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# Solvent Extraction Studies of Coprocessing Flowsheets — Results from Campaign 6 of the Solvent Extraction Test Facility (SETF)

D. E. Benker J. E. Bigelow F. R. Chattin E. D. Collins L. J. King R. G. Ross H. C. Savage R. G. Stacy



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#### Consolidated Fuel Reprocessing Program

SOLVENT EXTRACTION STUDIES OF COPROCESSING FLOWSHEETS, RESULTS FROM CAMPAIGN 6 OF THE SOLVENT EXTRACTION TEST FACILITY (SETF) D. E. Benker

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SOLVENT EXTRACTION STUDIES OF COPROCESSING FLOWSHEETS -RESULTS FROM CAMPAIGN 6 OF THE SOLVENT EXTRACTION TEST FACILITY (SETF)

D. E. Benker, J. E. Bigelow, E. D. Collins, F. R. Chattin, L. J. King, H. C. Savage, R. G. Ross, R. G. Stacy

#### ABSTRACT

A series of five solvent extraction tests were made in the Solvent Extraction Test Facility (SETF) during Campaign 6. Each test used a coprocessing flowsheet that included coextractioncoscrubbing of the heavy metals followed by partial partitioning of the uranium and plutonium into separate uranium and uraniumplutonium products. The separation of the uranium and plutonium was aided by the addition of  $HNO_2$  to the organic backscrub stream. Two of these tests compared the performance of the traditional Purex solvent, tri-n-butyl phosphate (TBP), with a potential replacement, tri-2-ethylhexyl phosphate (TEHP). The remaining three tests were made with a chemically-degraded TBP solvent to compare the effectiveness of two solvent cleanup methods — treatment with silica gel or scrubbing with sodium carbonate and water.

#### 1. INTRODUCTION

The Solvent Extraction Test Facility is located within one of the heavily shielded hot cells of the Transuranium Processing Plant at the Oak Ridge National Laboratory.<sup>1</sup> In the SETF, flowsheets for the reprocessing of irradiated nuclear reactor fuels are evaluated in mixer-settler contactors that have a processing capability of ~1 kg/d of heavy metals. The results from these tests provide information on uranium and plutonium recoveries, fission product removal, and the general operability of the system.

The broad objectives of studying coprocessing flowsheets, which was begun in the previous work,  $^{1-3}$  was continued in Campaign 6. For each of the tests, the solvent extraction flowsheet included coextraction and coscrubbing of the heavy metals (uranium and plutonium) in the first contactor, followed by back-extraction of the plutonium with part of the uranium (partial partitioning) in the second contactor. An organic scrub was used in the partition bank to control the amount of uranium that was recovered with the plutonium and to add excess nitrous acid (HNO<sub>2</sub>) to improve the uranium-plutonium separation by reducing some of the plutonium to Pu(III).

The five tests that were made in Campaign 6 were similar except for the type of organic extractant that was used. The first two tests were made to compare the performance of an alternative extractant, tri-2ethylhexyl phosphate (TEHP), with that of the standard Purex extractant, tri-<u>n</u>-butyl phosphate (TBP). The other three tests were made using a TBP-based solvent that had been chemically degraded to simulate a recycled solvent. These latter tests compared the performance of two solvent cleanup methods, (1) treatment with base-treated silica gel or (2) conventional scrubbing with sodium carbonate and water.

Although the program emphasis was on the reprocessing of fast breeder reactor (FBR) fuel, no such fuel was readily available when Campaign 6 was made in the fall of 1981. Approximately 10 kg of light water reactor (LWR) fuel from the H. B. Robinson Reactor was used for these tests which had been irradiated to a burnup of ~31 MWd/kg and discharged from the reactor in May 1974.

#### 2. EQUIPMENT AND OPERATIONAL PROCEDURES

The SETF equipment items and most of the operational procedures used during Campaign 6 for fuel dissolution, feed clarification and adjustment; and solvent extraction were similar to those described for previous campaigns, 1-3 except as noted below.

### 2.1 FUEL DISSOLUTION AND ADDITION OF <sup>95</sup>Zr TRACER

The basic procedure for dissolving LWR fuels has remained unchanged since the first dissolution in Campaign 1 and includes: (1) adding the sheared fuel pieces to 3 M nitric acid ( $HNO_3$ ), (2) heating to 50°C, (3) adding 11 M HNO3 at a controlled rate, and (4) heating and digesting 2 h at 90°C. The objective of this multi-step procedure was to maintain a slow, controlled dissolution rate. The final solution concentrations were typically 3 M HNO3 and 350 g/L of heavy metals. Since short-cooled fuel was not available for Campaign 6, a small amount of <sup>95</sup>Zr tracer was added during the dissolution procedure. Although it is unknown whether the tracer is yielding quantitative data on the behavior of fission product zirconium, the tracer was found to be useful in the previous campaign<sup>3</sup> for comparisons of decontamination factor values (DFs) with flowsheet changes. In Campaign 6, the tracer solution was added to the  $3 \text{ M HNO}_3$  solution in the dissolver prior to the dissolution, instead of after the fuel dissolution as was done in the previous campaign. It was hoped that this method of adding the 95Zr tracer would provide a better opportunity for isotopic exchange of zirconium between the tracer and the fuel.

