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for Plutonium and Uranium

Inv 36

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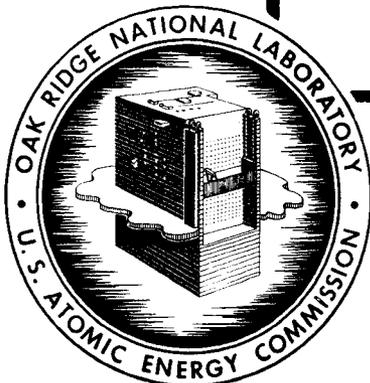
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DEVELOPMENT OF THE AMEX PROCESS  
FOR AMERICIUM RECOVERY

R. H. Rainey

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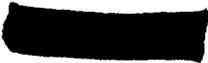
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CHEMICAL TECHNOLOGY DIVISION  
Chemical Development Section

DEVELOPMENT OF THE AMEX PROCESS FOR AMERICIUM RECOVERY

R. H. Rainey

DATE ISSUED

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Suggestions from other members of the Chemical Technology Division, K. M. Harmon of Hanford, and members of D. F. Peppard's group at Argonne, which contributed much to the Amex process, are gratefully acknowledged. The author also wishes to thank K. A. Kraus of ORNL and D. C. Stewart of Argonne for supplying the americium, and K. M. Harmon's group at Hanford for dissolving and shipping a crucible and its associated slag to be used in demonstrating the Amex process. Most of the laboratory work was done by J. M. Delozier and C. L. Ghann. J. H. Cooper's group of the Analytical Chemistry Division did the analytical work.

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1.0 ABSTRACT

The Amex process was developed for recovering americium from the accumulated Hanford slag and crucible waste. After the plutonium has been recovered by a 30% tributyl phosphate (TBP) extraction, the excess acid (5 M) in the aqueous waste is neutralized with calcium oxide or gaseous ammonia, and the americium is extracted with 30% TBP. The organic extract is scrubbed with ammonium nitrate, the americium is stripped with water, sorbed on Dowex 50W cation exchange resin, and eluted with ammonium acetate—acetic acid. Process losses are about 1%.

An alternate process of simultaneous extraction of plutonium and americium with partition of americium showed promise but will not be used in this recovery for reasons stated.

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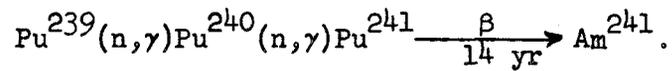
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## 2.0 INTRODUCTION

The purpose of the work reported here was to develop a process for recovery of the approximately 20 g of americium present in the 30,000 lb of accumulated Hanford slag and crucible waste. This waste will yield, on dissolution, about 80,000 gal of solution. The process will use as feed the aqueous effluent from an extraction column from which plutonium has been extracted with 30% tributyl phosphate (TBP).\*

The americium is formed from plutonium by the reaction



Most of the americium that has been recovered up to the present has been isolated from the plutonium peroxide precipitation filtrate. Americium recovery methods reported in the literature from this and other solutions include:

Coprecipitation with  $\text{LaF}_3$  (WASH-59, HW-22267)

Extraction with chelating agents such as thenoyltrifluoroacetone (ORNL-1088, ORNL-1423, CC-3874, BC-1)

Extraction with tributyl phosphate (ANL-4490, ANL-4545, ANL-4593, ANL-4667, AECD-3327)

Extraction with other solvents (ANL-4292, ANL-4593, ANL-4942, AECU-927)

Sorption on and elution from ion exchange resins (UCRL-923, UCRL-1054, UCRL-1796)

The high salt content and the large volume of the Hanford waste solution would make precipitation, chelation, or ion exchange methods difficult and economically impractical. Process development effort was therefore directed toward the extraction with 30% TBP to make the americium recovery similar to the plutonium recovery cycle.

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\*The process described in ORNL-1442 except that there will be no valence adjustment or feed filtration unless these are later shown to be necessary.

### 3.0 PROCESS DEVELOPMENT

The final Amex process flowsheet is shown in Fig. 1. The process development work was done with a synthetic solution of the same ionic composition as a solution of Hanford waste, spiked with  $2 \times 10^5$  Am<sup>241</sup> α c/m/ml (see Table 1), the average americium concentration of the solution of the Hanford material. The final demonstration of the process was made with a solution of a Hanford crucible and associated slag (see Appendix 1). This solution was treated by the plutonium extraction cycle before being fed to the Amex process extraction column (see Table 2).

