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MARTIN MARIETTA

Solvent Extraction Studies with Low-Burnup Fast Flux Test Facility Fuel in the Solvent Extraction Test Facility

D. E. Benker
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CONSOLIDATED FUEL REPROCESSING PROGRAM C F R P ORNL

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Chemical Technology Division

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CONTENTS

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ABSTRACT

A batch of irradiated Fast Flux Test Facility (FFTF) fuel was processed for the first time in the Solvent Extraction Test Facility (SETF) at the Oak Ridge National Laboratory (ORNL) during Campaign 7. The average burnup of the fuel was only 0.2 atom %, but the cooling time was short enough (~2 years) so that ^{95}Zr was detected in the feed. This short cooling permitted our first measurement of ^{95}Zr decontamination factors (DFs) without having to use tracers. No operational problems were noted in the operation of the extraction-scrubbing contactor, and low uranium and plutonium losses (<0.01%) were measured. Fission product DFs were improved noticeably by increasing the number of scrub stages from six to eight. Two flowsheet options for making pure uranium and plutonium products (total partitioning) were tested. Each flowsheet used hydroxylamine nitrate for reducing plutonium. Good products were obtained (uranium DFs of $>10^3$ and plutonium DFs of $>10^4$), but each flowsheet was troubled with plutonium reoxidation. Adding hydrazine and lowering the plutonium concentration lessened the problem but did not eliminate it. About 370 g of plutonium was recovered from these tests, purified by anion exchange, converted to PuO_2, and transferred to the fuel refabrication program.

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1. INTRODUCTION

The Solvent Extraction Test Facility is located in one of the heavily shielded hot cells of the Transuranium Processing Plant at the Oak Ridge National Laboratory.[1] This facility uses mixer-settler contactors to evaluate solvent extraction flowsheets for the reprocessing of irradiated nuclear reactor fuels. Results from these tests provide information on heavy metal recoveries, fission product behavior, comparisons of flowsheet options, and general operability of the system.

Previous work in Campaigns 1-5[1,2,3] and Campaign 6 had centered on the study of coprocessing flowsheets for both light-water reactor (LWR) and

fast breeder reactor (FBR) fuels. However, recent plans for future reprocessing plants, such as the Breeder Reprocessing Engineering Test (BRET) facility, require separate uranium and plutonium products; as a result, emphasis has been changed to flowsheets that completely partition the uranium and plutonium recovered from FBR fuels. In the current work, Campaign 7, a small batch of irradiated fuel from the Fast Flux Test Facility (FFTF) was used as feed for two solvent extraction tests that were made to determine the general solvent extraction behavior of the FFTF fuel and to further investigate two total partitioning methods. The fuel, which is from fuel assembly DEA-1, had been irradiated to an average burnup of 0.22 atom % or 0.18 TJ/kg (~2100 MWd/MT) and discharged from the reactor in January 1981. Although the burnup is quite low, the fuel was operated at full power for about 1 d and reached its peak operating temperature. Work with this fuel will provide a baseline for future tests with fuels of higher burnups. The fuel pin identification numbers are listed in the Appendix.

As in Campaign 5, the recovered plutonium from each solvent extraction test was purified using one cycle of anion exchange, and then converted to PuO_2 by precipitation and calcination of plutonium oxalate. A total of ~370 g of plutonium was shipped to the Hanford Engineering Development Laboratory (HEDL) for use in fuel fabrication studies.

2. EQUIPMENT AND OPERATIONAL PROCEDURES

Most of the equipment items and operational procedures used during Campaign 7 for feed clarification, solvent extraction, plutonium purification, and conversion to oxide were similar to those used before and described for previous campaigns.[1,2,3] However, some notable changes made in the fuel dissolution and feed adjustment procedures are explained below.

2.1 FUEL DISSOLUTION

In previous campaigns, irradiated LWR fuels had been successfully dissolved by: (1) adding a batch of ~3 M nitric acid to the chopped fuel

in the dissolver, (2) heating to ~50°C while metering in additional nitric acid to maintain the dissolver acidity near ~3 M, and (3) heating to 90°C and digesting ~2 h. The major objective of this procedure was to maintain a slow, controlled dissolution that did not create a sudden burst of activity to the vessel off-gas system. When a procedure similar to this was tried in Campaign 5 to dissolve mixed-oxide fuel (~20% Pu), a substantial portion of the heavy metals did not dissolve, and ~13% to 19% was recovered in a secondary dissolution.

In Campaign 7, the dissolution procedure was modified to use more concentrated nitric acid, a higher digestion temperature, and a longer digestion period in order to effect more complete dissolution. This procedure called for: (1) a single batch addition of 7.2 M nitric acid, and then (2) heating to 95°C for a 4-h digest. The volume of 7.2 M nitric acid was sized to make a final dissolver solution that would have ~300 g/L of heavy metals and ~3.5 M in nitric acid. After the dissolver solution was transferred and flushed from the tank, a hull leach was made with a much larger volume of 7 M nitric acid.

The results with this procedure were much improved, with 99.8% to 99.2% of the heavy metals that were recovered being contained in the primary dissolver solution and only 0.2% to 0.8% in the hull leach. Because the hull leach also includes some solution from the tank heel, the amount of fuel that was actually dissolved in this leach was less than the amount measured in the solution.

2.2 CLARIFICATION AND FEED ADJUSTMENT

The dissolver solutions were clarified by filtration through a deep bed of diatomaceous earth. This technique was first used in Campaign 4 (see ref. 2), and continues to be the most efficient procedure that has been tested at the SETF.

The adjustment of the plutonium valence to Pu(IV) in the clarified solutions usually has been done by sparging with N_2O_3 gas at ambient temperature (~35°C). After Run 7-1, N_2O_3 was no longer available and sparging with NO gas at ~60°C was substituted in the later runs (7-2 and 7-3). After the valence adjustment, the solution was adjusted to the desired heavy-metal concentration and acidity by addition of the appropriate nitric

acid solution. The addition of H_2O_2, which has been used in previous campaigns to help dissolve insoluble colloids, was omitted because of indications from previous runs that it may reduce the ruthenium DF for the plutonium product from the partition bank.

The adjusted solution was given a polishing filtration by passing it through a deep-bed filter of diatomaceous earth as it was metered to the mixer-settlers. This polishing filtration with a deep-bed filter was first used in Campaign 5; it is intended to remove any solids that might have passed through the primary filtration or that might have formed during the feed adjustment and waiting period before the mixer-settler run.

3. DESCRIPTION OF THE SOLVENT EXTRACTION FLOWSHEETS

Two first-cycle flowsheet options for the BRET facility were investigated (Figs. 1 and 2). Operating conditions and detailed stream analyses for each test are tabulated in the Appendix.

In each case, the first contactor was used to coextract the uranium and plutonium from the hot aqueous feed (HAF) into an organic solvent and then scrub the pregnant solvent with nitric acid to remove impurities. The organic solvent (HAX) was tri-n-butyl phosphate (TBP) at a concentration of 30 vol % in normal paraffin hydrocarbon (NPH) diluent. The use of two aqueous scrub solutions (HAS and HAIS) is now standard in all the SETF runs and is considered to be a desirable technique. The low-acid scrub not only increases the removal of zirconium but also reduces the amount of nitric acid that leaves the contactor in the organic product (HAP).

The extraction-scrub bank conditions for Run 7-1 were similar to those used previously in Run 5-1 (see ref. 3) that processed some mixed-oxide fuel from the EBR-II and GETR; these conditions were repeated for comparison. The only significant changes in the second run (7-2) were in the number of scrub/extraction stages and the concentrations of the scrub solutions (HAS and HAIS). From previous runs we know that all 10 extraction stages are not usually needed for good recovery of the heavy metals, so the number of scrub/extraction stages was changed from 6/10 to 8/8 in order to improve the removal of fission products. The nitric acid concentrations of the scrub streams were changed to better match flowsheets that were being proposed for BRET at the time.

