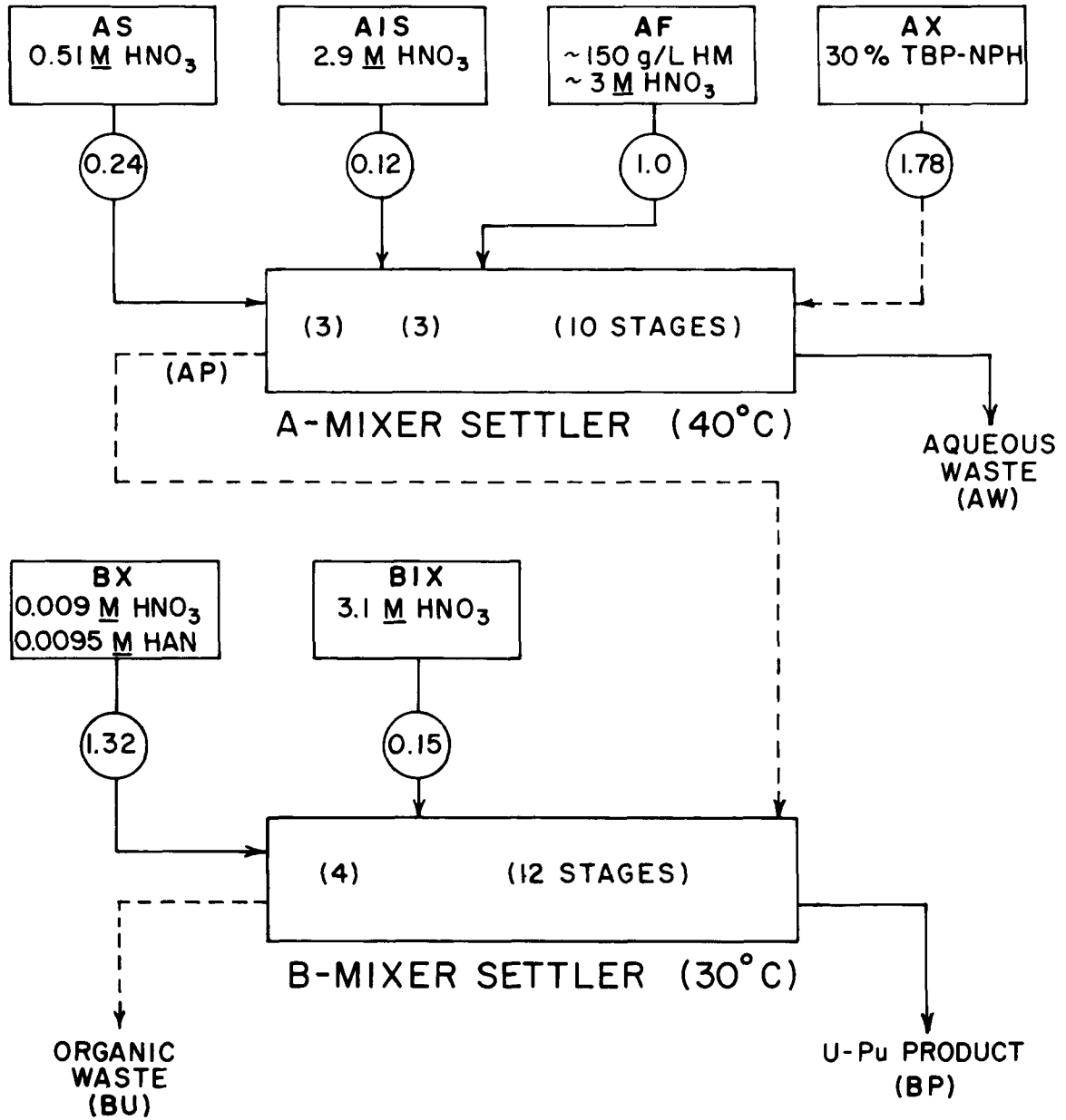


Fig. 2. FBR coprocessing flowsheet for Test 5-1 using split flows for nitric acid scrubbing and partial partitioning.



