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ARGONNE NATIONAL LABORATORY
P. O. Box 5207
Chicago 80, Illinois

RECOVERY OF NEPTUNIUM-237 FROM SPECIAL HANFORD WASTES

by

H. B. Evans, W. B. Seefeldt, H. H. Hyman

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
INTRODUCTION	5
I. ATTEMPTS AT CONCENTRATION OF FEED	7
II. CHOICE OF PROCESS CONDITIONS	7
III. RE-EXTRACTION OF NEPTUNIUM FROM HEXONE	11
IV. LABORATORY TESTS OF PROPOSED FLOWSHEET	12
V. PROCESSING OPERATIONS.	12
A. Preparation of Feed	12
B. Preparation of the Extractant	14
C. Preparation of the Strip Solution	14
D. Contacting Procedure	14
E. Equipment	14
F. Preliminary Test of Equipment	17
G. Results	19
H. Analytical Procedures	20
I. Product Purification	23
VI. FEASIBILITY OF COUNTERCURRENT SOLVENT EXTRACTION FOR NEPTUNIUM-237	23
VII. ALTERNATE PROCESS	25

SECRET

4

LIST OF TABLES

	<u>Page</u>
1 - Neptunium and Plutonium Distribution Ratios under Varying Process Conditions	8
2 - Efficiency of Various Strip Solutions on Neptunium	11
3 - Summary of Laboratory Runs	12
4 - Results of Neptunium Recovery Runs	18
5 - Composition of Hanford Solutions Before and After Processing for Neptunium	21

LIST OF FIGURES

	<u>Page</u>
I - Batch Solvent Extraction Scheme for Neptunium Recovery	13
II - Equipment for Separation of Neptunium from Plutonium	15
III - Flow Pattern in Strip Tank	16
IV - Effect of Absorbing Impurities on Plutonium Pulse Analyses	22
V - Enrichment of Neptunium by Scrubbing	24

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ABSTRACT

Neptunium-237 was recovered with moderate success from eight batches of special Hanford plutonium waste solutions by a batch solvent extraction process. The procedure utilized the behavior of neptunium-IV to form highly solvent-soluble nitrate complexes in the presence of certain organic amines or quarternary salts under conditions where plutonium-III can be stabilized. Some very preliminary work on an alternate batch solvent extraction process utilizing the solvent inextractability of neptunium-V is also reported. The feasibility of continuous countercurrent extraction for the separation of neptunium from plutonium is discussed.

INTRODUCTION

In the pile bombardment of uranium, at least three neptunium isotopes, of mass numbers 237, 238, and 239, are formed. Early investigations of the properties of this element were carried out with the short-lived neptunium-239. However, the isotope best suited for use in the investigation of neptunium chemistry is neptunium-237, an alpha emitter with a half-life of 2.25×10^6 years, produced in the pile in an amount estimated to be equivalent to about 0.3 per cent of the plutonium present.

The isolation and purification of neptunium has been reviewed by Magnusson, Hindman, and LaChapelle⁽¹⁾. These authors describe a process for the separation of neptunium from plutonium by extraction with a benzene solution of the chelating agent, thenoyl trifluoroacetone, in the presence of a reducing agent. The study of neptunium behavior in the Redox solvent extraction process⁽²⁾ has shown neptunium-VI nitrate to be readily extracted into hexone. Neptunium-IV nitrate is less extractable except in the presence of organic soluble basic reagents, e.g., tri-n-butyl amine⁽³⁾, and much less extractable in the presence of some aqueous complexing anions, e.g., sulfate or fluoride.

The present work was initiated to isolate neptunium-237 from eight batches of special Hanford plutonium waste solution with a total volume of about 230 liters. The composition of the original Hanford solution was approximately 3.0 M nitric acid and 0.4 M lanthanum nitrate. Each batch was estimated to contain from 300 to 600 mg. of neptunium-237, and 3.0 to 6.5 grams of plutonium. The goal was the recovery of the bulk of the neptunium decontaminated from plutonium by a factor of 50 or more. No effort was made to develop a completely satisfactory separations process, although information was obtained that might be useful in such a development.

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- (1) Magnusson, Hindman, and LaChapelle, ANL-4066, October 10, 1947.
 - (2) Blaedel and Hyman, CN-3525, June 25, 1946.
 - (3) Hyman and Vogler, ANL-WMM-231, August 15, 1947.

Efforts to concentrate the feed were relatively unsuccessful and the final process employed the following steps:

1. Neutralization of the excess acidity with ammonium hydroxide.
2. Addition of aluminum nitrate to complex traces of excess fluoride ion and increase the salting-out power.
3. Reduction of plutonium with ferrous sulfamate to the inextractable plutonium-III, at the same time quantitatively stabilizing neptunium-IV.
4. Batch extraction of the neptunium with hexone containing tri-n-butyl amine and nitric acid.
5. Stripping the neptunium from the hexone with sodium hydroxide solution.
6. Decanting the sodium hydroxide solution, leaving the product slurry.
7. Recycling the hexone and caustic solutions until three extractions and six strip operations are performed in processing each batch.