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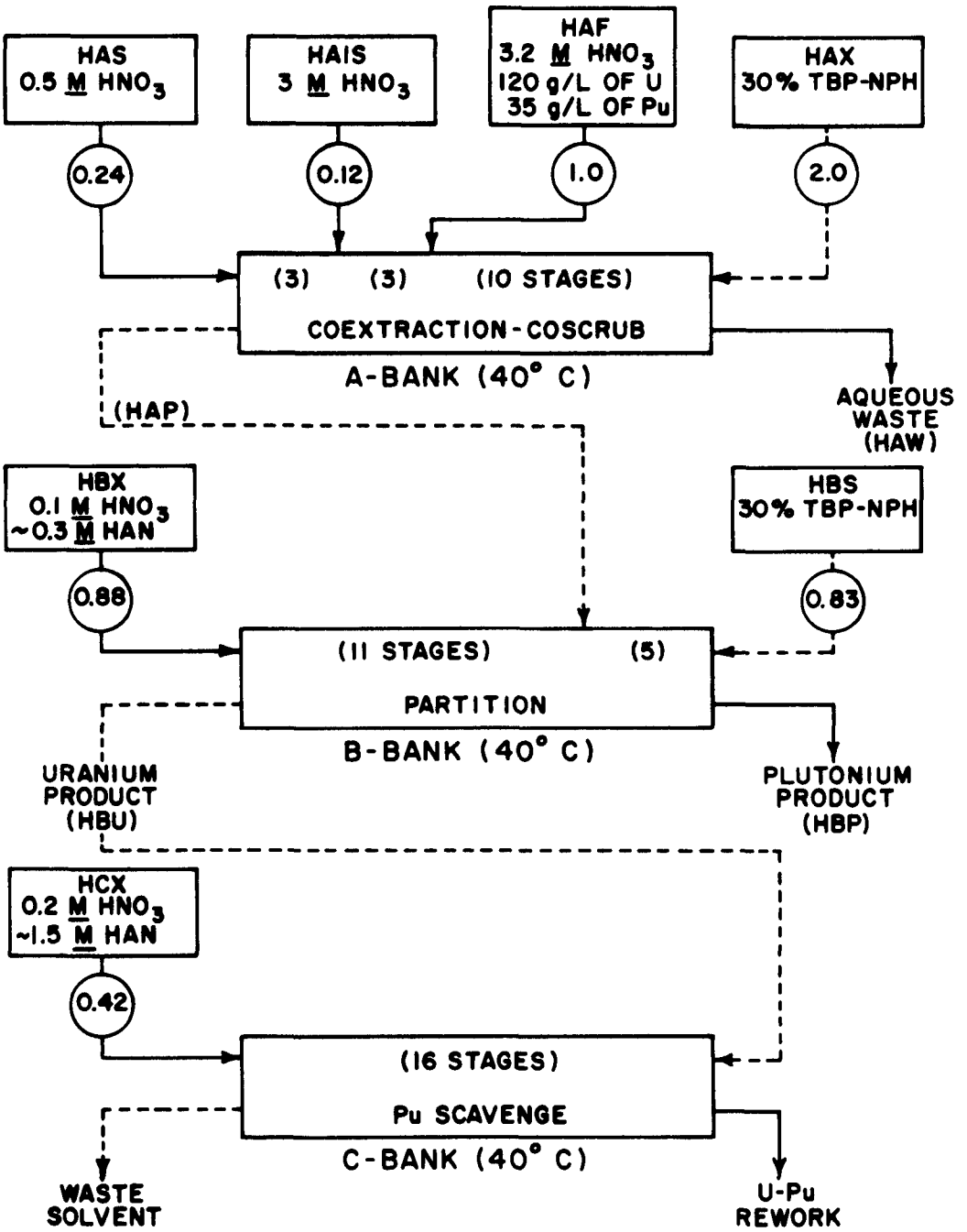

Fig. 1. FFTF solvent extraction flowsheet used for Tests 7-1, 7-3A, and 7-3B (flow ratios and stream concentrations shown are for Test 7-1) using the organic back-scrub method for partitioning.

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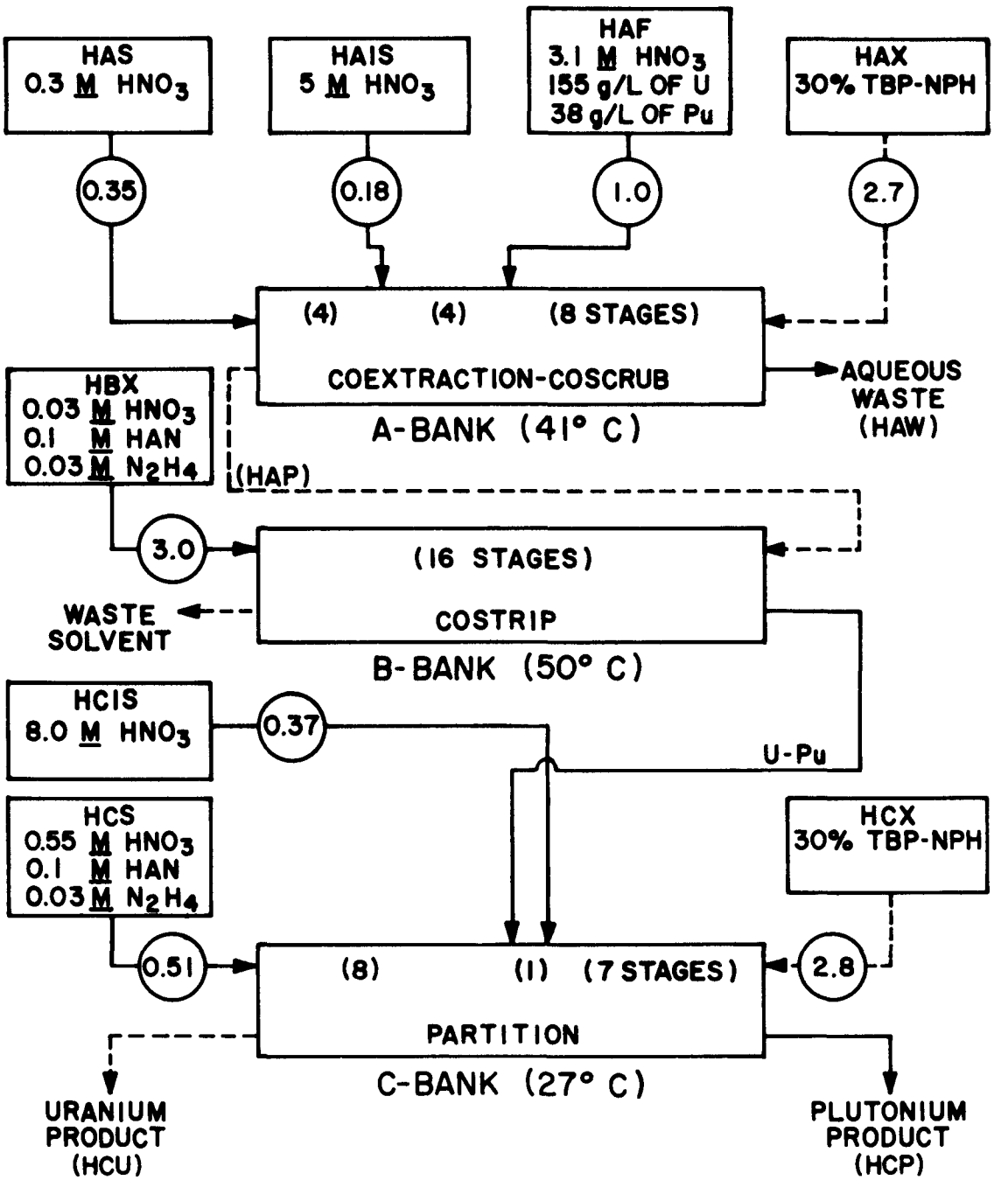

Fig 2. FFTF solvent extraction flowsheet used for Test 7-2 using the selective uranium extraction method for partitioning.

The organic products from the coextraction-coscrub bank (HAP) were processed to partition the uranium and plutonium into separate product streams. In each test, the separation was accomplished by reducing plutonium to the poorly extractable Pu(III) state; however, the arrangement of the system was different for each test.

In the first method, which is similar to the conventional Purex process, partitioning was accomplished in B-bank. The plutonium was stripped from the solvent using a dilute nitric acid stream containing hydroxylamine nitrate (HAN) to reduce the plutonium. The plutonium product stream (HBP) was scrubbed with TBP-NPH solvent to back-extract any uranium that stripped with the plutonium. One advantage of this flowsheet is that it is relatively simple to operate and can generate a plutonium product that is more concentrated than the organic feed stream.

In the second method, the heavy metals were first costripped from the solvent with dilute nitric acid in B-bank, which was operated at 50°C to take advantage of the lower uranium distribution coefficients. The aqueous strip contained HAN to reduce the plutonium and hydrazine to serve as a Pu(III) holding agent. The aqueous product from B-bank (HBP) was then routed to C-bank where the uranium was selectively extracted into a fresh TBP-NPH stream, leaving the reduced plutonium in the aqueous effluent (HCP). An aqueous stream (HCIS) containing strong nitric acid was added to acidify the aqueous in the extraction section to ~1 M to improve the efficiency of the uranium extraction. Also, the organic solvent that contained the uranium was scrubbed with nitric acid which had additional HAN and hydrazine to remove any reoxidized plutonium from the solvent. This second method is similar to flowsheets evaluated for the Hot Experimental Facility (HEF). Although this method appears to use an additional contactor (costrip, partition, and uranium strip compared to partition and uranium strip for the previous method), the partition contactor in this case does provide some additional uranium purification from fission products. This flowsheet, however, does not provide any concentration of the plutonium product.