#### 2.2 FEED CLARIFICATION AND ADJUSTMENT

The clarification of the dissolver solution was accomplished in two filtration steps. The first (primary) filtration was made after the fuel dissolution to remove the acid insoluble residues; the second (polishing) filtration was made after the feed adjustment as the feed was in transit to the mixer-settlers in order to remove solids that might have formed during the feed adjustment or by feed aging mechanisms during the period preceding mixer-settler start-up. Both filtrations were made with a deepbed type of filter that contains a bed of diatomaceous-earth filter aid as

the filtering medium. Although this deep-bed filter was used for the primary filtration in Campaign 4 and for the polishing filtration in Campaign 5, this was the first time deep-bed filters have been used for both filtrations.

The feed adjustment was effected by the usual procedure; (1) sparging with  $N_2O_3$  and air at ambient conditions to adjust the plutonium valence, and (2) addition of the appropriate HNO<sub>3</sub> solution to make the final concentrations ~3 <u>M</u> HNO<sub>3</sub> and ~150 g/L of heavy metals. The  $H_2O_2$  addition and digest step that was used in Campaigns 2 through 5 was omitted because it appeared to have had a detrimental effect on the ruthenium DFs in the strip contactor.

#### 3. DESCRIPTION OF THE SOLVENT EXTRACTION FLOWSHEETS

A diagram of the basic flowsheet used during Campaign 6 is shown in Fig. 1; the operating conditions and detailed stream analyses for each test are tabulated in the Appendix.

In each test, the first contactor was used to coextract the uranium and plutonium from the aqueous feed and coscrub the pregnant solvent with HNO<sub>3</sub> to remove impurities. Because the use of two aqueous scrub streams had provided better zirconium removal during the previous campaign, it was included in Campaign 6. Also, the number of low-acid scrub stages was increased from three to six, with a corresponding decrease in extraction stages from 10 to 7, in order to determine whether the additional stages would provide additional zirconium removal.

The second contactor was used to partially partition the uranium and plutonium. The two products desired from this type of flowsheet were, (1) a uranium stream (HBU) that was relatively free of plutonium, and (2) a mixed uranium-plutonium stream (HBP) that was enriched in plutonium. The amount of uranium that was stripped with the plutonium in the HBP was controlled in part by the organic backscrub stream (HBS). This stream was also used to add HNO<sub>2</sub>. At the H<sup>+</sup> concentrations used in these runs, HNO<sub>2</sub>

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### **FLOWSHEET FOR CAMPAIGN 6**

Fig. 1. Solvent extraction flowsheet used in Campaign 6.

reduces Pu(IV) to Pu(III) which improves the efficiency of plutonium stripping and improves uranium-plutonium separation.

In a reprocessing plant the third contactor would be used to strip the uranium into an aqueous product stream. In these tests, the third contactor was used as a backup strip contactor for plutonium; uranium stripping was not studied. This mode was used to allow more freedom in testing partitioning flowsheets while ensuring that the waste solvent would meet disposal limits for plutonium. In addition, hydroxylamine nitrate (HAN) was added to the aqueous strip solution to reduce plutonium to Pu(III) and ensure complete stripping of plutonium from the solvent. The relatively high concentration (1.5 M) of HAN acted as an inextractable nitrate salt that helped lessen the amount of uranium that would be stripped along with the plutonium. This simplified the subsequent recovery of plutonium from this stream.

The primary difference among the five runs was in the organic extractant that was used for each test. The first two runs (6-1 and 6-2) compared an alternative extractant, tri-2-ethyhexyl phosphate (TEHP), with the more common Purex extractant, tri-n-butyl phosphate (TBP). Laboratory and glove box studies with TEHP4,5 had proceeded to the point that further testing with irradiated fuel was desirable. Some of the possible advantages of TEHP over TBP, which had been indicated by the laboratory studies, include: (1) lower aqueous solubility, (2) higher extraction coefficients for heavy metals, (3) greater chemical stability, and, when processing thorium, (4) no third phase formation at high metal loadings. The typical extractant concentration for fuel reprocessing is 1.1 M (30 vol %) TBP; however, because the phase separation characteristics of TEHP are poor at this concentration, the extractant concentration was lowered to 0.6 M for these comparison runs; 0.6 M corresponds to 28 and 16.5 vol % for TEHP and TBP, respectively. The diluent for these extractants was normal paraffin hydrocarbon.

The first two runs were further subdivided into two parts, "A" and "B", in order to determine the effect on the partitioning of adding different amounts of  $HNO_2$ . In the "A" runs (6-1A and 6-2A), ~2 mol of  $HNO_2$  per mol of plutonium was added to the partitioning contactor, and in the

"B" runs (6-1B and 6-2B) five times as much, ~10 mol of  $HNO_2$  per mol of plutonium, was added. The  $HNO_2$  was added with the HBS stream, which contained ~0.008 <u>M</u>  $HNO_2$  in the "A" runs and ~0.04 <u>M</u>  $HNO_2$  in the "B" runs.