All eight batches were processed and attempts to recover additional material from the raffinate were unsuccessful. While this would imply that virtually all the extractable neptunium had been recovered, laboratory processing of samples from each batch indicated that higher yields should have been obtained. On the basis of the estimated yield from the $n, 2n$ reaction on uranium-238, still more neptunium should have been present than indicated by the laboratory batch experiments. However, no attempt was made to follow losses in the bulk isolation of the neptunium at Hanford so the reason for this discrepancy, while still obscure, may be completely outside the scope of the current investigation.

There were appreciable discrepancies found between assays at various steps in the processing operations. That is, compared to the 6 grams of neptunium which would be predicted by nuclear considerations only, the laboratory batch experiments indicated 3.92 grams to be present in the starting material; the solvent extract from the semi-works operation indicated 3.08 grams; and the isolated product assayed only 2.24 grams.

It is felt that losses in the various steps involved do not satisfactorily explain these differences.

The decontamination factor from plutonium for the eight runs averaged 65.

Preliminary data are presented suggesting the feasibility of a continuous process using chemical conditions similar to those described above. An alternate flow scheme using countercurrent solvent extraction and taking advantage of the solvent inextractability of neptunium-V is attractive in principle, but attempts to quantitatively stabilize neptunium-V under practical conditions proved unsuccessful.

I. ATTEMPTS AT CONCENTRATION OF FEED

Since the available equipment and space were limited, an effort was made to shorten the processing time by reducing the volume of the 230 liters of Hanford solution to the minimum compatible with good separation. The Hanford solutions were approximately 0.4 M in lanthanum nitrate and 3.0 M in nitric acid. Several experimental feeds were prepared by evaporation accompanied in most instances by neutralization with calcium hydroxide or ammonium hydroxide, either before or after the evaporation. In most cases, it was necessary to reject the final feed due to solid formation, high viscosity, or high nitrate concentration, but the physical feasibility of moderate concentration factors was established. In each run the distillates were caught in graduated cylinders and aliquots chosen for acid determination. The residues were used wherever possible in the preparation of feeds for testing the behavior of neptunium and plutonium. Both synthetic and process solutions were employed. However, as noted in Table 1, page 8, poor separation factors for neptunium from plutonium were obtained on these concentrated solutions and this approach was abandoned.

II. CHOICE OF PROCESS CONDITIONS

It has been known for some time that the extractability of many heavy metal nitrates including uranyl nitrate⁽⁴⁾, plutonium-IV nitrate⁽⁵⁾, thorium nitrate⁽⁶⁾, and neptunium-IV nitrate^(3, 7), from aqueous nitrate solutions is increased by the addition of a small amount of a high molecular weight amine or quarternary ammonium salt to the system. This effect has been attributed to the formation of stable anionic nitrate complexes, which, in combination with suitable organic cations, are highly solvent soluble. In the case of neptunium-IV, complex formation may be represented as:

where R is a substituted ammonium cation, and X is the number of nitrate ions combining with one molecule of neptunium-IV nitrate.

(4) Kaplan, L., and Hildebrandt, R., ANL-WMM-193; ANL-WMM-288.

(5) Evans, Brown, Hyman, and Kaplan - (To be published).

(6) Kaplan, L., ANL-WMM-193.

(7) Miles, et al, in Taylor, ORNL-65, July 9, 1948.

