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NEPTUNIUM BEHAVIOR IN SOLVENT EXTRACTION OF URANIUM AT SAVANNAH RIVER PLANT

[redacted]

by
H. E. Henry, D. G. Karraker, and C. S. Schlea
Separations Chemistry Division

September 1961

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ABSTRACT

The solvent extraction behavior of neptunium in the processing of irradiated natural uranium (Purex process) and irradiated enriched uranium (HM process) at Savannah River was studied in the laboratory. Conditions were demonstrated for extracting neptunium in the first solvent extraction contactor of each process, and two methods were developed for partitioning neptunium from uranium in the HM process.

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NEPTUNIUM BEHAVIOR IN SOLVENT EXTRACTION OF URANIUM AT SAVANNAH RIVER PLANT

INTRODUCTION

Several methods were investigated at the Savannah River Laboratory as possibilities for the recovery of neptunium during the processing of irradiated natural uranium (Purex process) or irradiated enriched uranium (HM process), and the results of these studies are reported here.

In the Savannah River production reactors, Np^{237} is produced by the following reactions:

$$U^{238} \xrightarrow{(n,2n)} U^{237} \xrightarrow{\beta^-} Np^{237} \qquad (1)$$

$$U^{235} \xrightarrow{(n,\gamma)} U^{236} \xrightarrow{(n,\gamma)} U^{237} \xrightarrow{\beta^-} Np^{237} \qquad (2)$$

Reaction (1) is the principal source of Np^{237} from the irradiation of natural uranium; reaction (2) predominates with enriched U^{235} fuel.

In the recovery of neptunium the first step is the isolation of a crude fraction of neptunium at some point in the solvent extraction process. This fraction is then purified in subsequent process steps. The design of the over-all recovery process involves the selection of the method for isolating neptunium from the solvent extraction process as well as the selection of the method for final purification. The numerous factors that are involved in these selections are not discussed in detail in this report. Rather, emphasis is placed on the solvent extraction behavior of neptunium with the intent of developing information that permits the routing of neptunium to that point in the process that is most advantageous for recovery under any given set of conditions. For example, in some instances it may be desirable to route neptunium directly to the aqueous effluent from the first solvent extraction contactor (1A bank), and then to recover neptunium from this "waste" after evaporation. Under different circumstances it may be advantageous to extract neptunium in the 1A bank and to separate the extracted neptunium from the other actinides at a subsequent stage in the process.

Hanford[1] has reported work on the recovery of neptunium by solvent extraction in the Purex process operated there. Solvent extraction flowsheets were suggested by the Oak Ridge National Laboratory (ORNL) for recovery of neptunium from the Purex process[2,3,4], and several special solvent extraction processes were developed for neptunium purification[3,4,5]. The recovery of neptunium from the ORNL process for recovery of irradiated enriched uranium was also reported.

The objective of the work reported here was to develop special conditions that would apply to Savannah River processes, equipment, and operating practices.

SUMMARY

A study was made of the solvent extraction behavior of neptunium in the Purex process and in the enriched uranium (HM) process at the Savannah River Plant. The objective of this study was to demonstrate conditions in the solvent extraction processes that would permit routing the neptunium to points that would be advantageous for subsequent isolation and purification.

In the Purex process, in which the majority of the neptunium is normally directed to the aqueous waste from the first solvent extraction contactor (1A bank), conditions were demonstrated for extracting the neptunium with the uranium and plutonium in the 1A bank or for refluxing the neptunium in the bank. Neptunium was extracted by adjusting the concentration of nitrous acid so that Np(VI) was present in the bank, and by adjusting the saturation of the solvent in the scrub section to prevent the reflux of nitrous acid which leads to reduction of Np(VI) to Np(V). Neptunium that was extracted in the 1A bank followed uranium through the first extraction cycle under normal process conditions. Neptunium was refluxed in the 1A bank by adding ferrous sulfamate to produce Np(IV) in the extraction section and by maintaining a high saturation in the solvent to prevent the extraction of Np(IV) in the scrub section.

Neptunium is normally extracted in the 1A bank of the HM process. In the second extraction cycle the final distribution of neptunium is about 10-25% in the aqueous waste from the 1A bank, about 50-60% in the aqueous waste from the 1D bank, and about 25-30% in the final uranium product. Conditions were demonstrated for increasing the extraction of neptunium as Np(IV) in the 1A bank and for partitioning the extracted neptunium from uranium in the 1B bank. The addition of ferrous sulfamate to the feed improved the extraction of neptunium, and an increase in the solvent flow resulted in a further improvement. In a 1B bank, neptunium was successfully stripped into 4M nitric acid; less than 2% of the neptunium remained with the uranium and less than 0.07% of the total uranium accompanied the neptunium. Conditions were also demonstrated for extracting and partitioning neptunium as Np(VI); however, this method of operation does not permit the required separation of uranium from plutonium in the first cycle.

If it is not feasible to partition neptunium from uranium in a 1B bank, it is necessary to control the route of neptunium in the second cycle of solvent extraction. Conditions were adjusted in the second cycle so that neptunium was routed to either the final uranium product or the aqueous waste from the first contactor (1D bank). Neptunium was routed to the aqueous waste by reducing the normal acidity of the scrub solution, and was routed to the uranium product by adding Ce(IV) to produce Np(VI) in the bank.

As in the Purex process, the selection of a method for the recovery of neptunium from the HM process depends on a number of factors, including constraints placed upon the process by other requirements and upon the availability of equipment for final purification. The demonstrated ability to control the route of neptunium in the solvent extraction processes is an important advantage in selecting the best over-all process for recovery and purification.

DISCUSSION

The extraction of neptunium in the solvent extraction processes depends upon the processing conditions, and the valence state of neptunium under these processing conditions. Neptunium is extractable in two valence states: Np(IV), which is about 1/5 as extractable as Pu(IV); and Np(VI), which is about as extractable as Pu(IV). Under normal process conditions, Fe(II) will reduce Np(V) and Np(VI) to Np(IV) and maintain this valence state; Np(VI) can be maintained by strong oxidizing agents such as Ce(IV), MnO_4^-, $Cr_2O_7^=$, and under special conditions by HNO_2-HNO_3. Thus, the problem of extracting neptunium in either solvent extraction process can be resolved into adjusting process conditions to extract either Np(IV) or Np(VI), and then taking the necessary measures to maintain neptunium in the proper valence state.

EXPERIMENTAL PROCEDURE

The solvent extraction process under investigation was operated in miniature mixer-settlers to determine the path of neptunium under varying process conditions. Similar equipment and run procedures were previously described.[6,7] In these experiments, no significant level of fission products was present, and the effect of the process changes on fission product decontamination was not determined. Two different isotopes of neptunium were used: Np^{239} in experiments with the Purex process, and Np^{237} in experiments with the HM process. Np^{239} was measured analytically with a gamma scintillation spectrometer, and Np^{237} was measured by standard alpha counting techniques.

To produce the feed solution for studies of the Purex process, UO_3 was irradiated for 2 to 10 kwh in the SRL Standard Pile. The U^{239} produced by the pile irradiation was allowed to decay to Np^{239}, and the irradiated material was dissolved in nitric acid. Silver iodide was precipitated from this solution to remove the 8-day I^{131} and to avoid interference of the I^{131} gamma with the Np^{239} gamma during the determination of neptunium. After filtration to remove the AgI precipitate, the solution was adjusted to the proper concentrations of acid and uranium for Purex feed.

Feed for experiments on the HM process was made by dissolving uranyl nitrate and aluminum nitrate in dilute nitric acid and adding a nitric acid solution of Np^{237}.