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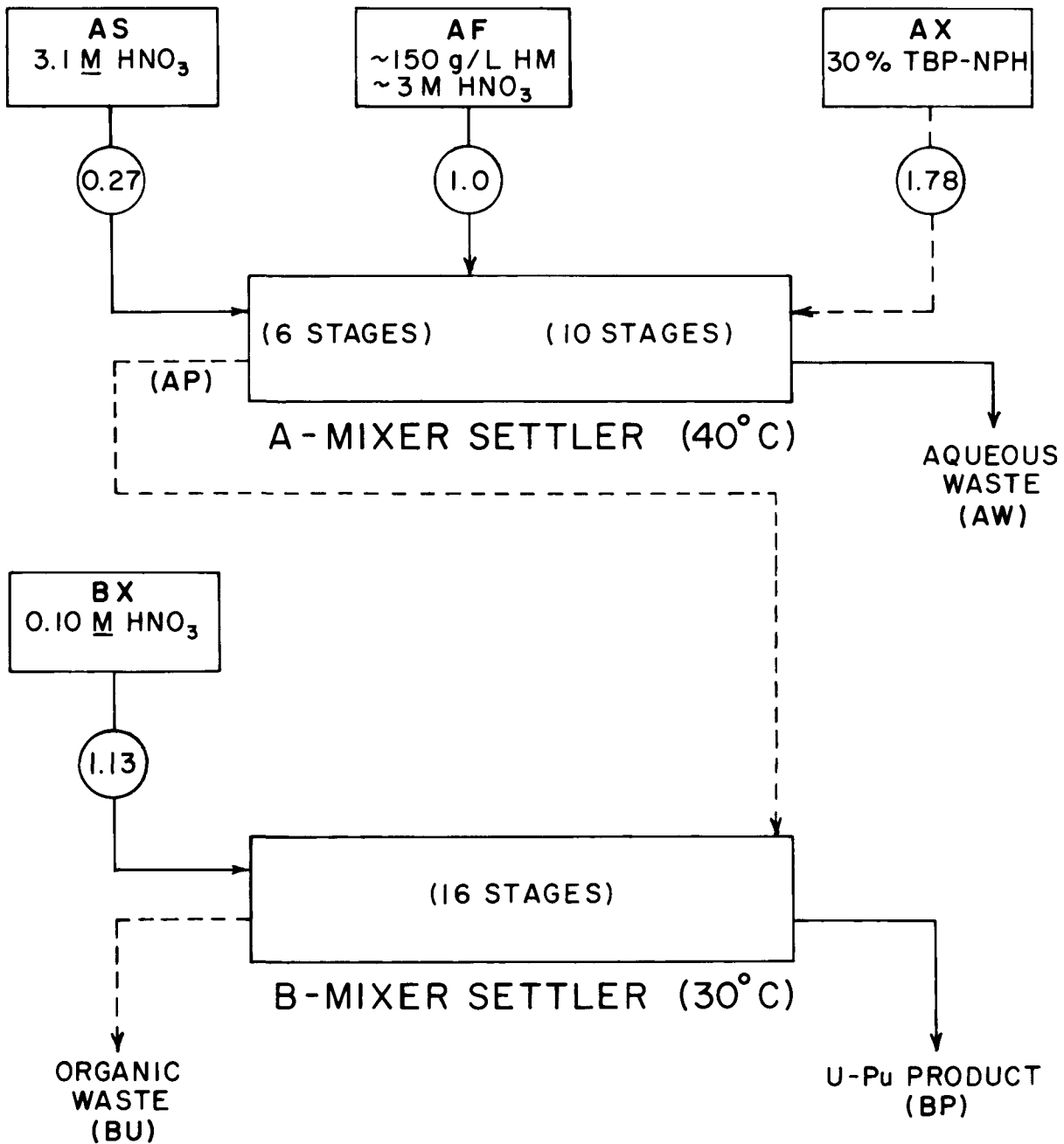


Fig. 3. FBR coprocessing flowsheet for Test 5-3 using single stream flow for nitric acid scrubbing and partial partitioning.

of aqueous stripping solutions permits a stagewise profile of aqueous phase nitric acid concentration that enhances stripping and yet is not conducive to plutonium polymer formation since significant concentrations of plutonium are confined to the higher acid region. The CFRP reference flowsheet also makes use of a low concentration of hydroxylamine nitrate (HAN) in the BX stream (Fig. 2) to reduce Pu(IV) and thus enhance the stripping of any small quantity of residual plutonium that may still be present in the last few stripping stages of the contactor. The use of HAN was omitted in Run 5-3 (Fig. 3).

Although the use of split scrubbing and split stripping streams offer potential advantages, flow rates must be closely controlled to obtain the desired results in costripping or partial partitioning. In Run 5-3 (Fig. 3), the use of a single strip stream (0.1 M HNO<sub>3</sub>) was employed in order to compare an alternative single stream stripping concept when partial partitioning. The principal purpose of using a single scrub stream (3.1 M HNO<sub>3</sub>) in Run 5-3 was to verify the expected poorer performance of high acid scrubbing on zirconium decontamination.

### 3.1 Results in Coextraction-Coscrubbing

General operability of the mixer-settler bank in regard to phase separations and the collection of emulsified solids at the aqueous-organic interface (crud) was good and was comparable to that observed previously<sup>1,2</sup> with LWR fuels. Interfacial crud formation was observed at the feed stage and in the adjacent extraction stage but did not progress any farther into the extraction section during the runs. The FBR fuels used for these tests had decayed for >6 years, and the activity levels were actually less than those encountered in previous<sup>1,2</sup> processing of LWR fuels (Table 1).

The final scrubbing of the organic phase with 0.5 M HNO<sub>3</sub> in Run 5-1 produced a better DF for zirconium than the 3 M HNO<sub>3</sub> scrub in Run 5-3 as expected (Table 2). Thus, the zirconium added as tracer showed the general behavior that is typical of the extractable zirconium species.<sup>5</sup> Its extractability is greatly enhanced by increasing the nitric acid concentration. Concentration profiles of <sup>95</sup>Zr, <sup>95</sup>Nb, and <sup>154</sup>Eu in the organic

Table 1. Comparison of radioactivity levels of the FBR dissolver solutions with those of the LWR dissolver solutions previously processed in the SETF

Radionuclide	Radionuclide activity, GBq/kg (U+Pu)	
	LWR	FBR
$^{60}\text{Co}$	11	<1.5
$^{95}\text{Zr}$		110 <sup>a</sup>
$^{95}\text{Nb}$		36 <sup>a</sup>
$^{106}\text{Ru}$	580	<44
$^{125}\text{Sb}$	81	38
$^{134}\text{Cs}$	960	
$^{137}\text{Cs}$	3000	2600
$^{144}\text{Ce}$	590	<22
$^{154}\text{Eu}$	120	20

<sup>a</sup> $^{95}\text{Zr}$ - $^{95}\text{Zb}$  tracer was added to the dissolver solution product.