In a reprocessing plant, the organic uranium products from each flowsheet (HBU and HCU) would, of course, be sent to a strip bank to recover the uranium from the solvent in a stream of dilute nitric acid. In these tests, uranium stripping was not studied; the uranium was instead discarded with the solvents.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS OF SOLVENT EXTRACTION TESTS

During the operation of the mixer-settlers, no significant problems were noted with respect to phase separations, gassing, or formation of solids. This was expected because of the low burnup of the fuel. However, the cooling time was short enough so that ^{95}Zr could still be detected in the feed (Table 1), which permitted our first measurements of zirconium DFs without having to use tracers.

Table 1. Comparison of fission product concentrations of the FFTF dissolver solutions with FBR and LWR dissolver solutions previously processed in the SETF

Radionuclide	Radionuclide activity, GBq/kg (U+Pu)		
	LWR	FBR[a]	FFTF
^{95}Zr		110[b]	2
^{95}Nb		36[b]	3
^{106}Ru	580	<44	180
^{125}Sb	81	38	18
^{137}Cs	3000	2600	160
^{144}Ce	590	<22	480
^{154}Eu	120	20	0.7

[a]EBR-II and GETR fuel from Campaign 5.
[b]^{95}Zr-Nb tracer was added to the dissolver product solution.

4.1 RESULTS FROM THE COEXTRACTION-COSCRUBBING CONTACTOR

Losses of uranium and plutonium to the aqueous waste (HAW) were quite low for both runs and comparable to previous runs with FBR fuel (Table 2). The run conditions for the extraction-scrub bank were conservatively chosen to ensure that there would be excess extraction stages. The HAP products contained 75 and 67 g/L of heavy metals (or 58% and 52% of saturation for 30 v/o TBP) for Runs 7-1 and 7-2, respectively. The peak saturation in the contactor was estimated by SEPHIS[4] calculations to be ~65% and 60% in the low-acid scrub section because the low-acid scrub causes some reflux of the heavy metals.

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

	Run No.			
	EBR-II		FFTF	
	5-1	5-3	7-1	7-2
Extraction losses				
Uranium	0.23%	0.001%	0.002%	0.003%
Plutonium	0.004%	0.019%	0.011%	0.012%
Fission product DFs				
^{95}Zr	7.5E2[a,b]	1.8E2[a]	9E1	7E2
^{95}Nb	2E3[a]	2E3[a]	2E2	4E3
^{106}Ru			6E2	3E3
^{125}Sb	>3E4	>9E3	>9E3	>2E4
^{137}Cs	5E5	3E5	>4E5	>7E5
^{144}Ce			>1E5	>2E5
^{154}Eu	>7E4	>1E4		

[a] ^{95}Zr-Nb tracer was added to the dissolver solution product.

[b] To be read as 7.5×10^2.

For both runs, the DFs for rare earths (cerium) and cesium were satisfactorily high (Table 2). However, the zirconium and niobium DFs in Run 7-1 were poorer than those measured in Run 5-1, which had a similar flowsheet configuration, and in Run 5-3, which did not have a low-acid scrub section. These lower DFs may represent differences in the chemical form of the ^{95}Zr and ^{95}Nb compared to that supplied as tracer in Runs 5-1 and 5-3. In the second run (7-2), the zirconium, niobium, and also the ruthenium DFs improved, which may have been the result of using two additional scrub stages (i.e., eight stages instead of six as used in 7-1). Concentration profiles of H^+, ^{95}Zr and ^{106}Ru are shown in Figs. 3 and 4.

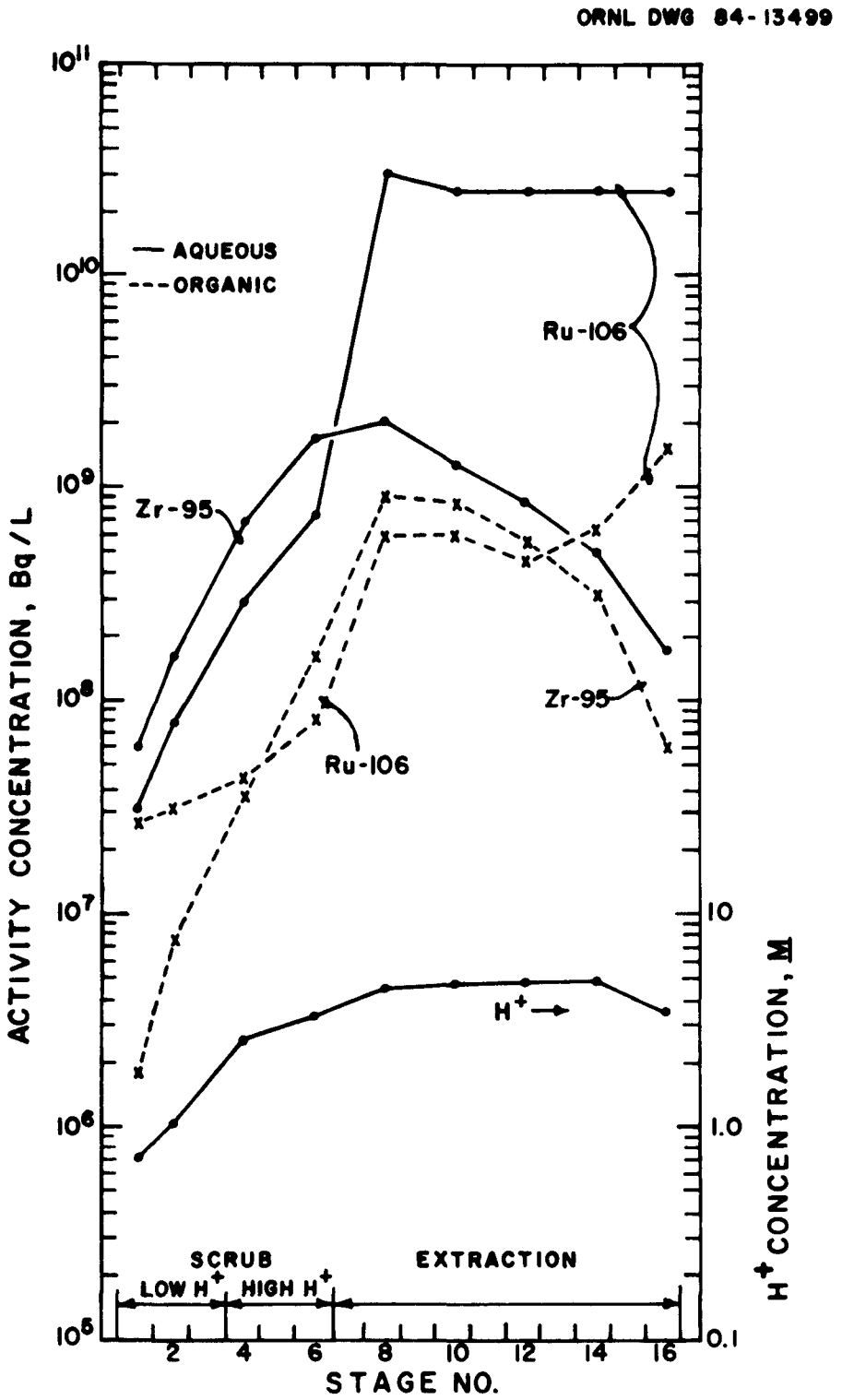

Fig 3. Concentration profiles of ^{95}Zr, ^{106}Ru, and H^+ in the extraction-scrubbing contactor for Test 7-1.