The other three runs were made using 30 vol % TBP (the diluent was again normal paraffin hydrocarbon) that had been chemically degraded (described below) in order to simulate a recycled solvent. Two solvent cleanup methods were evaluated — (1) scrubbing with sodium carbonate and water and (2) treatment with base-treated silica gel. Sodium carbonate scrubbing is the traditional method for solvent treatment in a reprocessing plant; the silica gel method is a relatively new method developed by Tallent et al.<sup>6</sup> for possible application in fuel reprocessing. The chemical degradation step was necessary because the SETF has no means for recycling solvent or of using alpha-contaminated solvents; all previous runs have been made with new solvent that was used once and then discarded.

The degraded solvent was prepared by refluxing a small batch of 30% TBP in 8  $\underline{M}$  HNO<sub>3</sub> while sparging with NO<sub>2</sub>, and then diluting this concentrate with new 30% TBP to make a final solution that was ~0.003  $\underline{M}$  dibutyl phosphate (DBP) and ~0.8% diluent degradation products.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS OF SOLVENT EXTRACTION TESTS

4.1 RESULTS USING TRI-2-ETHYLHEXYL PHOSPHATE

The initial use of TEHP in the SETF equipment caused problems that required some minor operational changes. During the solvent cleanup step (sodium carbonate and water scrubs), a slower agitator speed was needed to prevent the water scrubs from forming a stable emulsion. More batch contacts were used to compensate for the less vigorous mixing. Also, in order to achieve proper hydraulic operation in the SETF mixer-settlers, minor adjustments of the agitator positions were required to improve the pumping action from the mixers. On the other hand, the TEHP run did seem qualitatively to have less interfacial crud than did the later run with TBP (6-2).

#### 4.1.1 Coextraction-Coscrub

The overall results from these runs indicated similar results for both solvents, except for uranium losses and zirconium DFs (Table 1). For the run with TEHP solvent (6-1), uranium was not detected in the aqueous raf-finate (HAW); the results shown are the limits of detection for the given samples. Because the uranium loss is so much lower than the plutonium loss in Run 6-1, it may be the result of sampling or analysis problems rather than from using TEHP. Concentration profiles for uranium, pluto-nium, and free H<sup>+</sup> are shown in Fig. 2.

The concentration profile for the  ${}^{95}$ Zr tracer is shown in Fig. 3. The higher  ${}^{95}$ Zr DF in the TBP run was not only the result of less  ${}^{95}$ Zr extracting but also of better  ${}^{95}$ Zr removal in the scrub section. The  ${}^{95}$ Zr concentration in Run 6-2 was 2.6 x 10<sup>7</sup> Bq/L in the solvent at stage 10 (aqueous feed inlet) and dropped by a factor of ~1000 across the scrub section. In the run with TEHP, the feed stage had twice as much  ${}^{95}$ Zr, 6.4 x 10<sup>7</sup> Bq/L, and the concentration only dropped by a factor of 200 across the scrub section. No significant difference was noted in the behavior of  ${}^{106}$ Ru,  ${}^{137}$ Cs,  ${}^{144}$ Ce, or  ${}^{154}$ Eu for either solvent.

The 95Zr DFs measured for Run 6-2 (2 x 10<sup>4</sup>) is significantly higher than the DF measured in Run 5-1 (750) during Campaign 5 and may be the result of using additional low-acid scrub stages for Campaign 6 (six instead of three). Other differences that might have also influenced the 95Zr behavior include: the fuel (Campaign 5 used EBR-II fuel), the addition of the tracer at a different point in the dissolution, and the lower TBP concentration (although Run 6-3, which used 30% TBP and is discussed below in section 4.2.1, had the same DF as Run 6-2).

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Fig. 2. Concentration profiles for the coextraction-coscrub contactor for the runs with TEHP and TBP.

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	Run	No.
	6-1 (TEHP)	6-2 (TBP)
Extraction losses, %		<u></u>
Uranium	<0.001	0.040
Plutonium	0.031	0.038
ission product DFs		
<sup>95</sup> Zr	1E3	<b>2E4</b>
<sup>95</sup> NЪ	7E3	5E3
106 <sub>Ru</sub>	<9E3	<4E3
<sup>137</sup> Cs	>2E7	>2E7
<sup>144</sup> Ce	~2E4	~1 E 4
154 <sub>Eu</sub>	>3E5	>2E5

Table 1. Uranium and plutonium losses and fission product decontamination results in coextraction-coscrubbing for the runs with TEHP and TBP.

#### 4.1.2 Partitioning

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Although a slightly larger flow rate for the aqueous strip was used in the runs with TEHP in order to compensate for its higher extraction coefficients, the losses of plutonium into the uranium product (HBU) were still excessive, 1 to 2% of the total plutonium (Table 2). On the other hand, slightly less uranium was stripped into the plutonium product (HBP). The net result was poorer U-Pu separation with TEHP; the overall U-Pu separation factors (Table 2) were lower by a factor of ~10.

Increasing the  $HNO_2/Pu$  mol ratio from ~2 (Runs 6-1A and 6-2A) to a mol ratio of ~10 (Runs 6-1B and 6-2B) decreased the plutonium losses to the uranium product by a factor of about 2; but, at the same time, increased the amount of uranium stripped to the plutonium product by factors of 1.2 and 1.4.

Concentration profiles for uranium, plutonium, nitric acid, and nitrous acid are shown in Fig. 4.



