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Report Number: ORNL-2235

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section

RECOVERY OF Np^{237} BY THE NEPTEX SOLVENT-EXTRACTION PROCESS

J. R. Flanary
J. H. Goode
R. G. Mansfield
R. P. Wischow

Classification cancelled (or changed to UNCLASSIFIED)
Ltr. Fr. Declassification
by authority of Branch, dtd 5-6-59
by J. C. Ridenour TISOR, date 5-13-59

DATE ISSUED:

APR 3 1957

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0.0 ABSTRACT

Flowsheets are presented for the solvent-extraction recovery of uranium and Np^{237} from special highly irradiated MTR fuel elements and from nonvolatile fluoride residues from the Oak Ridge Gaseous Diffusion Plant. In both cases the material containing the neptunium and uranium is dissolved and digested to inactivate emulsion-forming impurities, the neptunium and uranium are extracted with tributyl phosphate solvent, using aluminum nitrate as the primary salting agent, scrubbed free of fission products and/or ionic contaminants, and finally separated and recovered by selective stripping with nitric acid.

1.0 INTRODUCTION

Early in 1955 two widely different sources of the 2.2×10^6-year half-life α emitter Np^{237} became available, namely, twelve special spent fuel elements and shim rods from the MTR reactor, which contained a calculated 1.15 g of Np^{237}, and an accumulation of nearly 5000 lb of nonvolatile fluoride residues from the Oak Ridge Gaseous Diffusion Feed Plant, which contained 0.05-75 g of neptunium per ton.

The recovery of trace amounts of Np^{237} has been investigated by a number of workers.[1-15] At Oak Ridge National Laboratory solvent-extraction and ion-exchange techniques were developed[9-11] by which 30-40 g of neptunium have been isolated from radioactive wastes and by-product streams from radiochemical processes operated by the Chemical Technology Division. At Chalk River, 30% TBP in a kerosene-type diluent was used to extract Np^{237} from plant waste solutions.[3] In this process the neptunium was reduced to the tetravalent state by the addition of ferrous sulfamate to the feed before extraction and separated from the inextractable Pu(III) by

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scrubbing the extract with nitric acid containing ferrous sulfamate. A separation factor of neptunium from plutonium of 10^3 was reported. Some of the other reagents used for the extraction of neptunium are thenoyltrifluoroacetone (TTA) dissolved in chloroform or other inert solvent,[4] tributylamine in hexone,[5] hexone alone,[6] and triglycol dichloride.[7,8] The cost of the first two methods is sufficient to rule them out for large-scale operations. The main disadvantage of hexone as an extractant is that the neptunium must be oxidized to Np(VI) before extraction; this oxidation also increases the extraction of ruthenium and plutonium and results in contamination of the product stream with these elements.

The similarity between the Chalk River TBP process, which was salted with zinc nitrate, and the ORNL 25-TBP process,[12] in which enriched uranium is recovered by extraction with 6% TBP from an aluminum nitrate—salted solution, suggested that modifications of the 25-TBP process might be used to recover the neptunium and uranium, partially decontaminated from fission products, from the uranium-aluminum alloy MTR fuel elements. A second solvent extraction cycle could then be used to further decontaminate and separate the two products in a partitioning column (Part I). A process similar to the second solvent-extraction cycle could also be used for recovery of the neptunium and uranium in fluorination ash (Part II).

In the primary extraction of either process, uranium and neptunium must be coextracted quantitatively from the aluminum nitrate—salted feed, then scrubbed with aluminum nitrate—nitric acid solution to backwash any impurities that may have been extracted. Previous studies[9] of neptunium chemistry have shown that Np(VI) is the form most readily extracted by tributyl phosphate (TBP), but it is difficult to hold neptunium in the hexavalent state. Since the oxidants required, 0.1 M bromate or permanganate, may also be extracted by TBP, it was considered advisable to reduce the neptunium and extract it in the tetravalent state. Ferrous sulfamate, 0.01-0.02 M, was therefore added to the aqueous feeds and scrubs to keep the neptunium reduced to the tetravalent state.

The contributions of the ORNL Analytical Chemistry Division in the development of methods for the analysis of Np^{237} and Np^{239} and nonradioactive constituents under process conditions, especially the groups of W. L. Laing, F. L. Moore, G. R. Wilson, and E. I. Wyatt, are acknowledged.

Part I. THE RECOVERY OF Np^{237} AND ENRICHED URANIUM FROM URANIUM-ALUMINUM FUEL ELEMENTS

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2.0 FLOWSHEET FOR MTR FUEL ELEMENT FEED

In the Neptex process first-cycle flowsheet (Fig. 1), the fuel elements are dissolved in 8 $\underline{M}$ HNO_3, containing 0.005 $\underline{M}$ $Hg(NO_3)_2$ as a catalyst for the dissolution of the aluminum. The nitric acid/aluminum mole ratio is 4.45/1.00, yielding a solution 1.8 $\underline{M}$ in aluminum after dissolution is complete. The solution thus obtained is 1.1-1.3 $\underline{M}$ in HNO_3 and contains all the neptunium, uranium, and fission products from the fuel elements.

Emulsion-forming siliceous matter in the feed is dehydrated, and thus rendered inactive, by adding 1 vol of 13 $\underline{M}$ HNO_3 for each 3 vol of solution, boiling the mixture down to a liquid temperature of 136°C, and diluting with water to the original volume of dissolver solution used. Ferrous sulfamate and oxalic acid are then added and the solution is held at room temperature for 1 hr in order to reduce the neptunium to the tetravalent state and to complex the radioactive zirconium.

This solution is fed to the IA column together with a countercurrent 2% solution of tributyl phosphate in Amsco 125-82, an inert

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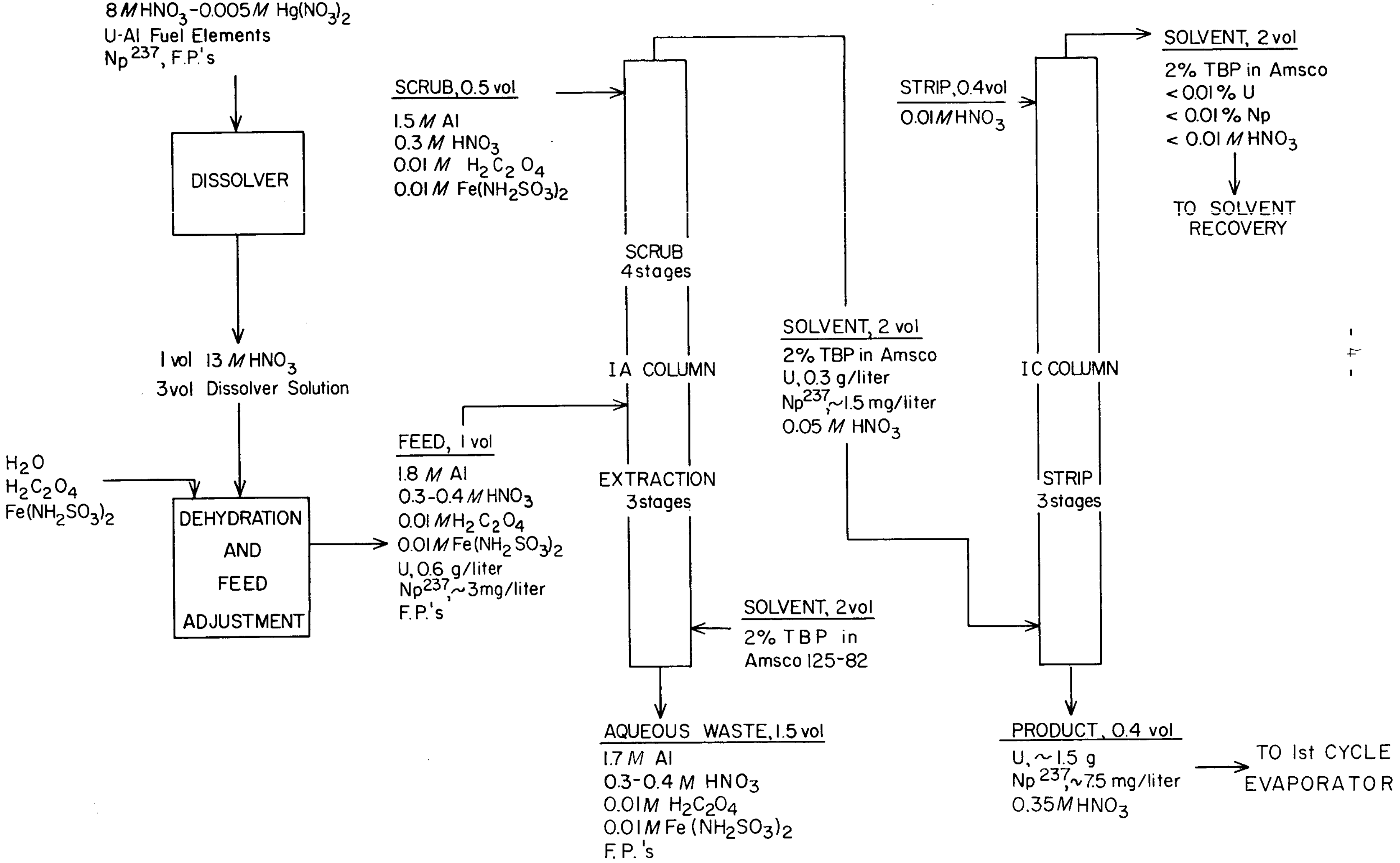

Fig. 1. Neptex Process First Cycle Flowsheet.

alkane diluent. The IA column product is fed to the IC column, in which the uranium and neptunium are stripped from the tributyl phosphate solution with 0.01 M HNO_3. The IC column product flows to an evaporator for concentration and then to the second solvent extraction cycle, where the neptunium and uranium are further decontaminated and partitioned (Fig. 2).