PUREX PROCESS

GENERAL

In the Purex process at the Savannah River Plant, Np^{237} is normally discharged in the aqueous waste stream (1AW) from the initial mixer-settler bank (1A bank) (see Figure 1). Recovery of neptunium from this waste stream can be accomplished by an anion exchange process; however, this waste stream contains virtually all the fission products and requires a maximum effort to decontaminate and purify neptunium by anion exchange. Two methods for improvement of this process were studied: (1) the extraction of the neptunium with uranium in the 1A bank to permit the eventual separation from a second solvent extraction cycle waste concentrate by anion exchange; and (2) the accumulation of neptunium in the 1A bank by reflux, the periodic removal of neptunium from the bank in the aqueous waste, and recovery of neptunium from this waste stream. The advantage of the first method is that the fission product level is decreased by a factor of about 10^3 before anion exchange processing, thus simplifying the processing required. The second method achieves a separation of neptunium from fission products in the solvent extraction process, and also decreases the volume of solution to be processed by the anion exchange by a factor of 5 to 10.

EXTRACTION OF Np(VI) IN THE 1A BANK

The extraction of Np(VI) in the 1A bank depends upon oxidizing neptunium to Np(VI) and adjusting the extractant flow so that Np(VI) is extracted. The oxidizing agents investigated were nitric acid catalyzed by HNO_2, and Ce(IV). Prior studies at Hanford[1] showed that the addition of 10^{-3}M HNO_2 as a catalyst to the extractant stream (1AX) and elimination of HNO_2 from the feed stream (1AF) permitted excellent extraction of neptunium. These results were in accord with the study of Siddall and Dukes[8], who found that low concentrations of HNO_2 catalyzed the oxidation of Np(V) to Np(VI) but that higher concentrations of HNO_2 reduced Np(VI) to Np(V). Oxidation by Ce(IV) was investigated to determine the behavior of Np(VI) when no HNO_2 was present.

In the solvent extraction tests two mixer-settler banks, of 16 and 12 stages, were connected to simulate a 28-stage 1A bank. The organic stream from the 1A bank was fed to the center of a 16-stage 1B bank and was then stripped in a 16-stage 1C bank (Figure 2), as in the normal Purex process. The 1A and 1B banks (Figure 2) were operated at 35°C, and the 1C bank at 45°C. The process flowsheet for these tests is shown in Table I.

TABLE I

Purex Test Flowsheet

Stream	Relative Flow	Process Entry	Composition
1AF	100	1A-13	1.5M UNH, 1-2M HNO_3, 5×10^5 γ c/(min)(ml) of Np^{239}
1AS	76.5	1A-1	3M HNO_3
1AS'	(a)	1A-27	(b)
1AX	340-480(a)	1A-28	30% TBP
1BS	83.3	1B-16	30% TBP
1BX	50	1B-1	0.1M HNO_3, 0.04M $Fe(SO_3NH_2)_2$
1CX	710	1C-1	0.05M HNO_3

(a) Flow adjusted as process variable
(b) Composition adjusted as process variable

The results of these tests are summarized in Table II.

TABLE II

Extraction of Neptunium in Purex Process

1AS' Composition	1AS' Relative Flow	1AX Relative Flow	Organic Phase (1AP) Saturation, %	Np, % of Total in Feed	
				1CU	1AW
0.01M $NaNO_2$	37.8	378	73	-	20(a)
0.01M $NaNO_2$	40	400	70	72	28
0.01M $NaNO_2$	44	440	63	93	7
0.01M $NaNO_2$	48	480	58	100	-
0.1M $Ce(NO_3)_4$	21	386	72	100	-
No 1AS' Fed	-	378	73	4	20(a)
No 1AS' Fed	-	420	66	16	60(a)

(a) Neptunium was accumulating in the 1A bank by reflux; steady-state conditions were not reached in the end streams.

The results of the tests with $NaNO_2$ are in agreement with the results obtained in similar experiments at Hanford: Np(VI) was produced in the 1A bank by the HNO_2-catalyzed oxidation of Np(V) by HNO_3 and was recovered with the uranium when the saturation of the extractant with uranyl nitrate was about 65% or less. In the absence of nitrous acid, neptunium extraction was poor because the principal species present were Np(V) and Np(IV). The extraction of Np(VI) with Ce(IV) as the oxidant indicates clearly that inability to recover Np(VI) from a saturated (75%) organic phase was not caused by a low Np(VI) distribution coefficient. Complete recovery was obtained with Ce(IV) as an oxidizing agent at 72% saturation; with HNO_2-HNO_3 as oxidant, there was essentially no extraction of neptunium at 72% saturation. The probable explanation for this result is that high saturation conditions cause the reflux of HNO_2 at the feed point, and HNO_2 accumulates until its concentration is high enough to reduce Np(VI) to Np(V) by the reaction

$$2NpO_2^{++} + HNO_2 + H_2O \longrightarrow 2NpO_2^{+} + NO_3^{-} + 3H^{+}$$

The conditions for extraction of Np(VI) with HNO_2 present requires low enough saturation in the scrub section to prevent reflux of HNO_2. Ce(IV) can be used to recover Np(VI) with any operable Purex process, since Ce(IV) oxidizes HNO_2 to HNO_3, and prevents the accumulation of HNO_2. Np(VI) should be recovered under any process conditions that will recover Pu(IV).

These tests also showed that when neptunium was extracted in the 1A bank, it followed the uranium through the 1B bank and was stripped with the uranium into the 1CU stream. Np(VI) is reduced to Np(IV) by Fe(II) in the 1B bank. Np(IV) is sufficiently extractable to be recovered with uranium in the 1B bank, but is stripped out of the organic phase with dilute acid in the 1C bank. Conditions in the 1B bank can be altered to route the neptunium with the plutonium product stream (1BP); a higher 1BX flow and a lower 1BS flow will accomplish this. Under the conditions used in these tests, however, no neptunium was found in the 1BP product stream.

REFLUX OF Np(IV) IN THE 1A BANK

A second scheme for neptunium recovery from the Purex process is to reflux neptunium in the 1A bank by adjusting conditions to extract Np(IV) in the extraction section of the bank while maintaining a high uranium saturation in the organic phase to prevent the extraction of Np(IV) in the scrub section. After the desired amount of neptunium has been accumulated, fission products can be flushed from the bank by feeding an inactive uranyl nitrate solution, and the neptunium can be removed from the bank in either the 1AP or the 1AW by an appropriate change in oxidation state. Neptunium can then be recovered from the first or second cycle aqueous waste streams by anion exchange.

The test of this process was made with the basic Purex flowsheet (Table I); a 1AX flow of 368 corresponded to 75% saturation of the organic phase. Np(IV) was produced in the extraction section by introducing a stream of 0.25M $Fe(SO_3NH_2)_2$ (relative flow, 24.2) into the 1A bank at stage 20, 7 stages below the feed stage. The process was operated under these conditions until about 70 bank throughputs of the aqueous streams (1AF and 1AS) had flowed through the extraction section. Analysis of the end streams at this point showed a loss of 14% of the neptunium in the feed to the aqueous waste (1AW) and 4% to the 1CU. Samples of the organic phase in the 1A bank (Figure 3) showed that neptunium concentrations 120 times greater than feed concentration were reached by the end of the experiment. Sufficient samples were not taken to measure the total neptunium loss during the run, but a linear interpolation indicates a loss of 7% of the total neptunium to the 1AW, and 2% to the 1CU. This experiment was performed under conditions of low efficiency for mass transfer; samples showed that the stage efficiency was about 30-35%, rather than the normal 85-95%. With normal stage efficiencies, it is probable that the loss of neptunium to both end streams would be substantially less.

This method for concentrating neptunium requires further laboratory investigation before it is used in a separations plant. The chief items requiring investigation are the effect of Np(IV) on plutonium recovery, and the effects of HNO_2 (introduced with the feed) on the loss of neptunium. Demonstrations of the methods for removing neptunium from the bank are also desirable. Experiments with this method, in which there is no steady state, are necessarily long, and development has not been completed. The method is presented in this report because of its novelty and potential value as a plant process.