Fig. 4. Concentration profiles for the partition contactor for the runs with TEHP and TBP.

		Ru	n No.	
	6-1Aa	6-1B <sup>b</sup>	6-2A <sup>C</sup>	6-2B <sup>d</sup>
Feed solution (HAF)			·······	
Pu, g/g of U	~0.008	~0.008	~0.008	~0.008
Phase ratio (O/A) <sup>e</sup>				
Scrub	1.9	1.9	2.1	2.1
Strip	6.8	6.9	7.2	7.2
% of Pu in				
U-Pu product (HBP)	97.4	98.5	99.72	99.88
U product (HBU)	2.6	1.5	0.28	0.12
Uranium product (HBU)				
Pu, µg/g of U	238	154	26	12
Pu DF	34	52	310	670
U-Pu product (HBP)				
Pu, g/g of U	0.081	0.074	0.071	0.049
U DF	10	9.2	8.9	6.1
U-Pu separation factor <sup>f</sup>	340	480	2700	4100

Table 2. Results from partial partitioning contactor for comparison runs using TEHP and TBP solvents.

aSolvent was 0.6 <u>M</u> (28%) TEHP with a  $HNO_2/Pu$  mol ratio of ~2. bSolvent was 0.6 <u>M</u> (28%) TEHP with a  $HNO_2/Pu$  mol ratio of ~10. <sup>c</sup>Solvent was 0.6 <u>M</u> (16.5%) TBP with a  $HNO_2/Pu$  mol ratio of ~2. dSolvent was 0.6 <u>M</u> (16.5%) TBP with a  $HNO_2/Pu$  mol ratio of ~10. e(organic flow rate)/(aqueous flow rate) fProduct of the U and Pu DFs.

4.2 RESULTS USING DEGRADED SOLVENT

#### 4.2.1 Coextraction-Coscrub

The flowsheet conditions were initially set to achieve a higher solvent loading than was used in previous SETF runs in an attempt to improve the efficiency of the coextraction-coscrub contactor. Unfortunately, the conditions were set too close to the maximum loading, and minor uncertainties in the feed composition and minor variations in the flow rates allowed the solvent loading to reach about 115 g/L (90% saturation) at stages 10 and 12 for Runs 6-3 and 6-4, respectively. This led to unacceptable losses of heavy metals to the aqueous raffinate (the very low uranium number in Table 3 for Run 6-3 is probably caused by an analysis or sampling problem). The flowsheet conditions were corrected in Run 6-5. The peak solvent loading was lowered to about 70% of saturation, and the loss of heavy metals was reduced to about 0.04%, which is similar to previous SETF runs. As a result, there were significant variations in the solvent loading during these runs, as shown in Fig. 5.

The DFs for  $^{137}$ Cs,  $^{144}$ Ce, and  $^{154}$ Eu were similar for each solvent and are apparently unaffected by the presence of solvent degradation products or by the type of cleanup method used. However, the DFs for  $^{95}$ Zr,  $^{95}$ Nb, and  $^{106}$ Ru were noticeably worse (by factors of about 1000, 100, and 10, respectively) when using the unpurified degraded solvent (Run 6-5). The two treatment methods (sodium carbonate or silica gel) yielded similar DFs for  $^{95}$ Nb and  $^{106}$ Ru, which were also similar to the DFs measured for new solvent. However, the  $^{95}$ Zr DF was a factor of 10 lower for the solvent that was treated with silica gel. After reviewing the purification procedure, it was determined that the poorer DF was probably the result of inadequate water scrubbing of the silica gel product, which would leave some DBP in the solvent. If better water scrubbing had been used for the silica gel treatment, it might have yielded  $^{95}$ Zr results similar to the sodium carbonate treatment. Concentration profiles for  $^{95}$ Zr,  $^{95}$ Nb, and  $^{106}$ Ru are shown in Figs. 6 through 8.



Fig. 5. Concentration profiles for the coextraction-coscrub contactor for the runs with chemically degraded solvent.





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10<sup>10</sup> RUN 6-3 RUN 6-4 **-**10<sup>9</sup> **RUN 6-5**  $^{106}$ Ru ORGANIC PHASE CONCENTRATION (Bq/L) 10<sup>8</sup> 10' 10<sup>6</sup> 105 LOW H<sup>+</sup> EXTRACTION HIGH





ORNL DWG 86-15342

Table 3. Uranium and plutonium losses and fission product decontamination results in coextraction-coscrub contactor for runs with degraded solvent and previous runs with new solvent.

	_		Run No	•
	New solvent <sup>a</sup>	6-3 <sup>b</sup>	6-4°	6-5d
Extraction losses, %				
Uranium	~0.01	<8E-4	4.6	0.03
Plutonium	~0.01	0.3	4.2	0.04
Fission product DFs				
<sup>95</sup> Zr	-	2E4	2E3	4
<sup>95</sup> NЪ	-	7E3	3E3	50
106 <sub>Ru</sub>	1E3-1E4	<2E3	1E4	5E2
<sup>137</sup> Cs	1E6-1E7	1E7	3E7	>1E6
<sup>144</sup> Ce	1E4-1E5	~2E5	~2E4	~4E3
154 <sub>Eu</sub>	1E4-1E5	>3E4	>5E5	>9E4

<sup>a</sup>Used new solvent that was purified with sodium carbonate and water scrubs. <sup>b</sup>Used degraded solvent that was purified with sodium carbonate and water scrubs.