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Table 1

NEPTUNIUM AND PLUTONIUM DISTRIBUTION RATIOS UNDER VARYING PROCESS CONDITIONS

Run No.	Feed Composition (M)						Volume Ratio (Hex./Aq.)	Hexone Composition (M)		Type of Feed	Distribution Ratio (Hexone/Aqueous)		
	HNO ₃	NH ₄ NO ₃	La(NO ₃) ₃	Al(NO ₃) ₃	Fe(SO ₃ NH ₂) ₂	Fe ^o		HNO ₃	2 Hexylpyridium Nitrate		Pu	Np	Fission Products
1	1.0	7.3	0.9	-	0.10	-	0.2	0.1	-	Hanford	0.01	-	-
2	1.0	7.3	0.9	-	0.10	-	0.2	0.1	0.1	Hanford	1.0	8	-
3	1.0	7.3	0.9	-	0.10	0.1	0.2	0.1	0.1	Hanford	0.5	-	-
4	1.0	7.3	0.9	-	0.10	-	0.2	0.1	0.5	Hanford	11	68	-
5	1.0	7.3	0.9	-	0.10	0.1	0.2	0.1	0.5	Hanford	6	-	-
6	0.6	7.3	1.0	-	0.10	-	0.2	0.1	-	Hanford	-	2.5	-
7	0.5	7.3	1.0	-	0.10	-	0.2	0.3	0.2	Synthetic	0.01	18	-
8	0.6	7.3	0.9	-	0.10	-	0.2	-	-	Synthetic	0.008	-	0.007
9	0.6	7.3	0.9	-	0.10	0.1(3)	0.2	-	-	Hanford	0.007	-	0.01
10	0.6	7.3	0.9	-	0.10	(4)	0.2	-	0.1(1)	Hanford	3.70	-	0.02
11	0.6	7.3	0.9	-	0.10	0.1	0.2	0.3	0.2	Hanford	0.7	-	-
12	0.35	2.20	0.34	-	0.10	-	0.14	0.005	-	Hanford	0.0001	0.0006	0.0008
13	0.35	2.20	0.34	-	0.10	-	0.14	0.25	0.2	Hanford	0.0016	0.04	0.002
14	0.35	2.20	0.34	-	0.10	-	0.10	0.25	0.2	Hanford	0.008	0.14	-
15	0.35	2.20	0.34	-	0.10	-	0.10	0.25	0.2	Hanford	0.001	0.034	-
16	0.35	2.20	0.34	-	0.10	-	0.14	0.25	0.2(2)	Hanford	0.04	0.9	-
17	0.4	3.5	0.35	-	0.10	-	0.2	0.25	0.2	Hanford	0.0005	0.5	-
18	0.4	3.5	0.35	-	0.10	-	0.2	0.25	0.2	Synthetic	0.0001	5.6	-
19	0.35	2.1	0.32	0.2	0.10	-	0.2	0.25	0.2	Hanford	0.02	8	-
20	0.35	2.1	0.32	0.2	0.10	-	0.2	0.25	0.2(5)	Hanford	0.15	40	-
21	0.35	2.1	0.32	0.2	0.10	-	0.2	0.25	0.1(5)	Hanford	0.04	12	-
22	0.3	8.0	-	-	0.10	-	1	-	-	Synthetic	-	0.06	-
23	0.3	8.0	-	-	0.15	(3)	1	-	-	Synthetic	-	0.004	-
24	0.5	1.8	0.27	0.17	0.15	-	0.2	0.15	0.1(5)	Hanford	0.012	9	-
25	0.5	1.7	0.26	0.35	0.15	-	0.2	0.15	-	Hanford	0.025	30	-
26	0.5	1.7	0.23	0.46	0.15	-	0.2	0.15	-	Hanford	0.05	35	-
27	0.5	1.6	0.22	0.55	0.15	-	0.2	0.15	-	Hanford	0.09	-	-
28	0.33	1.9	2.0	-	0.1	-	1.0	0.1	0.1	Synthetic	-	5	-
29	0.33	1.9	2.0	-	0.1	-	1.0	0.1	0.2	Synthetic	-	9	-
30	0.33	1.9	2.0	-	0.1	-	1.0	0.1	0.3	Synthetic	-	17	-
31	0.33	1.9	2.0	-	0.1	-	1.0	0.1	0.2(2)	Synthetic	-	12	-
32	0.65	7.3	1.0	-	0.1	-	0.2	0.1	-	Synthetic	-	2.5	-
33	0.65	7.3	1.0	-	0.1	-	0.2	0.1	0.1	Synthetic	-	60	-
34	0.65	7.3	1.0	-	0.1	-	0.2	0.1	0.3	Synthetic	-	290	-
35	0.65	7.3	1.0	-	0.1	-	0.2	0.1	0.5	Synthetic	-	742	-
36	0.52	7.3	0.9	-	0.1	-	0.2	0.1	-	Hanford	0.013	0.56	-
37	0.52	7.3	0.9	-	0.1	-	0.2	0.1	0.1	Hanford	0.92	5	-
38	0.52	7.3	0.9	-	0.1	-	0.2	0.1	0.3	Hanford	7.2	46	-
39	0.52	7.3	0.9	-	0.1	-	0.2	0.1	0.5	Hanford	17	48	-

(1) 0.1 M N₂H₄

(2) 2 (5 nonyl) pyridine

(3) 0.1 M sulfamic acid + 0.1 M Fe(NH₄)₂(SO₄)₂(4) 0.05 M Fe(NH₄)₂(SO₄)₂

(5) Tri-n-butyl amine

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Since neptunium-IV is known to be formed in aqueous nitrate solutions by reduction of higher valence states with ferrous ion, and since, under these conditions, plutonium is reduced to the inextractable (III) state, the extraction-separation of neptunium from plutonium can be effected. Such an approach was preferred to a number of possible alternatives, involving the extraction of solvent-soluble plutonium valence states from less-soluble neptunium species. The neptunium could thus be separated from the bulk of the plutonium, as well as from most of the other salts present, in a single operation and with a minimum handling of the rather large amounts of plutonium present.

In order to determine the conditions necessary for the maximum decontamination of neptunium from plutonium consistent with high recovery for the neptunium and simplicity of operation, the distribution ratios for these elements in systems which could be readily prepared from the Hanford solutions were measured. Both synthetic and Hanford solutions were employed. Plutonium was followed by lanthanum fluoride alpha assay making corrections for neptunium-237 where necessary. The behavior of neptunium was followed utilizing the 56-hour beta emitting neptunium-239 tracer prepared by the bombardment of depleted U_3O_8 in the Argonne pile. The tracer was isolated by a sequence of precipitation and solvent extraction cycles and added to the systems being studied as a nitric acid solution. The valence state of the tracer was not controlled since ferrous ion was found to reduce neptunium-VI and V to neptunium-IV equally well.

Ferrous sulfamate was chosen as the reducing agent for neptunium and plutonium because of its success as a holding reductant for plutonium in the Redox process(8). Most of the preliminary experiments were carried out using 2-hexylpyridine as the complexing amine; a few employed 2-5(nonyl)-pyridine or tri-n-butylamine. The results are shown in Table 1, page 8.

In order to recover a minimum of 95 per cent of the neptunium with a maximum of 2 per cent of the plutonium, the distribution coefficients for neptunium and plutonium must be of the order of 15 and 0.02, respectively, for three batch extractions using a 1:5 volume ratio of hexone to aqueous. Salting out strengths and amine concentration were varied over a fairly wide range in an attempt to find a combination of coefficients of this order of magnitude.