HM PROCESS

GENERAL

In the HM process (Figure 4) 75-90% of the neptunium is normally recovered in the first cycle with the uranium product (1CU) stream. During the purification of the uranium in the second solvent extraction cycle, the neptunium divides, one-third following the uranium into the final uranium product, and two-thirds following the aqueous waste (1DW) stream. The objectives of the laboratory studies were to extract all the neptunium in the 1A bank, and to direct the extracted neptunium through solvent extraction to a single stream. To achieve these objectives, the first cycle required modification to increase the extraction of neptunium, and a further modification of the process was necessary, either to partition neptunium from uranium in the first cycle or to divert the neptunium in the second cycle so that it followed either the 1DW stream or the uranium product. A restriction on the possible process changes was that process modifications should not prevent the removal of plutonium from uranium in both cycles of solvent extraction. A variety of

tests were made, and the success of most of these tests allows considerable choice of a method for neptunium recovery from the HM process.

EXTRACTION OF NEPTUNIUM IN THE 1A BANK

The feed (1AF) stream to the 1A bank contains Np, probably as a mixture of Np(VI) and Np(V). The scrub section (1AS) contains Fe(II) to reduce Pu(IV) to the inextractable Pu(III) and permit its separation from uranium. The reducing conditions assure that Np(IV) will be the predominant species in the organic (1AP) stream leaving the bank. Conditions were tested for the extraction of either Np(VI) or Np(IV) in the 1A bank. The tests involved modifications of the standard HM process flowsheet (Table III) in miniature mixer-settler equipment.

TABLE III

HM Flowsheet, 1A Bank

Stream	Relative Flow	Composition
1AF[a]	100	1.2M $Al(NO_3)_3$, 0.5M HNO_3 2.9 g U/l, 10 mg Np/l
1AS[a]	35	1.2M $Al(NO_3)_3$, pH 1.3
1AX	210	2.5% TBP in "Ultrasene"

(a) Oxidizing or reducing agents were added to these streams for control of Np valence.

The valence of neptunium was controlled with appropriate oxidizing and reducing agents - Fe(II) to produce Np(IV), Ce(IV) to produce Np(VI). The tests with Np(IV) were successful in extracting most of the neptunium, and in the tests with Np(VI) virtually all the neptunium was extracted. Results are shown in Table IV, and stage profiles for the neptunium concentration in the organic phase are shown in Figures 5 and 6.

TABLE IV

Extraction of Neptunium in 1A Bank in HM Process

Oxidizing or Reducing 1AF	Composition 1AS	Temp., °C	Np, % of Total in Feed 1AW	1AP
-	0.04M $Fe(SO_3NH_2)_2$	45	40	60
0.01M $Fe(SO_3NH_2)_2$	0.01M $Fe(SO_3NH_2)_2$	30	12	88
0.01M $Fe(SO_3NH_2)_2$	0.01M $Fe(SO_3NH_2)_2$	52	28	72
0.03M Ce(IV)	-	52	<2.5	~100
0.0003M Ce(IV)	0.04M $Fe(SO_3NH_2)_2$	50	45	55

Tests showed that extraction of Np(IV) was improved by adding Fe(II) to the feed solution, presumably because the rate of reduction of Np(V) by Fe(II) in the bank was not rapid enough to prevent loss to the aqueous waste. A test with Ce(IV) in the feed and Fe(II) in the 1AS gave identical results as would be predicted considering that Np(VI) must be reduced through Np(V) to Np(IV) for its recovery. Np(IV) distribution coefficients of about 0.6 in the extraction section of the bank (stages 8 to 16) and 0.18 or greater in the scrub section (stages 1 to 8) were measured in the run at 52°C; these are consistent with the observed losses.

When Ce(IV) was used as the oxidant, the extraction of Np(VI) in the 1A bank was essentially quantitative; distribution coefficients for Np(VI) were greater than one throughout the bank. However, these conditions cannot be applied to the HM process without other changes to prevent the recovery of plutonium with uranium.

Increasing the temperature to 52°C, when Fe(II) was added to both the 1AS and 1AF, decreased the extraction of Np(IV). Distribution measurements showed an increase in the extraction of Np(IV) from synthetic feed solution as the temperature was increased, but there was also a decrease in the extraction from the scrub (1AS) solution (Figure 7). The distribution coefficient for Np(IV) from 1AS solution was obtained by extrapolation of data obtained at lower temperatures and from the distribution coefficient obtained from the miniature mixer-settler run at 52°C. The extrapolation is shown in Figure 8. The distribution coefficient of 0.09 at 60°C is in accord with the extraction of neptunium that was observed during a plant test of operation at 60°C.

To permit calculation of the effect of process variations without repeated miniature mixer-settler runs, distribution coefficients for Np(IV) were measured in the laboratory under conditions applicable to the HM process. These data are shown in Figures 7 through 12.

It was concluded that increased extraction of Np(IV) in the 1A bank can be achieved by adding Fe(II) to the feed solution and by increasing the flow of solvent or the concentration of TBP in the solvent. The measured distribution coefficients of Np(IV) between aluminum nitrate solutions and 2-3.5% TBP indicate that a 30% increase in the flow of the solvent (1AX) or a 30% increase in the TBP concentration should give essentially 100% extraction of Np(IV).

PARTITION OF NEPTUNIUM FROM URANIUM IN THE 1B BANK

The partitioning of extracted neptunium from uranium in a 1B (partition) bank depends upon providing extraction conditions in the bank to retain uranium in the solvent and to strip neptunium from the solvent into the aqueous phase. The distribution coefficients of uranium and Np(IV) between 4M HNO_3 and 2.5% TBP are 1.3 and 0.04,[e] respectively, indicating that a satisfactory partition could be obtained. Additional distribution data for uranium, showing the effects of HNO_3, TBP, and temperature are shown in Figures 13, 14, and 15.

TABLE V

Partition of Np(IV) from Uranium in 1B Bank

Stream	Flow (1AF = 100)	Composition
1AP (organic stream from 1A bank)	210-270	2.5% TBP, 1.5 g/l U, 5 mg/l Np
1BX	70	4M HNO_3
1BS	250	2.5% TBP

In miniature mixer-settler tests, Table V, Np(IV) was successfully stripped into 4M HNO_3 and separated from uranium. The loss of neptunium to the uranium (organic) stream was less than 2% at 35°C, and the aqueous neptunium product stream contained less than 0.07% of the total uranium.

When Np(VI) was extracted in the 1A bank, the extracted Np(VI) was successfully partitioned from uranium in the 1B bank by adding 0.1-0.2M $NaNO_2$ to the 1BX to reduce Np(VI) to the inextractable Np(V). Because HNO_2 is extracted into the solvent, it is probable that a smaller quantity of $NaNO_2$ added near the feed stage of the bank would have been just as effective. Under the conditions tested, about 97% of the Np(VI) was reduced and recovered in the aqueous stream. With no sodium nitrite added, nearly all the neptunium followed the uranium stream through the 1B bank.

EXTRACTION OF NEPTUNIUM IN THE 1D BANK

The extraction of neptunium with the uranium in the 1D bank was tested with the intent of permitting the later separation of neptunium from the uranium product by cation exchange. The easiest method for recovering neptunium depends upon maintaining neptunium as Np(VI); the extraction of Np(VI) by 7.5% TBP is sufficient (distribution coefficient is 1.3 in 3M HNO_3) to assure virtually complete extraction. The extraction of Np(VI) was tested in miniature mixer-settlers; Ce(IV) and HNO_2 were used to maintain Np(VI). Extraction was quantitative when Ce(IV) was used as an oxidant, but was only about 85% when HNO_2 was used.