Table 2. Uranium and plutonium losses and fission product decontamination results in coextraction-coscrubbing

Test run	5-1	5-3
Extraction losses		
Uranium	0.23%	0.001%
Plutonium	0.004%	0.019%
Fission product DFs		
$^{95}\text{Zr}$	7.5E2 <sup>a</sup>	1.8E2
$^{95}\text{Nb}$	2E3	2E3
$^{125}\text{Sb}$	>3E4	>9E3
$^{137}\text{Cs}$	5E5	3E5
$^{154}\text{Eu}$	>7E4	>1E4
$^{155}\text{Eu}$	5E4	>2E4

<sup>a</sup>To be read as  $7.5 \times 10^2$ .

phase are shown in Fig. 4. The ruthenium activity level in the feed solutions was too low to permit the determination of the DF for ruthenium in Runs 5-1 and 5-3.

Plutonium losses to the aqueous waste were quite low (Table 2). The higher uranium loss in Run 5-1 is difficult to understand when such low losses of plutonium were obtained. The plutonium losses from the current processing of FBR fuels were the same order of magnitude as were observed previously<sup>1,2</sup> when processing LWR fuels (Table 3).

Table 3. Typical losses of plutonium obtained in solvent extraction processing of LWR and FBR fuels at the SETF

Fuel	Extraction bank aqueous waste loss (%)	U-Pu strip bank organic waste loss (%)
LWR fuel (~1% plutonium)	0.007	0.008
LWR fuel spiked with recovered plutonium (~10% plutonium)	0.02	0.002
FBR core fuel (~22% plutonium)	~0.01	0.004

### 3.2 Partial Partitioning Results

In both runs, the plutonium loss to the stripped extractant was <0.005%, and the uranium-plutonium product contained ~32% plutonium. The uranium and plutonium stripping results (Figs. 5-7) were nearly identical as evidenced by the plutonium and uranium concentration profiles, although the aqueous nitric acid concentration profiles are quite different. In both runs, the stagewise stripping of plutonium was more complete than SEPHIS<sup>8</sup> calculations predicted. Stripping possibly was partially assisted by hydroxylamine reduction (Run 5-1), nitrous acid reduction, or by disproportionation of tetravalent plutonium at the low acidity used in each run. However, no measurements were made in regard to plutonium valence in any of the stage samples to determine if any Pu(III) stripping had occurred.

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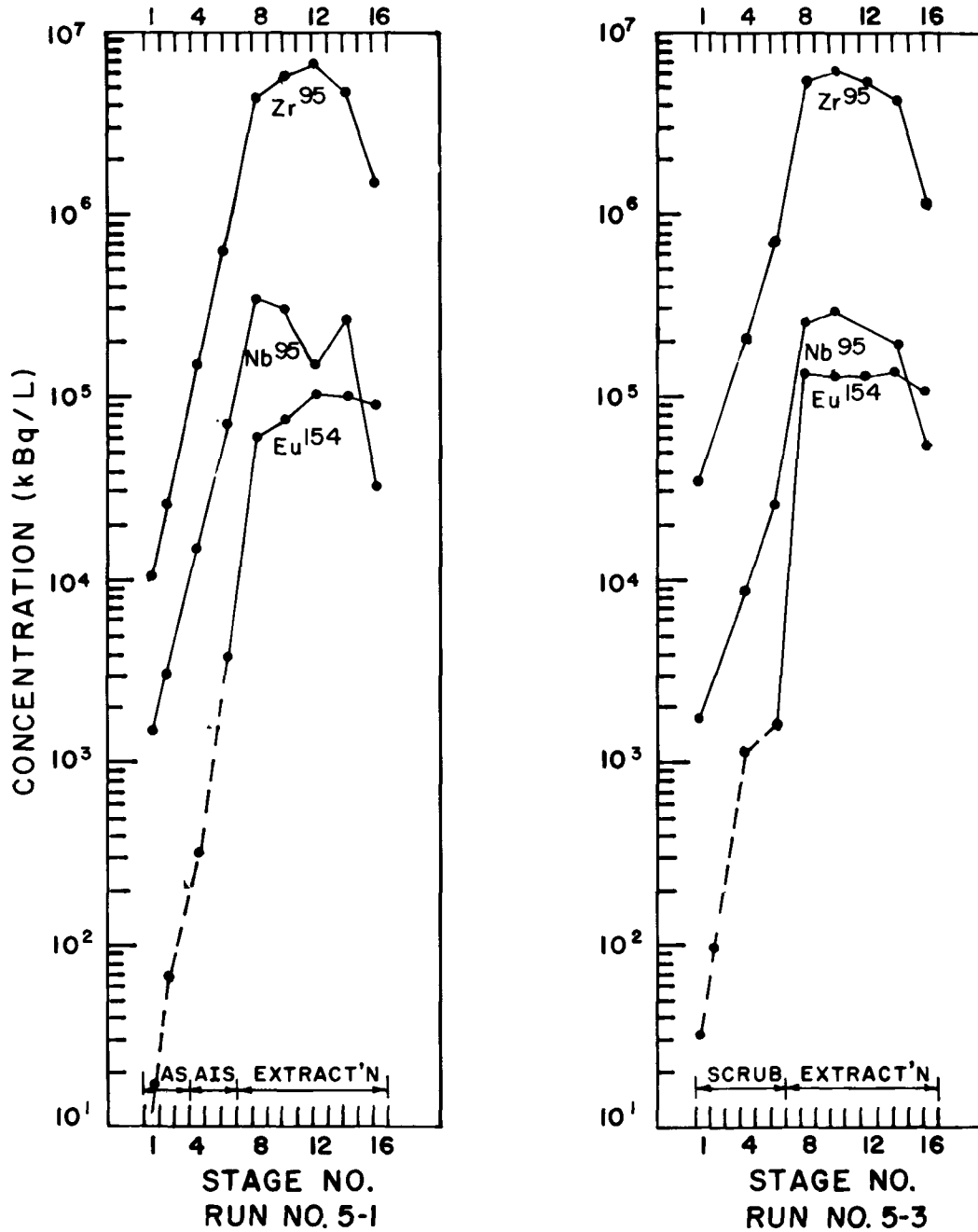