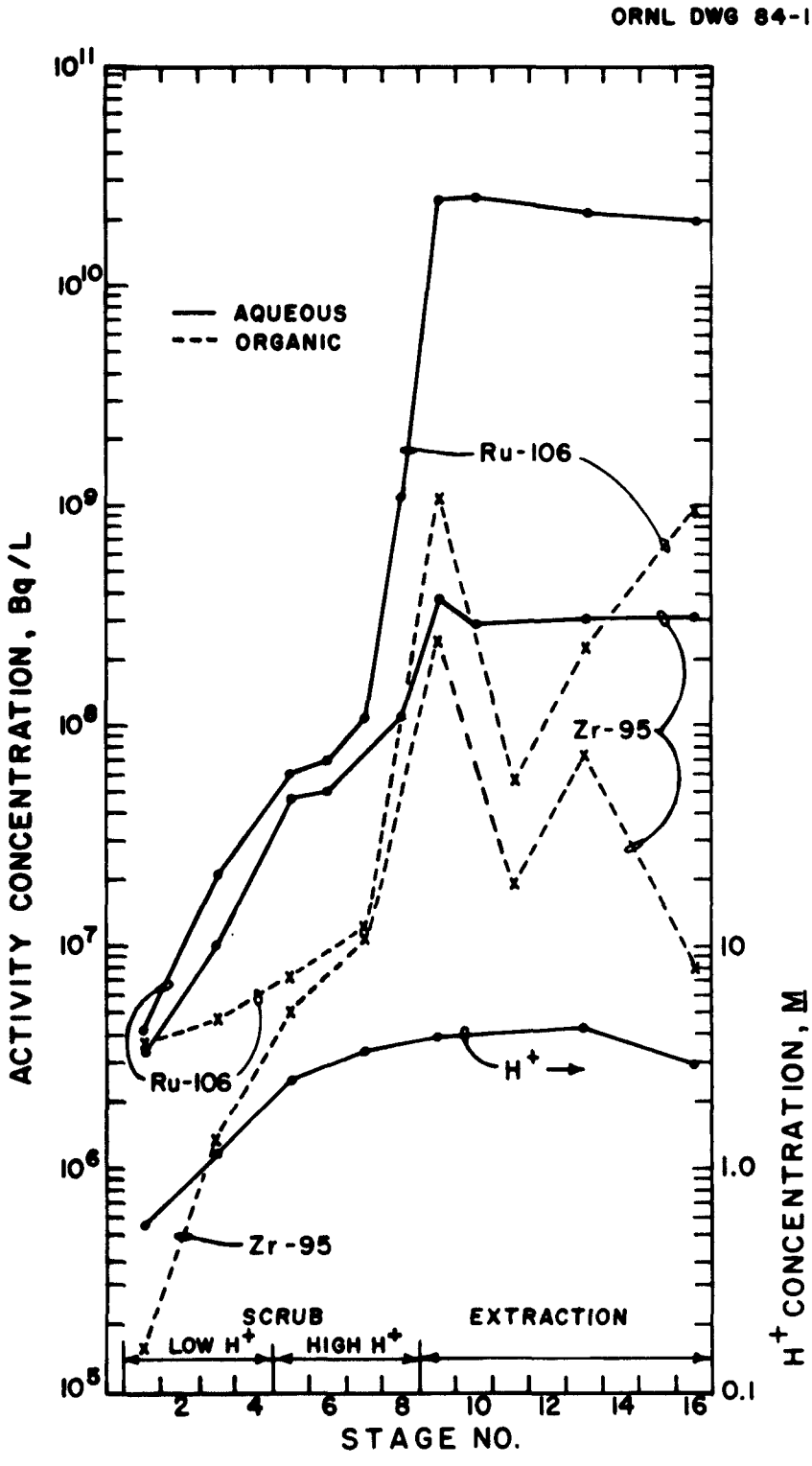

Fig 4. Concentration profiles of ^{95}Zr, ^{106}Ru, and H^+ in the extraction-scrubbing contactor for Test 7-2.

4.2 Partitioning Results

4.2.1 Organic Back-Scrub

Run 7-1 was made to test total partitioning of FFTF fuel with the organic back-scrub flowsheet using HAN (without hydrazine) as the plutonium reductant. In this test, a HAN/Pu mol ratio of only ~2 was used, which was a little more than the ratio (~1.5) proposed for BRET when this test was made. Unfortunately, the plutonium was not adequately reduced and a significant amount of plutonium was left in the uranium stream (HBU). However, the overall plutonium loss to the waste solvent was very low because the plutonium was stripped in the backup strip contactor (C-bank) in which a much higher HAN/Pu mol ratio was used.

To investigate this flowsheet further, a synthetic feed was prepared using the plutonium product solution from Run 7-2 (discussed below). Depleted uranium was added to the solution to make the plutonium ~20% of the heavy metals, and the solution was then concentrated by evaporation. A rerun (labeled Run 7-3A) of this flowsheet with the synthetic feed solution and a HAN/Pu ratio of ~2 verified the unsatisfactory plutonium stripping behavior. The run was interrupted and the heavy metals were purged from the partition contactor. The run was restarted (labeled Run 7-3B) with these changes: the HAN concentration in the HBX was increased from 0.3 to 0.5 M, and the HBX flow rate was increased by ~15%. These increases led to a doubling of the HAN addition rate (HAN/Pu = ~4), and the remaining feed was processed while yielding quite satisfactory products (Table 3). However, whether steady-state operation was achieved in this short run is uncertain; an alpha monitor in the plutonium product stream was still increasing slightly at the end of the run, indicating a slightly increasing plutonium concentration.

Concentration profiles for the partition contactors are shown in Figs. 5 and 6. Also included as dotted lines are estimated concentrations as calculated by the SEPHIS computer code.

Although satisfactory products were obtained, significant reoxidation of plutonium was occurring in the contactor, as shown in the concentration profile (Fig. 5). The SEPHIS code does not include provision for reoxidation.

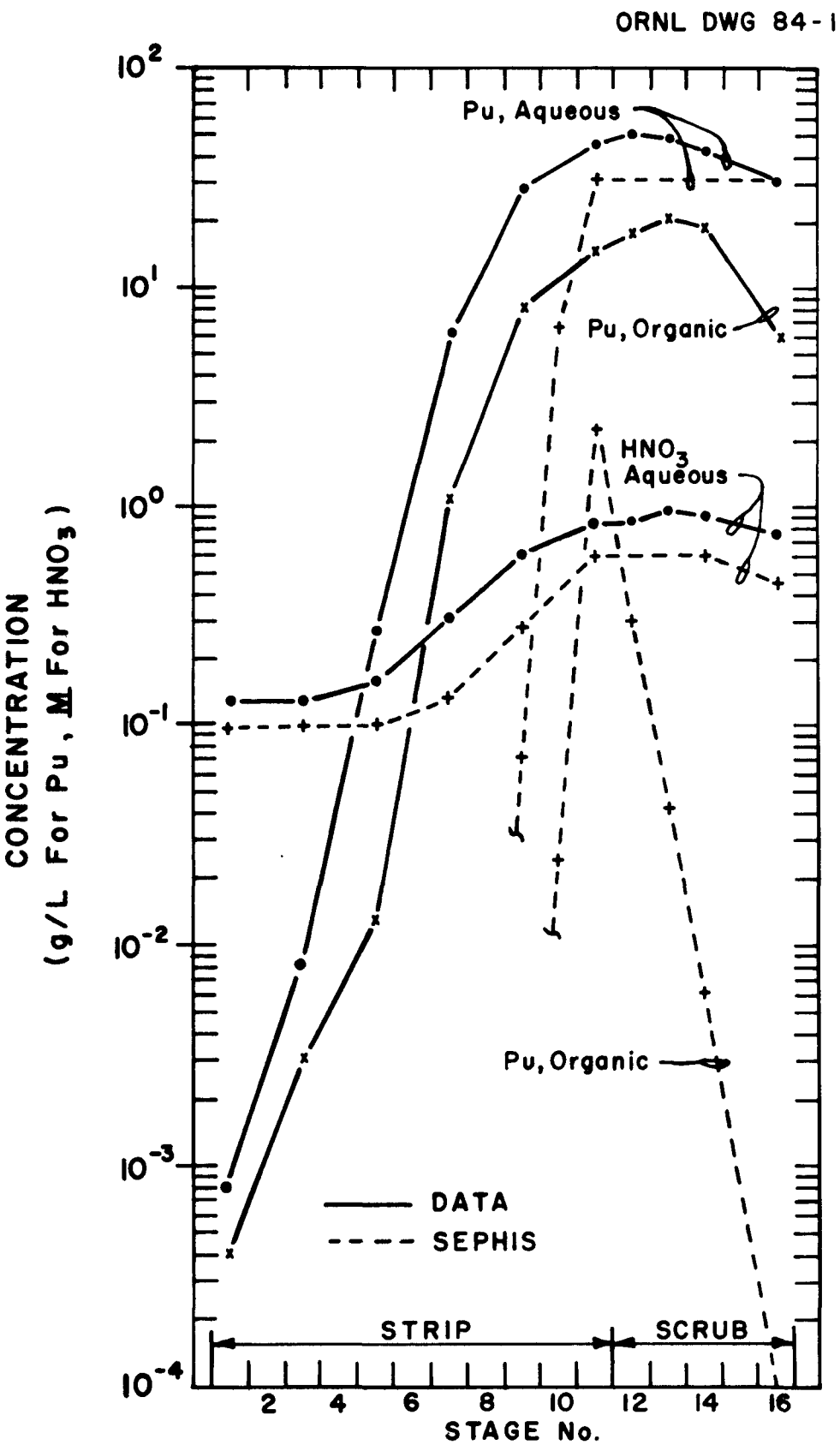

Fig 5. Concentration profiles of plutonium and nitric acid in the partition contactor for Test 7-3B.