The feed solution for the mixer-settler tests contained 3.2 g U/l, 4.1M HNO_3 and about 10^4 α d/(min)(ml) of Np^{237}. The mixer-settler experiments were performed by operating the process with Ce(IV) as an oxidant until steady-state concentrations of neptunium were reached in the end streams, sampling the organic phase in all stages of the 1D bank, and then operating to steady-state conditions with nitrous acid as an oxidant. The flowsheets for the tests are given in Table VI.

TABLE VI

Test Flowsheet, 1D Bank

Stream	Relative Flow	Enters 1D Bank at Stage	Composition	Temp., °C
1DF	100	8	3.2 g U/l, 4.2M HNO_3 1.1×10^4 α d/(min)(ml) of Np(V)	
1DS	48	1	1.2M HNO_3	
1DX	286	16	7.5% TBP	
Tests with Oxidizing Agent				
Test No. 1	26	9	0.2M Ce(IV), 4.2M HNO_3	35
2	28.6	14	0.005M $NaNO_2$, 4.2M HNO_3	42
3(a)	28.6	14	0.01M $NaNO_2$, 4.2M HNO_3	35

(a) 1DS 2M HNO_3

The test of Ce(IV) as an oxidizing agent was quite successful; loss of neptunium to the 1DW was below detectable limits. Supplementary experiments indicated that 10^{-3}M Ce(IV) is sufficient to stabilize Np(VI) long enough to permit its extraction in the 1D bank. Distribution data are shown in Figure 16 and a stage profile for Np(VI) in the organic phase is shown in Figure 17.

The oxidation of Np(V) to Np(VI) by HNO_2-HNO_3 was not as successful; 85% recovery of neptunium was obtained with concentrations of 10^{-3}M and 5×10^{-4}M HNO_2 in the organic phase. Stage samples (Figures 18 and 19) showed that there was some reflux of neptunium in the organic phase. The poorer recovery of neptunium is believed to be the result of the slow rate of oxidation of Np(V) to Np(VI) by HNO_2-HNO_3; the half-time for the oxidation is about 7 minutes at 35°C in 3M HNO_3[8]. From this rate and a residence time of 3 minutes per stage, a pseudo-extraction factor of 1.4 was calculated. The predicted neptunium loss for an extraction factor of 1.4 is about 13%, in reasonable agreement with the experimental loss of 15%. Assuming this explanation is correct, the rate of oxidation could be increased by raising the operating temperature, thus leading to increased recovery.

This processing scheme was not considered for use in the Plant because other factors led to the need for increased separation of plutonium from uranium in the 1D bank, and the addition of oxidants to the bank precludes this separation. It is probable that cation exchange separation of neptunium from uranium would also separate plutonium from uranium.

PARTITION OF NEPTUNIUM FROM URANIUM IN THE 1D BANK

The normal 1D bank flowsheet uses reducing conditions to complete the partition of plutonium from the recovered uranium. Under such conditions, neptunium is present as Np(IV). The effect of scrub (1DS) acidity on the behavior of neptunium in the 1D bank was calculated from extrapolated distribution data. The calculated results agreed well with data obtained in plant operation and indicate that a satisfactory partition of neptunium from uranium can be obtained in the 1D bank at low scrub (1DS) acidity. The flowsheet used for these calculations was as follows.

Stream	Relative Flow	Composition
1DF	100	4.1M HNO_3
1DS	56	0.8-1.5M HNO_3
1DX	330	7.5% TBP

The calculated recovery of neptunium at three different 1DS acidities is tabulated in Table VII below, together with representative data from the plant operation.

TABLE VII

Partition of Np(IV) from Uranium in 1D Bank

1DS Acid Concentration, M	Per cent of Total Np in Aqueous Waste		Per cent of Total Np in Uranium Product	
	Calc.	Plant	Calc.	Plant
0.80	99.5	96(a)	0.5	4(a)
1.2	77	70	23	30
1.5	23	-	67	-

(a) This value may not represent steady-state operation; the trend of the data was toward a lower percentage of neptunium in the uranium product.

The calculations indicated a substantial reflux of neptunium at about the middle of the 1D bank with the peak concentration at the seventh stage from product end of the bank (Figure 20). The inventory of neptunium in the bank, in both phases, is 3-to-7-fold greater than the feed concentration.

These calculations show that relatively minor changes in the flowsheet could achieve an adequate partition of neptunium from the uranium, and indicate that the conditions could be adjusted (higher acidity in feed, higher solvent flow) for essentially complete extraction of neptunium. The changes required to partition neptunium from uranium,

according to plant experience, would tend to improve the decontamination performance and increase the inventory of uranium in the bank; the process changes required to extract neptunium with the uranium would tend to decrease both the decontamination performance and the bank inventory of uranium. The usefulness of either partition or extraction in the 1D bank depends upon the other constraints placed upon the process, but both methods have the advantage of achieving the goal of removing neptunium without requiring an expenditure for new capital equipment.

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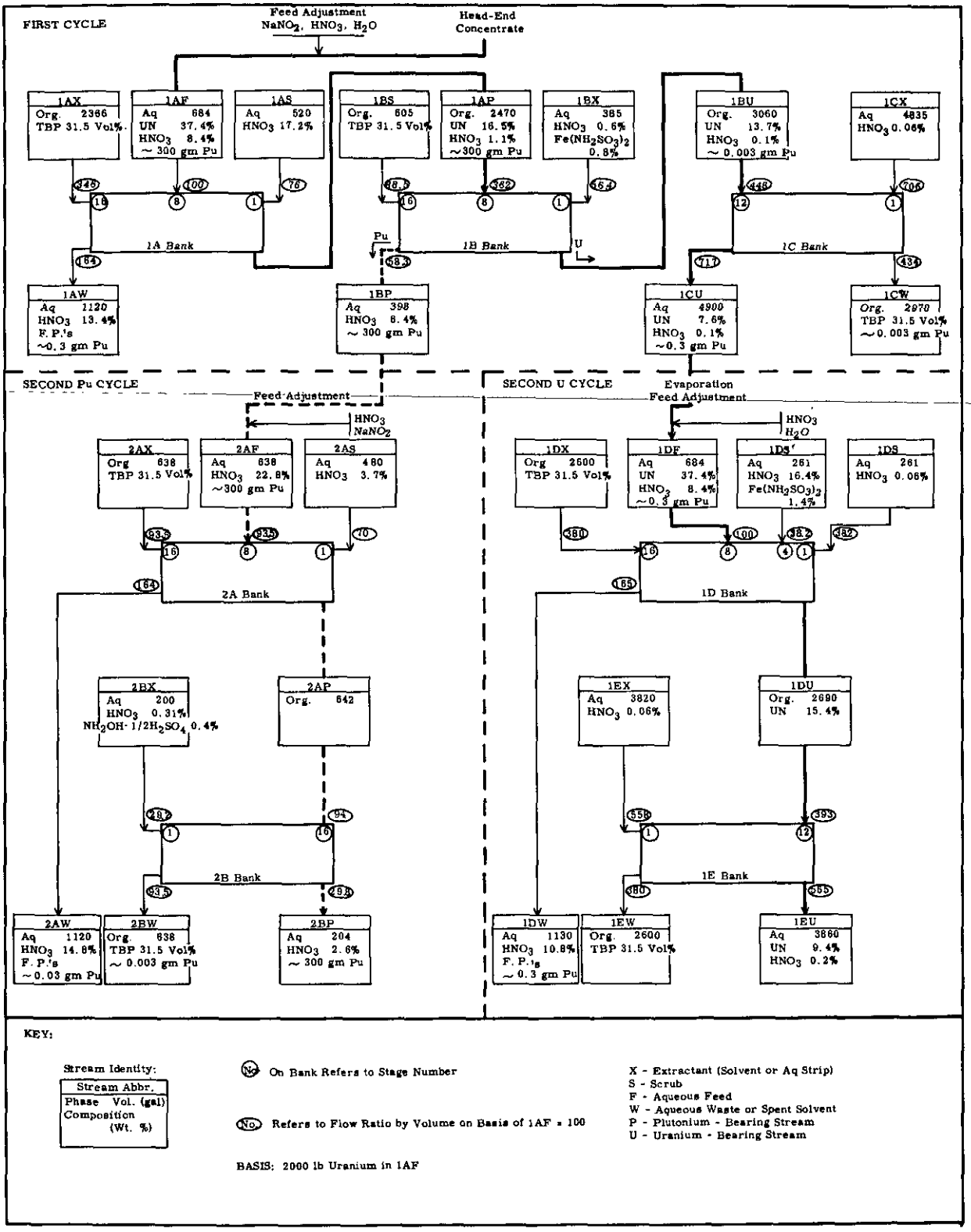