Fig. 4. Concentration profiles of <sup>95</sup>Zr, <sup>95</sup>Nb, and <sup>154</sup>Eu in the extraction-scrubbing contactor for Tests 5-1 and 5-3.

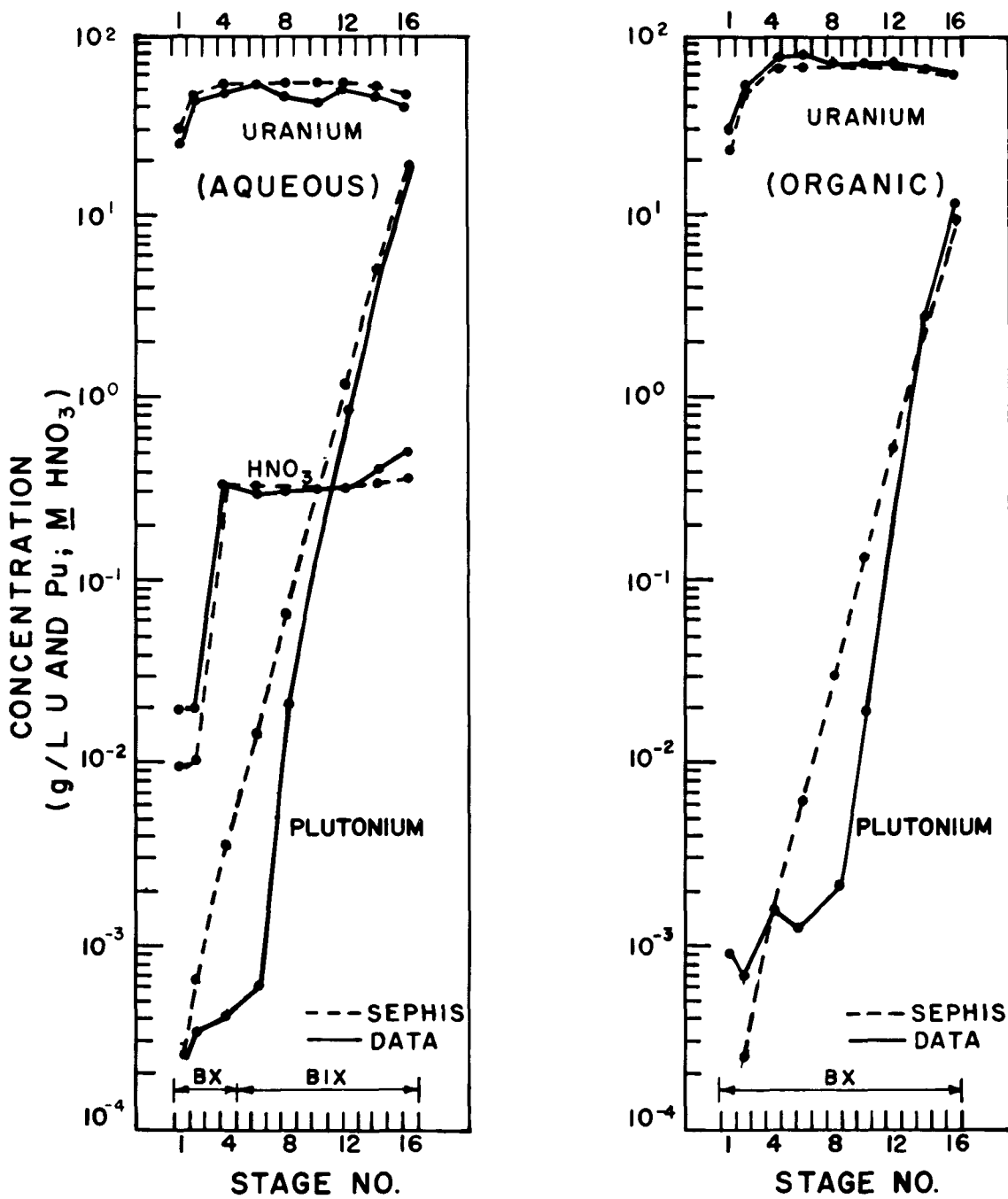


Fig. 5. Concentration profiles of uranium, plutonium, and nitric acid in the partial-partitioning contactor (Test 5-1).