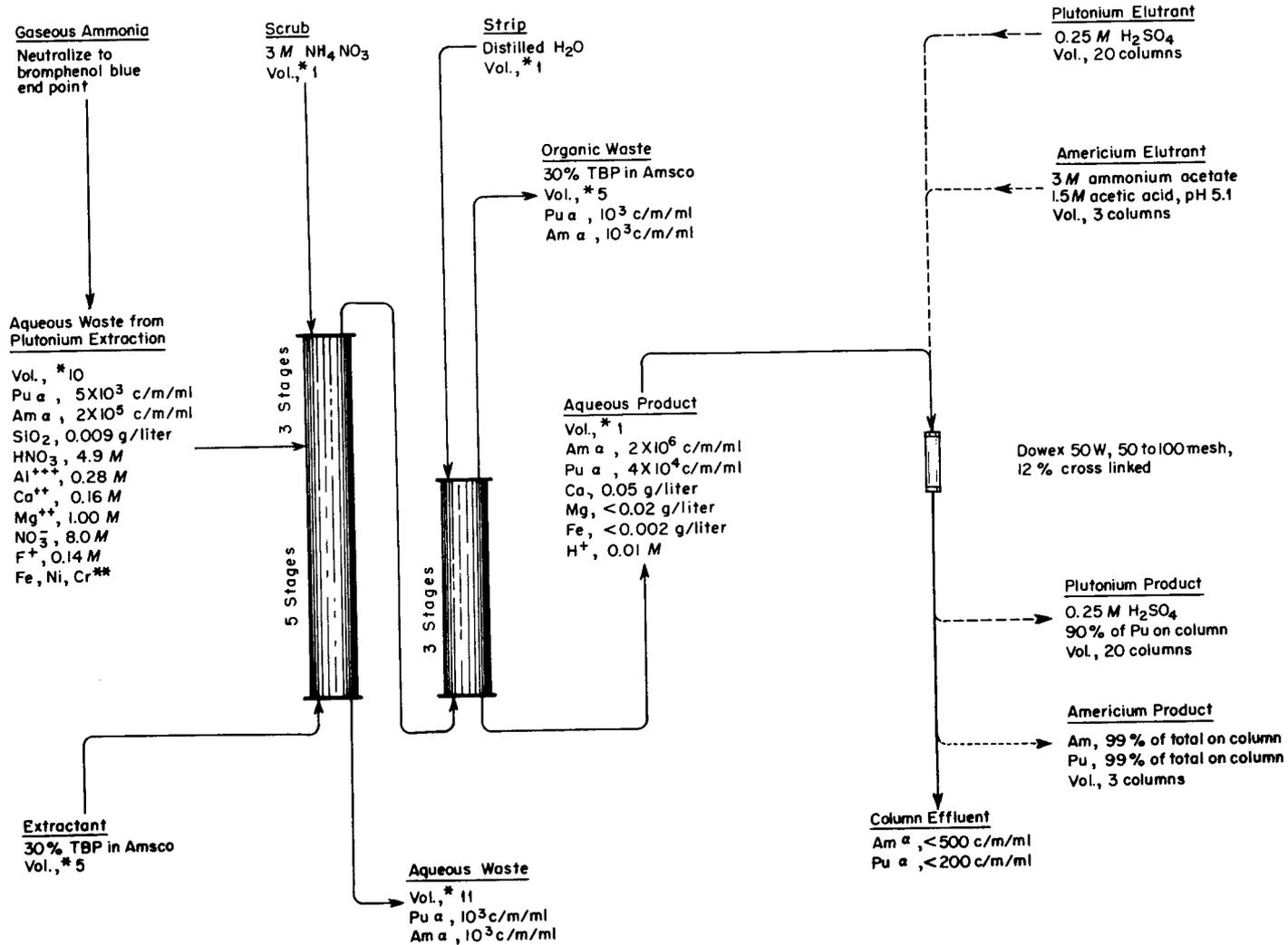
#### 3.1 Feed Preparation

The plutonium cycle aqueous effluent is neutralized with gaseous ammonia. Although the americium DC O/A (distribution coefficient, organic/aqueous) with ammonia is less than with some of the other neutralizing agents studied (see Sect. 3.2), there are fewer engineering problems associated with the continuous addition of a gaseous reagent on a plant scale.

The Unit Operations Section is designing a pH meter control for continuous neutralization of the feed. Until this unit has been developed, however, the neutralization will be controlled by the use of bromophenol blue indicator, which has a sharp color change coinciding with the neutral point of the feed.

#### 3.2 Isolation of Americium by Extraction

The plant extraction-scrub column will be 6 5/8 in. in diameter and will have a 24-ft extraction section and a 16-ft scrub section. The strip column will be 6 5/8 in. in diameter and 15 ft long.



\* Volume ratios  
 \*\* Dependent upon corrosion rate

Fig. 1. Flowsheet for Amex Recovery of Americium from Hanford Slag and Crucible Waste

Table 1

Composition of Aqueous Waste from 30% TBP Extraction of  
Plutonium from Hanford Slag and Crucible Solution

(taken from ORNL-1442, p. 84)

Basis: One 350-g plutonium reduction batch

Volume	24.5 liters		
Pu	$< 5 \times 10^3 \alpha$ c/m/ml		
Am	$\sim 2 \times 10^5 \alpha$ c/m/ml		
SiO <sub>2</sub>	0.009 g/liter	NO <sub>3</sub> <sup>-</sup>	8.0 <u>M</u>
HNO <sub>3</sub>	4.9 <u>M</u>	F <sup>-</sup>	0.14 <u>M</u>
Al <sup>+++</sup>	0.28 <u>M</u>	SO <sub>4</sub> <sup>=</sup>	0.009 <u>M</u>
Ca <sup>++</sup>	0.16 <u>M</u>	Fe, Ni, Cr	Dependent on corrosion rate
Mg <sup>++</sup>	1.00 <u>M</u>		

Table 2

Typical Countercurrent Batch Extraction of Plutonium  
from Solution of Hanford Crucible and Slag

Feed:  $3.00 \times 10^7$   $\alpha$ /m/ml; 5.5 N  $H^+$

Extractant: 30% TBP in Amsco

Scrub: 0.5 N  $HNO_3$

Strip: 0.05 M hydroxylamine sulfate

Stages: feed, 6; extraction, 2; scrub, 1; strip, 1

Stage	Aqueous Phase ( $\alpha$ c/m/ml)	Organic Phase ( $\alpha$ c/m/ml)	DC	EF
E-4	$2.38 \times 10^5$	$1.7 \times 10^5$	0.7	0.2
E-3	$3.05 \times 10^5$	$1.1 \times 10^6$	3.6	1.2
E-2	$3.1 \times 10^5$	$8.27 \times 10^6$	26.7	8.9
E-1	$2.5 \times 10^6$	$7.34 \times 10^7$	29.4	9.8
Sc-1	$1.24 \times 10^7$	$8.74 \times 10^7$	7.0	14.0
Sc-2	$2.57 \times 10^7$	$8.11 \times 10^7$	3.2	6.4
Sc-3	$4.3 \times 10^7$	$8.13 \times 10^7$	1.9	3.8
St-1	$1.96 \times 10^8$	$1.34 \times 10^6$	146	73
St-2	$3.38 \times 10^6$	$2.03 \times 10^4$	167	84
St-3	$5.18 \times 10^4$	$3.13 \times 10^3$	16.5	8.3
St-4	$4.24 \times 10^3$	$1.68 \times 10^3$	2.5	1.3
AW Composite	$3.06 \times 10^5$			
BP Composite	$1.68 \times 10^8$			
BW Composite		$1.25 \times 10^4$		