FIG. 1 OUTLINE OF SRP PUREX PROCESS

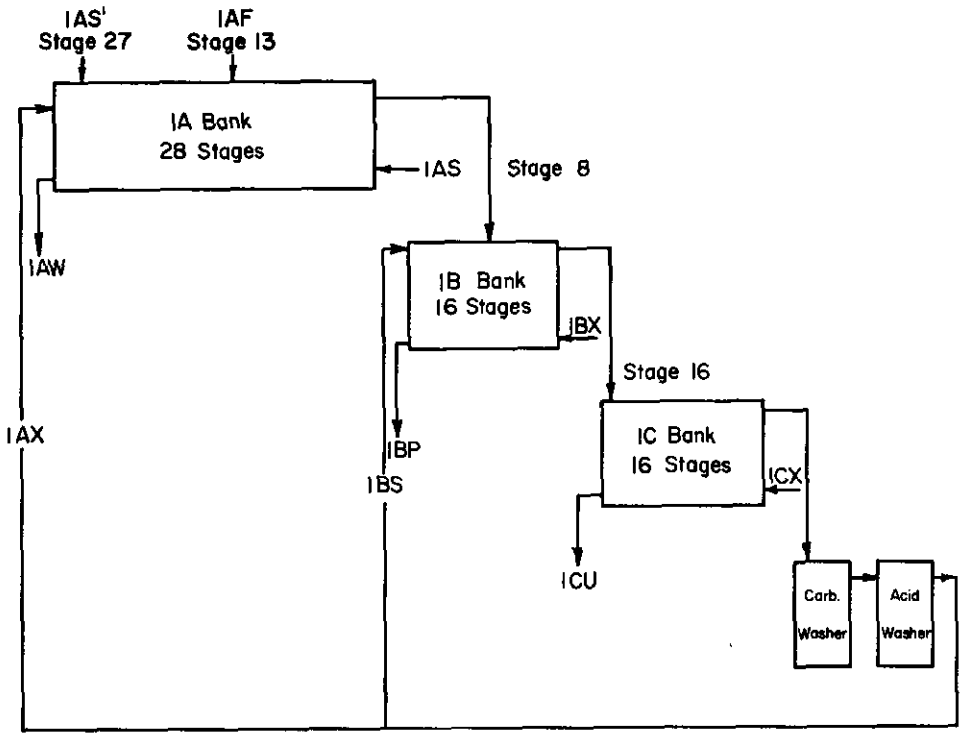

FIG. 2 FLOW DIAGRAM FOR PUREX TEST FLOWSHEET

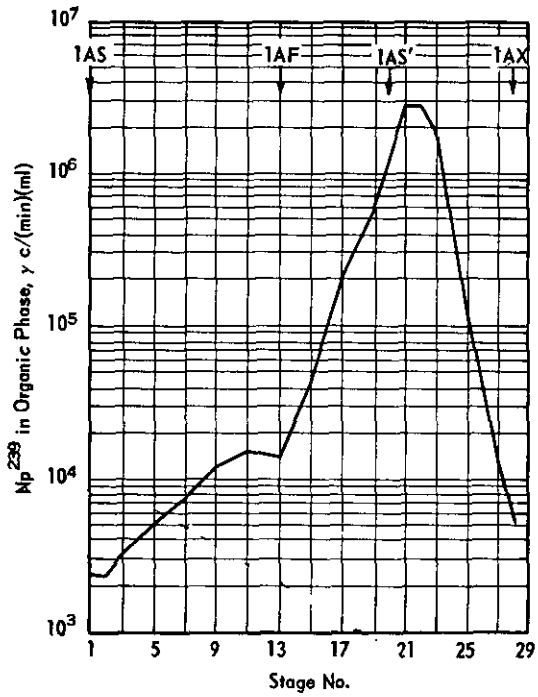

FIG. 3 STAGE PROFILE OF NEPTUNIUM IN ORGANIC PHASE OF 1A BANK, PUREX PROCESS

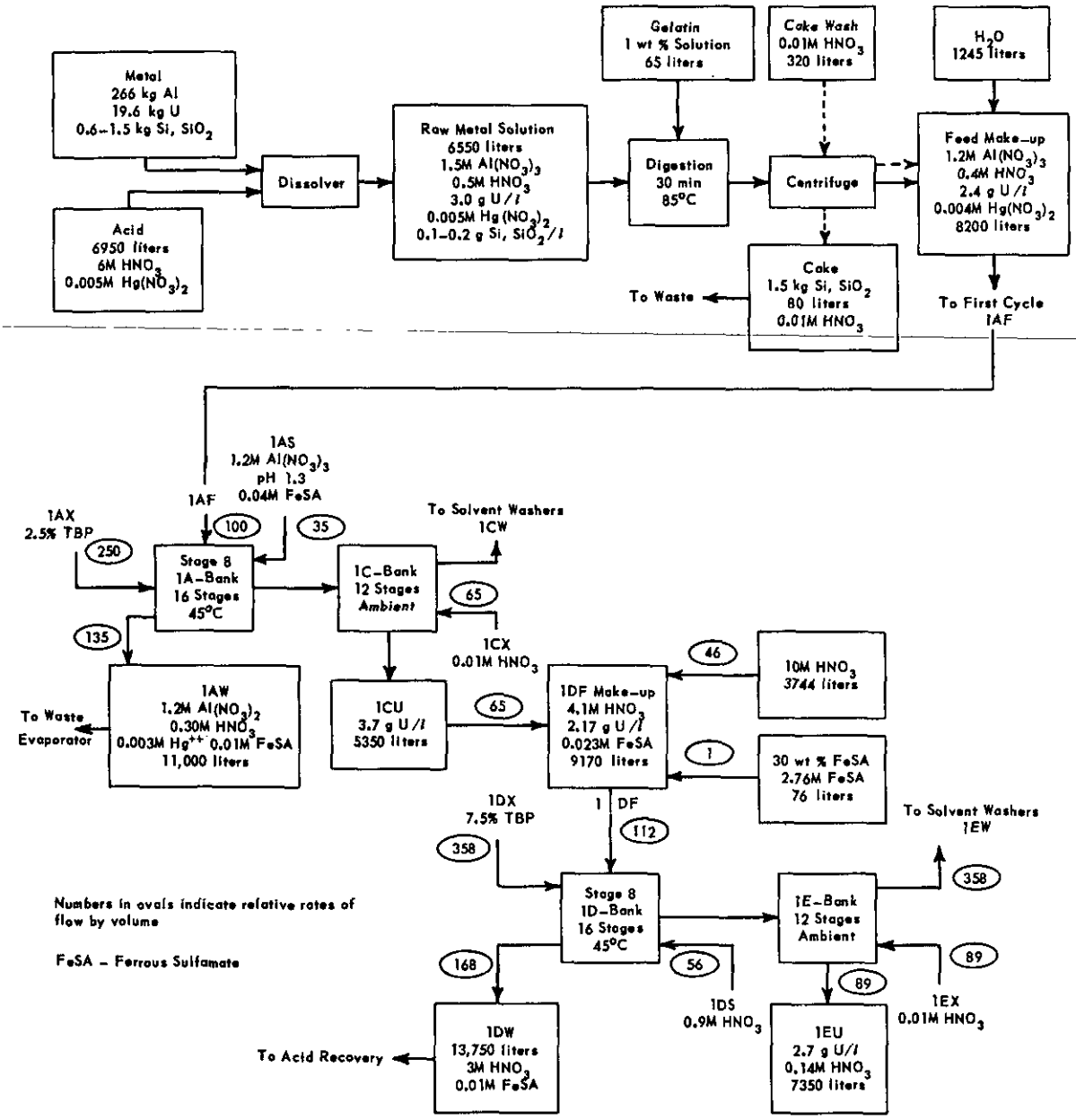

FIG. 4 OUTLINE OF HM PROCESS

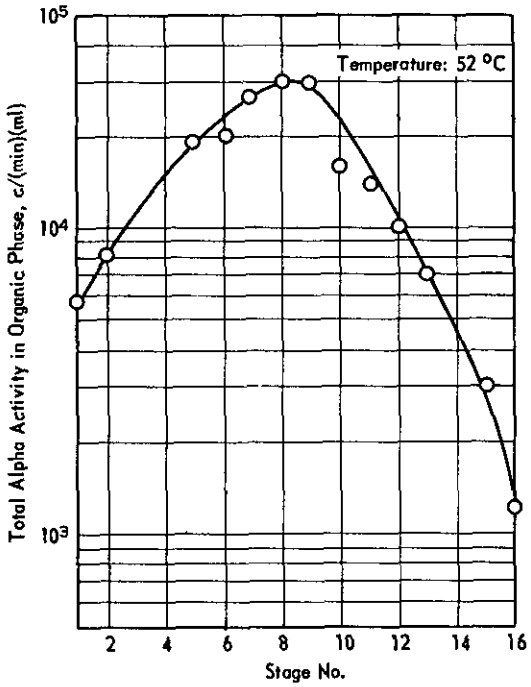

FIG. 5 STAGE PROFILE OF Np(IV) IN ORGANIC PHASE OF 1A BANK, HM PROCESS

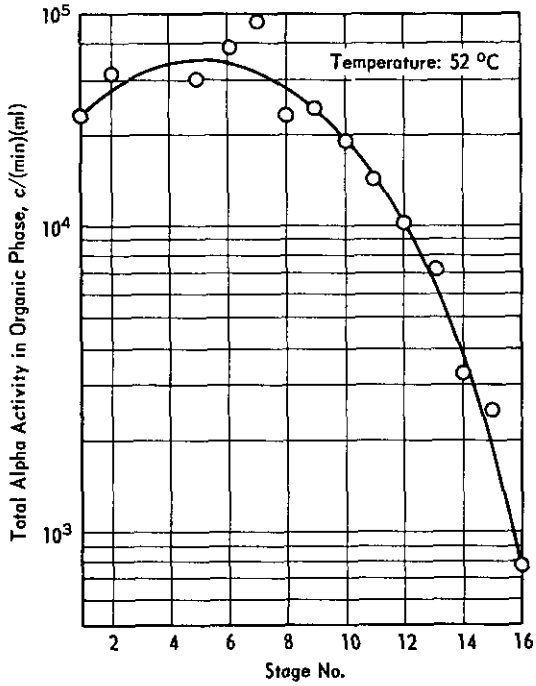

FIG. 6 STAGE PROFILE OF Np(VI) IN ORGANIC PHASE OF 1A BANK, HM PROCESS