The evaporated first cycle product is adjusted to the second cycle feed composition by dissolving 2S aluminum barstock in the solution after the addition of an amount of concentrated nitric acid calculated to leave a 1 M excess and mercuric nitrate catalyst. This method was chosen in order to consume excess nitric acid from the evaporation and to obtain the highest possible uranium concentration and aluminum salting strength with minimum volume increase. After digestion to coagulate silica, the feed is made 0.02 M in ferrous sulfamate to hold the neptunium in the tetravalent state, and adjusted to 1.8 M $Al(NO_3)_3$, 1 M HNO_3, and 15 g of uranium per liter. The uranium and neptunium are extracted from the feed by an equal volume of 15% TBP in Amsco 125-82 and scrubbed free of fission products in the IIA column. The neptunium is selectively stripped from the uranium by 0.5 M HNO_3 in the top of the IIB column; the neptunium is freed of uranium by back-extraction of the uranium into more solvent in the bottom of the IIB column. The neptunium product is purified and isolated by ion exchange. The solvent is stripped of uranium in the IIC column and then sent to a solvent recovery system. The enriched uranium product is finally concentrated by evaporation.

The second-cycle flowsheet may be varied to accommodate different uranium concentrations in the feed by changing the solvent/feed volume ratio to maintain a uranium concentration of 15 g/liter in the organic phase leaving the IIA column.

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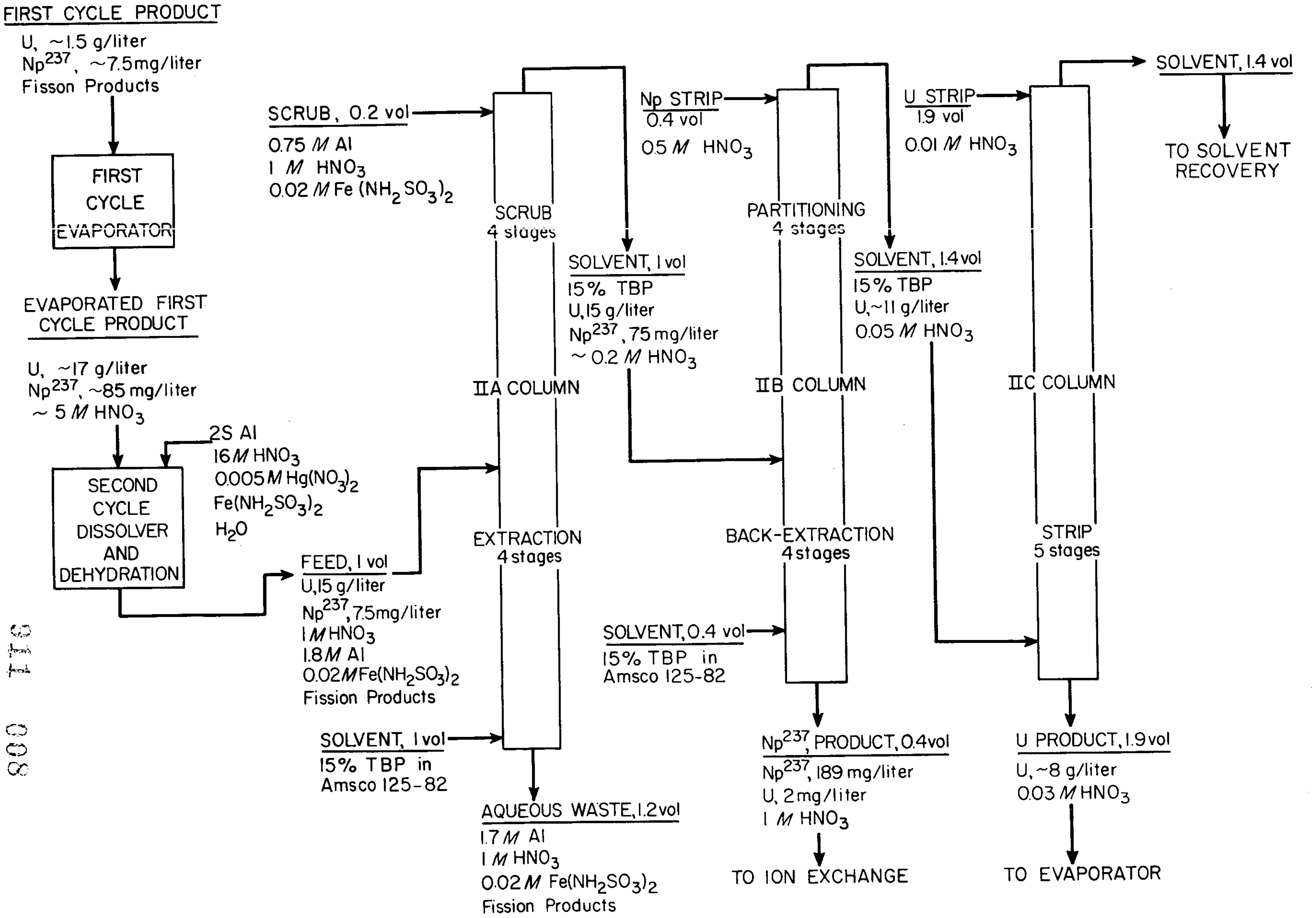

Fig. 2. Neptex Process Second Cycle Flowsheet.

3.0 FLOWSHEET OPERATION

3.1 First Cycle

The Pilot Plant Section of the ORNL Chemical Technology Division processed the 12 irradiated fuel elements and shim rods in two batches, based on different uranium burnups, during the summer of 1955 by the 2% TBP first-cycle flowsheet. A typical feed analysis was:

U	0.11 g/liter	Np α	2.47×10^3 c/m/ml
HNO_3	0.41 M	Gross γ	3×10^9 c/m/ml
$Al(NO_3)_3$	1.80 M	Ru γ	2×10^8 c/m/ml
$H_2C_2O_4$	0.01 M	Zr-Nb γ	2×10^8 c/m/ml
$Fe(NH_2SO_3)_2$	0.01 M	Total rare earth β	5×10^9 c/m/ml

Approximately 2.2 g of Np^{237} and 670 g (99.3%) of uranium were recovered. Fission product decontamination factors across the first cycle were 2×10^4 for gross γ, 4×10^5 for ruthenium, 10^3 for zirconium-niobium, and 7×10^6 for total rare earths, which generally confirmed or bettered the decontamination found in the tracer level experiments (Sec. 4.3).

Pilot Plant operation during the processing was essentially routine, except for the necessity of careful control of the reducing normality of the feed. The intense radioactivity of the feed appeared to result in oxidation of the neptunium reductant, 0.01 M ferrous sulfamate, and periodic additions of ferrous sulfamate were necessary to maintain reducing conditions.

The recovery of 2.2 g of Np^{237}, rather than the calculated 1.15 g, indicated that many of the assumed values for the radiation history of the elements were in error. This was further confirmed by the recovery of 471 g of U^{235}, rather than the 285 g that had been estimated.

3.2 Second Cycle

The Np^{237} and enriched uranium products that had been processed through one cycle by the Pilot Plant, by the 2% TBP first-cycle flowsheet, were reduced in volume by evaporation and delivered to the Chemical Development Section for smaller-scale separation of neptunium and uranium and additional decontamination from fission products. From the product of the batch containing the low-burnup material, approximately 90 g of uranium and 225 mg of Np^{237} were recovered; the high-burnup material yielded about 580 g of uranium and about 2 g of neptunium. Mass assays of the uranium from the two batches are shown in Table 1.

The small quantity of low-burnup material was processed batch countercurrently, but the high-burnup material was processed in 0.75-in.-dia pulsed columns. The recovery operation was difficult owing to interfacial emulsions generated by colloidal silica in the feed, possibly picked up from the Pilot Plant evaporators. Attempts to reduce emulsification by increasing the A-column acidity resulted in rather high neptunium and uranium losses, 13.8 and 0.51%, respectively. Similar losses were incurred in the batch countercurrent operation, 10% for neptunium and 0.1% for uranium.

Decontamination of uranium and neptunium from fission products was erratic and lower than expected (Table 2); however, the uranium product met activity specifications of less than 130% of the β and 200% of the γ background activity of unirradiated U^{235}. The neptunium product was sufficiently decontaminated for direct handling.