Although adequate extraction of neptunium is easily obtained, careful selection of conditions is necessary in order to obtain the desired separation factors.

The feed used in Runs 1 - 12 (Table 1, page 8) would correspond to a concentration factor of 2.5 for the original Hanford solution. Under these conditions it was found that the plutonium was too solvent-soluble in the presence of an amine (Runs 2 - 5 and 10 - 11). Attempts to reduce the Fe III/Fe II ratio with added iron powder were not successful (Runs 3, 5, 9, and 11). The high distribution ratios (hexone/aqueous) for plutonium at the higher nitrate concentrations may be associated with the nitrate complexing

(8) Zebroski and Feber, KAPL-89.

of plutonium-IV, resulting in incomplete reduction to the inextractable (III) state. Because of this effect, efforts to obtain a large volume reduction in the Hanford solution before processing were abandoned. In Runs 12 - 18 the original Hanford solution was used after adjusting the acid concentration with ammonium hydroxide. In these runs the plutonium coefficients were of the desired order of magnitude, but the neptunium distribution coefficients were much too low for effective extraction.

All of the amines tested gave essentially equivalent results; the choice of tri-n-butylamine was based largely on its greater availability. Runs 20 and 21 (Table 1) indicate no great change in separation factor with amine concentration. It is of interest that the approximately fourfold increase in neptunium distribution ratio with a twofold increase in amine concentration in these experiments corresponds to a formula $R_2Np(NO_3)_6$ for the complex; analogous to that of plutonium-IV(5, 9). The rather large differences in behavior between the synthetic and the Hanford solution (Runs 28 - 39) may be attributable to the presence of small amounts of complexing anions, e.g., fluoride in the Hanford material.

A "crud" layer was noted in the Hanford solution which was not readily removed by filtration, centrifugation, or extraction with organic solvents. The addition of aluminum nitrate to the Hanford material reduced the amount of "crud", increased the solubility of neptunium in hexone, and improved material balances in laboratory experiments. This behavior and the nature of the process by which the Hanford solutions were prepared suggests the presence of fluoride. In Runs 24 - 26, the effect of varying concentrations of aluminum nitrate on the distribution coefficients was measured. The conditions of Run 25, in which a separation factor of 1200 between neptunium and plutonium was obtained, were found to satisfy best the requirements set for the separation process. Three such extractions with a hexone to aqueous volume ratio of 1:5 would give, assuming equilibrium were established, a recovery of 99.5 per cent of the neptunium and decontamination from plutonium by a factor of 60. Rate studies on this system revealed that equilibrium values for both neptunium and plutonium are reached in less than thirty minutes with no appreciable change in coefficients over an additional five-hour period. The stability of the system over even longer periods was subsequently established in semi-works runs.

There was a beta activity of unknown origin of approximately 1×10^5 cts./min./ml. associated with all of the Hanford solutions. This activity was only slightly extractable into the solvent phase under any of the conditions tested in these experiments. Where necessary, an appropriate correction was applied to the neptunium-239 activity in the aqueous phase.

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- (9) Berkman and Kaplan, Quarterly Report for January, February, and March, 1948, ANL-4171.

III. RE-EXTRACTION OF NEPTUNIUM FROM HEXONE

The adaptability of an alkaline strip operation to the proposed batch extraction process was explored. It was hoped that a large volume reduction might be attained and at the same time the hexone and amine might be recycled with only a minor adjustment of the acidity. Aluminum and lanthanum nitrate are slightly soluble in the solvent phase. Upon equilibrating this organic phase with a caustic solution, the hydroxide precipitates formed served as carrier for the neptunium, thus giving additional volume reduction.

The stripping operations were tested by adding neptunium-239 tracer to a highly salted aqueous solution and extracting twice with a hexone solution containing 0.1 M tri-n-butylamine and 0.3 M nitric acid. Portions of this hexone solution were equilibrated for fifteen minutes with various aqueous strip solutions and the amount of neptunium retained in the hexone was determined. The results are given in Table 2.

Table 2

Efficiency of Various Strip Solutions on Neptunium

Run No.	Volume Ratio (hex./aq.)	Aqueous Composition (M)	% Retained After (n) Extractions		
			n = 1,	2,	3
1	0.20	0.1 M HNO ₃	50	15	4
2	0.25	0.1 M H ₂ SO ₄	16	0.01	-
3	1.0	2.56 M NaOH	5	1	-
4	1.0	2 M NaOH + 0.5 M sodium tartrate	<1	-	-
5	1.0	2 M NaOH + 0.5 M sodium citrate	<1	-	-
6	1.0	2 M NaOH + 0.5 M sodium acetate	<1	-	-
7	1.0	2 M NaOH + 0.5 M (NH ₄) ₂ SO ₄	<1	-	-
8	2.0	Distilled Water	0.1	0.01	-
9	2.0	2 M NH ₄ OH	2.0	0.01	-
10	1.0	7 M NaOH	65	43	-
11	1.0	1 M NaOH + 6 M NaNO ₃	3.1	0.04	-

IV. LABORATORY TESTS OF PROPOSED FLOWSHEET

Several laboratory runs were made using neptunium-239 tracer to test the feasibility of the proposed flowsheet which is shown in Figure 1, page 13. The results are given in Table 3.