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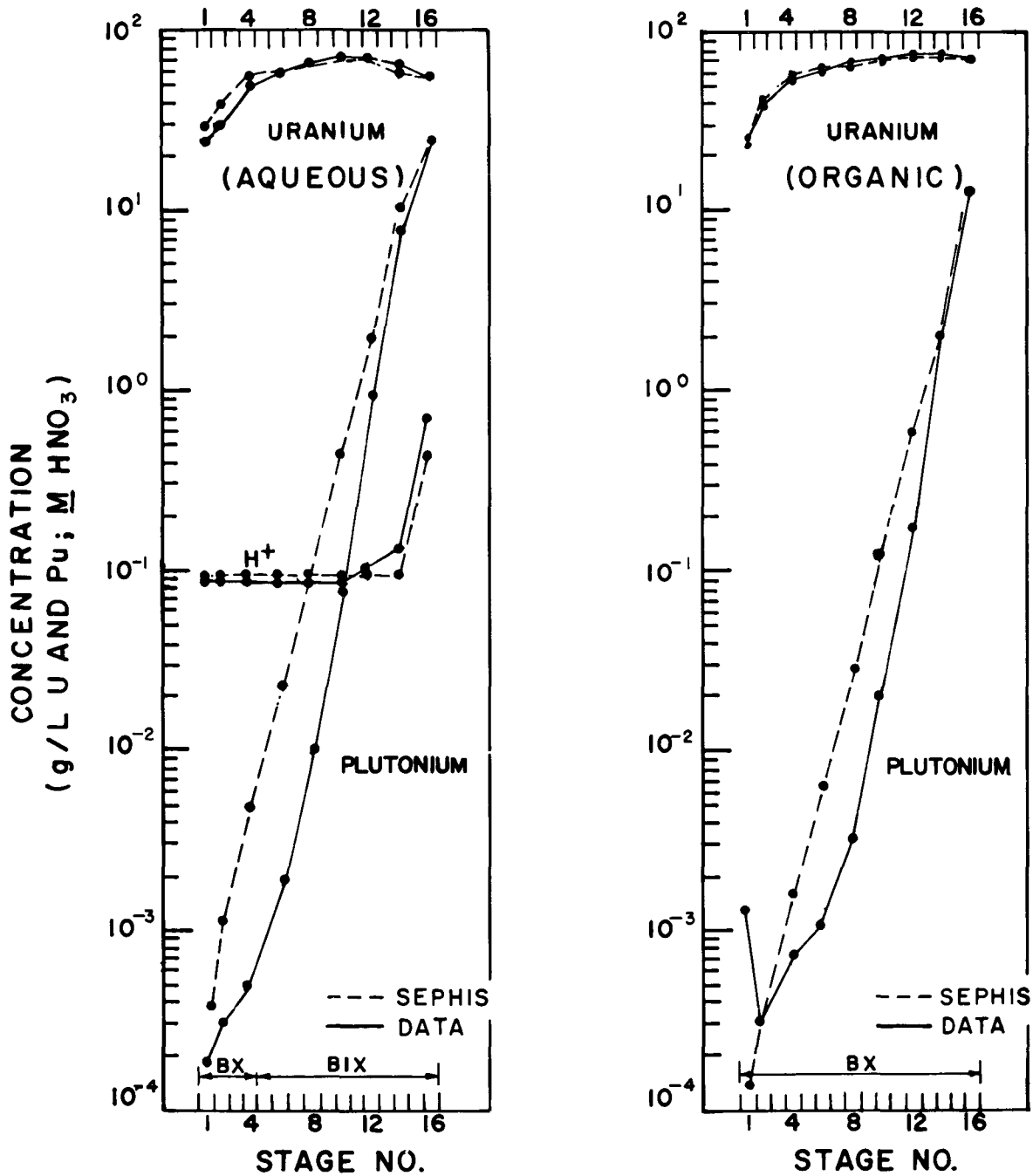


Fig. 6. Concentration profiles of uranium, plutonium, and nitric acid in the partial-partitioning contactor (Test 5-3).