The decontaminated uranium products from the neptunium partitioning runs were transferred to the Special Separations Section of the ORNL Electronuclear Research Division for further purification and isotope separation, while the recovered neptunium was transferred to the Isolation Laboratory of the Chemical Technology Division for final concentration and purification.

Table 1. Mass Assays of MTR Neptex Uranium Product

	U^{234} (%)	U^{235} (%)	U^{236} (%)	U^{238} (%)
Low burnup	1.14	80.70	9.38	8.78
High burnup	1.70	68.20	18.26	11.84

Table 2. Second-cycle Decontamination Factors and Losses

	Low-burnup Material			High-burnup Material		
	Loss (%)	Decontamination Factor		Loss	Decontamination Factor	
		Gross γ	Gross β		Gross γ	Gross β
Neptunium	10	14	70	13.8	---	---
Uranium	0.1	11	18	0.51	44	1.1×10^3

3.2.1 Recovery of Low-burnup Material

Since less than 100 g of uranium comprised the low-burnup material and provided insufficient volume for column operation under second-cycle flowsheet conditions, the Pilot Plant product (45.6 liters) was evaporated to about 2 liters, and then adjusted to make two feeds containing about 25 g of uranium per liter. This feed was processed in two batch countercurrent experiments as a final check on a proposed flowsheet with actual feed. Five extraction, four scrub, five partitioning, and four back-extraction stages were used, plus a batch uranium stripping operation. Very bad emulsions occurred in the extraction section of the system during the initial part of the first experiment, and the acid concentration of the feed had to be increased from 0.3 M to 1 M HNO_3 before the phases would disengage rapidly. The originally proposed flowsheet was modified to that shown in Fig. 2 for processing the remainder of the material.

Material balances accounted for 98% of the uranium and 81% of the neptunium, which is within the limits of analytical accuracy. About 5% and 75% of the neptunium appeared in the uranium and neptunium products, respectively. A total of 0.224 g of Np^{237}, in association with 0.011 g of uranium, was separated as the product from the processing of the low-burnup material.

3.2.2 Recovery of High-burnup Material

A total of 60.7 liters of evaporated first-cycle product was received from the Pilot Plant. The material was filtered to remove a highly radioactive black precipitate and evaporated to 34 liters. After analysis enough 2S aluminum barstock was dissolved into the solution with the aid of mercuric nitrate catalyst to achieve the desired feed conditions. Aluminum barstock was used rather than $Al(NO_3)_3$ and base, to minimize volume increase.

The original flowsheet was changed to conform to the conditions developed during the processing of the low-burnup material. Column operation was begun under the following conditions:

Feed, 30 ml/min: 15 g U/l, 1.8 $\underline{M}$ $Al(NO_3)_3$, 1 $\underline{M}$ HNO_3, 0.02 $\underline{M}$ Fe^{++}

Scrub, 6 ml/min: 1.5 $\underline{M}$ $Al(NO_3)_3$, 1 $\underline{M}$ HNO_3, 0.02 $\underline{M}$ Fe^{++}

Extractant, 45 ml/min: 15% TBP

Back-extractant, 12 ml/min: 15% TBP

Np strip, 12 ml/min: 0.5 $\underline{M}$ HNO_3

U strip, 57 ml/min: 0.1 $\underline{M}$ HNO_3

As the run progressed, the flowsheet conditions were changed several times to make the columns perform satisfactorily. Severe emulsification problems, primarily in the extraction-scrub column, necessitated the addition of more nitric acid to the feed, and the run was completed with a feed containing 1.85 $\underline{M}$ HNO_3. At the same time, the scrub composition was changed to 0.75 $\underline{M}$ $Al(NO_3)_3$—1 $\underline{M}$ HNO_3. The solvent flow rate was decreased from 45 to 30 ml/min because of flooding in the strip column. These changes appeared to smooth out column operation, and the run was completed in about 30 hr of actual operating time, including startup and shutdown periods. The total processing time, including downtime, was about 70 hr.

Although the addition of more nitric acid to the feed permitted the extraction column to function, the acid carry-over in the organic stream from the A column increased the neptunium losses to the solvent stream from B column by increasing the neptunium extraction coefficient in the B column. About 20% of the neptunium was found in two batches of the uranium product; this material was evaporated and reprocessed after the feed had been concentrated to 25 g of uranium per liter.

A third run was made to process all analytical wastes, samples, tank rinsings, and the black precipitate filtered from the Pilot Plant product. The precipitate was dissolved in 14 $\underline{M}$ HF, neutralized with $Al(OH)_2NO_3$, and added to the feed. The precipitate, thought to be an iron-nickel silicate, carried the bulk of the fission products present in the Pilot Plant material and had an activity greater than 50 r/hr measured at several inches.

It is felt that colloidal silica from the aluminum barstock was the chief cause of the emulsification in the extraction column under the low (1 M) acid conditions. The drastic Thorex feed pretreatment procedure, in which the feed is evaporated, dehydrated at 160°C, and then diluted to feed concentrations, would probably eliminate the emulsification difficulties; the lower feed and scrub acidities in the original flowsheet would decrease neptunium losses.

4.0 EXPERIMENTAL WORK

4.1 Fuel Element Dissolution

In previous studies,[12] 8 M HNO_3 catalyzed with 0.005 M $Hg(NO_3)_2$ had been found optimum for dissolving 5-15% uranium-aluminum alloy fuel elements. This strength acid dissolved ~45-g test samples of nonirradiated MTR fuel elements in 2 hr and left no residue. With 6, 10, and 12 M HNO_3, up to 12 hr was required for complete dissolution.

4.2 Feed Adjustment

The dissolver solution prepared with 8 M HNO_3 is about 1.8 M in $Al(NO_3)_3$ and ~1 M in HNO_3. When this solution was extracted with tributyl phosphate, severe emulsions formed at the organic-aqueous interface and phase disengagement was very slow. Addition of 13 M HNO_3, to an acidity of about 4 M, evaporation until the liquid temperature reached 136°C, and addition of water to the original dissolver solution volume destroyed the emulsion formers. It is believed that these emulsion formers are hydrous soluble silicates or silicic acid, which are dehydrated during the heating. The final feed solution to

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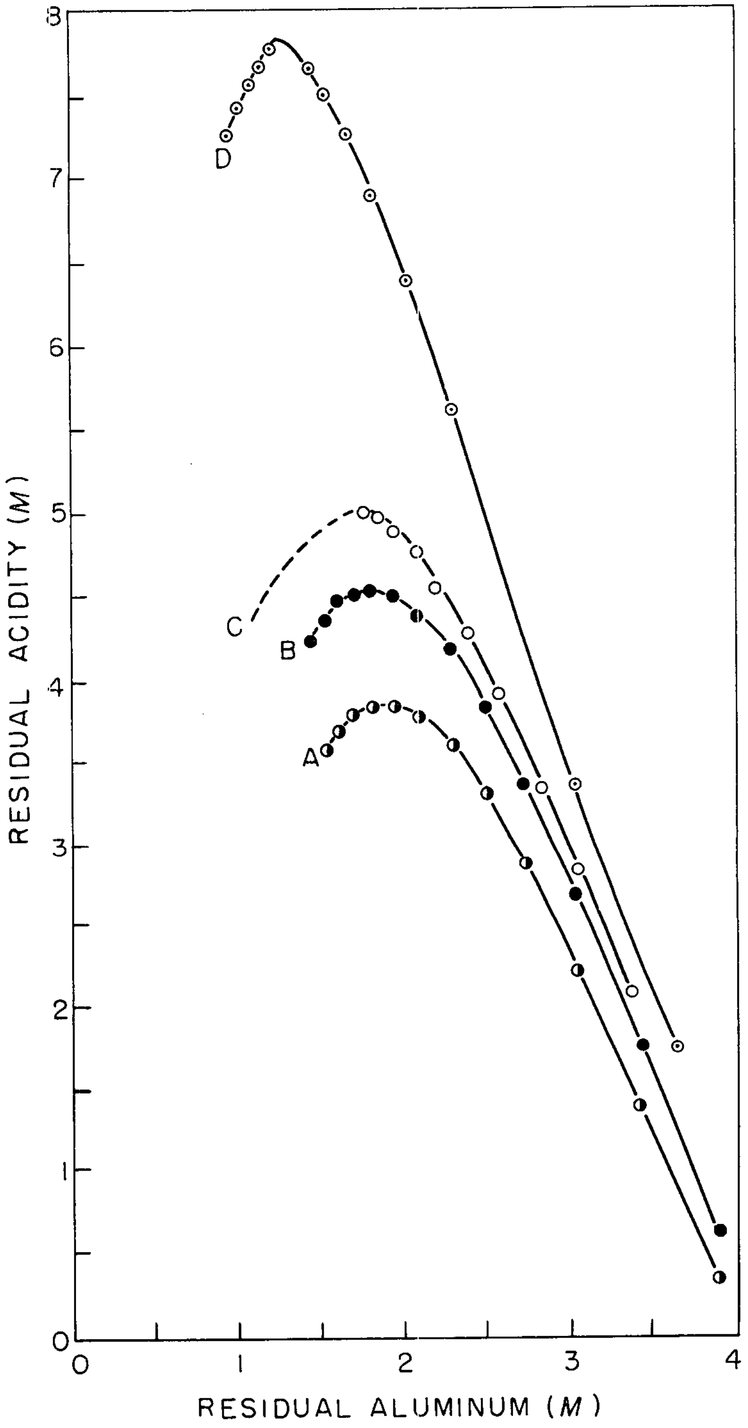

Fig. 3. Neptex Process Feed Adjustment. Residual Acidity as a Function of Residual Aluminum Concentration During Evaporation to 136°C of Dissolver Solutions of Different Initial Compositions.

the extraction column was about 1.8 M in $Al(NO_3)_3$ and 0.4 M in HNO_3. It contained an insoluble flocculent precipitate which did not interfere with the solvent-extraction system.