Table 3

Summary of Laboratory Runs

Run No.	<u>Extraction-Distribution Ratio</u>						<u>% Loss in Strip Operation</u>		<u>% Recovery</u>
	<u>Neptunium</u>			<u>Plutonium</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>1</u>	<u>2</u>	
1	16	4	1	0.03	0.04	0.04	0.4	0.1	83
2	32	15	4	0.03	0.04	0.04	-	-	96
3	30	30	16	-	-	-	-	-	97

In Run 1 a decided drop was noted in the distribution ratio after the first extraction. This was attributed to the presence either of an in-extractable neptunium species or an impurity in the neptunium-239 tracer.

In Run 2, the neptunium-239 tracer was repurified by solvent extraction. This run was carried through the extraction stages with 96 per cent recovery. In Run 3, the neptunium-239 tracer was added to the original solution and the feed prepared as usual in order to determine if any in-extractable species of neptunium were formed during the various steps involved in the preparation of the feed. The distribution ratios given here (Run 3) are values corrected for the fission product activity associated with the Hanford solution.

V. PROCESSING OPERATIONS

The flowsheet used in the semi-works operations is outlined in Figure 1, page 13.

A. Preparation of Feed

The composition of the feed for the extraction was as follows:

ca. 0.5 - 0.65 M nitric acid
 ca. 0.3 M lanthanum nitrate
 ca. 1.4 M ammonium nitrate
 0.35 M aluminum nitrate
 0.20 M ferrous sulfamate.

Figure I

BATCH SOLVENT EXTRACTION SCHEME FOR NEPTUNIUM RECOVERY

(1) This sequence of steps is repeated 3 times. The final concentrations are given in parenthesis.

(2) This sequence of steps is repeated 2 times.

* Product as hydroxide slurry.

The acidity was first adjusted by the addition of the required amount of concentrated ammonium hydroxide to the Hanford solution. After the solution had cooled to room temperature the aluminum nitrate was added as a 2.5 M solution and the ferrous sulfamate as a 2.5 to 3.0 M solution. The ferrous sulfamate was prepared from metallic iron and sulfamic acid. The other solutions were prepared directly from reagent grade chemicals.

B. Preparation of the Extractant

Water-saturated, pretreated hexone was used throughout. Concentrated nitric acid and tri-n-butylamine (obtained from Sharples Chemicals, Incorp.) were added to give a concentration of 0.15 M and 0.10 M, respectively. After each extraction, the hexone was stripped of neptunium and the solvent was analyzed for tri-n-butylamine. Where necessary, amine was added, the acidity adjusted, and the hexone recycled. No noticeable deterioration in the effectiveness of these hexone-amine solutions was noted upon standing for a month.

C. Preparation of the Strip Solution

The original flowsheet required two batches of strip solution, each consisting of 5 liters of 2 M sodium hydroxide. In order to permit re-using the caustic, it was decided to use 7 M sodium hydroxide in the first run. This solution was not satisfactory. However, it was shown that sodium hydroxide could be added after each batch was processed and the buildup of nitrate in the strip solution could be tolerated up to a concentration of 6 M sodium nitrate and 1.0 M sodium hydroxide (see Table 2, page 11).

D. Contacting Procedure

The feed and hexone were contacted in a stainless steel tank for thirty minutes. The phases were allowed to settle for thirty minutes before removing the solvent phase, which was then contacted for fifteen minutes with 2 M sodium hydroxide in a glass carboy. These phases were allowed to settle until the hexone phase was clear, and the latter was transferred to a second carboy where the stripping process was repeated. This entire procedure was repeated three times for each batch. Enough nitric acid was added to the hexone after the second strip and before recycling to keep the acid concentration of the aqueous feed constant.

E. Equipment

The equipment used for the actual operations is shown in Figure II, page 15. It was installed in a ventilated hood (44" x 29" x 60") located in an isolated cell. A 30-gallon stainless steel drum was used as the extractor and a 1/8 H.P. explosion-proof motor was used for stirring. The length of the stirrer was adjusted so that the two-blades were positioned at the interface. Two 5-gallon glass carboys were used as the strip vessels, and 1/20 H.P. explosion-proof motors were used for stirring. To obtain satisfactory stirring in the strip tanks, stirrers with three sets of blades (4 blades per set) tilted to give the flow pattern as shown in Figure III, page 16, were used. These proved very efficient in producing a completely homogeneous mixture of aqueous and organic phases. A stainless

FIGURE II
EQUIPMENT FOR SEPARATION OF NEPTUNIUM FROM PLUTONIUM

16
FIGURE III

FLOW PATTERN IN STRIP TANK

steel tray, having a capacity of 60 liters was used as a secondary container for the strip vessels. This arrangement permitted direct observation of the operations.

To facilitate the transfer of the organic phases, adjustable downlegs with inverted ends as shown in Figure II, page 15, were used. A phase separator consisting of a 10" length of 1" Pyrex pipe was installed in conjunction with the adjustable leg on the extractor tank. This was done to preclude transfer of any aqueous solution from the extractor to the first strip vessel since the position of the downleg with respect to the interface could not be determined visually as in the case of the strip vessels. The transfer assemblies for the strip vessels were kept in dilute nitric acid during stirring operations, as were the stirrers during transfer operations. All material transfers were effected by vacuum regulated to a maximum of 10 inches of mercury.