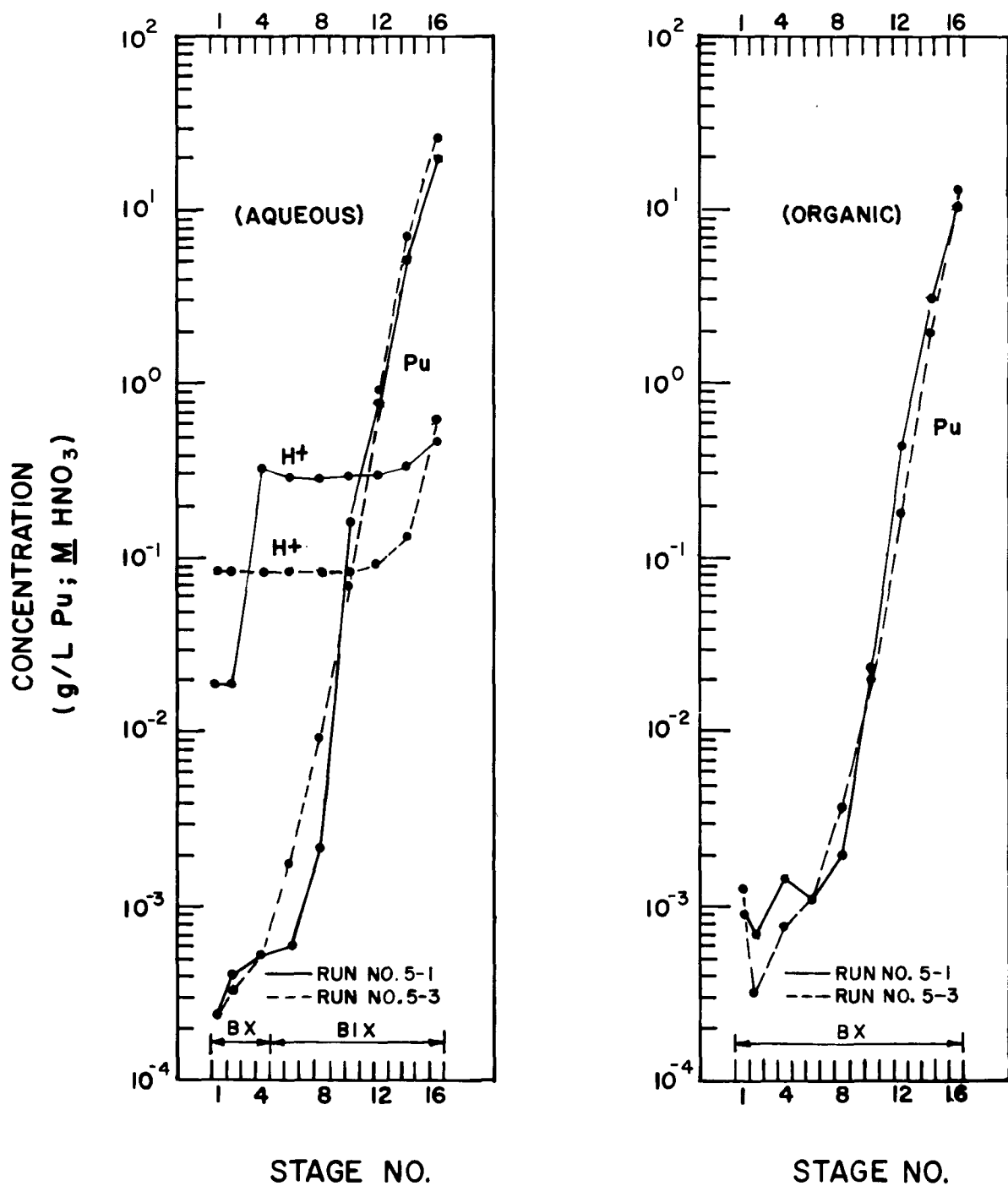


Fig. 7. Concentration profiles of plutonium and nitric acid in the partial-partitioning contactor (Tests 5-1 and 5-3).



## 4. PLUTONIUM PURIFICATION AND OXIDE CONVERSION RESULTS

One cycle of anion exchange gave satisfactory recovery and purification of plutonium from the aqueous uranium-plutonium solutions generated by the solvent extraction processing (Runs 5-1 through 5-4). The DF values for uranium and fission products for the two anion exchange runs are shown in Table 4. Purified product recovery was 99%, and the average product concentration was ~27 g/L Pu. The satisfactory, but relatively poor decontamination from  $^{125}\text{Sb}$ , resulted from carrying out these two runs after the column of resin had been previously used to recover plutonium from a dirty composite of many rework solutions. About 18 GBq of the  $^{125}\text{Sb}$  remained sorbed on the column and a small fraction of this  $^{125}\text{Sb}$  slowly eluted in the subsequent runs (which included Runs 5-AX-4 and 5-AX-5). Fortunately, most of the  $^{125}\text{Sb}$  was eluted to the waste stream and only a small quantity was eluted with the product.

Table 4. Fission product radionuclide and uranium decontamination factors obtained in anion exchange processing runs

Impurity	Radioactivity level in product (MBq/kg Pu)		DF	
	Run 5-AX-4	Run 5-AX-5	Run 5-AX-4	Run 5-AX-5
Fission product radionuclide				
$^{95}\text{Zr}$	25	41	260	140
$^{106}\text{Ru}$	18	<30	<20	
$^{125}\text{Sb}$	80	94	<2	<2
$^{137}\text{Cs}$	3.1	6.8	240	28
$^{154}\text{Eu}$	<1	<2		
Uranium			1300	280

The purified plutonium product solutions were then converted to oxide by batch precipitation of Pu(III) oxalate, which was subsequently calcined to  $\text{PuO}_2$ . Recovery of plutonium by the batch oxalate precipitation was satisfactory, and the loss to the supernatant liquid was only about 1%.