During the evaporation and dehydration the acidity of the solution passed through a maximum and then dropped rapidly to near neutrality as denitration took place. When the initial acidity was 3.5 M (curve A, Fig. 3), the emulsion formers were not always destroyed. With solution of initial acid concentration of 4.25 M or higher (curves B, C, and D, Fig. 3), the digestion procedure was satisfactory.

4.3 Solvent Extraction

Because of the similarity of the ORNL 25-TBP process feed[12] to one that could be obtained by acid dissolution of MTR fuel elements, the first investigations of the Neptex solvent-extraction system were carried out under conditions similar to those of the 25-TBP process. Calculations based on the approximate aluminum and uranium content of the MTR elements showed that, at the 25-TBP process feed aluminum concentration of 1.8 M, a Neptex IA column feed would contain ~0.6 g of uranium per liter.

In preliminary Neptex extraction studies a 6% TBP solution was used, as in the 25-TBP process. The TBP concentration was later decreased to 2%, in order to obtain greater decontamination from fission products.

The behavior of neptunium was studied by means of Np^{239} tracer which was produced by neutron-irradiation of U^{235}-depleted U_3O_8. In preliminary experiments, where Np^{239} was the only radioactive material present, the path of neptunium was traced by gross β or gross γ analysis. This was sufficiently accurate for approximate determinations of distribution coefficients, but, when fission products were present, it was necessary to chemically separate the neptunium before determining its concentration by scintillation γ counting.

4.3.1 IA (Extraction-Scrubbing) Column Conditions

Batch countercurrent experiments showed that the following IA column conditions yielded 98-100% extraction of neptunium and uranium:

Feed: 1.7-1.8 M $Al(NO_3)_3$, 0.3-0.5 M HNO_3, 0.01 M $Fe(NH_2SO_3)_2$, 0.01 M $H_2C_2O_4$, 0.5-1.5 g of uranium per liter, Np^{239} tracer

Scrub: 1.5 M $Al(NO_3)_3$, 0.4-0.5 M HNO_3, 0.01 M $Fe(NH_2SO_3)_2$, 0.01 M $H_2C_2O_4$

Extractant: 2% TBP-98% Amsco 125-82

Feed/scrub/extractant flow ratios: 1.0/0.5/2.0

3 extraction stages, 4 scrub stages

Decontamination factors were 10^4-10^5 for ruthenium, 2 x 10^4 for zirconium, 10^4 for niobium, 10^4-10^5 for total rare earths, and 5 x 10^3 for plutonium under these conditions.

4.3.2 IC (Stripping) Column Conditions

The uranium and neptunium were stripped from the IA-column organic stream by 0.01 M HNO_3. In batch countercurrent studies the uranium and neptunium distribution coefficients,* O/A, were low enough that stripping was complete in 3 stages with an organic/aqueous flow ratio of 5/1. No further decontamination was achieved in the IC column.

4.3.3 Effect of First-cycle Process Variables

Tributyl Phosphate Concentration. The organic/aqueous distribution coefficient of Np(IV) increased as the tributyl phosphate concentration increased (Fig. 4) according to the relation Np(IV) D.C. = 0.57 (% of TBP)$^{2.3}$ or 1140 (molarity of TBP)$^{2.3}$. The experiments were made with feed solutions 0.3 M in HNO_3, 1.8 M in aluminum nitrate, and 0.01 M in ferrous sulfamate. These were equilibrated with equal volumes of TBP in Amsco 125-82, the TBP concentration varying from 1.7 to 6.4%.

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*The distribution coefficient, O/A, is defined as the equilibrium ratio of the concentration of solute in the solvent phase to that in the aqueous phase.

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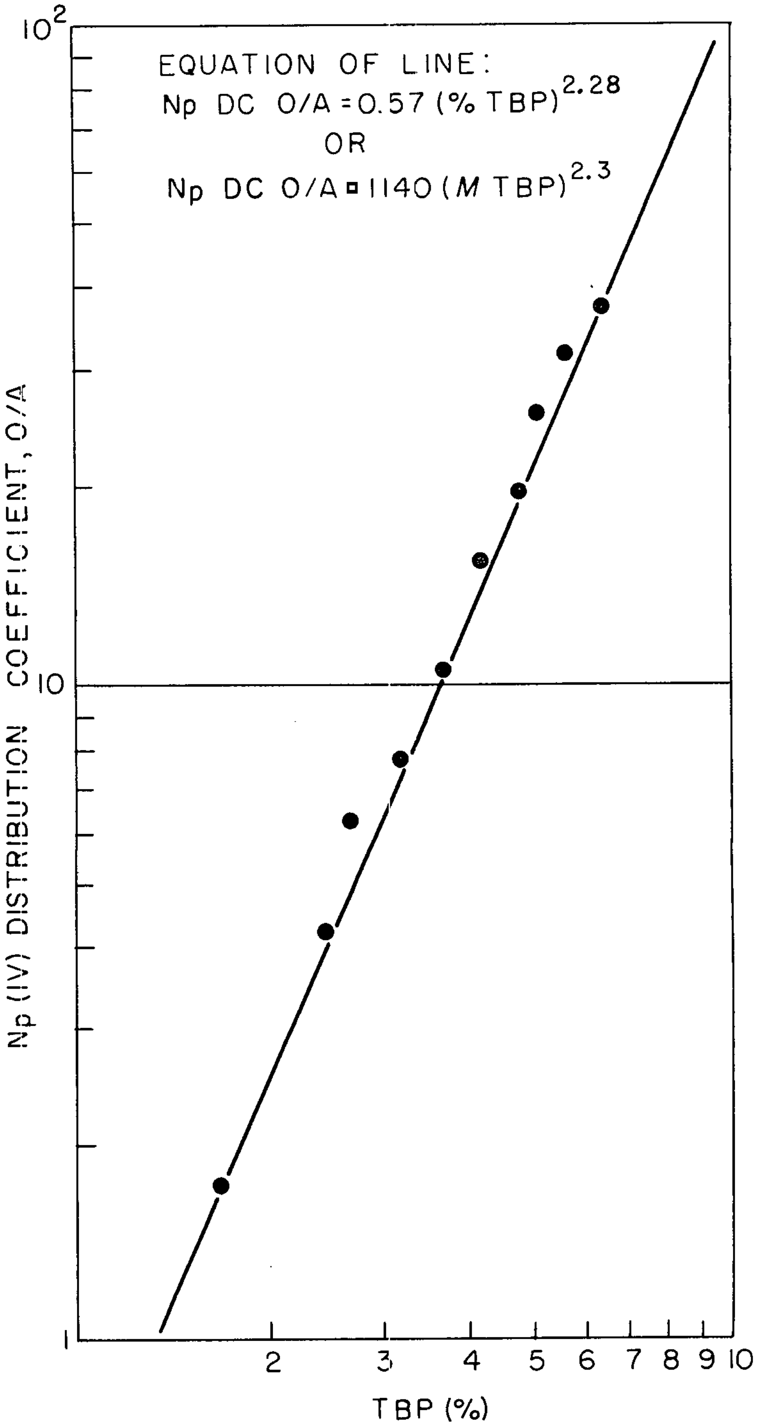

Fig. 4. Np(IV) Distribution Coefficient, O/A, vs % TBP at Constant Feed Conditions.

Nitric Acid and Ferrous Sulfamate Concentrations of A-Column Feed. The Np(IV) distribution coefficient increased as the feed HNO_3 concentration increased from 0.1 to 0.2 M, and then decreased with further increase in the acid concentration (Fig. 5). Increasing the ferrous sulfamate concentration from 0.01 M to 0.1 M did not increase the distribution coefficient. The lower value at 0.002 M ferrous sulfamate may not be significant since the analytical method was not highly accurate. With 0.1 M ferrous sulfamate there were emulsions in the extractions which took several minutes to break; no emulsifying effect was noted from the lower sulfamate concentrations.

In the experiments, feed solutions containing approximately the same concentration of all components except nitric acid were equilibrated with equal volumes of 6% TBP. The aluminum concentration of the feeds was maintained at 1.8 M, while the nitric acid was varied from 0.1 M to 3.0 M. Np^{239} tracer and ferrous sulfamate (0.01 M) were added to each feed solution prior to extraction. Neptunium distribution coefficients were determined by gross β activity ratios.