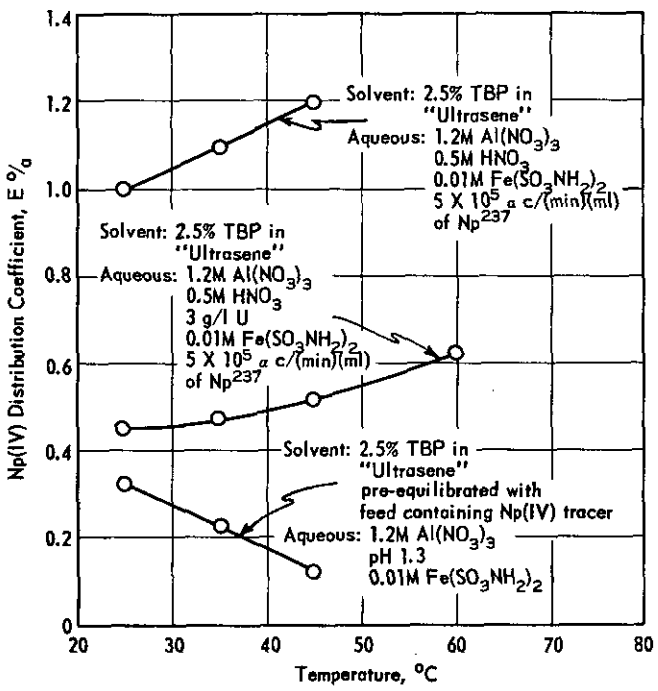

FIG. 7 EFFECT OF TEMPERATURE ON DISTRIBUTION OF Np(IV), HM PROCESS

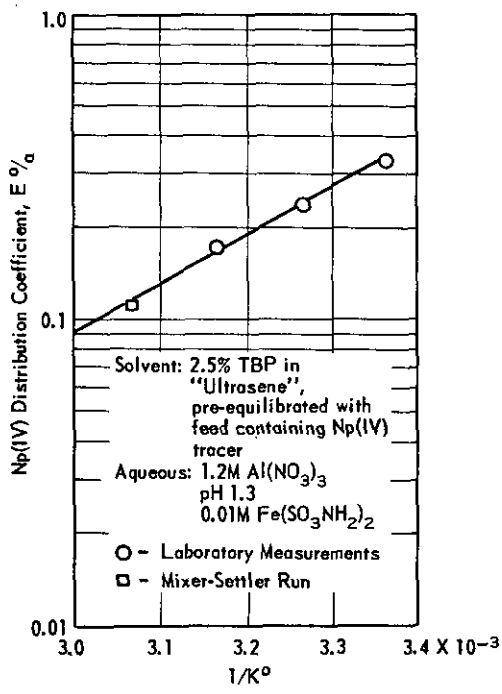

FIG. 8 EXTRAPOLATION OF DISTRIBUTION DATA FOR Np(IV), HM PROCESS

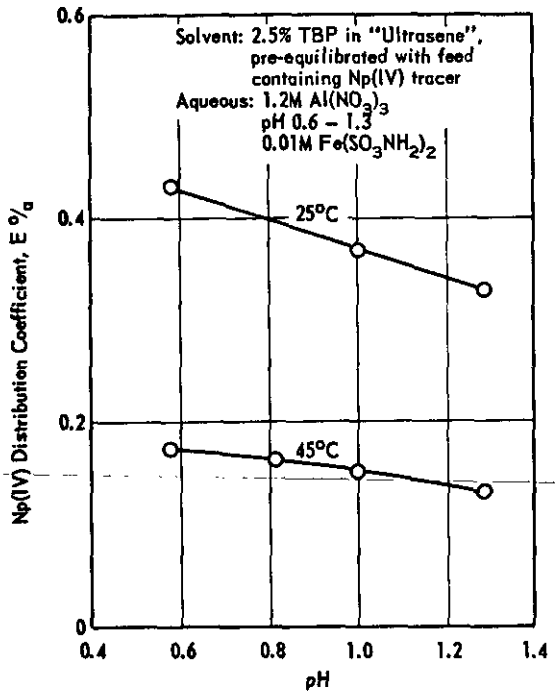

FIG. 9 EFFECT OF pH ON DISTRIBUTION OF Np(IV), HM PROCESS

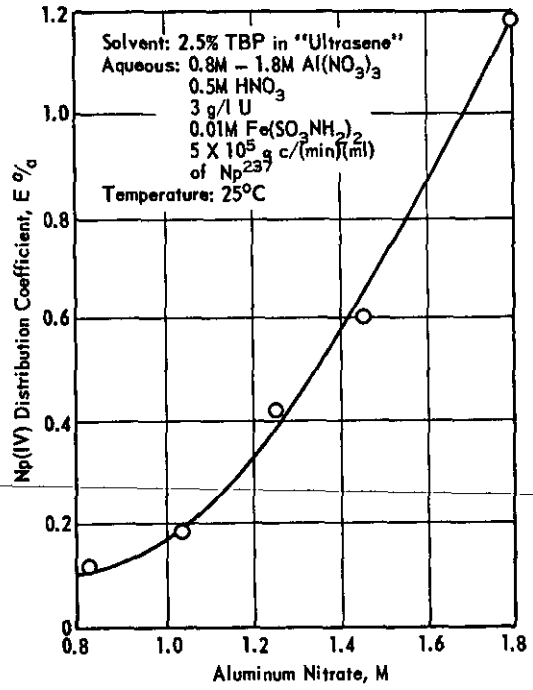

FIG. 10 EFFECT OF ALUMINUM NITRATE ON DISTRIBUTION OF Np(IV), HM PROCESS

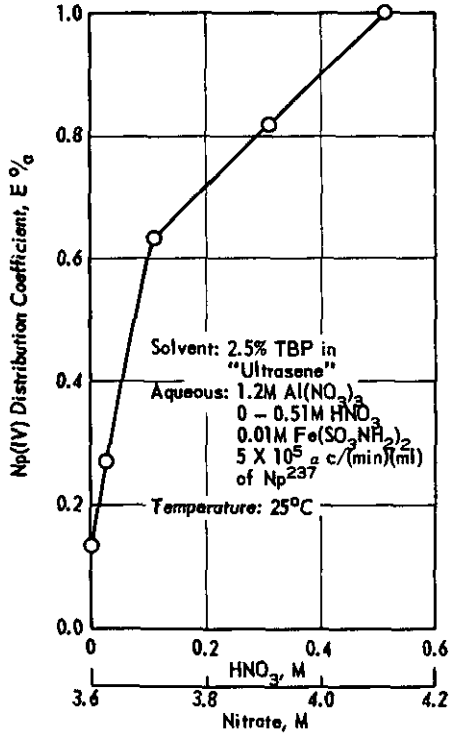

FIG. 11 EFFECT OF NITRIC ACID (NITRATE) ON DISTRIBUTION OF Np(IV), HM PROCESS