<sup>C</sup>Used degraded solvent that was purified by base-treated silica gel. <sup>d</sup>Used degraded solvent without purification.

#### 4.2.2 Partitioning

Concentration profiles for the partitioning bank are shown in Fig. 9. The plutonium losses to the uranium product during the runs with degraded solvent were larger than those measured during a previous run with new solvent (Table 4). Using degraded solvent without purification yielded the largest loss,  $\sim 7\%$ . When the degraded solvent was purified by one of the treatment methods (sodium carbonate or silica gel), the plutonium loss was  $\sim 0.5\%$ , which is only slightly poorer than the 0.1% that was measured for the run with new solvent.

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Fig. 9. Concentration profiles for the partition contactor for the runs with new solvent and chemically degraded solvent.

Although the plutonium content in the degraded solvent was larger, the plutonium was not irreversibly lost. It was successfully stripped in the backup strip contactor  $(0.2 \text{ M} \text{ HNO}_3 \text{ and } 1.5 \text{ M} \text{ hydroxylamine nitrate aqueous strip})$ . The plutonium content of the final waste solvent from this contactor was <1 mg/L, which is similar to the plutonium concentrations achieved when using new solvent.

		Run No.				
	3-2C <sup>a</sup>	6-3b	6-4c	6-5d		
Phase ratio (0/A) <sup>e</sup>			<u> </u>			
Scrub section	1.1	0.99	0.93	0.99		
Strip section	4.0	3.5	2.8	3.0		
% of Pu in						
U-Pu product (HBP)	99.9	99.6	99.5	93.1		
U product (HBU)	0.1	0.4	0.5	6.9		
% of U in						
U-Pu product (HBP)	10.6	10.8	16.9	10.7		
U product (HBU)	89.4	89.2	83.1	89.2		
Uranium product						
Pu, µg/g of U	9	37	55	589		
U-Pu product						
Pu, g/g of U	0.082	0.070	0.051	0.066		

Table 4. Results from partial partitioning contactor for comparison runs using degraded and new solvents.

<sup>a</sup>Used new solvent purified with sodium carbonate and water scrubs. <sup>b</sup>Used degraded solvent purified with sodium carbonate and water scrubs. <sup>C</sup>Used degraded solvent purified by base-treated silica gel. <sup>d</sup>Used degraded solvent without purification.

e(Organic flow rate)/aqueous flow rate).

#### 4.3 TECHNETIUM DISTRIBUTION

The distribution of technetium was measured in the outlet streams for Run 6-2 (Table 5). This had not been done before because technetium is not detectable in routine gamma-scans and special analytical techniques are required to measure it. In the coextraction-coscrub bank, about 86% of the technetium was measured in the aqueous waste which corresponds to a technetium DF of  $\sim$ 7 for the coextraction-coscrub bank. In the partitioning contactor, no significant separation of technetium and uranium was noted.

## Table 5. Distribution of technetium and uranium in outlet streams for Run 6-2.

	Tc	U
	(%)	(%)
Coextraction-coscrub bank	· · · · · · · · · · · · · · · · · · ·	<del> </del>
Aqueous waste (HAW)	86	0.04
U-Pu product (HAP)	14	99.96
artial partitioning bank		
U-Pu product (HBP)	19	12
Uranium product (HBU)	81	88

#### 5. SUMMARY AND CONCLUSIONS

The most significant results and conclusions from SETF Campaign 6 are as follows:

The extractant TEHP was tested and compared with the traditional TBP extractant for fuel reprocessing. Its use yielded no major advantages compared with TBP. The raffinate losses and fission product removals were similar; and although TEHP did initially cause some hydraulic problems, they were corrected by minor changes in equipment and operational procedures. The only significant disadvantage was the poorer U-Pu separation with TEHP, which was primarily the result of poorer plutonium stripping. Using a different plutonium reductant or different flowsheet conditions might mitigate this difference with TBP.

Several tests were made to compare the solvent extraction behavior of (1) new solvent, (2) chemically degraded solvent (0.003 <u>M</u> DBP and 0.8% diluent degradation products), and (3) chemically degraded solvent that had been purified by either sodium carbonate or base-treated silica gel. When the degraded solvent was left unpurified, it yielded poorer DFs for 95Zr, 95Nb, and 106Ru, in addition to much higher plutonium retention in the solvent from the partitioning bank (7% plutonium loss versus 0.1% for new solvent). Treating the solvent with either of the above purification methods, restored the fission product DFs to values similar to those obtained with new solvent, but still left a small amount of plutonium in the solvent from the partitioning contactor (0.5%). Little difference was noted between the runs that used sodium carbonate or silica gel treated solvent, except for the 95Zr DF; the lower 95Zr DF for the silica-treated solvent may have resulted from inadequate water scrubbing following the treatment.