Degree of Saturation of Extractant. As the degree of saturation of the extractant increased, the Np(IV) distribution coefficient decreased (Table 3). The experiments were batch extractions of feeds in which all components were maintained constant except the uranium, which was varied from 3.56% to 550% of the concentration necessary to saturate an equal volume of 2% TBP. The feed solution was nearly neutral, but the contribution of nitric acid to the total saturation was taken into account. The "percent total saturation" was taken as the sum of the percent saturation with uranium plus the percent saturation with nitric acid.

Studies on the extraction of low concentrations of uranium from solutions containing high concentrations of fission products have shown that the greater the degree of saturation of the extractant with uranium, the greater is the decontamination from fission products. Therefore, because of the expected high level of fission product activity in the solution produced by dissolution of the MTR fuel elements, it would be

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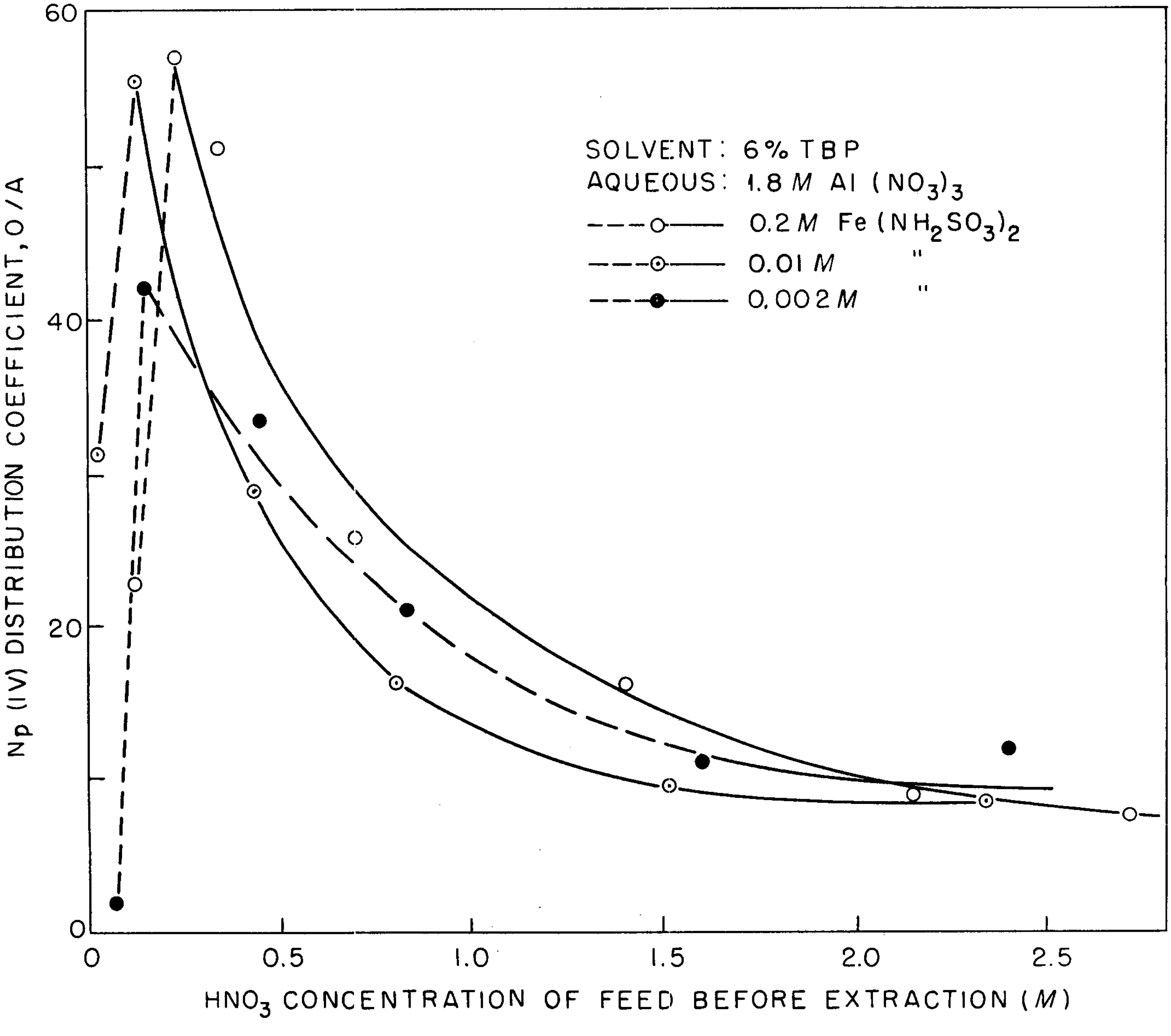

Fig. 5. Effect of Nitric Acid Concentration on the Np(IV) Distribution Coefficient.

Table 3. Effect of Degree of Saturation of 2% TBP Solvent on Np(IV) Distribution Coefficient

Feed: 1.91 M $Al(NO_3)_3$, 0.03 M HNO_3, 0.01 M $Fe(NH_2SO_3)_2$; Np^{239} tracer, 1.3 x 10^7 γ c/m/ml

Uranium varied from 0.32 to 49.6 mg/ml

Extractant: 2.0% TBP--98% Amsco 125-82

Single batch equilibrations using equal volumes of feed and organic

Saturation of Organic Phase after Equilibration (%)	Np(IV) D.C., O/A	Saturation of Organic Phase after Equilibration (%)	Np(IV) D.C., O/A
23.0	2.63	82.3	0.122
27.0	3.22	89.0	0.017
32.4	1.81	90.0	0.0074
33.9	1.62	91.3	0.00064

desirable to use the lowest concentration of TBP which would still yield a satisfactory distribution coefficient for neptunium.

Aluminum Nitrate Concentration. The Np(IV) distribution coefficient varied with the aluminum nitrate concentration of the feed according to the relation

$$\text{Np(IV) D.C., O/A} = 0.1\,[\text{Al(NO}_3)_3]^{5.5}$$

in the $Al(NO_3)_3$ range 0.45-1.87 M (Fig. 6).

Scrub Aluminum Nitrate Concentration. The neptunium distribution coefficient varied with varying scrub aluminum nitrate concentration (Fig. 7) according to the relations

$$\text{For 6\% TBP, Np(IV) D.C.} = 0.021\,e^{4.89\,[\text{Al(NO}_3)_3]}$$

$$\text{For 2\% TBP, Np(IV) D.C.} = 0.0019\,e^{4.76\,[\text{Al(NO}_3)_3]}$$

Scrub conditions of the IA column were simulated by batch contacting of extractant that had been previously equilibrated with feed solutions of constant acidity and varying aluminum nitrate concentration.

Complexing Agents. Sulfate, as sodium sulfate, has been used to inhibit extraction of zirconium by tributyl phosphate. However, in countercurrent experiments zirconium decontamination was not significantly increased by adding sodium sulfate.

Oxalic acid, which has been used in solvent extraction processes

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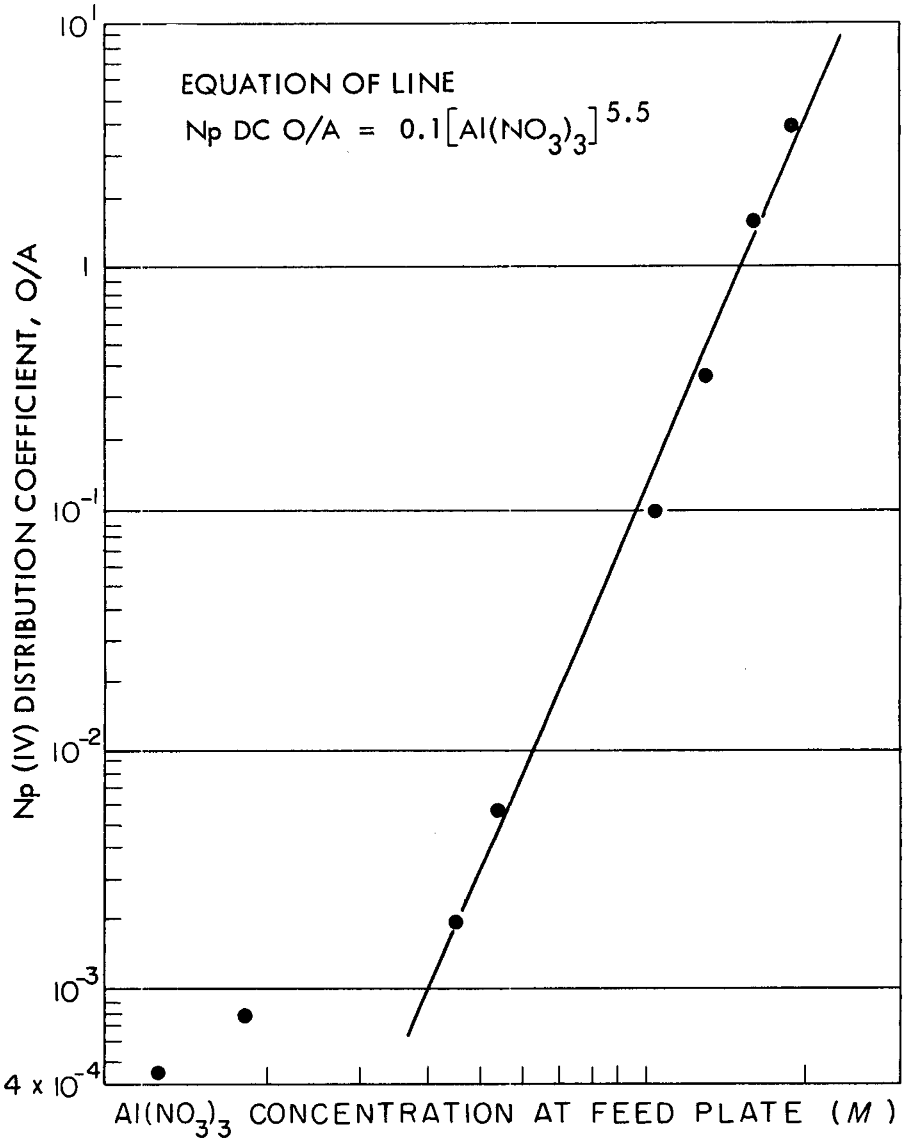

2% TBP EQUILIBRATED WITH FEED CONTAINING 0.01*M* $Fe(NH_2SO_3)_2$, 0.25*M* HNO_3, VARIABLE Al^{3+}

Fig. 6. Effect of Feed $Al(NO_3)_3$ Concentration on Np(IV) Distribution Coefficient at Feed Plate.