F. Preliminary Test of Equipment

All transfer lines and valves were tested for leaks before any runs were made. Two stirrer efficiency tests were conducted on the extractor using a dummy feed and hexone in order to determine equilibrium time. The acid distribution ratios were determined for two hours at varying time intervals. These ratios indicated that 30 minutes would be sufficient to reach an equilibrium condition. To further check equilibrium time, samples of feed and solvent were taken at varying intervals through the first and second runs (1N8 and 2N1), Table 4, page 18.

Other tests were conducted in order to obtain a blade tilt on the strip stirrers that would produce homogeneous mixtures of the two phases in the strip vessels, and to determine a satisfactory stirring time for the strip operation. In order to decrease the volume of caustic solution containing the final product, an attempt was made to increase the concentration of sodium hydroxide up to 6.0 M. Stripping with this solution proves very unsatisfactory and the lower concentration was employed. A third strip was necessary on the first run in order to recover the product. In the subsequent runs the caustic concentration was adjusted by adding solid sodium hydroxide to the strip vessel.

Analysis of samples taken during the strip operations on the fourth and fifth runs (4N3 and 5N4) were indicative of a decreasing strip efficiency. Since this seemed to be due to an impurity concentrating in the solvent, fresh hexone and caustic solutions were used for the last three runs (6N5, 7N6, and 8N7). It was observed that the color of the extractant in runs 4N3 and 5N4 changed from yellow to a deep orange-red on standing, the color disappearing on contact with the caustic strip solution.

Three operational changes were made after Run 1:

1. The concentrated nitric acid used to adjust the acidity of the feed following an extraction was added to the hexone instead of to the feed in order to eliminate any possible oxidation of Fe-II that might occur as a result of the contact with concentrated nitric acid.

Table 4

Results of Neptunium Recovery Runs

Run No.	Ext'n. Stage	Initial Pu (g.)	Lab.* Np (mg)	Neptunium Recovery		Apparent* Recovery (%)	Plutonium Extracted (%)	Strip Efficiency (%)
				Semi-Works Np (mg)	Semi-Works Pu (mg)			
1N8	1X			226	17			99.7
	2X			85	32			99.6
	3X			40	28			99.6
	Total	6.52	591			59.4	1.2	
2N1	1X		410	287	11			99.8
	2X		70	46	9			99.6
	3X		20	15	12			99.9
	Total	3.28	500	348	32	69.6	1.0	
3N2	1X		314	317	21			99.8
	2X		44	51	26			98.5
	3X		28	27	25			98.9
	Total	2.98	386	395	72	102.3	2.4	
4N3	1X		456	342	28			99.7
	2X		68	60	33			100
	3X		16	13	9			98.6
	Total	4.66	540	415	70	76.8	1.5	
5N4	1X		305	269	26			98.5
	2X		52	75	29			97.7
	3X		20	54	29			99.6
	Total	4.80	377	398	84	105.6	1.7	
6N7	1X		374	307	22			100
	2X		70	100	27			100
	3X		0	0	25			100
	Total	3.56	444	407	74	91.7	2.0	
7N6	1X		434	357	11			99.2
	2X		63	37	13			99.8
	3X		0	0	17			100
	Total	3.42	497	394	41	79.3	1.2	
8N7	1X		520	327	21			99.8
	2X		59	38	17			99.4
	3X		10	6	21			99.8
	Total	3.95	589	371	59	63.0	1.5	
Total		33.17	3924	3079	508	78.5	1.54	

* These figures, on which recoveries are based, were calculated from data obtained on parallel laboratory runs using small aliquots of semi-works feed.

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2. Since the neptunium recovery of the first run did not come up to expectations, the aluminum nitrate concentration in the feed was increased to 0.50 M following the first extraction of the second run (2N1). This did not appreciably affect recovery, and the original flowsheet concentration of 0.35 M was resumed for the remaining runs.
3. The extraction stirring time was increased from 30 to 45 minutes in order to insure the attainment of true equilibrium.

G. Results

The results of processing the eight batches are summarized in Table 4, page 18. In general the larger scale runs were accompanied by parallel runs in the laboratory on identical feed material. The apparent neptunium recovery in the semi-works was considerably lower than in the laboratory runs. However, a careful search for neptunium in all waste fractions showed that losses in full-scale operations could not account for the difference between the semi-works and laboratory results.

It will be noted from Table 4 that 6 of the 8 batches showed from 10 - 40 per cent less neptunium in the solvent extract than was predicted on the basis of the laboratory run, yet further extraction of the raffinate in each of these cases yielded no detectable amount of neptunium. Since each 10-liter solvent extract contained 10 - 30 mg. of plutonium which is 100 times as effective an alpha emitter, simple pulse analysis probably could not guarantee the absence of up to 30 mg. of neptunium under these conditions. As will be discussed in the following section however, the pulse analyzer tended to give high results for small amounts of neptunium, so that the losses of extractable neptunium were probably much less than this figure.