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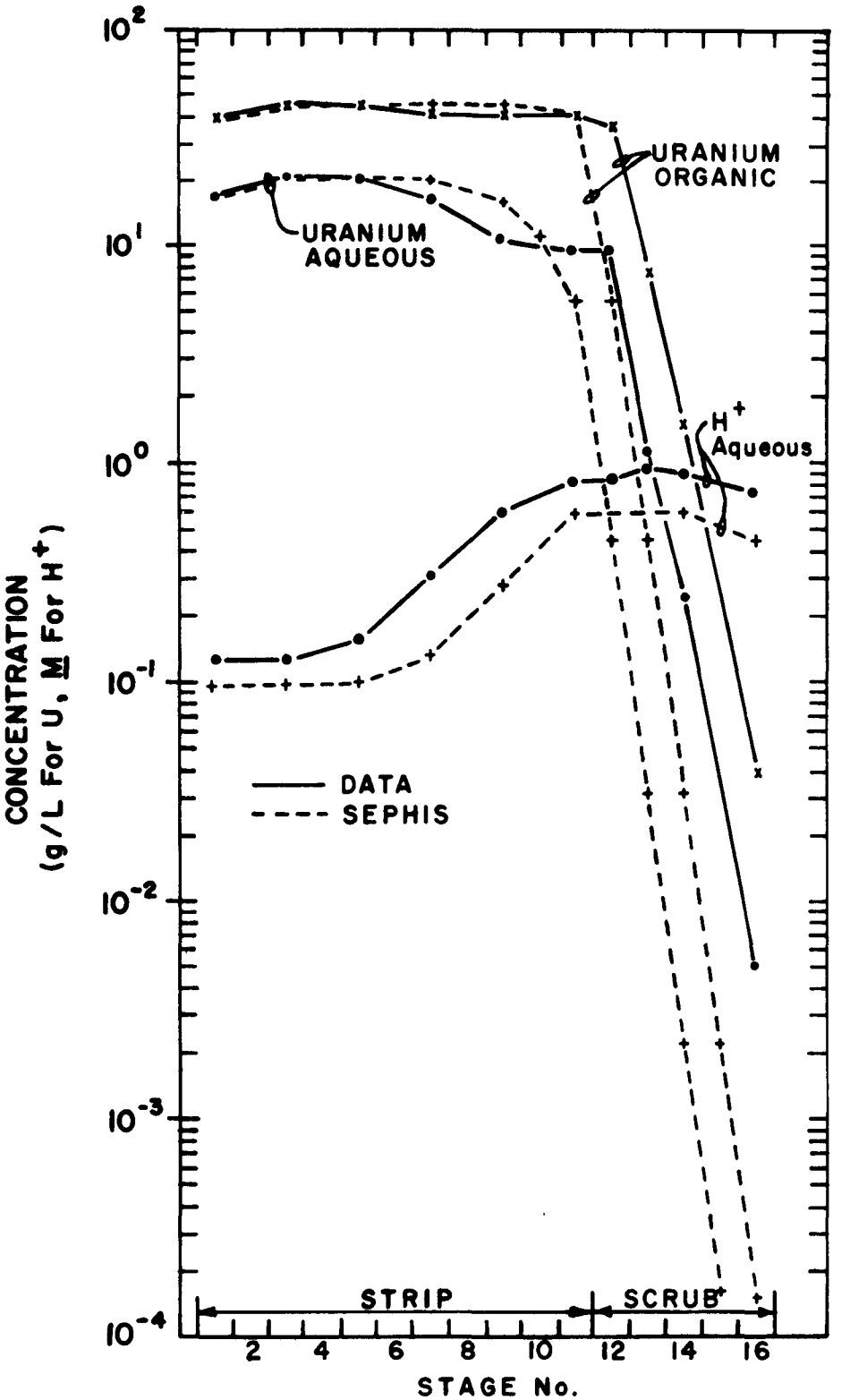

Fig 6. Concentration profiles of uranium and nitric acid in the partition contactor for Test 7-3B.

Table 3. Results of tests with total partitioning

Stream	Run No. 7-2	Run No. 7-3B[a]
Feed solution (HAF)		
Pu, g/g of U	0.249	0.268
Plutonium aqueous product[b]		
Pu, g/L	9.4	30.3
U, μg/g of Pu	650	180
U DF	6.2E3	2.1E4[c]
Uranium organic product[d]		
U, g/L	52	39
Pu, μg/g of U	16	23
Pu DF	1.6E4	1.2E4

[a]Second cycle run using 7-2 Pu product plus depleted uranium.
[b]HCP stream for 7-2 and HBP stream for Run 7-3B.
[c]To be read as 2.1×10^4.
[d]HCU stream for 7-2 and HBU stream for Run 7-3B.

The plutonium concentration in the organic phase and the plutonium extraction coefficients varied from a low of 5.8 g/L and 0.19, respectively, at stage 16, to a high of 21 g/L and 0.45 at stage 13. These relatively high plutonium extraction coefficients in the scrub section imply that a significant amount of Pu(IV) was present. Furthermore, the H^+ balance (Table 4) for the run shows that ~4.8 mol of H^+ were made per mol of plutonium added to the contactor. According to the rate law proposed by Barney,[5] only 2 mol of H^+ should be made per mol of plutonium reduced when there is excess HAN. The HNO_2 content in the organic feed stream (HAP) was only ~0.001 M. Apparently, large amounts of HAN were consumed by something other than reaction with the Pu(IV) and HNO_2 that was originally present in the organic feed. This observation may suggest that some cyclic reactions are in progress. One likely reaction may be the reoxidation of Pu(III) in the solvent.[6]

Table 4. Acid balance and estimated production in partition and costrip contactors

	Run No.			
	7-2 (costrip)	7-2 (partition)	7-2 (combined[a])	7-3B (partition)
Input Pu, mol/h	0.0561	0.0561	0.0561	0.0640
Input (mol ratio)				
$HAN/N_2H_4/Pu$	2/0.6/1	0.3/0.1/1	2.3/0.7/1	4.1/0/1
H^+/Pu	1.83	24.8	26.7	1.64
Output (mol ratio)				
H^+/Pu	4.10	26.4	30.5	6.48
Increase (mol ratio)				
H^+/Pu	2.3	~1.6	~3.9	4.8

[a]Acid balance for the combined costrip and partition bank.

4.2.2 Selective Uranium Extraction

For Run 7-2, no operational problems were noted with the selective uranium partitioning method, and good products were collected (Table 3). Concentration profiles for the costrip contactor are shown in Fig. 7 and for the partition contactor in Figs. 8 and 9.

In the costrip contactor (Fig. 7) the plutonium strips very rapidly from the solvent because of the very low aqueous acidity and the HAN-hydrazine reductant in the strip solution. Only six stages were needed to lower the plutonium concentration in the solvent to <1 mg/L, which is close to the background concentration level. The acid balance (Table 4) indicates that 2.3 mol of H^+ was produced per mol of plutonium strip, which is close to the value predicted by the Barney rate law.

However, the uranium did not strip as quickly, which is not unusual for a costripping flowsheet because a higher free acid concentration than is desired for uranium stripping is needed to prevent plutonium hydrolysis. In this case, however, the uranium stripping was not inhibited as much by the free acid, which was only 0.03 M in the HBX, as by the reductant. The 0.1 M HAN added to the strip solution acts as an inextractable