The activity levels of fission product radionuclides in the plutonium oxide product from each batch of fuel processed and the overall DF values achieved by the combined sequence of processing (solvent extraction, anion exchange, and oxide conversion) are shown in Table 5. The only measurable gamma-emitting fission products that remained in the oxide product were  $^{95}\text{Zr}$  and  $^{125}\text{Sb}$ , and these nuclides were present in satisfactorily low concentrations. Cross-contamination of the oxide products with  $^{244}\text{Cm}$  from the precipitation equipment, which had previously been used to recover  $^{244}\text{Cm}$ , was not a problem. The  $^{244}\text{Cm}$  concentration in the product was 1 to 4  $\mu\text{g}$  per g of plutonium. The concentrations of some miscellaneous impurities, as analyzed by routine spark-source mass spectrometry (SSMS) methods, in the dissolver feed solution and the oxide product are shown in Table 6 and indicate an acceptable product purity. Oxide products totaling 392 g of plutonium were packaged and shipped to HEDL.

Table 5. Radioactivity levels of fission product radionuclides in plutonium oxide products and the overall DF values achieved

Fission product radionuclide	Radioactivity level in product (MBq/kg Pu)		Overall DF <sup>a</sup>	
	Batch 1	Batch 2	Batch 1	Batch 2
$^{95}\text{Zr}$	13	25	$4\text{E}4$ <sup>b</sup>	$2\text{E}4$
$^{106}\text{Ru}$	<10	<15		
$^{125}\text{Sb}$	17	50	$1\text{E}4$	$4\text{E}3$
$^{137}\text{Cs}$	<2	<2	$>6\text{E}6$	$>8\text{E}6$
$^{154}\text{Eu}$	<4	<4	$>2\text{E}4$	$>2\text{E}4$

<sup>a</sup>The overall DF is defined as the ratio of the radionuclide concentration (MBq/kg Pu basis) in the fuel dissolver solution to its concentration in the  $\text{PuO}_2$  product.

<sup>b</sup>To be read as  $4 \times 10^4$ .

Table 6. Miscellaneous impurities in the first FBR plutonium oxide product as measured by SSMS

Element	Dissolver solution <sup>a</sup> ( $\mu\text{g/g Pu}$ )	Oxide product <sup>b</sup> ( $\mu\text{g/g Pu}$ )	DF
Na	$1 \times 10^4$	20	500
Al	$2 \times 10^3$	<0.2	$>9 \times 10^3$
P	100	1	100
S	300	10	30
K	200	0.6	350
Ca	900	6	150
Cr	$1 \times 10^3$	1	$1 \times 10^3$
Fe	$3 \times 10^3$	3	800
Co	20	<0.1	>200
Ni	$1 \times 10^3$	1	$1 \times 10^3$
Zr	$2 \times 10^3$	0.4	$4 \times 10^3$
Mo	$3 \times 10^3$	<1	$>3 \times 10^3$
Tc	300	<0.2	$>1 \times 10^3$
Ru	600	<2	>300
Cd	200	<2	>100
U	$3 \times 10^6$	<300	$>1 \times 10^4$

<sup>a</sup> From first dissolution of the initial batch of fuel (Run 5-DS-1).

<sup>b</sup> Oxide product made from initial batch of fuel (Run 5-OX-5,6,7).

## 5. SUMMARY AND CONCLUSIONS

The most significant results and conclusions regarding the two solvent extraction flowsheet tests with irradiated FBR fuel are as follows:

1. Approximately 90% of the plutonium recovered from the dissolution of the mixed-oxide fuel was successfully purified and converted to an oxide product. About 15 g of this plutonium was sent to the ORNL Metals and Ceramics Division for characterization. The rest, 392 g of plutonium, was sent to HEDL for refabrication studies.

2. Solvent extraction operations with FBR fuel were equivalent to those experienced previously with LWR fuels with respect to phase separations, accumulation of interfacial solids, uranium and plutonium losses, and fission product decontamination. Operations were smooth, and the losses of plutonium were low (<0.01%). Phase separations were good, and there was little accumulation of interfacial solids.

3. An extractant backscrubbing stream is not needed to produce partially partitioned uranium-plutonium products containing 30–35% plutonium when processing core FBR fuel (22% Pu). The necessary enrichment factor (~1.5) can be attained by maintaining the temperature at 25–30°C in partial partitioning and adjusting the relative flow rates of the aqueous and organic phases.

4. The concentration of nitric acid used in scrubbing had a major impact on DF values of zirconium as expected. Six stages of scrubbing with 3 M HNO<sub>3</sub> were not as effective for zirconium decontamination (DF = 180) as three stages of intermediate acid scrubbing with 3 M HNO<sub>3</sub> followed by three stages of scrubbing with 0.5 M HNO<sub>3</sub> (DF = 750).

## 6. ACKNOWLEDGMENTS

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7. APPENDIX

Table A-1. Campaign 5 first-cycle tests — extraction scrub bank conditions and results

	Run number	
	5-1	5-3
Dates	6/24/81	8/5/81
Bank temp., °C	41	40-41
Number of stages:		
final scrub/intermediate scrub/extraction	3/3/10	6/0/10
AX stream flow rate, L/h	1.518	1.39
Flow ratios:		
AS/AX	0.133	0.150
AIS/AX	0.065	
AF/AX	0.563	0.563
<u>Inlet stream compositions:</u>		
AS stream, HNO <sub>3</sub> , <u>M</u>	0.51	3.1
AIS stream, HNO <sub>3</sub> , <u>M</u>	2.9	
AX stream, % TBP	30±0.5	30±0.5
AF stream		
HNO <sub>3</sub> , <u>M</u>	3.3	2.8
U, g/L	119	106
Pu, g/L	35	31
<sup>241</sup> Am, mg/L	362	319
<sup>95</sup> Zr, GBq/L	16.8	13.3
<sup>95</sup> Nb, GBq/L	5.4	7.5
<sup>106</sup> Ru, GBq/L	<7	<5
<sup>125</sup> Sb, GBq/L	5.7	6.5
<sup>137</sup> Cs, GBq/L	393	455
<sup>144</sup> Ce, GBq/L	<3	<2
<sup>154</sup> Eu, GBq/L	2.98	3.1
<sup>155</sup> Eu, GBq/L	13.5	16