The americium is extracted with 30% tributyl phosphate (TBP) in Amsco.\* The used solvent will be treated with caustic (ORNL-1442, p. 54) and recycled continuously. The use of the same solvent for both americium and plutonium extractions permits simplification of equipment and a saving in solvent treatment.

a. Distribution of Americium in Extraction Step. The loss of americium in the extraction step is less than 1%. The distribution of americium between the two phases is a function of the concentration of the acid (see Fig. 2) and of the nitrate ion and to a lesser extent of the type of cation present (see Fig. 3). The americium is not extracted in the plutonium cycle because the americium DC (O/A) is only 0.02 in the highly acidic slag and crucible solution. This DC, however, is increased to about 60 at the Amex feed plate if the feed is neutralized with calcium oxide and to about 25 if it is neutralized with gaseous ammonia. The advantages of using ammonia over calcium oxide include not only the greater ease of addition of a gaseous reagent (Sect. 3.1) but also the lowered calcium content of the extraction column product (see Fig. 4). In addition, the ammonium ion is less objectionable than calcium as a contaminant in the influent to the ion exchange resin column used for final americium isolation.

The effect of increasing the nitrate ion concentration in the absence of free acid is to increase the americium DC (O/A). The best salting agent in common use is aluminum nitrate, but calcium, magnesium, and ammonium nitrate (see Fig. 3) all proved to have more than sufficient salting strength to provide adequate extraction of americium.

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\*In previous Pilot Plant studies Amsco-123-15 and Amsco-125-90W were tried, with no observable differences in operation or results. The type of Amsco to be used is therefore not specified.

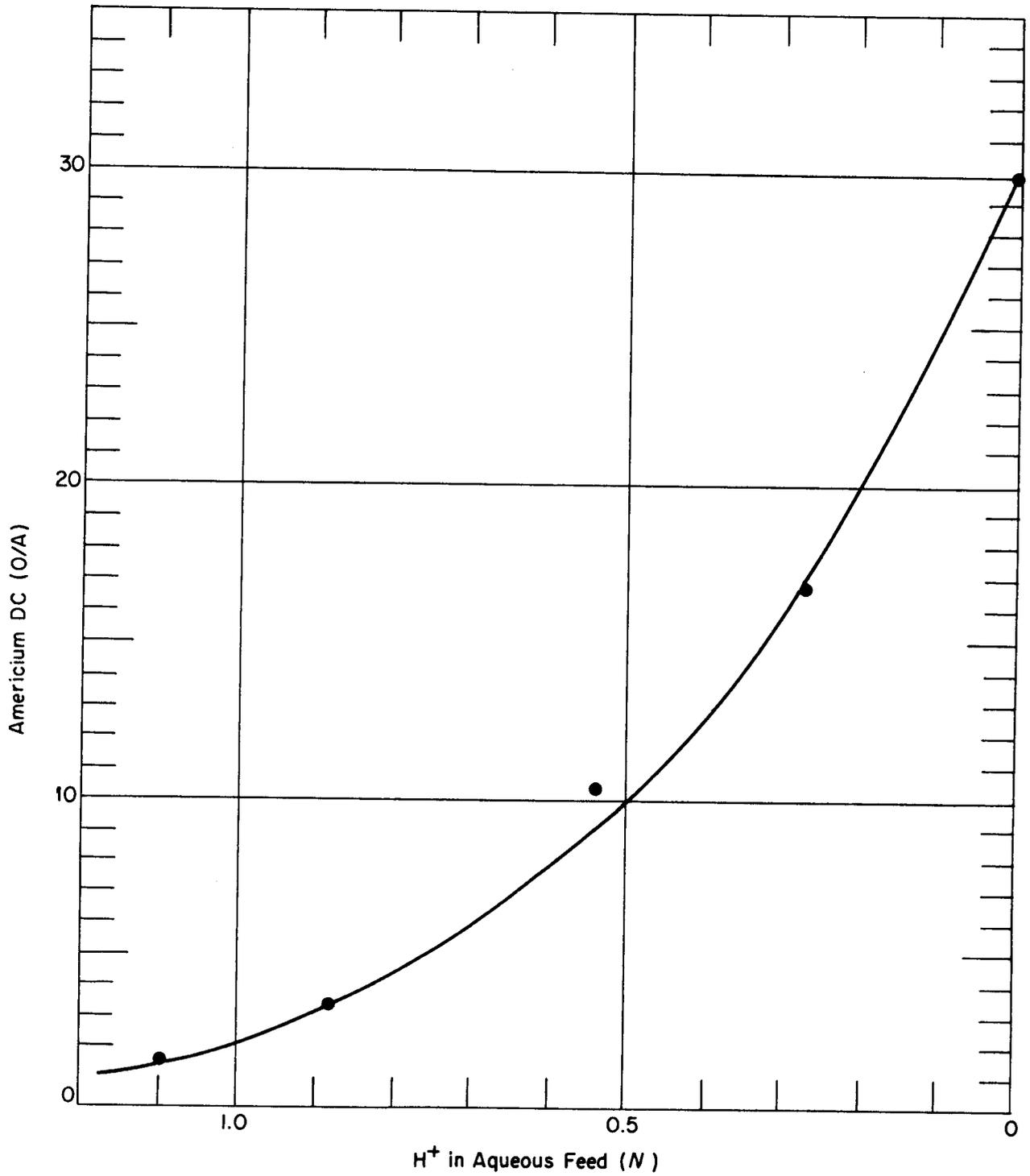


Fig. 2. Distribution of Americium between Aqueous Solution and 30% TBP as a Function of the Free Acid Concentration in the Aqueous Feed. Constant Total Nitrate Concentration; Lime Neutralized