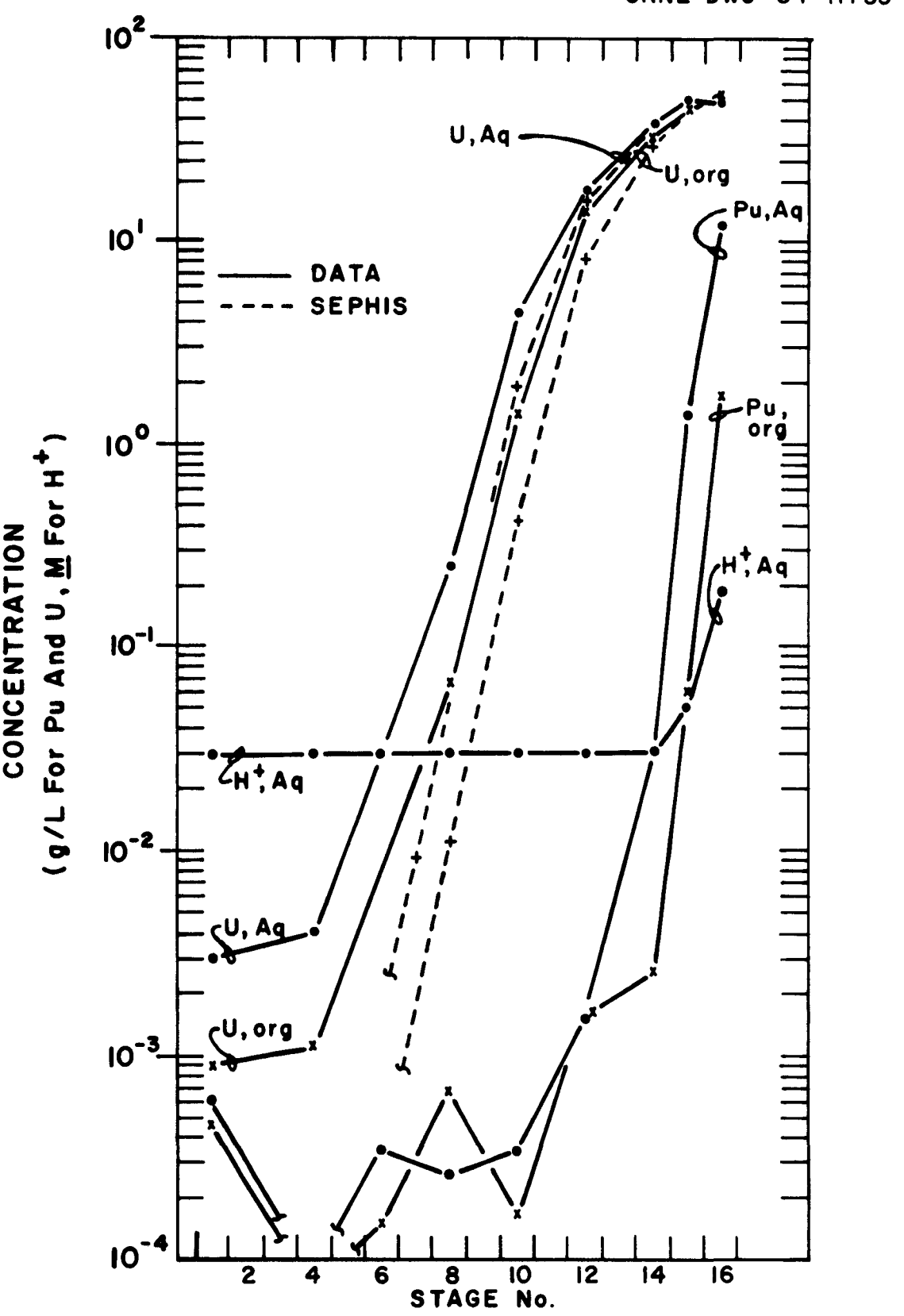

Fig 7. Concentration profiles of uranium, plutonium, and nitric acid in the costrip contactor for Test 7-2.

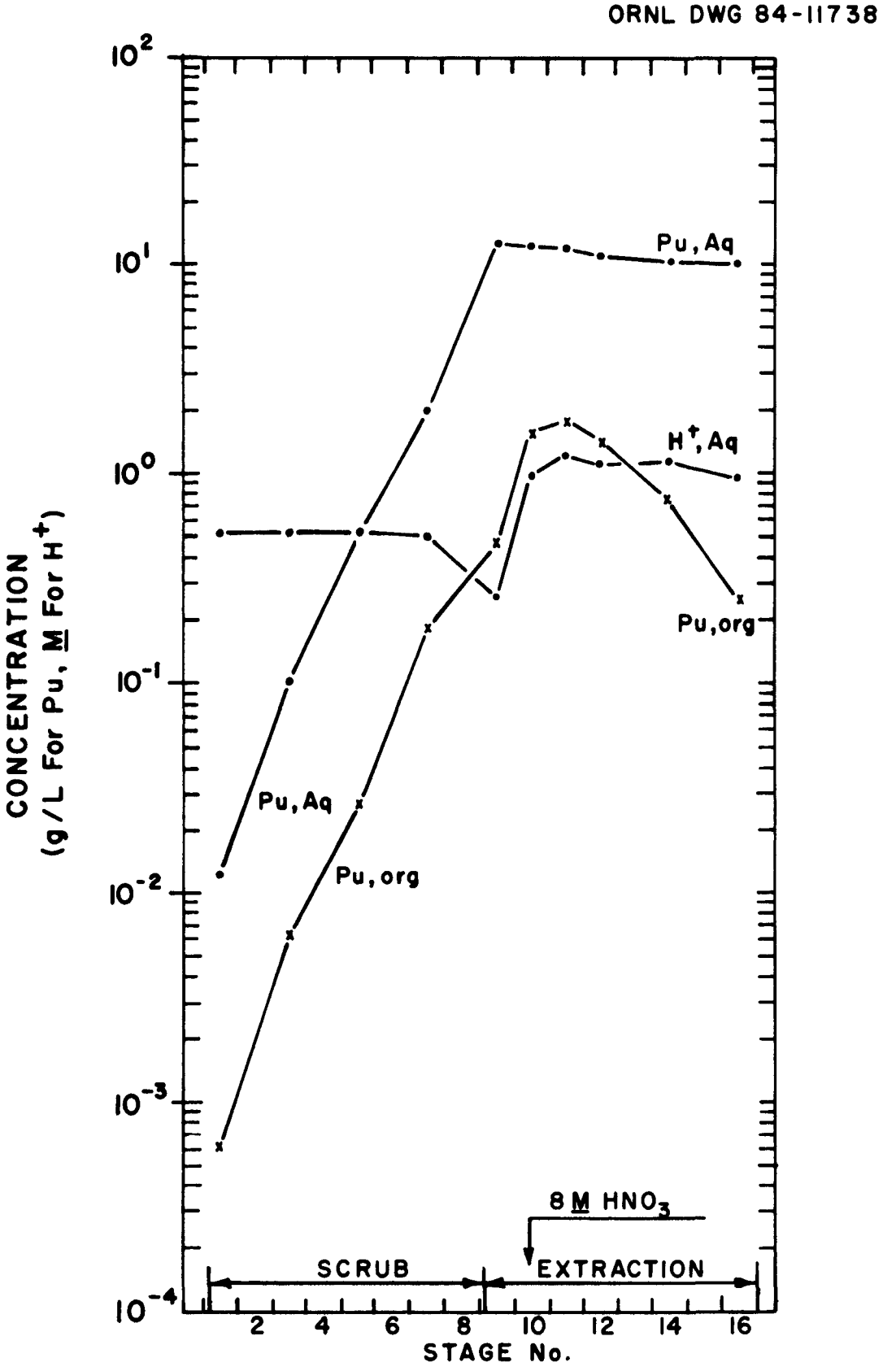

Fig. 8. Concentration profiles of plutonium and nitric acid in the partition contactor for Test 7-2.