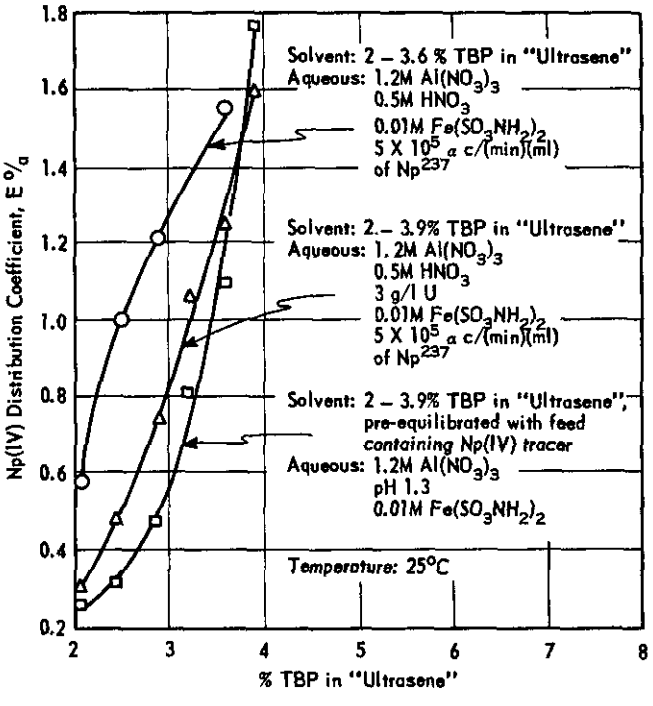

FIG. 12 EFFECT OF TBP ON DISTRIBUTION OF Np(IV), HM PROCESS

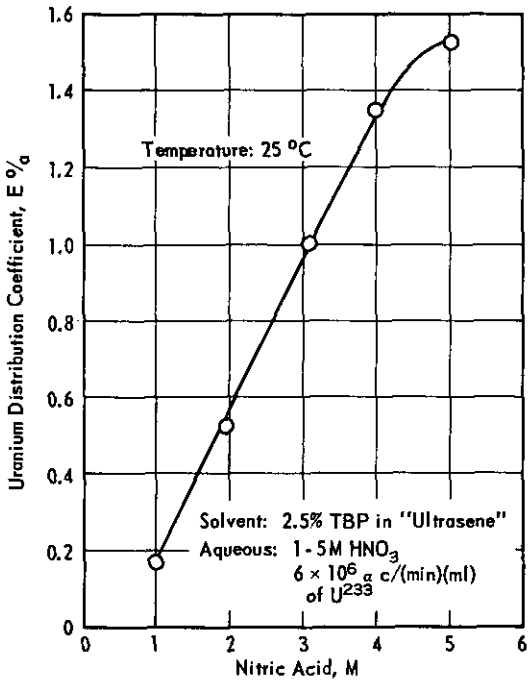

FIG. 13 EFFECT OF NITRIC ACID ON DISTRIBUTION OF URANIUM, HM PROCESS

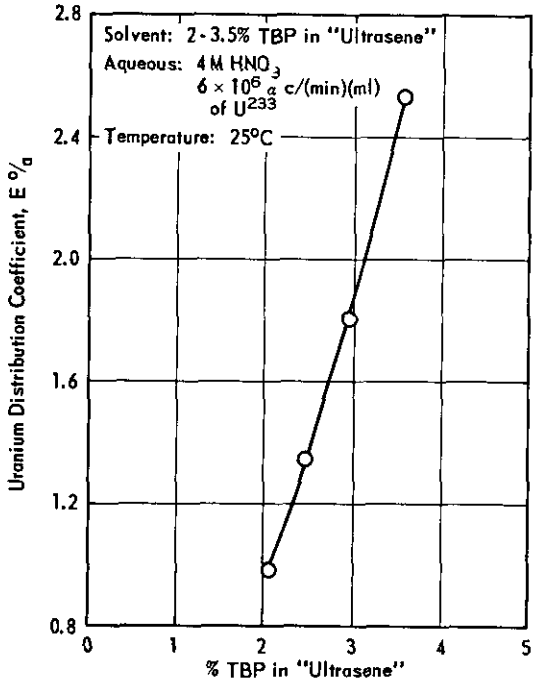

FIG. 14 EFFECT OF TBP ON DISTRIBUTION OF URANIUM, HM PROCESS

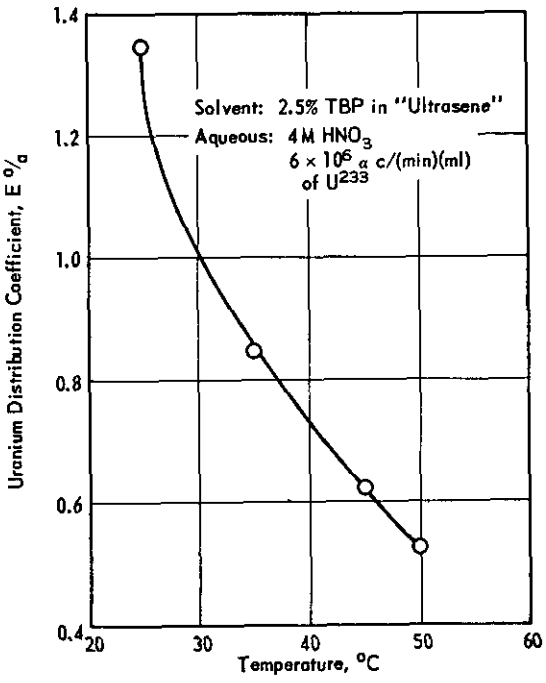

FIG. 15 EFFECT OF TEMPERATURE ON DISTRIBUTION OF URANIUM, HM PROCESS

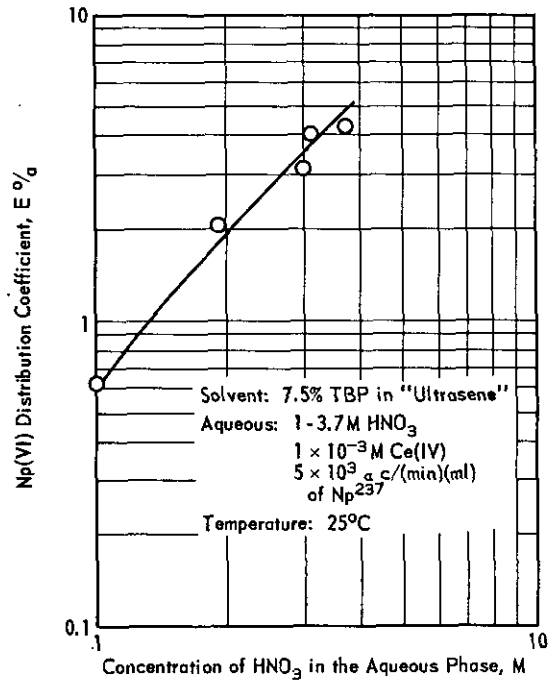

FIG. 16 DISTRIBUTION OF Np(VI), HM PROCESS