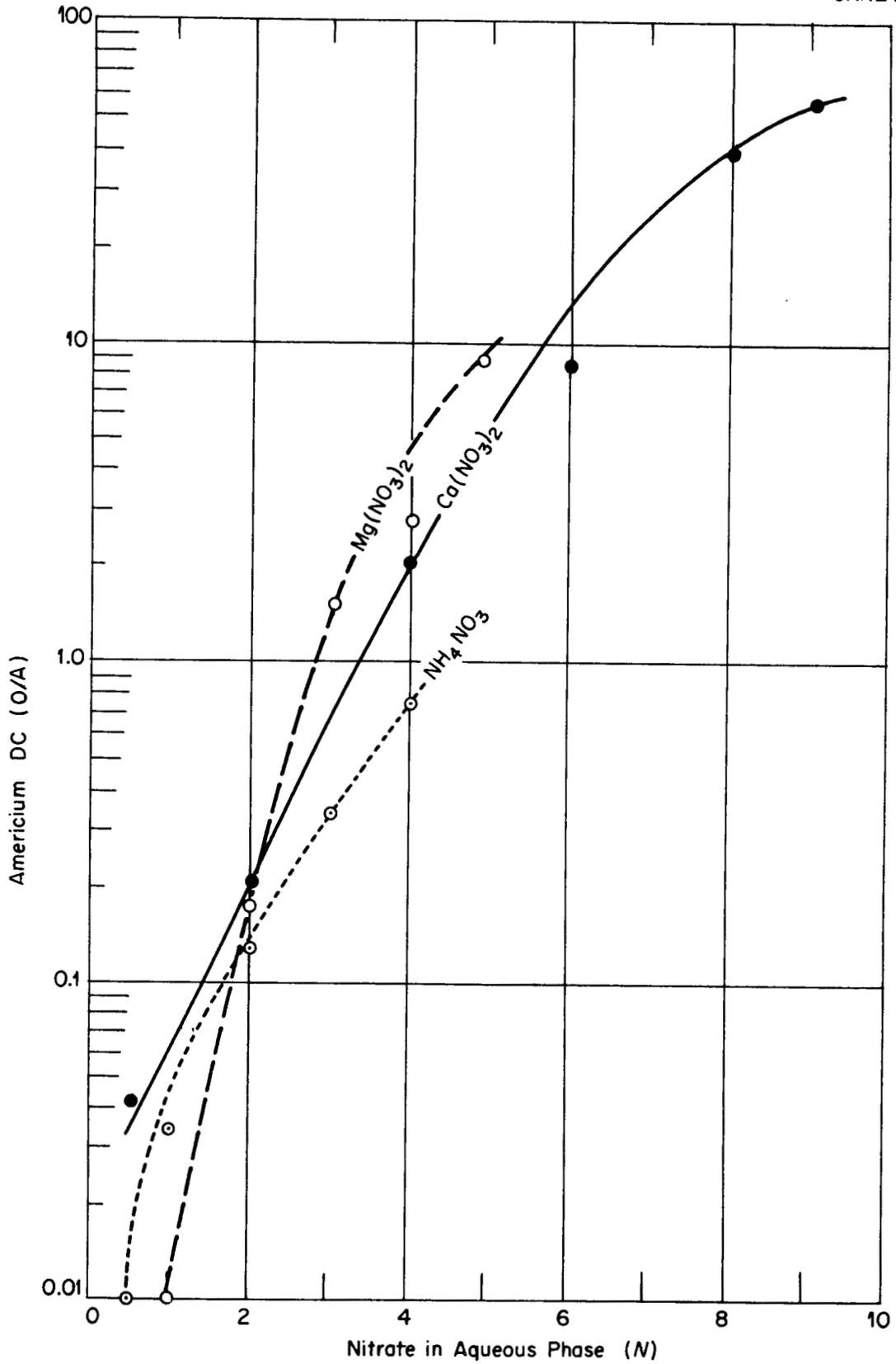


Fig. 3. Distribution of Americium between Aqueous Solution and 30% TBP as a function of Concentration of Ammonium, Calcium, and Magnesium Nitrates in the Aqueous Phase.