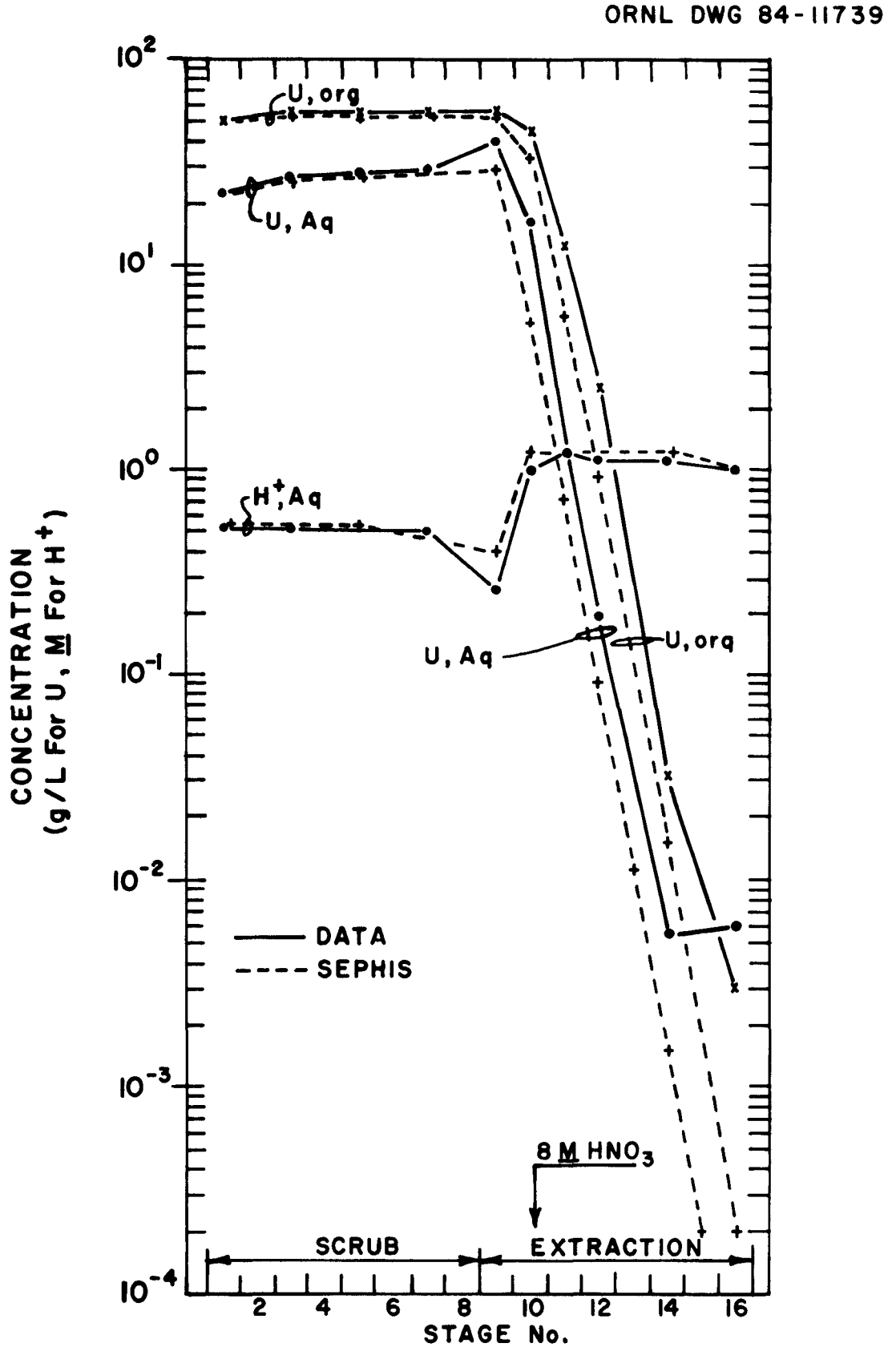

Fig. 9. Concentration profiles of uranium and nitric acid in the partition contactor for Test 7-2.

nitrate salting agent and hinders the uranium stripping. The agreement of the data with a SEPHIS estimate was not as good as one might desire; however, the flowsheet was run relatively conservatively, and we still obtained good results.

The uranium-plutonium product stream from the costrip contactor was continuously fed to stage 9 of the partition contactor (Fig. 8). The plutonium, at this point, should be essentially all Pu(III) and should stay primarily in the aqueous phase that eventually exits the contactor at stage 16. However, some reoxidation and reflux of the plutonium did occur in the extraction section, but this was less severe than in the organic back-scrub test (Run 7-3B) because of the lower plutonium concentration (by almost a third, which would decrease the Pu(III) concentration in the solvent) and the addition of hydrazine to the strip solutions. The organic plutonium concentration in the extraction section varied from a low of 0.25 g/L (extraction coefficient of 0.025) at stage 16 to a peak of 1.8 g/L (extraction coefficient of 0.16) at stage 11. This plutonium was easily removed from the solvent in the scrub section, which had additional HAN-hydrazine reductant and a lower H^+ concentration. The acid balance (Table 4) for the partition contactor indicates that ~1.6 mol of H^+ were generated per mole of plutonium partitioned, even though the feed to this contactor was Pu(III). This observation may demonstrate, as in the other flowsheet test (7-3B), that some cyclic reactions are in progress, possibly including the reoxidation of Pu(III) in the solvent.

4.2.3 Mitigating the Plutonium Reoxidation

According to Sze,[6] the reoxidation of Pu(III) in TBP solutions is catalyzed by HNO_2 and proceeds rapidly when the HNO_3 concentration in the organic is >0.2 M. Therefore, to prevent the plutonium reoxidation, the concentration of Pu(III), HNO_2, and HNO_3 in the organic solution should be minimized. Traditionally, reoxidation has been controlled by adding hydrazine to scavenge HNO_2 from the system. However, the results from Run 7-2 indicate that this still allows considerable plutonium reoxidation when processing breeder fuels. In these flowsheets, significant amounts of Pu(III) extracts to the solvent because of the very high concentrations of plutonium, while the hydrazine stays in the aqueous phase.

Lowering the HNO_3 concentration in the partitioning system so that the organic solutions contain <0.2 M HNO_3 would make separating the uranium from the plutonium difficult. However, one alternative may be to replace some of the HNO_3 with an inextractable salt. A coprocessing flowsheet proposed by Okamoto[7] used excess HAN to help salt uranium into the organic phase. For total partitioning, an organic scrub would be needed to improve the uranium separation, and the HNO_3 concentration in the strip reagent would be kept low (~0.01 M). The HAN reaction with Pu(IV) would make HNO_3 and prevent plutonium hydrolysis in the same way as in the costrip bank in Run 7-2.

5. PLUTONIUM PURIFICATION AND OXIDE CONVERSION RESULTS

The two aqueous plutonium product solutions that were recovered from the solvent extraction processing (Runs 7-1 and 7-3) were each purified by one cycle of anion exchange. The purified plutonium solutions were then converted to oxide by batch precipitation of Pu(III) oxalate followed by calcination of the oxalate to PuO_2. Recovery of plutonium by the anion exchange and oxalate precipitation-calcination runs was adequate, ~99% and 95%, respectively. Table 5 lists the activity levels of some of the fission product radionuclides in the final plutonium oxide product and the overall DF values achieved by the combined processing steps — solvent extraction, anion exchange, and oxalate precipitation. The only measurable gamma-emitting fission product left in the oxide product was ^{95}Zr, which was present in satisfactorily low concentrations. However, the ^{95}Zr content in the batch 2 oxide was lower than the batch 1 oxide by a factor of ~10. This difference is significant and is probably the result of making two solvent extraction runs (7-2 and 7-3) during the processing of the second batch as compared to one (7-1) for the first batch. The oxide products contained a total of 374 g of plutonium, which represents about ~78% of the plutonium originally measured in the dissolver solutions. These products were subsequently packaged and sent to HEDL.

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

Fission product radionuclides	Radioactivity level in product (MBq/kg Pu)		Overall DF[a]	
	Batch 1	Batch 2	Batch 1	Batch 2
^{95}Zr	6.62	0.61	2E3[b]	2E4
^{106}Ru	<6	<3	>2E5	>3E5
^{125}Sb	<3	<2	>3E4	>5E4
^{137}Cs	<1	<4	>8E5	>2E5
^{144}Ce	<5	<6	>5E5	>4E5
^{154}Eu	<2	<1	>8E5	>3E4

[a]The overall DF is defined as the ratio of the radionuclide concentration relative to the plutonium in the dissolver solution to the concentration relative to the plutonium in the PuO_2 product.

[b]To be read as 2×10^3.

6. SUMMARY AND CONCLUSIONS

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

1. A batch of FFTF fuel was processed in the SETF for the first time. Mixer-settler operation was good in regard to phase separations and solids accumulation. The gas liberated by the HAN reduction of plutonium, when producing product streams with plutonium concentrations up to 30 g/L plutonium, posed no significant problems in the mixer-settlers.

2. The coextraction-coscrubbing bank operated well and yielded low uranium and plutonium losses. The DFs for zirconium and niobium were poorer than those measured previously using tracer zirconium-niobium. DFs for zirconium, niobium, and ruthenium were improved in the second run by using eight scrub stages instead of six.

3. Partitioning with the organic back-scrub and the selective uranium extraction method both yielded good products. However, both flowsheets

were plagued to some degree by a plutonium reoxidation problem. The organic back-scrub method, which had the higher plutonium concentrations and no hydrazine, had a very significant problem; adding hydrazine may solve this problem. The selective uranium extraction method, which had hydrazine and lower plutonium concentrations, also had some reoxidation. An alternative may be to reduce the HNO_3 concentration and add more HAN to help salt the uranium into the organic phase.

4. Approximately 78% of the plutonium recovered from the dissolution of the fuel was successfully purified and converted to an oxide product. The oxide product, which contained 374 g of plutonium, was packaged and sent to HEDL for refabrication studies.