#### 6. ACKNOWLEDGMENTS

The experimental work done in the SETF was performed by the Chemical Technology Division staff of the Transuranium Processing Plant. The preparation of the degraded solvent and the purification by silica gel was performed by O. K. Tallent and J. C. Mailen of the Chemical Technology Division. The extensive analytical work was carried out by Analytical Chemistry Division personnel, primarily under the supervision of J. H. Cooper and J. M. Peele. Engineering and maintenance services were provided by personnel from the ORNL Engineering Division, the Instrumentation and Controls Division, and Plant and Equipment Division, under the supervision of S. O. Lewis, A. A. Shourbaji, E. M. Shuford, and B. R. Scarborough.

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#### 7. REFERENCES

- E. D. Collins, D. E. Benker, J. E. Bigelow, F. R. Chattin, M. H. Lloyd, L. J. King, R. G. Ross, H. C. Savage, <u>Solvent Extraction</u> <u>Studies of Coprocessing Flowsheets - Results from Campaigns 1 and 2 of</u> <u>the Solvent Extraction Test Facility (SETF)</u>, ORNL/TM-7080, Oak Ridge National Laboratory, July 1982.
- 2. E. D. Collins, D. E. Benker, J. E. Bigelow, F. R. Chattin, L. J. King, R. G. Ross, H. C. Savage, <u>Solvent Extraction Studies of Coprocessing</u> <u>Flowsheets - Results from Campaigns 3 and 4 of the Solvent Extraction</u> <u>Test Facility (SETF)</u>, ORNL/TM-7991, Oak Ridge National Laboratory, May 1982.
- 3. W. D. Bond, D. E. Benker, J. E. Bigelow, F. R. Chattin, E. D. Collins, L. J. King, R. G. Ross, H. C. Savage, <u>Solvent Extraction Studies of</u> <u>Coprocessing Flowsheets - Results from Campaign 5 of the Solvent</u> <u>Extraction Test Facility (SETF)</u>, ORNL/TM-8598, Oak Ridge National Laboratory, November 1983.
- W. D. Arnold and D. J. Crouse, <u>Evaluation of Alternate Extractants to</u> <u>Tributyl Phosphate - Phase I</u>, ORNL/TM-7536, Oak Ridge National Laboratory, April 1981.
- 5. B. A. Hannaford and G. D. Davis, <u>Plutonium Flowsheet Development in</u> <u>Miniature Mixer-Settlers. Part II: Coextraction-Costripping</u> <u>Experiments with Fast Breeder Reactor Fuel Composition</u>, ORNL/TM-8856, Oak Ridge National Laboratory, August 1984.
- O. K. Tallent, J. C. Mailen, K. D. Pannell, <u>Solvent Cleanup Using</u> <u>Base-Treated Silica Gel Solid Adsorbent</u>, ORNL/TM-8948, Oak Ridge National Laboratory, June 1984.

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### APPENDIX A

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			Run No.		
	6-1	6-2	6-3	6-4	6-5
Dates	10/19-21/81	10/29-31/81	11/9-10/81	11/17-18/81	12/7-8/81
Bank temperature, °C	51	51	51	52	51
Number of stages final scrub/intermediate					
scrub/extraction	6/3/7	6/3/7	6/3/7	6/3/7	6/3/7
HAX stream flow rate, L/h	1.50	1.56	1.52	1.45	1.54
Flow ratios					
HAS/HAX	0.118	0.118	0.121	0.126	0.118
HAIS/HAX	0.0609	0.060	0.060	0.064	0.064
HAF/HAX	0.259	0.230	0.564	0.591	0.525
Inlet stream compositions					
HAS Stream, HNO <sub>3</sub> , mol	/L 0.51	0.49	0.48	0.48	0.52
HAIS Stream, HNO <sub>3</sub> , mol	/L 3.0	3.0	3.0	3.0	3.0
HAX Stream					
% TBP		16.5 <u>+</u> 0.5	30 <u>+</u> 0.5	30 <u>+</u> 0.5	30 <u>+</u> 0.5
% ТЕНР	28 <u>+</u> 0.5				
HAF Stream					
$HNO_3, mol/L$	3.08	3.04	2.84	2.88	2.76
U, g/L	149	153	163	158	144
Pu, g/L	1.31	1.18	1.17	1.31	1.21
$^{241}$ Am, mg/L	49	48	56	52	53
<sup>244</sup> Cm, mg/L	2.77	2.53	2.59	2.68	2.44
<sup>95</sup> Zr, GBq/L	1.48	2.18	1.32	0.895	0.87
<sup>95</sup> Nb, GBg/L	1.34	1.05	1.57	1.23	0.90
$106_{Ru}$ , GBg/L	<13	<10	<5	7.14	7.7
<sup>125</sup> Sb, GBq/L		<6	<3	3.8	<6
<sup>137</sup> Cs, GBq/L	411	375	389	403	348
<sup>144</sup> Ce, GBq/L	<6	<6	<3	<4	<6
154Eu, GBq/L	15.2	13.0	12.4	14.8	13