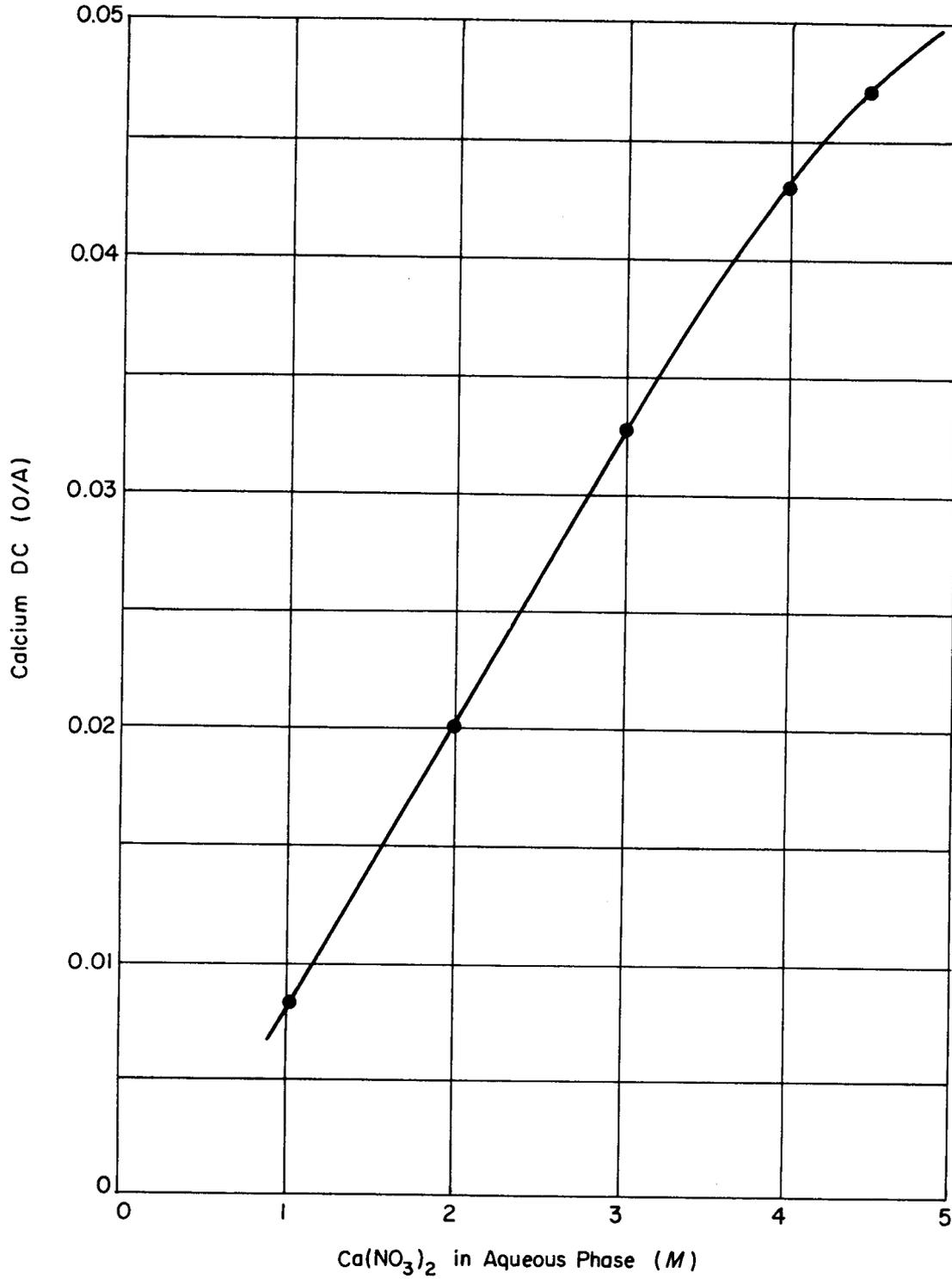


Fig. 4. Distribution of Calcium between Aqueous Solution and 30% TBP as a Function of the Calcium Nitrate Concentration in the Aqueous Phase.

b. Scrubbing Step. The organic extract is scrubbed with 3 M ammonium nitrate. Both calcium and magnesium are slightly extractable with 30% TBP. Although the distribution coefficients at the feed plate for these ions are quite small (about 0.068 for calcium and 0.0045 for magnesium), this is sufficient extractability to give a calcium plus magnesium concentration of 10 g/liter in the unscrubbed product, while the americium concentration is only  $5 \times 10^{-4}$  g/liter. The scrubbing step reduced the calcium and magnesium content of the final product to less than 0.01 g/liter, the lower limit of the analytical method used. The DC (O/A) of ammonium from the 3 M ammonium nitrate scrub solution is 0.003, thereby giving about 1.2 g/liter ammonium nitrate in the product.

c. Stripping Step. The americium is stripped from the organic solvent with distilled water. The strip DC (O/A) in the first stage is about  $10^3$ .

d. Flow Ratios. The concentration of americium in the product is determined by the ratio of feed to product flow rate in the solvent extraction system. The distribution coefficients of the americium for both the extraction (about 25) and strip (about  $10^3$ ) are high enough that the extraction and stripping flow ratios are limited only by operational characteristics of the pulse columns. On the recommendation of the plant engineers, the feed-to-extractant flow ratio was set at 2 and the extraction-to-strip at 5, thus giving an overall concentration factor of 10 for the solvent extraction system.

The maximum ratio of extractant to scrub was set by the plant engineers at 5. Since an extraction factor of at least 1 in the scrub is required, the concentration of the scrub solution was set at 3 M ammonium nitrate. As can be seen from Fig. 3, the distribution coefficient (O/A) of americium in 3 M ammonium nitrate is about 0.35. Thus with a flow ratio of extractant to scrub of 5, the extraction factor in the scrub section is 1.7.

e. Theoretical Stages Required. The numbers of theoretical stages that would be required in the three sections of the pulse columns were determined by laboratory countercurrent extraction experiments to be five extraction, three scrub, and three strip stages. This number of stages gives americium losses of less than  $10^3 \alpha$  c/m/ml in both aqueous and organic waste streams. The countercurrent batch extraction experiment closely approximates the operation of a continuous countercurrent column and allows an evaluation of the number of theoretical stages that would be needed at steady-state conditions in the column. To supplement these runs, faster and simpler exhaustive extractions were used for preliminary evaluation of the operation for some parts of the system. In this way (Table 3) three stages of 0.1 vol. of 3 M ammonium nitrate was shown to give satisfactory calcium removal from pregnant organic. To allow for differences between laboratory and plant conditions, 0.2 vol. of 3 M ammonium nitrate will be used.

f. Pulse Column Operation. In several runs made under flowsheet conditions in 0.5-in.-diam. pulse columns, there were no mechanical difficulties. The extraction column operated at 11 ml/m/cm<sup>2</sup> total flow (about 700 gal/hr/ft<sup>2</sup>) without flooding, and there were no stable emulsions formed. The height of a theoretical stage for plant-size columns could not be determined from the small-column tests, but the batch countercurrent data reported in Sect. 3.2 e. indicate that the columns that are to be used for the separation (see Sect. 3.2) have a sufficient number of stages. Multiple feed inlets are to be built into the extraction column to adjust the length of the scrub section if this is shown to be necessary.

g. Simultaneous Extraction of Plutonium and Americium. One run was made in which the americium and plutonium were extracted simultaneously. Such a process was not considered desirable, however, for the recovery of the americium in the present program (see Appendix 2).