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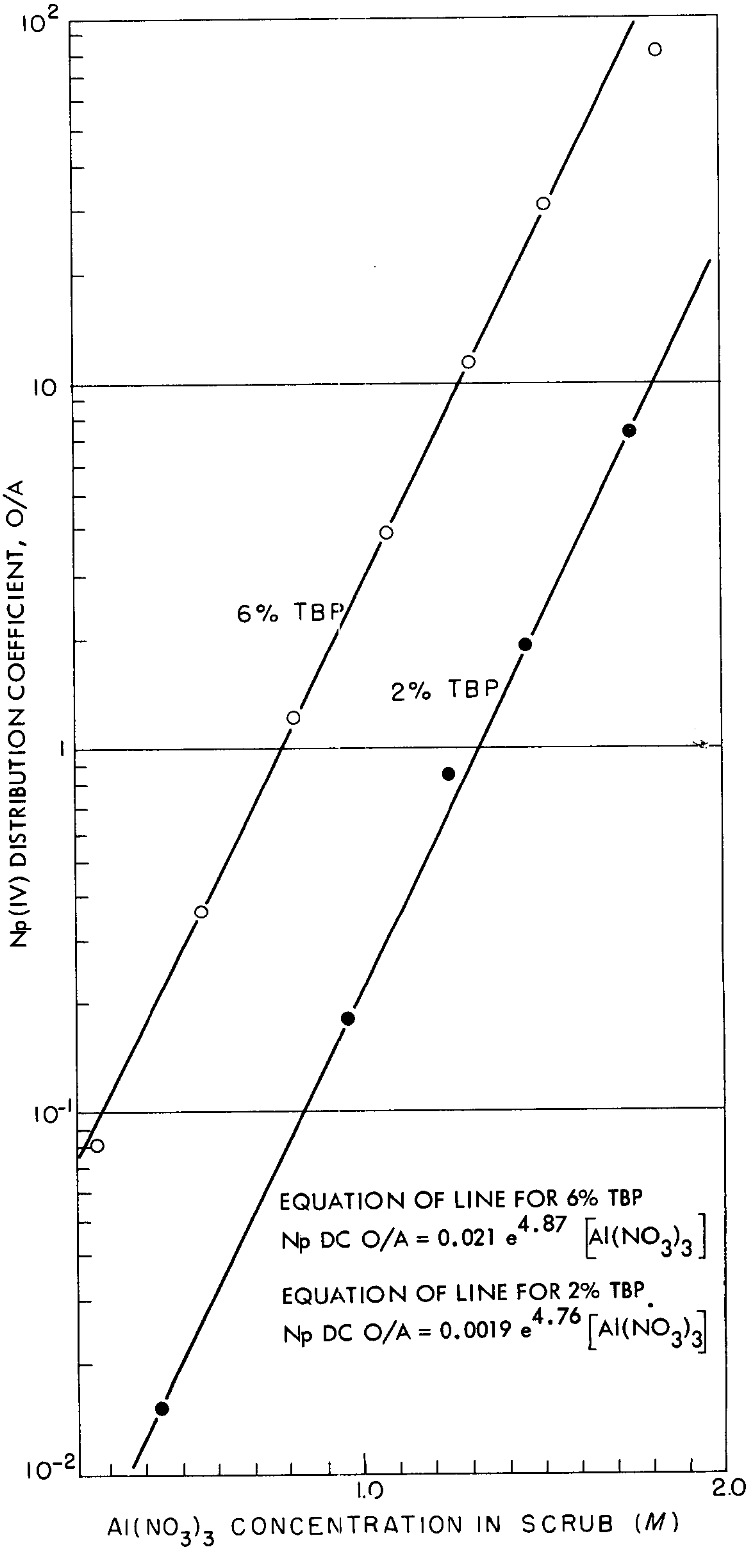

Fig. 7. Np(IV) Distribution Coefficient as a Function of $Al(NO_3)_3$ Concentration of Scrub (*M*).

to inhibit extraction of zirconium by formation of a complex, increased the zirconium decontamination factor by a factor of 10^3 without any noticeable effect on the extraction of neptunium or uranium (Table 4, Fig. 8).

4.3.4 Pulsed-column Tests of First-cycle Flowsheet

Tracer runs were made in 0.75-in.-dia pulsed columns to test the Neptex flowsheet in process equipment. In the first run less than 0.01% of either the uranium or the neptunium was lost to the extraction column aqueous waste; 1% of the neptunium and 0.1% of the uranium were found in the stripped solvent and 99% of the neptunium and uranium were in the IC column product. The loss to the solvent was due to a poor pulsing action in the IC column, which resulted in only one stripping stage; this defect was later corrected. The run lasted 11 hr and the feed contained no oxalic acid. The flow rates were set just below flooding conditions and provided one volume change per hour. A steady state with respect to uranium and neptunium was reached by the end of 4 hr.

In a second test conditions were the same as the first except that 0.01 M oxalic acid was added to both the feed and scrub. Results were the same as those of the first run except that the neptunium loss to the aqueous waste increased to 0.03%. This small increase may not be significant when compared with the larger zirconium decontamination factor obtained in the presence of oxalic acid.

Table 4. Effect of Oxalic Acid on Zirconium Decontamination Factor across the A-column

Batch countercurrent experiments
3 extraction; 4 scrub stages

Conditions of Addition of $H_2C_2O_4$	Zr-Nb γ Decontamination Factor in A-column[a]
0.01 M $H_2C_2O_4$ in feed only	1.3×10^4
0.01 M $H_2C_2O_4$ in scrub only	7.6×10^3
0.001 M $H_2C_2O_4$ in feed and scrub	3.0×10^3
0.005 M $H_2C_2O_4$ in feed and scrub	7.2×10^3
0.01 M $H_2C_2O_4$ in both feed and scrub	1.8×10^4

[a] Zirconium-niobium scan was used since insufficient sample available for separate zirconium determination.

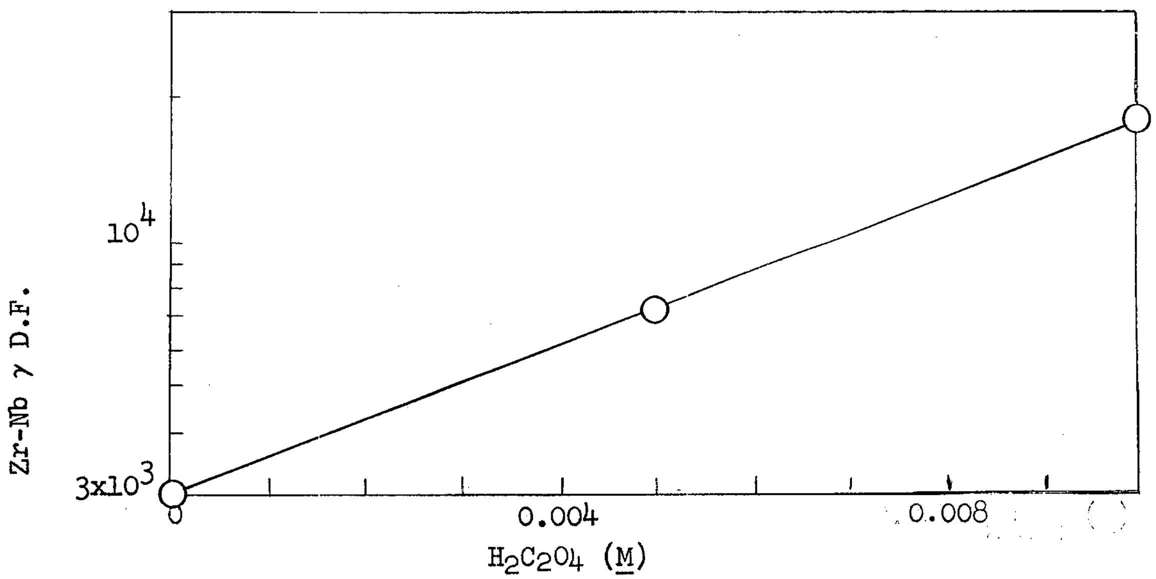

FIG. 8. EFFECT OF OXALIC ACID ON ZIRCONIUM-NIOBIUM γ DECONTAMINATION FACTOR IN A-COLUMN.