# Table A.1. Campaign 6 first cycle tests — extraction/scrub bank conditions and results

-			Run No.		
	6-1	6-2	6-3	6-4	6-5
utlet stream composit	ions		<del>7 <b></b></del>		
HAW stream					
HNO <sub>3</sub> , mol/L	2.5	2.35	2.6	2.7	2.8
U, mg/L	<1	31	<1	4990	30
Pu, $mg/L$	0.23	0.24	2.25	39	0.35
241Am, $mg/L$	35	34	44	49	44
<sup>2</sup> <sup>-+</sup> Cm, mg/L	0.919	1.6	1.9	2.1	2.1
<sup>95</sup> Zr, GBq/L		0.57	0.74	1.14	0.418
106Ru, GBq/L 125cl GBq/L	0.703 <4	0.55 <4	0.97 5.95	1.25	0.698
137Cs, GBq/L	240	224	3.67	296	281
<sup>154</sup> Eu, GBq/L	<2 8•4	7.52	10.2	11.8	10.8
HAP stream					
HNO3, mol/L	0.01	0.01	0.02	0.03	0.05
HNO2, mol/L	0.00045	0.00078	0.0019	0.0030	0.0028
U, g/L	37.5	31.4	86.9	80.3	73.5
Pu, g/L	0.327	0.262	0.63	0.69	0.60
<sup>95</sup> Zr, MBg/L	0.294	0.020	0.035	0.251	109
<sup>95</sup> Nb, MBq/L	0.048	0.050	0.12	0.211	9.47
<sup>106</sup> Ru, MBq/L	0.358	0.729	1.56	0.387	7.0
<sup>125</sup> Sb, MBq/L	<0.02	<0.02	<0.03	<0.03	<0.5
<sup>137</sup> Cs, MBq/L	<0.005	<0.005	0.016	0.0076	<0.1
<sup>144</sup> Ce, MBq/L	<0.06	<0.1	<0.1	<0.09	<0.6
<sup>154</sup> Eu, MBq/L	<0.01	<0.02	<0.02	<0.02	<0.07

Table A-1 (continued)

				Run	No.		
	6-1A	6-1B	6-2A	6-2B	6-3	6-4	6-5
Dates	10/19-20/81	10/20-21/81	10/29-30/81	10/30-31/81	11/9-10/81	11/17-18/81	12/7-8/81
Bank temperature, °C	25	25	32	32	25-26	25	25
Number of stages							
Strip/scrub	13/3	13/3	13/3	13/3	13/3	13/3	13/3
BX stream flow rate, L/h	0.307	0.303	0.304	0.304	0.616	0.760	0.752
Flow ratios							
HAP/HBX	4.89	4.95	5.12	5.12	2.47	1.91	2.04
HBS/HBX	1.93	1.95	2.07	2.07	0.989	0.933	0.989
Inlet stream compositions	6						
HBX stream, HNO <sub>3</sub> , mol/	'L 0.10	0.10	0.10	0.10	0.10	0.10	0.10
HBS stream	·						
% TBP			16.5+0.5	16.5+0.5	30+0.5	30+0.5	30+0.5
% TEHP	28+0.5	28+0.5	-		—	—	-
$HNO_3$ , $mo1/L$	<0.01	<0.01	<0.01	<0.01	0.02	0.01	0.02
$HNO_2$ , $mo1/L$	0.0085	0.043	0.0085	0.040	0.083	0.089	0.099
HAP Stream							
% TBP			16.5+0.5	16.5+0.5	30+0.5	30+0.5	30+0.5
% TEHP	28+0.5	28+0.5				<b>—</b> .	_
HNO <sub>3</sub> , mol/L	0.01	-	0.01		0.02	0.03	0.05
$HNO_2$ , $mo1/L$	0.00045		0.00078		0.0019	0.0030	0.0028
U, g/L	37.5		31.4		86.9	80.3	73.5
Pu, g/L	0.327		0.262		0.63	0.69	0.60
<sup>95</sup> Zr, MBq/L	0.294		0.020		0.035	0.251	109
<sup>95</sup> Nb, MBq/L	0.048		0.050		0.12	0.211	9.47
106Ru, MBq/L	0.358		0.729		1.56	0.387	7.0
125Sb, MBq/L	<0.02		<0.02		<0.03	<0.03	<0.5
137Cs, MBq/L	<0.005		<0.005		0.016	0.0076	<0.1
<sup>144</sup> Ce, MBq/L	<0.06		<0.1		<0.1	<0.09	<0.6
<sup>154</sup> Eu, MBq/L	<0.01		<0.02		<0.02	<0.02	<0.07