Table 3

Exhaustive Extractions of Pregnant Organic to Determine Ammonium Nitrate Concentration and Number of Stages Needed in Scrub Section

Organic/aqueous vol. ratio: 10 in each stage

Extractant: 31.5% TBP-Amsco which had been equilibrated with calcium oxide—neutralized feed

Stage	Aqueous Phase		Organic Phase		Am		Ca	
	$\alpha$ Activity (c/m/ml)	Ca (g/liter)	$\alpha$ Activity (c/m/ml)	Ca (g/liter)	DC	EF	DC	EF
2 M Ammonium Nitrate								
1st	$3.98 \times 10^5$	53.6	$6.0 \times 10^5$	0.83	1.51	15.2	0.02	0.2
2nd	$2.11 \times 10^5$	8.46	$4.39 \times 10^5$	0.05	0.21	2.1	0.006	0.06
3rd	$1.8 \times 10^6$	0.45	$2.35 \times 10^5$	< 0.02	0.13	1.3	---	---
3 M Ammonium Nitrate								
1st	$2.72 \times 10^5$	52.9	$5.55 \times 10^5$	1.06	2.02	20.2	0.02	0.2
2nd	$1.08 \times 10^6$	10.3	$5.34 \times 10^5$	0.07	0.50	5.0	0.007	0.07
3rd	$9.96 \times 10^5$	0.6	$6.64 \times 10^5$	< 0.02	0.67	6.7	---	---
4 M Ammonium Nitrate								
1st	$2.0 \times 10^5$	52.3	$6.38 \times 10^5$	1.07	3.2	32.0	0.02	0.2
2nd	$8.75 \times 10^5$	10.8	$6.19 \times 10^5$	0.07	0.71	7.1	0.007	0.07
3rd	$8.48 \times 10^5$	0.6	$4.98 \times 10^5$	< 0.02	0.59	5.9	---	---

### 3.3 Countercurrent Demonstration of Amex Process

a. Normal Plutonium Concentration in the Amex Feed. Under normal conditions more than 99.8% of the plutonium will be extracted from the slag and crucible solution before the Amex process. Most of the plutonium left in the Amex feed will be discharged in the Amex aqueous waste. In a run (Table 4) using Hanford slag and crucible solution from which 99.9% of the plutonium had been extracted and in which the acid had been neutralized with ammonia, only 2% of the plutonium which was in the Amex feed was extracted with the americium while the remainder was in the Amex waste. Radiochemical analyses showed that  $\sim 400$  c/m/ml of americium was in the aqueous waste. The alpha activity of the organic waste in this run was  $\sim 30$  c/m/ml.

b. High Plutonium Concentration in the Amex Feed. In case of operational difficulty in the plutonium extraction cycle, the plutonium content of the Amex feed would be increased. In a run in which  $\sim 1\%$  of the total plutonium remained in the Amex feed (Table 5), about 28% of the plutonium was extracted with the americium while the remainder was in the Amex aqueous waste. An apparently high americium loss in the aqueous waste of this run can be accounted for as analytical background, since an analysis of a pure plutonium sample for americium will show as much as 1% of the plutonium alpha to be americium. (For analytical methods used in this program see CF-53-1-235.) The americium balance without this analysis indicates complete americium extraction. For further study on the extraction of plutonium from Amex feed, see Appendix 3.

c. Synthetic Feed Neutralized with Calcium Oxide. A typical run using a lime-neutralized synthetic feed containing no plutonium (Table 6) produced waste streams containing less than  $10^3$  Am  $\alpha$  c/m/ml (less than 1% of the total americium). The feed plate DC (O/A) was 50,

Table 4

Countercurrent Batch Extraction of Americium from Ammonia-Neutralized  
Aqueous Waste from Countercurrent Batch Extraction of Plutonium  
from Solution of Hanford Waste

Feed: gross  $\alpha$ ,  $1.7 \times 10^5$ ; 0.005 N basic

Extractant: 30% TBP in Amsco

Scrub: 3 M  $\text{NH}_4\text{NO}_3$

Strip: distilled water

Flow ratio: feed, 10; extraction, 5; scrub, 1; strip, 1

Stage	$\alpha$ Activity (c/m/ml)		DC	EF
	Aqueous Phase	Organic Phase		
E-4	$1.65 \times 10^4$	$2.98 \times 10^3$	0.18	0.09
E-3	$2.80 \times 10^4$	$1.62 \times 10^4$	0.58	0.29
E-2	$2.1 \times 10^4$	$1.08 \times 10^5$	5.14	2.57
E-1	$5.2 \times 10^4$	$9.26 \times 10^5$	17.8	8.90
Sc-1	$2.6 \times 10^6$	$7.38 \times 10^5$	0.28	1.40
Sc-2	$2.46 \times 10^6$	$6.70 \times 10^5$	0.27	1.35
Sc-3	$1.44 \times 10^6$	$3.83 \times 10^5$	0.26	1.30
St-1	$2.13 \times 10^6$	920	2320	464
St-2	$1.5 \times 10^4$	1950	---	---
St-3	$8.0 \times 10^3$	300	---	---

AW composite: gross  $\alpha$ ,  $5.1 \times 10^4$  c/m/ml; Pu  $\alpha$ ,  $1.38 \times 10^4$  c/m/ml;  
 Am  $\alpha$ , 412 c/m/ml

BP composite: gross  $\alpha$ ,  $1.39 \times 10^6$  c/m/ml; Pu  $\alpha$ ,  $3.58 \times 10^4$  c/m/ml;  
 Am  $\alpha$ ,  $1.45 \times 10^6$  c/m/ml; Mg, < 0.02 g/liter; Fe, < 0.002  
 g/liter; Ca, 0.05 g/liter

Table 5

Countercurrent Batch Extraction of Americium from Ammonia-Neutralized  
Aqueous Waste from Pulse Column Extraction of Plutonium from  
Solution of Hanford Waste

Feed: gross  $\alpha$ ,  $2.34 \times 10^6$  c/m/ml; Pu  $\alpha$ ,  $2.16 \times 10^6$  c/m/ml; Am  $\alpha$ ,  
 $1.82 \times 10^5$  c/m/ml; 0.17 N basic