Although no good method was found for determining the possible presence of inextractable neptunium, the discrepancy between laboratory and larger scale runs cannot readily be explained on this basis. The laboratory runs were designed to simulate the larger scale operations as closely as possible. For example, stainless steel was added in some runs, but no special effect was noted. It is possible that the discrepancies were due to faulty analyses as the result of letting samples from the large scale runs stand for some time before analysis. It has been pointed out that these recoveries are based on analysis of the solvent phase after extraction (and then after stripping) because the final product is obtained as a questionably analyzable slurry. It is known from previous solvent extraction experience that wet hexone solutions of the heavy metals often are unstable in that an aqueous phase may settle out. This often results in stripping out a high percentage of the heavy metal. As a result, solvent analyses are often low and for routine analytical procedures where samples may be retained for days before analysis, analytical results may be grossly in error.

While an effort was made to prepare plates from the solvent samples as rapidly as practical, it was felt that this source of error may still have

crept in. Since there was no way to check this at the time, it seemed reasonable to place more credence in the laboratory samples which were finally checked as stable aqueous solutions of the product precipitate.

In view of the failure of subsequent processing to yield even the lower figures of neptunium content there may have been other factors contributing to erratic results. It has been suggested by J. C. Hindman that the presence of solid extractable impurities, also carried by LaF_3 (Th, Bi), might increase the weight of absorbent on a sample plate to the point where plutonium counts are slowed down and counted as neptunium. The appearance of the pulse analysis curves should, in this case, show much more smearing than was actually observed. Of course, a slight segregation of phases so that plutonium were deposited and covered with an inert layer could conceivably account for the observed phenomena and enormously increase the estimate of neptunium content. If this is the proper explanation, all analytical data as to recoveries prior to final purification are rather meaningless. While this explanation may appear plausible, it was not substantiated by evidence.

In order to eliminate any mechanical loss of neptunium, all waste materials, other than the aqueous raffinate, were re-processed. The spent hexone was washed and filtered. The caustic waste solutions were treated with lanthanum nitrate and the resulting precipitate filtered out. The filters were washed with nitric acid, as well as all equipment used in the processing. The combined washings contained only a negligible quantity of neptunium.

The aqueous raffinates from the hexone extractions were analyzed and returned to their original containers. The composition of the raffinates, as well as of the original solutions, are summarized in Table 5, page 21.

H. Analytical Procedures

Plutonium analyses were made where possible, either by direct mounting of small aliquots or by lanthanum fluoride procedures, slightly modified to reduce interference from aluminum. The neptunium/plutonium ratio was determined by the use of the alpha pulse analyzer. While this instrument has been described in some detail by A. Ghiorso, A. H. Jaffey, H. P. Robinson, and B. Weissbourd (AECD-2508), its use in chemical analysis is worth discussing.

This device (the 48-channel unit described in the above report is the prototype of the one actually employed) records on 48 fast mechanical registers every alpha pulse of enough energy to trip the specific circuit associated with the register and of insufficient energy to trip the one above. No single pulse registers on two recorders. The 48-channels may be arranged to cover a rather narrow energy band of maximum interest rather than the entire alpha energy spectrum. A weightless sample of a mono-energetic alpha emitter will record almost entirely in a single channel, with a slight amount of low-side counting due to reflected alpha particles which have lost some of their energy (see Figure IV, page 22).

Composition of Hanford Solutions Before and After Processing for Neptunium

Composition of Original Solution							Composition of Aqueous Raffinate ⁽¹⁾					
Run No.	Tank No.	HNO ₃ (M)	La(NO ₃) ₃ (M)	Sp. Gr. 25°C	Total Pu (gms)	Volume (l.)	HNO ₃ (M)	NH ₄ NO ₃ (M)	Al(NO ₃) ₃ (M)	Fe(SO ₃ NH ₂) ₂ (M)	Sp. Gr. 25°C	Volume (l.)
1N8	8	2.96	0.41	1.1982	6.52	24.94 ⁽²⁾	0.55	1.43	0.35	0.20	1.2133	36.24
2N1	1	3.10	—	1.1968	3.28	27.3	0.60	1.51	0.35	0.20	1.215	39.9
3N2	2	2.95	—	1.2182	2.98	27.3	0.50	1.41	0.50	0.20	1.2325	40.14
4N3	3	3.18	—	1.2035	4.66	27.9	0.50	1.44	0.35	0.20	1.2207	44.4
5N4	4	3.23	0.36	1.2048	4.80	25.2 ⁽²⁾	0.54	1.49	0.35	0.20	1.2249	37.8
6N5	5	3.12	—	1.2096	3.56	27.3	0.46	1.45	0.35	0.20	1.2275	40.1
7N6	6	3.24	—	1.1989	3.42	27.6	0.52	1.56	0.35	0.20	1.2154	40.9
8N7	7	3.02	—	1.2110	3.94	26.9	0.53	1.44	0.35	0.20	1.2197	39.6 ⁽³⁾
						33.17 ⁽⁴⁾	214.4					

(1) Aqueous raffinate is hexone saturated; about 1 to 2% of initial Pu was removed during Np processing.

(2) After removal of samples for laboratory experiments.

(3) Includes 2.6 liters of waste from laboratory experiments.

(4) Based on the figure 7.1×10^6 c/min/mg.