7. ACKNOWLEDGMENTS

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APPENDIX

APPENDIX

Table A-1. Campaign 7 – fuel pin identification numbers

Run number	
7-1	7-2
N2J 124	N2I 963
N2J 139	N2I 964
N2J 163	N2I 970
N2J 171	N2J 431
N2J 262	N2S 551
N2J 542	N2S 667
N2J 625	N2T 013

Table A-2. Campaign 7 first-cycle tests – extraction scrub bank conditions and results

	Run number	
	7-1	7-2
Dates	4/13/83	5/18-19/83
Bank temperature, °C	40-43	40-41
Number of stages:		
final scrub/inter. scrub/extr'n.	3/3/10	4/4/8
HAX stream flow rate, L/h	1.02	0.995
Flow ratios:		
HAS/HAX	0.122	0.128
HAIS/HAX	0.062	0.064
HAF/HAX	0.499	0.357
Inlet stream compositions:		
HAS stream, HNO_3, mol/L	0.50	0.30
HAIS stream, HNO_3, mol/L	3.1	5.05
HAX stream, % TBP	30.0 ± 0.5	30.0 ± 0.5
HAF stream:		
HNO_3, mol/L	3.2	3.1
U, g/L	120	155
Pu, g/L	33.9	38.5
^{241}Am, g/L	0.24	0.31
^{95}Zr, GBq/L	0.56	0.37
^{95}Nb, GBq/L	0.75	0.52
^{106}Ru, GBq/L	34.6	34.9
^{125}Sb, GBq/L	3.14	3.72
^{137}Cs, GBq/L	28.1	33.7
^{144}Ce, GBq/L	93.1	100.0
^{154}Eu, GBq/L	<0.1	<0.08

Table A-2. (continued)

	Run number	
	7-1	7-2
Outlet stream compositions:		
HAW stream		
HNO_3, mol/L	3.1	3.0
U, mg/L	2.0	2.6
Pu, mg/L	2.5	2.3
^{241}Am, g/L	0.17	0.21
^{95}Zr, GBq/L	0.27	0.23
^{95}Nb, GBq/L	0.32	0.27
^{106}Ru, GBq/L	24.2	20.7
^{125}Sb, GBq/L	2.22	2.23
^{137}Cs, GBq/L	19.8	20.2
^{144}Ce, GBq/L	62.3	60.8
^{154}Eu, GBq/L	<0.04	<0.1
HAP stream		
HNO_2, mol/L	[a]	0.0011
HNO_3, mol/L	0.08	0.07
U, g/L	59.8	54.2
Pu, g/L	15.3	13.3
^{95}Zr, MBq/L	2.76	0.18
^{95}Nb, MBq/L	2.11	0.043
^{106}Ru, MBq/L	25.9	4.58
^{125}Sb, MBq/L	<0.2	<0.07
^{137}Cs, MBq/L	<0.04	<0.02
^{144}Ce, MBq/L	<0.3	<0.2
^{154}Eu, MBq/L	<0.04	<0.03

[a] Not requested.

Table A-3. Campaign 7 first-cycle tests — strip bank conditions and results

	Run number	
	7-1	7-2
Dates	4/13/83	5/18-19/83
Bank temperature, °C	40-43	50-51
Number of stages:		
strip/scrub	11/5	16/0
HBX stream flow rate, L/h	0.569	1.105
Flow ratios:		
HAP/HBX	1.786	0.900
HBS/HBX	0.801	
Inlet stream compositions:		
HBX stream		
HNO_3, mol/L	0.1	0.03
HAN,[a] mol/L	0.3	0.1
N_2H_4, mol/L		0.03
HBS stream, % TBP	30.0 ± 0.5	
HAP stream		
HNO_3, mol/L	0.08	0.07
U, g/L	59.8	54.2
Pu, g/L	15.3	13.3
^{95}Zr, MBq/L	2.76	0.18
^{95}Nb, MBq/L	2.11	0.043
^{106}Ru, MBq/L	25.9	4.58
^{125}Sb, MBq/L	<0.2	<0.07
^{137}Cs, MBq/L	<0.04	<0.02
^{144}Ce, MBq/L	<0.3	<0.2
^{154}Eu, MBq/L	<0.04	<0.03

Table A-3. (continued)

	Run number	
	7-1	7-2
Outlet stream compositions:		
HBP stream		
HNO_3, mol/L	0.38	0.20
U, g/L	2.6	48.8
Pu, g/L	19	12.3
^{95}Zr, MBq/L	6.3	0.168
^{95}Nb, MBq/L	4.6	0.047
^{106}Ru, MBq/L	14.6	0.885
^{125}Sb, MBq/L	<0.7	<0.03
^{137}Cs, MBq/L	0.30	0.012
^{144}Ce, MBq/L	<0.8	<0.1
^{154}Eu, MBq/L	<0.5	<0.02
HBU stream		
HNO_2, mol/L	b	0.00056
HNO_3, mol/L	0.06	<0.01
U, g/L	40	0.0009
Pu, mg/L	4900	0.18
^{95}Zr, MBq/L	<0.03	<0.01
^{95}Nb, MBq/L	0.083	0.0078
^{106}Ru, MBq/L	11.1	2.79
^{125}Sb, MBq/L	<0.09	<0.03
^{137}Cs, MBq/L	<0.02	<0.006
^{144}Ce, MBq/L	<0.2	<0.04
^{154}Eu, MBq/L	<0.03	<0.01

[a]Hydroxylamine nitrate.

[b]Not requested.

Table A-4. Campaign 7 first-cycle tests – selective uranium extraction, bank conditions, and results

	Run number 7-2
Dates	5/18-19/83
Bank temperature, °C	26-27
Number of stages:	
scrub/acid addition/extraction	8/1/7
HCX stream flow rate, L/h	1.005
Flow ratios:	
HCS/HCX	0.18
HCIS/HCX	0.13
HBP/HCX	1.10
Inlet stream compositions:	
HCS stream	
HNO_3, mol/L	0.55
HAN,[a] mol/L	0.10
N_2H_4, mol/L	0.03
HCIS stream, HNO_3, mol/L	8.0
HCX stream, % TBP	30.0 ± 0.5
HBP stream	
HNO_3, mol/L	0.20
U, g/L	48.8
Pu, g/L	12.3
^{95}Zr, MBq/L	0.168
^{95}Nb, MBq/L	0.047
^{106}Ru, MBq/L	0.885
^{125}Sb, MBq/L	<0.03
^{137}Cs, MBq/L	<0.012
^{144}Ce, MBq/L	<0.1
^{154}Eu, MBq/L	<0.02

Table A-4. (continued)

	Run number 7-2
Outlet stream compositions:	
HCW stream	
HNO_2, mol/L	0.00057
HNO_3, mol/L	0.07
U, g/L	52.4
Pu, mg/L	0.86
^{95}Zr, kBq/L	<10
^{95}Nb, kBq/L	<4
^{106}Ru, kBq/L	<100
^{125}Sb, kBq/L	<10
^{137}Cs, kBq/L	<4
^{144}Ce, kBq/L	<80
^{154}Eu, kBq/L	<20
HCP stream	
HNO_3, mol/L	1.0
U, mg/L	6.1
Pu, g/L	9.4
^{95}Zr, kBq/L	90
^{95}Nb, kBq/L	28
^{106}Ru, kBq/L	570
^{125}Sb, kBq/L	<20
^{137}Cs, kBq/L	23
^{144}Ce, kBq/L	<80
^{154}Eu, kBq/L	<10

[a]Hydroxylamine nitrate.

Table A-5. Campaign 7 second-cycle tests – extraction scrub bank conditions and results

	Run number	
	7-3A	7-3B
Dates	5/25/83	5/25/83
Bank temperature, °C	42-43	42-43
Number of stages:		
scrub/inter. scrub/extr'n.	3/3/10	3/3/10
HAX stream flow rate, L/h	1.01	1.00
Flow ratios:		
HAS/HAX	0.119	0.121
HAIS/HAX	0.059	0.060
HAF/HAX	0.753	0.798
Inlet stream compositions:		
HAS stream, HNO_3, mol/L	0.49	0.49
HAIS stream, HNO_3, mol/L	3.0	3.0
HAX stream, % TBP	30.0 ± 0.5	30.0 ± 0.5
HAF stream		
HNO_3, mol/L	3.3	3.3
U, g/L	76	76
Pu, g/L	20.4	20.4
Outlet stream compositions:		
HAW stream		
HNO_3, mol/L	3.1	3.1
U, mg/L	<1	<1
Pu, mg/L	<0.04	<0.03
HAP stream		
HNO_2, mol/L	0.00078	0.00075
HNO_3, mol/L		0.05
U, g/L	52.4	56.3
Pu, g/L	14.6	16.2

Table A-6. Campaign 7 second-cycle tests – strip bank conditions and results

	Run number	
	7-3A	7-3B
Dates	5/25/83	5/25/83
Bank temperature, °C	42-43	42-43
Number of stages:		
strip/scrub	11/5	11/5
HBX stream flow rate, L/h	0.439	0.505
Flow ratios:		
HAP/HBX	2.308	1.990
HBS/HBX	1.055	0.990
Inlet stream compositions:		
HBX stream		
HNO_3, mol/L	0.097	0.11
HAN,[a] mol/L	0.31	0.53
HBS stream, % TBP	30.0 ± 0.5	30.0 ± 0.5
HAP stream		
HNO_2, mol/L	0.00078	0.00075
HNO_3, mol/L	[b]	0.05
U, g/L	52.4	56.3
Pu, g/L	14.6	16.2
Outlet stream compositions:		
HBP stream		
HNO_3, mol/L	0.6	0.81
U, g/L	0.2	0.005
Pu, g/L	12	30.3
HBU stream		
HNO_3, mol/L	[b]	[b]
U, g/L	40	38.6
Pu, mg/L	20	0.9

[a] Hydroxylamine nitrate.

[b] Not requested.

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