Extractant: 30% TBP in Amsco

Scrub: 3 M  $\text{NH}_4\text{NO}_3$

Strip: distilled water

Flow ratio: feed, 10; extraction, 5; scrub, 1; strip, 1

Stage	$\alpha$ Activity (c/m/ml)		DC	EF
	Aqueous Phase	Organic Phase		
E-4	$1.78 \times 10^6$	$1.50 \times 10^5$	0.08	0.04
E-3	$1.71 \times 10^6$	$2.17 \times 10^5$	0.13	0.06
E-2	$1.87 \times 10^6$	$4.23 \times 10^5$	0.23	0.12
E-1	$1.83 \times 10^6$	$1.39 \times 10^6$	0.76	0.38
Sc-1	$3.98 \times 10^6$	$1.09 \times 10^6$	0.27	1.35
Sc-2	$3.16 \times 10^6$	$9.16 \times 10^5$	0.29	1.45
Sc-3	$1.80 \times 10^6$	$5.38 \times 10^5$	0.30	1.50
St-1	$3.42 \times 10^6$	$1.32 \times 10^4$	259	52
St-2	$8.34 \times 10^4$	$4.95 \times 10^3$	16.8	3.4
St-3	$2.92 \times 10^4$	$8.0 \times 10^3$	3.65	0.73

AW composite: gross  $\alpha$ ,  $1.65 \times 10^6$  c/m/ml; Pu  $\alpha$ ,  $1.60 \times 10^6$  c/m/ml;  
Am  $\alpha$ ,  $1.19 \times 10^4$  c/m/ml

BP composite: gross  $\alpha$ ,  $2.44 \times 10^6$  c/m/ml; Pu  $\alpha$ ,  $6.15 \times 10^5$  c/m/ml;  
Am  $\alpha$ ,  $2.07 \times 10^6$  c/m/ml

BW composite: gross  $\alpha$ ,  $5.54 \times 10^6$  c/m/ml

Table 6  
Countercurrent Batch Extraction of Americium from a  
Lime-Neutralized Synthetic Feed

Feed: Am  $\alpha$ ,  $1.3 \times 10^5$  c/m/ml; 0.04 M basic

Extractant: 30.6% TBP in Amsco

Scrub: 3 M  $\text{NH}_4\text{NO}_3$

Strip: distilled water

Flow ratio: feed, 10; extraction, 5; scrub, 1; strip, 1

Stage	$\alpha$ Activity (c/m/ml)		DC	EF
	Aqueous Phase	Organic Phase		
E-4	400	160	---	---
E-3	300	$1.43 \times 10^3$	---	---
E-2	800	$2.12 \times 10^4$	---	---
E-1	$8.1 \times 10^3$	$4.27 \times 10^5$	52.6	26.3
Sc-1	$6.42 \times 10^5$	$5.7 \times 10^5$	0.89	4.45
Sc-2	$1.9 \times 10^6$	$4.52 \times 10^5$	0.24	1.20
Sc-3	$1.05 \times 10^6$	$2.97 \times 10^5$	0.28	1.40
St-1	$1.31 \times 10^6$	185	7100	1600
St-2	$3.03 \times 10^3$	0	---	---
St-3	$1.34 \times 10^3$	10	---	---

AW composite: Am  $\alpha$ , 200 c/m/ml

BP composite: Am  $\alpha$ ,  $1.2 \times 10^6$  c/m/ml; Ca, 0.034 g/liter

BW composite: Am  $\alpha$ , 0 c/m/ml

and the composited product contained 0.034 g of calcium and/or magnesium per liter.

d. Synthetic Feed Neutralized with Gaseous Ammonia. The above run may be compared with a run (Table 7) in which a similar feed was neutralized with gaseous ammonia. The aqueous waste stream contained  $8 \times 10^3$  Am  $\alpha$  c/m/ml, the DC (O/A) at the feed plate was 22, and the product contained 0.006 g of calcium and/or magnesium and 0.4 g of  $\text{NH}_4$  ion per liter.

### 3.4 Concentration of Americium by Ion Exchange

Two ion exchange columns, each 4 in. in diameter and with a resin bed 12 in. high, have been prepared for use in the plant. The columns were filled with Dowex 50W resin, 12% cross linked, 50 to 100 mesh, which had been treated according to the resin preparation procedure described in ORNL-1449, p. 55. Based on 6% theoretical saturation of the resin with americium, as was determined from small scale tests, and 100% excess resin, one such column will hold 22 g of americium, about the amount expected to be recovered. The second column is a stand-by.

The concentrations of the americium, plutonium, and inert ions such as calcium, magnesium, and iron will depend on operating conditions in the plant. Under laboratory conditions the americium product from the solvent extraction cycle had the following composition:

Am	$1.5 \times 10^6 \alpha$ c/m/ml	Mg	<0.02 g/liter
Pu	$4 \times 10^4 \alpha$ c/m/ml	Fe	<0.002 g/liter
Ca	0.05 g/liter	H <sup>+</sup>	0.01 <u>N</u>

This product was successfully sorbed on a resin column 2 mm in diameter and 50 mm long at a flow rate of about 10 ml/m/cm<sup>2</sup>. The effluent stream had an activity of 500  $\alpha$  c/m/ml. Since the feed to the ion exchange

Table 7  
Countercurrent Batch Extraction of Americium from  
Ammonia-Neutralized Synthetic Feed

Feed: Am  $\alpha$ ,  $5.25 \times 10^5$  c/m/ml; neutral

Extractant: 30.6% TBP in Amsco

Scrub: 3.0 M  $\text{NH}_4\text{NO}_3$

Strip: distilled water

Flow ratio: feed, 10; extraction, 5; scrub, 1; strip, 1

Stage	$\alpha$ Activity (c/m/ml)		DC	EF
	Aqueous Phase	Organic Phase		
E-4	$7.5 \times 10^3$	$3.0 \times 10^3$	0.4	0.2
E-3	$7.5 \times 10^3$	$3.15 \times 10^4$	4.2	2.1
E-2	$1.68 \times 10^4$	$3.0 \times 10^5$	17.6	8.8
E-1	$1.15 \times 10^5$	$2.54 \times 10^6$	22.1	11.1
Sc-1	$8.07 \times 10^6$	$2.44 \times 10^6$	0.30	1.50
Sc-2	$7.31 \times 10^6$	$1.76 \times 10^6$	0.24	1.20
Sc-3	$3.86 \times 10^6$	$9.49 \times 10^5$	0.25	1.25
St-1	$4.99 \times 10^6$	$5 \times 10^3$	998	199
St-2	$5.22 \times 10^3$	885	5.9	1.2
St-3	560	370	---	---