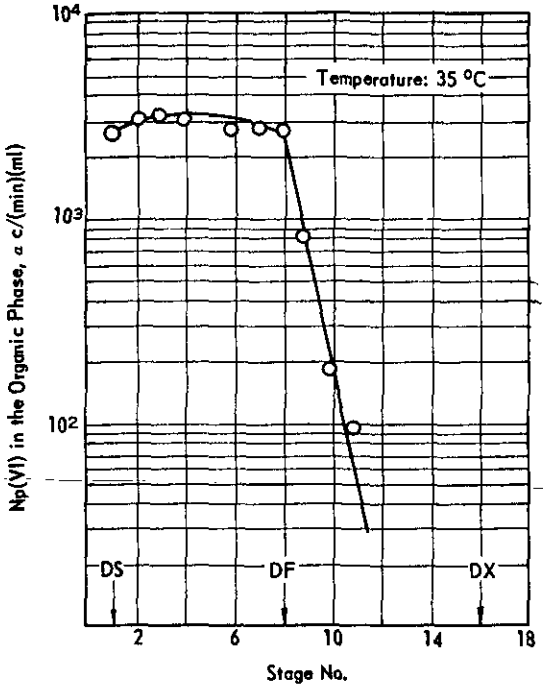

FIG. 17 STAGE PROFILE OF Np(VI) IN ORGANIC PHASE OF 1D BANK, OXIDATION WITH Ce(IV), HM PROCESS

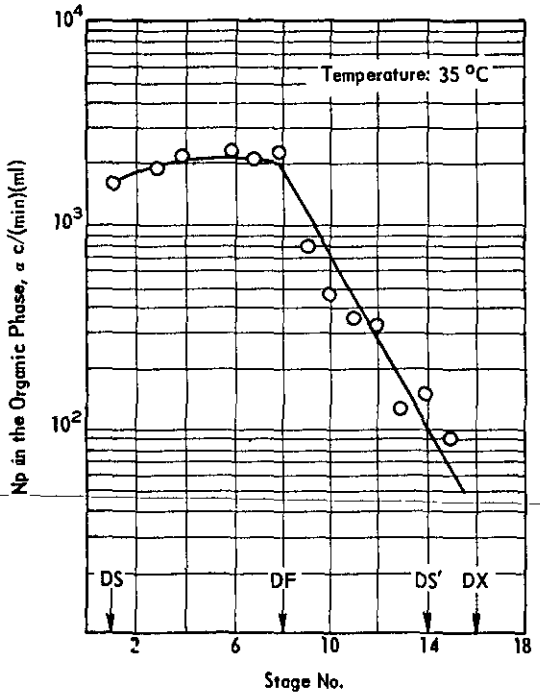

FIG. 18 STAGE PROFILE OF Np IN ORGANIC PHASE OF 1D BANK, 0.001M HNO_2 IN THE ORGANIC PHASE, HM PROCESS

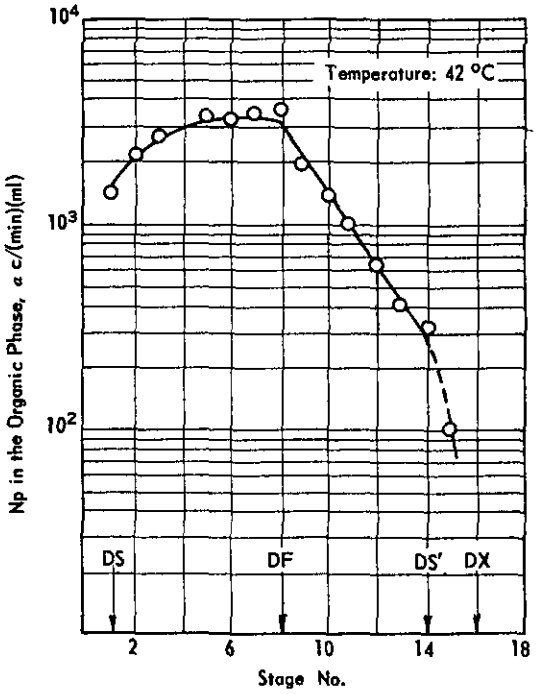

FIG. 19 STAGE PROFILE OF Np IN ORGANIC PHASE OF 1D BANK, 0.0005M HNO_2 IN THE ORGANIC PHASE, HM PROCESS

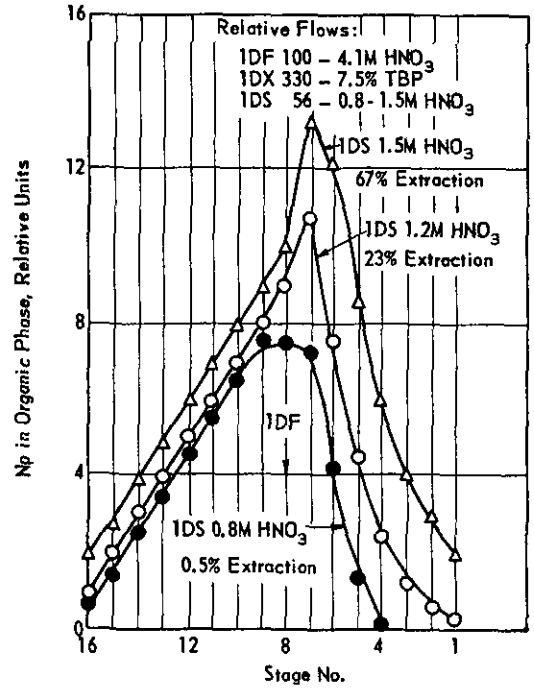

FIG. 20 CALCULATED STAGE PROFILE OF Np(IV) IN ORGANIC PHASE OF 1D BANK, HM PROCESS