22

FIGURE IV
EFFECT OF ABSORBING IMPURITIES
ON PLUTONIUM PULSE ANALYSES

If the sample plate contains an appreciable amount of absorbing impurities, alpha particles will be found with net energies below the maximum energy. To include most of the resulting pulses in a single channel, the sensitivity of the instrument must be reduced and therefore the sharpness of separation between two materials is smaller. Furthermore, a substantial amount of a higher energy alpha particle may be confused with a lower one. Since neptunium pulses are found in lower energy registers, a bad plate might give an erroneously high neptunium-to-plutonium alpha ratio. Ordinarily this effect would be detected by a large number of counts between the neptunium and plutonium maxima. However, with a coarse grained, poorly dispersed plate it could be possible in any one case for erroneous conclusions to be drawn. Poor plates were not consistently obtained in this investigation and there is no reason to believe they were even common. In general, such plates show marked visible non-homogeneity of deposits and this was not observed in the current work. Neglecting the effects of poor sample preparation, the accuracy inherent in this instrument is similar to ordinary air alpha counting.

The acid and amine content of the solvent phases were determined by direct titration for total acid to the phenolphthalin end point, followed by an acid titration to the brom-thymol blue end point in order to determine the tri-n-butylamine concentration. The latter titration for amine was made after the addition of 25 - 35 ml. of acetone in order to give a single phase.

I. Product Purification

The combined product slurries were transferred to the Chemistry Division for final purification and eventual isolation of neptunium as neptunium tetrachloride⁽¹⁰⁾. A small portion of this crude product was retained by the Chemical Engineering Division for further investigation.

VI. FEASIBILITY OF COUNTERCURRENT SOLVENT EXTRACTION FOR NEPTUNIUM-237

A continuous countercurrent extraction process, particularly one employing a scrub tower, may have some advantages over the batch process employed in this work. The choice of a batch process in this work was based on the earlier availability of suitable equipment. Some preliminary laboratory experiments were performed to indicate the feasibility of a continuous process.

The effectiveness of scrubbing to complete the removal of plutonium from neptunium was demonstrated by shaking a hexone extract (from Run 2, Table 3, page 12) successively with equal volumes of an aqueous solution of the following composition: 0.75 M aluminum nitrate, 0.10 M nitric acid, 0.02 M tri-n-butylamine, and 0.10 M ferrous sulfamate. The alpha activity in the hexone solution consisted initially of 15 per cent neptunium and the remainder plutonium. After three scrubs, pulse analyses showed that only 0.25 per cent of the residual activity was plutonium. (This corresponds to about 0.002 per cent plutonium by weight in the neptunium.) Pulse analyses of the hexone solution before and after scrubbing are shown in Figure V, page 24.

(10) S. Fried, ANL-4225.

24

FIGURE V
ENRICHMENT OF NEPTUNIUM BY SCRUBBING

Presumably, additional scrubs would further reduce the plutonium carry-over, but this would be difficult to detect by the analytical methods employed. The neptunium concentration after three scrubs was 99 per cent of that initially present.

A rather simple and effective flowsheet for a continuous process may be outlined as follows:

The feed and extractant are prepared as described for the batch operations. The scrub solution has the composition of that employed in the experiment described above. A suitable ratio of flow rates would be four volumes of feed and one volume of scrub to one volume of extractant. The neptunium is stripped from the hexone in a second tower with either water or dilute sulfuric acid, depending on what subsequent treatment is proposed. With five extraction stages and five scrub stages, it is expected that the loss of neptunium would be less than 0.1 per cent, with a decontamination factor from plutonium greater than 10^7 .

Factors other than distribution ratios, such as reaction kinetics and physical properties of the solutions, would have to be investigated to determine their effect on the operation of a continuous process. No measurements were made of the viscosities and surface tensions of the process solutions. Visual examination, however, showed no evidence of emulsification in any of the two-phase systems, and phase separations appeared to be reasonably fast.

VII. ALTERNATE PROCESS

Instead of extracting neptunium-IV away from plutonium-III, it should be possible to extract the solvent-soluble plutonium-IV or VI under conditions such that the neptunium would remain behind in the inextractable (V) state. Such a procedure would have the additional advantage of removing thorium from the neptunium. Since the neptunium-237 produced in this work was found to be contaminated with appreciable amounts of thorium, preliminary experiments were performed on the use of such a process as a second cycle. The neptunium hydroxide was dissolved in nitric acid, the solution heated to depolymerize any plutonium or neptunium polymer, treated with hydrogen peroxide, and salted up with aluminum nitrate. The plutonium and thorium were readily extracted by a 0.1 M solution of tri-n-butylamine in hexone. However, the extraction of neptunium was greater than that expected for neptunium-V and varied considerably with the history of the solution. In the best experiments five per cent of the neptunium was extracted with the plutonium and thorium. It was not established whether the difficulty was due to the presence of neptunium-IV or VI, or whether the (V) state was disproportionating under the conditions of the experiment. Treatment of the solution with nitrite instead of hydrogen peroxide did not improve matters. Treatment of the aqueous solution, after the extraction of the plutonium, thorium, and some of the neptunium, with ferrous sulfamate made it possible to extract quantitatively the residual neptunium with a

SECRET

26

hexone-tri-n-butylamine solution. Thus, if the neptunium-V can be stabilized, an effective second cycle can be devised in which the plutonium and thorium are extracted from the neptunium, and the latter is then reduced and extracted away from inextractable impurities.

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