Part II. RECOVERY OF Np^{237} FROM FLUORINATION ASH

J. R. Flanary and J. H. Goode

5.0 FLOWSHEET FOR FLUORINATION ASH FEED

The accumulated fluorination ash from the UF_6 feed plant at the Oak Ridge Gaseous Diffusion Plant (about 5000 lb) was found to be a potential source of neptunium. In the fluorination of UF_4 to UF_6 a quantity of nonvolatile fluoride ash, with both uranium and ionic impurities (Table 8, Appendix), collects at the bottom of the fluorination tower. Additional ash is separated from the UF_6 in a cyclone collector and a barrier filter. The amount of neptunium in the ash, which had been carried along with the uranium through the solvent extraction and gaseous diffusion feed preparation processes, varied from as low as 0.05 g/ton at the bottom of the fluorination tower to as high as 75 g/ton in some lots which were collected in the barrier filter (Table 9, Appendix). A second solvent-extraction process was developed for the recovery of both the neptunium and depleted uranium from these fluorination residues.

The flowsheet for recovery and purification of Np^{237} and depleted uranium from K-25 fluorination ash provides for dissolution of the ash and one cycle of solvent extraction (Fig. 9). The ash is dissolved in boiling aluminum nitrate—nitric acid solution and refluxed 2-4 hr to coagulate and dehydrate silica. This provides a stable, nonemulsifying feed solution of high nitrate salting strength and maximum uranium and neptunium concentrations.

The uranium and neptunium are recovered in a battery of three pulsed columns arranged in cascade. In the first column they are coextracted (4 theoretical stages) from the feed with 15% tributyl phosphate (TBP) and scrubbed with aluminum nitrate—nitric acid solution to remove extracted impurities. The organic phase then flows to a

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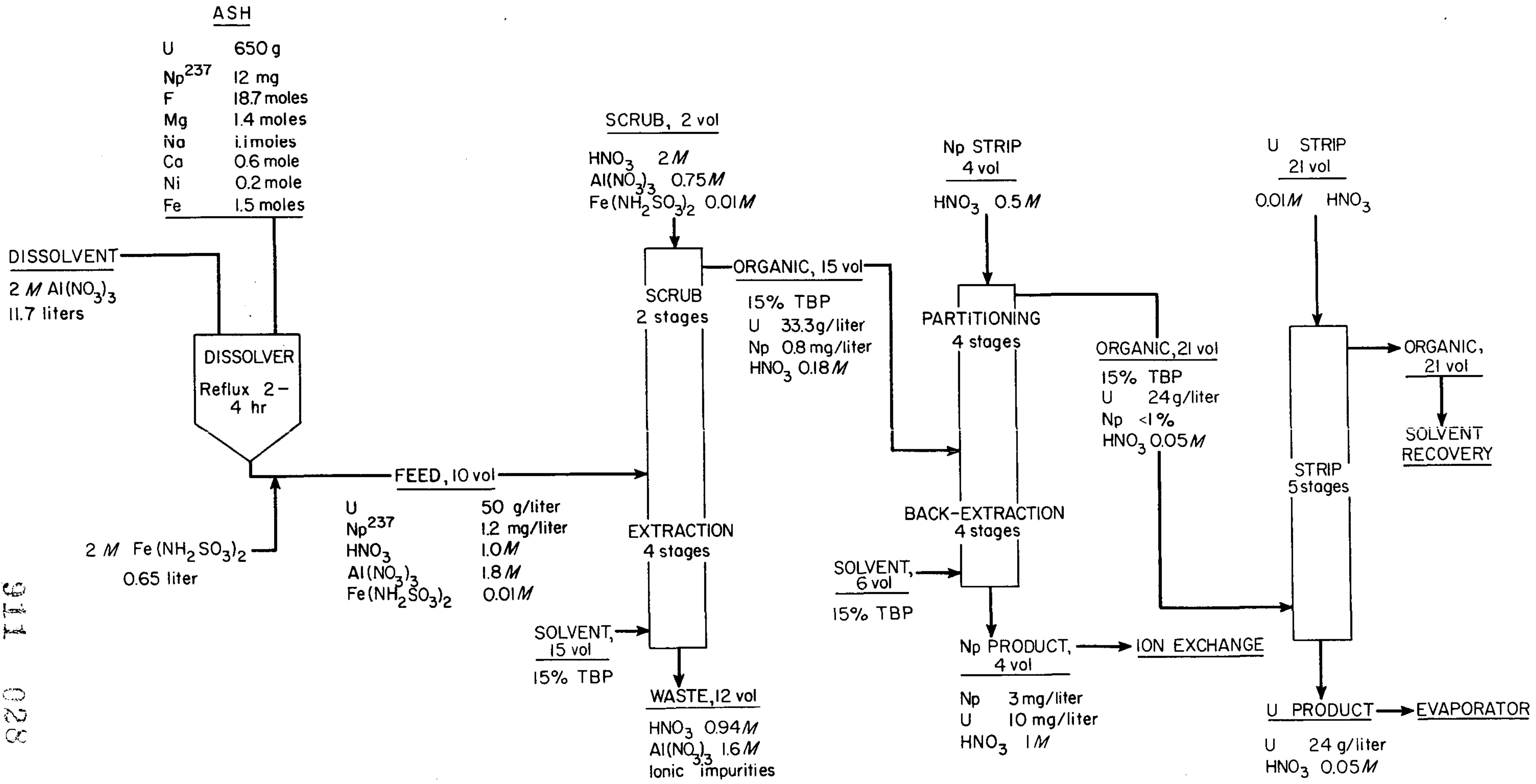

Fig. 9. Flowsheet for Recovery of Neptunium from K-25 Fluorination Ash. Basis: 1 kg of ash.

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second column where neptunium is preferentially stripped (4 theoretical stages) from the solvent with 0.5 M HNO_3. Finally, the organic phase flows to a third column where uranium is stripped with 0.01 M HNO_3 (5 theoretical stages).

In tests in 3/4-in.-dia pulsed columns the system operated successfully for 30 hr, with no interfacial precipitates or emulsions. Approximately 85 mg of Np^{237} and 4.55 kg of depleted uranium were recovered free of elemental impurities. Neptunium was separated from uranium by a factor of 2.4×10^3. The average flowing stream loss of uranium was 0.02%; neptunium in the waste streams was below the limits of analytical detection.

6.0 PULSED-COLUMN FLOWSHEET DEMONSTRATIONS

A number of test runs were made with K-25 fluorination ash in the 0.75-in.-dia pulsed-column equipment to demonstrate flowsheets developed in the laboratory in batch countercurrent experiments. In initial test runs nitric acid carryover from the extraction column in the solvent to the partitioning column failed to provide sufficient nitrate ion salting strength for adequate uranium re-extraction, resulting in excessive uranium contamination of the neptunium product. The acidity of the A-column scrub was increased from an initial 0.5 M HNO_3 to 2 M HNO_3 to achieve the optimum concentrations of 0.18 M HNO_3 in the solvent from the A-column and 1 M HNO_3 in the neptunium product. Under these conditions the uranium concentration in the neptunium product averaged about 0.040 mg/ml with 6 ft of back-extraction height. Batch countercurrent data showed that a uranium concentration of 0.01 mg/ml could be reached in 4 stages.

In an extended run, 6-12 hr was required to bring the neptunium to a steady state, while the uranium reached equilibrium in about

4 hr. After 12 hr of operation, the neptunium material balance (feed to product) was >99%. The uranium-neptunium separation factor was 2.4×10^3 under the following conditions:

Feed, 100 vol: 50 g U/l, 1.8 M $Al(NO_3)_3$, 1 M HNO_3, 0.01 M $Fe(NH_2SO_3)_2$

Scrub, 20 vol: 0.75 M $Al(NO_3)_3$, 2 M HNO_3, 0.01 M $Fe(NH_2SO_3)_2$

Extractant, 150 vol: 15% TBP

Back-extractant, 60 vol: 15% TBP

Np strip, 40 vol: 0.5 M HNO_3

U strip, 210 vol: 0.01 M HNO_3

Uranium losses were quite low, totaling 0.023%. Table 5 shows typical analytical data from flowing stream samples taken after 12 and 24 hr of operation with the above flowsheet.

Column operation also showed that a feed digestion step was necessary to prevent intolerable interfacial emulsions in all three columns. Undigested feed often resulted in column shutdowns due to failure of interface controls after only a few hours' operation. Digestion for 2-4 hr coagulated and dehydrated siliceous materials so that only the usual small amounts of dense solids formed at the interfaces. Runs as long as 30 hr were made without emulsion formation.