Table A-2. Campaign 6 first-cycle tests — strip bank conditions and results

		Run No.						
	.`	6-1A	6-1B	6-2A	6-2B	6-3	6-4	6-5
		,						
Outlet	stream composition							
HBP	Stream							
	HNO <sub>3</sub> , mol/L	0.18	0.16	0.14	0.20	0.19	0.26	0.20
	U, g/L	19.0	21.3	19.4	29.4	23.3	26.4	17.4
	Pu, g/L	1.54	1.58	1.38	1.44	1.64	1.34	1.14
	% Pu(IV)					42	47	44
	<sup>95</sup> Zr, MBq/L	1.84	1.56	0.0674	0.047	0.0365	0.398	188
	95Nb, MBg/L	0.373	0.334	0.0399	0.0442	0.0581	0.128	5.8
	$106_{Ru}$ , MBg/L	<0.1	<0.1	<0.06	<0.06	<0.05	<0.08	<0.9
	<sup>125</sup> Sb, MBg/L	<0.04	<0.05	<0.02	<0.02	<0.02	<0.02	<0.5
	<sup>137</sup> Cs, MBq/L	0.039	0.060	0.0208	0.0101	0.0156	0.070	0.28
	<sup>144</sup> Ce, MBg/L	<0.1	<0.1	<0.1	<0.25	<0.1	<0.1	<0.5
	<sup>154</sup> Eu, MBq/L	<0.02	<0.02	<0.01	<0.02	<0.01	<0.02	<0.08
HBU	stream							
	HNO <sub>3</sub> , mol/L	<0.01	<0.01			0.01	0.02	0.03
	HNO <sub>2</sub> , mol/L	0.0020	0.0083	0.0024	0.0080	0.018	0.024	0.024
	U, g/L	25.6	21.8	20.2	20.5	55.2	45.8	47
	Pu, mg/L	6.1	3.4	0.53	0.24	2.1	2.5	27.8
	<sup>95</sup> Zr, MBq/L	0.039	0.020	0.0164	0.0092	0.022	0.0507	20.9
	<sup>95</sup> Nb, MBq/L	0.012	0.012	0.0237	0.0284	0.0774	0.158	5.06
	<sup>106</sup> Ru, MBq/L	0.320	<0.24	0.536	0.554	1.42	0.266	5.2
	<sup>125</sup> Sb, MBq/L	<0.02	<0.02	<0.02	0.02	<0.03	<0.02	<0.2
	$^{137}$ Cs, MBq/L	<0.006	<0.003	<0.004	0.0037	<0.006	0.0059	<0.04
	<sup>144</sup> Ce, MBq/L	<0.04	<0.03	<0.04	<0.03	<0.06	<0.05	<0.2
	<sup>154</sup> Eu, MBq/L	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.02

Table A-2 (continued)

 $\mathbf{31}$ 

			Run No.		
	6-1A	6-2A	6-3	6-4	6-5
Dates	10/19-20/81	10/29-30/81	11/9-10/81	11/17-18/81	12/7-8/81
Bank temperature, °C	40	31-32	41-42	41	41
Number of stages	16	16	16	16	16
HCX stream flow rate, L/h	0.195	0.762	0.205	0.203	0.203
Flow ratios					
HBU/CX	10.7	2.87	10.4	10.6	.11.2
Inlet stream compositions					
HCX Stream					
HNO <sub>2</sub> , mol/L	0.17	0.10	0.2	0.21	0.22
HAN, mol/L	1.7		1.6	1.5	1.5
HBU Stream					
% TBP		16.5+0.5	30+0.5	30+0.5	30+0.5
% ТЕНР	28+0.5	. —	-	-	
$HNO_3$ , $mo1/L$	<0.01		0.01	0.02	0.03
$HNO_2$ , $mo1/L$	0.0020	0.002	0.018	0.024	0.024
U, g/L	25.6	20.2	55.2	46	47
Pu, mg/L	6.1	0.53	2.1	2.5	27.8
<sup>95</sup> Zr, MBq/L	0.039	0.016	0.022	0.051	20.9
<sup>95</sup> Nb, MBq/L	0.012	0.024	0.0774	0.158	5.1
<sup>106</sup> Ru, MBq/L	0.320	0.54	1.42	0.266	5.2
125Sb, MBq/L	<0.02	<0.02	<0.03	<0.02	<0.2
<sup>137</sup> Cs, MBq/L	<0.006	<0.004	<0.006	0.0059	<0.04
<sup>144</sup> Ce, MBq/L	<0.04	<0.04	<0.06	<0.05	<0.2
<sup>154</sup> Eu, MBq/L	<0.01	<0.01	<0.02	<0.01	<0.02

# Table A-3. Campaign 6 first cycle tests — Pu scavenging bank conditions and results

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		Run No.					
	6-1A	6-2A	6-3	6-4	6-5		
utlet Stream Composi	tions	<u>*********</u> ***************************					
HCP Stream							
$HNO_3, mol/L$		0.08		0.15	0.14		
U, g/L	5.8	43		9.9	11		
Pu, mg/L	36	1.6		34.7	404		
<sup>95</sup> Zr, MBq/L				0.317	97		
<sup>95</sup> Nb, MBg/L		4		0.298	6.3		
<sup>106</sup> Ru, MBq/L				0.25	0.73		
<sup>125</sup> Sb, MBq/L				<0.03	<0.4		
137Cs, MBq/L				0.13	<0.2		
<sup>144</sup> Ce, MBq/L		•		<0.04	<0.4		
<sup>154</sup> Eu, MBq/L				<0.02	<0.05		
HCW Stream							
U.g/L		4.41		47.5	46.5		
Pu, mg/L		0.14		0.21	0.43		
<sup>95</sup> Zr, MBg/L				0.033	15.7		
<sup>95</sup> Nb, MBg/L				0.082	4.46		
106 <sub>Ru</sub> , MBa/L				0.28	4.88		
125Sb, MBa/L				<0.02	<0.2		
<sup>137</sup> Cs, MBa/L				<0.006	<0.04		
<sup>144</sup> Ce, MBa/L				<0.05	<0.2		
154Eu MBg/L				<0.02	<0.02		

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