Table A-1. Continued

	Run number	
	5-1	5-3
<u>Outlet stream compositions:</u>		
AW stream		
HNO <sub>3</sub> , <u>M</u>	2.8	2.7
U, mg/L	204	<1
Pu, mg/L	0.97	4.6
<sup>241</sup> Am, mg/L	257	276
<sup>95</sup> Zr, GBq/L	11.3	10.6
<sup>95</sup> Nb, GBq/L	3.6	6.8
<sup>106</sup> Ru, GBq/L	<2	<4
<sup>125</sup> Sb, GBq/L	3.8	5.8
<sup>137</sup> Cs, GBq/L	257	378
<sup>144</sup> Ce, GBq/L		<2
<sup>154</sup> Eu, GBq/L	1.8	2.8
<sup>155</sup> Eu, GBq/L	8.9	13.1
AP stream		
HNO <sub>3</sub> , <u>M</u>	0.07	0.25
HNO <sub>2</sub> , <u>M</u>	<0.002	0.0017
U, g/L	64	59
Pu, g/L	18	18
<sup>95</sup> Zr, MBq/L	10.2	38.4
<sup>95</sup> Nb, MBq/L	1.42	1.44
<sup>106</sup> Ru, MBq/L	0.73	<1
<sup>125</sup> Sb, MBq/L	<0.1	<0.4
<sup>137</sup> Cs, MBq/L	<0.03	<0.1
<sup>144</sup> Ce, MBq/L		<0.6
<sup>154</sup> Eu, MBq/L	<0.02	<0.06
<sup>155</sup> Eu, MBq/L	<0.2	<0.4

Table A-2. Campaign 5 first-cycle tests – strip bank conditions and results

	Run number	
	5-1	5-3
Dates	6/24/81	8/5/81
Bank temp., °C	25-28	28-30
Number of strip stages	16 <sup>a</sup>	16
BX stream flow rate, L/h	1.130	0.887
Flow ratios:		
AP/BX	1.343	1.567
BIX/BX	0.113	
<u>Inlet stream compositions:</u>		
BX stream:		
HNO <sub>3</sub> , <u>M</u>	0.009	0.1
HAN, <u>M</u>	0.0095	
BIX stream:		
HNO <sub>3</sub>	3.1	
AP stream		
% TBP	30±0.5	30±0.5
HNO <sub>3</sub> , <u>M</u>	0.07	0.25
HNO <sub>2</sub> , <u>M</u>	<0.002	0.0017
U, g/L	64	59
Pu, g/L	18	18
<sup>95</sup> Zr, MBq/L	10.2	38.4
<sup>95</sup> Nb, MBq/L	1.42	1.4
<sup>106</sup> Ru, MBq/L	0.73	<1
<sup>125</sup> Sb, MBq/L	<0.1	<0.4
<sup>137</sup> Cs, MBq/L	<0.03	<0.1
<sup>144</sup> Ce, MBq/L		<0.6
<sup>154</sup> Eu, MBq/L	<0.02	<0.06
<sup>155</sup> Eu, MBq/L	<0.2	<0.4



Table A-2. Continued

	Run number	
	5-1	5-3
<u>Outlet stream compositions:</u>		
BP stream		
HNO <sub>3</sub> , <u>M</u>	0.54	0.73
U, g/L	41	58
Pu, g/L	21	27
<sup>95</sup> Zr, MBq/L	13.4	63.2
<sup>95</sup> Nb, MBq/L	2.1	3.1
<sup>106</sup> Ru, MBq/L	<0.4	<2
<sup>125</sup> Sb, MBq/L	<0.1	<0.6
<sup>137</sup> Cs, MBq/L	0.44	1.47
<sup>144</sup> Ce, MBq/L	<0.2	<1.1
<sup>154</sup> Eu, MBq/L	<0.03	<0.2
<sup>155</sup> Eu, MBq/L	<0.2	<0.6
BU stream		
HNO <sub>3</sub> , <u>M</u>	0.006	
HNO <sub>2</sub> , <u>M</u>		0.0021
U, g/L	29	25
Pu, mg/L	0.88	0.5
<sup>95</sup> Zr, MBq/L	0.43	0.194
<sup>95</sup> Nb, MBq/L	0.18	0.154
<sup>106</sup> Ru, MBq/L	<0.6	0.26
<sup>125</sup> Sb, MBq/L	<0.03	<0.03
<sup>137</sup> Cs, MBq/L	<0.01	<0.007
<sup>144</sup> Ce, MBq/L		<0.08
<sup>154</sup> Eu, MBq/L	<0.02	<0.02
<sup>155</sup> Eu, MBq/L	<0.05	<0.06

<sup>a</sup> Consisted of four low-acid strip stages and twelve high-acid strip stages.

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