Approximately 85 mg of Np^{237} was recovered and purified in the process demonstration runs along with 4.55 kg of uranium. The average flowing stream loss of uranium was 0.02%; the neptunium loss was below the limit of analytical detection.

Table 5. Data from Extended Column Operation in Recovery of Neptunium from Fluorination Ash

Flowsheet: see Fig. 9

Flowing Stream	Composition					
	12 hr			24 hr		
	U (mg/ml)	HNO_3 (M)	Np (c/m/ml)	U (mg/ml)	HNO_3 (M)	Np (c/m/ml)
Organic from A-column	29.4	0.16	532	29.7	0.18	---
Aqueous from A-column	0.0015	0.99	0	0.0009	0.99	0
Np product from B-column	0.024	0.95	1432	0.060	0.89	1497
U product from C-column	13.7	0.08	11	16.6	0.07	0
Organic from C-column	0.001	<0.02	0	0.001	<0.02	0

7.0 EXPERIMENTAL WORK

7.1 Dissolution of Ash and Digestion of Feed

Dissolution of the ash in various reagents, including nitric acid, aluminum nitrate, and dibasic aluminum nitrate, was studied. Boiling aluminum nitrate—nitric acid mixtures appeared most satisfactory from the standpoint of solubility, chemical costs, and ease of handling. The simplest procedure consisted in adding 1 kg of ash to 13 liters of 1.8 M $Al(NO_3)_3$—1 M HNO_3, mixing, and digesting at the boiling point under full reflux for 2-4 hr. The digestion coagulated and dehydrated silica in the feed so that emulsions and column operational difficulties were minimized or eliminated. Lower concentrations of aluminum nitrate and nitric acid could also be used, and the final concentrations, 1.8 M $Al(NO_3)_3$ and 1 M HNO_3 for a uranium concentration of 50 g/liter, obtained by an evaporation-digestion step.

7.2 Solvent Extraction

7.2.1 IA (Extraction-Scrubbing) Column Conditions

Solvent Concentration. Since the ash dissolution procedure is expected to yield a feed containing approximately 50 g of uranium per liter, 15 vol % TBP in Amsco 125-82 was chosen as an optimum solvent concentration based on the complexing power of TBP for uranium and satisfactory organic/aqueous flow ratios for smooth column operation.

The conditions specified for A-column operation in the chemical flowsheet (Fig. 9) with respect to uranium and Np(IV) extraction and general operability were tested in a laboratory-scale batch countercurrent run. The results were highly satisfactory. Only two extraction stages were needed to reduce the uranium extraction loss to 0.01%. For Np(IV), the extraction loss after four stages was 0.7%. Uranium and neptunium reflux values in the scrub section were about 1 and 2%, respectively.

The feed for the experiment was prepared from dissolved ash and spiked with Np^{239} tracer. Four extraction and four scrub stages were used, and the operation was carried through five column changes. These conditions are normally sufficient to approach a steady state in solvent-extraction systems involving little reflux.

Uranium Saturation. In order to define A-column extraction conditions more closely, it was necessary to determine the effect on Np(IV) extraction of percentage saturation of the solvent by uranium. Batch equilibration data (Table 6) showed that Np(IV) extraction is favorable up to, but not appreciably above, 60% uranium saturation. At 60% uranium saturation the Np(IV) distribution coefficient is 1.9. From previous experience with 15% TBP systems, 60% uranium saturation of the solvent is known to be satisfactory for uranium extraction.

A 15 vol % solution of TBP containing 62.5 g of uranium per liter is saturated with uranium; a 60% saturated solution would therefore contain 40 g/liter. As the percentage saturation of the solvent with uranium increases, the uranium extraction coefficient slowly decreases. More important, the Np(IV) extraction coefficient decreases very rapidly. This is expected since, as the percentage uranium saturation increases, less and less uncomplexed TBP remains for neptunium extraction.

The equilibration data were obtained with synthetic feed spiked with Np^{239} tracer, containing 50 g of uranium per liter, 1.8 M $Al(NO_3)_3$, 1 M HNO_3, and 0.01 M ferrous sulfamate. Aliquots of this feed (25 ml) were batch-extracted with 20 to 50 ml of solvent. The uranium and Np(IV) extraction coefficients were calculated from analyses of the organic and aqueous phases after equilibration.

7.2.2 IB (Partitioning) Column Conditions

The data from a series of batch equilibrations (Table 7) indicate that an aqueous phase concentration of 1 M HNO_3 should be near optimum for separation of neptunium and uranium. At this concentration the neptunium extraction coefficient is low, 0.05, while that of uranium is 1.5. This condition is favorable for back-extraction of uranium. The aqueous strip volume can be as low as 1/5 or 1/6 of the organic phase volume, permitting about threefold concentration of the neptunium. Five volume changes were sufficient for close approach to steady state. After four stripping stages the neptunium loss was 1.1%, and after four back-extraction stages the aqueous neptunium product contained 0.01 g of uranium per liter, showing a separation factor of 2.1×10^4. Under these conditions, with ash containing 12 g of neptunium per ton, the product U/Np weight ratio would be about 3/1, and further processing, e.g., by solvent extraction or ion exchange, would be needed to complete the separation.

For these tests, aqueous feed containing 50 g of uranium per liter, 1.8 M $Al(NO_3)_3$, and 1 M HNO_3 was spiked with Np^{239}, reduced with ferrous sulfamate, and extracted with 1.5 vol of 15% TBP. It is assumed that the neptunium remains in the tetravalent state in the B-column, and no holding reductant is used.

The organic phase, containing 35 g of uranium per liter, 0.10 M HNO_3, and Np(IV), was blended with 0.3 vol of additional solvent to simulate the organic phase at the feed stage. Aliquots of the organic phase were equilibrated for 3 min with 1/6 volume of aqueous neptunium strip solution, 0.1-5 M in HNO_3. After separation, the organic and aqueous phases were analyzed for uranium, neptunium, and nitric acid.

7.2.3 IC (Stripping) Column Conditions

After the neptunium is stripped from the solvent stream, the solvent is cascaded into the C-column where the uranium is stripped into 0.01 M HNO_3. With equal volumes of strip solution, five stripping stages were needed to reduce the uranium loss to 0.01%. The stripped solvent is reconditioned by washing with dilute sodium carbonate and nitric acid and returned to process.

Table 6. Effect of Percentage Uranium Saturation of 15% TBP on Np(IV) Extraction

Aqueous feed: 50 g U/l, 1.8 M $Al(NO_3)_3$, 1 M HNO_3, 0.01 M
$Fe(NH_2SO_3)_2$, 1.8 x 10^7 Np^{239} γ c/m/ml

Solvent: 15% TBP in Amsco 125-82

25-ml aliquots of feed equilibrated 3 min with 20-50 ml of solvent

Solvent/Aqueous Volume Ratio	Uranium Saturation of Solvent (%)	Uranium Concentration in Solvent (g/liter)	D.C., O/A	
			U	Np
0.8	86.5	54	5.7	0.15
1.0	72	45	22.5	0.72
1.2	61	38	54	1.93
1.4	54	34	103	3.81
1.6	50	31.3	130	5.64
1.8	45.5	28.5	158	6.55
2.0	36	22.5	187	10.5

Table 7. Neptunium Separation from Uranium with Nitric Acid in the 15% TBP System

B-column solvent phase: 15% TBP in Amsco 125-82, 28 g U/l,
0.08 M HNO_3, Np^{239} tracer

Organic/aqueous vol ratio: 6/1

Equilibration time: 3 min

HNO_3 Strip Solution (M)	Distribution Coefficient, O/A		Separation Factor U D.C./Np D.C.
	Uranium	Neptunium	
0.1	0.8	0.02	40
0.5	1.1	0.03	37
1	1.5	0.05	30
3	4.9	0.2	24
5	7.5	0.4	19

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9.0 APPENDIX

Table 8. Chemical Analyses of Initial Samples of Fluorination Ash from the K-25 UF_6 Feed Plant

Component	Sample Composition (wt %)	
	B-Tower Cyclone	B-Tower Barrier Filter
U	29.50	46.70
Fe	8.55	0.09
F	35.54	24.61
Ni	0.87	0.79
Ca	2.52	1.91
Mg	3.28	2.37
Na	2.06	2.57
	82.4[a]	79.1[a]
PO_4	330 ppm	225 ppm
SiO_2	524 ppm	240 ppm
Np^{237}	12.7 g/ton	34.5 g/ton

[a] Remainder probably oxygen and water.

Table 9. Np^{237} Analyses for Typical Batches of Fluorination Ash

Batch Number	Np^{237} α (c/m/g Ash)	Np^{237} g/ton[a]	Total Wt of Ash (kg)	Total Np^{237} (g)
BF-1	2.21×10^3	2.73	---	---
F-3	43	0.05	---	---
F-171	1.07×10^4	13.2	101.4	1.34
F-231	2.63×10^3	3.24	18.2	0.06
F-281	1.25×10^4	15.4	356.4	5.49
F-619	195	0.24	65.5	low
F-708	8.49×10^3	10.5	15.9	0.17
F-760	1.37×10^3	1.69	25.5	0.04

[a] Calculated on basis of 8.1×10^5 α c/m/mg Np^{237}.