AW composite: Am  $\alpha$ ,  $8.8 \times 10^3$  c/m/ml

BP composite: Am  $\alpha$ ,  $3.02 \times 10^6$  c/m/ml; Ca and/or Mg, 0.006 g/liter,  
 $\text{NH}_4$ , 0.4 g/liter

BW composite: Am  $\alpha$ , 230 c/m/ml

column in the plant may be somewhat different from that used in the laboratory studies, a solution of lower americium concentration and higher plutonium and inert ion concentrations, namely,

Am,  $1.1 \times 10^5$   $\alpha$  c/m/ml      Pu,  $9.5 \times 10^4$   $\alpha$  c/m/ml      Ca + Mg, 0.1 g/liter

was sorbed on a similar column. Under these conditions the americium band represented about 6% of the theoretical capacity of the resin, and the effluent had an alpha activity of about  $10^3$   $\alpha$  c/m/ml. It should be emphasized that these test columns were very much shorter than the plant-size column, and the effluent would be expected to contain much more americium than the plant effluent.

The elution scheme of the americium from the resin has not been definitely set and will depend on the anion desired in the final product and the impurities cosorbed on the resin. Acetate, nitrate, and chloride were used successfully to remove americium from small resin columns. The most promising scheme uses 0.25 M  $H_2SO_4$  for the selective elution of Pu(IV), followed by elution of the americium with ammonium acetate--acetic acid solution.

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Appendix 1

PROCEDURE USED BY HANFORD IN DISSOLVING SLAG AND CRUCIBLE FOR ORNL\*

The dissolution flowsheet in ORNL-1442, p. 80, was used. A slag and crucible from reduction run Y-9-8-2, August, 1949 (225 Mwd/ton), was obtained. It contained a pressed crucible weighing about 1800 g. To conform with flowsheet requirements, 800 g of crucible fragments was removed, leaving the slag, sand, and about 1000 g of magnesium oxide crucible. The material was charged to the dissolver, and the following reagents were added:

12.5 liters of 60% (13 M)  $\text{HNO}_3$   
4.0 liters of water  
0.5 liter of 50% (1.7 M) aluminum nitrate nonahydrate

The solution was heated without reflux until all iodine was removed. During this period 3 liters of solution distilled off. The total dissolution time was 2 hr.

The following reagents were then added:

3.5 liters of 50% aluminum nitrate nonahydrate and 1.0 liter of water and the solution was refluxed for 6 hr. Analysis of samples taken at this time showed:

Plutonium (radioassay), 0.470 g/liter                      Hydrogen ion, 5.05 M.

The volume was 18 liters. To conform to requested final volume and acidity, nitric acid and water were added to bring the final volume to 20 liters and the hydrogen ion concentration to 5.7 M.

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\*This section is taken from HW-30036.

17.5 liters of this solution was transferred to the polythene bottles furnished. The solution was agitated during transfer to achieve uniform distribution of solids to all five bottles. The balance of the solution remained as a heel which could not be transferred because of equipment difficulties. The final analysis\* of the solution showed:

Plutonium (radioassay)	0.420 g/liter
Assumed isotope correction factor	0.88
Plutonium concentration	0.37 g/liter
Volume	17.5 liters
Plutonium content	6.5 g
Hydrogen ion	5.7 <u>M</u>

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\* Analysis of this material at ORNL showed:

Gross $\alpha$ , $3.00 \times 10^7$ c/m/ml
Pu $\alpha$ , $3.27 \times 10^7$ c/m/ml
Am $\alpha$ , $2.71 \times 10^5$ c/m/ml
Ca, 11.29 g/liter
Mg, 22.8 g/liter
Fe, 0.63 g/liter
Ni, 0.05 g/liter
Al, 8.75 g/liter
F <sup>-</sup> , 4.67 g/liter
H <sup>+</sup> , 5.50 <u>N</u>

Appendix 2

SIMULTANEOUS EXTRACTION OF PLUTONIUM AND AMERICIUM

In a meeting held on September 16, 1953 consideration was given to a process\* for the simultaneous extraction of plutonium and americium. The plutonium recovery cycle had had extensive development (ORNL-1442), and the plans for conversion of ORNL facilities for this use had been made prior to receipt of the authorization for the americium recovery. Therefore, it was decided that the recovery of the americium should be made on the aqueous waste solution from the plutonium cycle so as not to interfere with the plutonium recovery schedule.

The feasibility of extracting plutonium and americium simultaneously from a partially neutralized solution of Hanford slag and crucible waste was demonstrated in a single countercurrent batch extraction experiment. When the slag and crucible solution was neutralized to 0.6 N acid, the gross alpha DC (O/A) with 30% TBP was 442; at 0.19 N acid, the DC (O/A) was 170; but at 0.07 N acid the DC (O/A) had dropped to 0.64. The americium product from a run made using feed at 0.19 N acid (Table 8) contained essentially all the americium and 9% of the plutonium. The plutonium product contained the remainder of the plutonium.

A considerably better partitioning agent would be a properly adjusted concentration of ammonium nitrate since the 3 N acid used interferes with the plutonium strip.

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\*A process using the simultaneous extraction of americium and plutonium and separation of the americium with 10 M HNO<sub>3</sub> was reported in the Los Alamos Scientific Laboratory Progress Report of Aug. 20, 1953 (WASH-137), but this information was not received at this laboratory until after Sept. 30, 1953 (CF-53-9-187).

Table 8

Countercurrent Batch Extraction Demonstrating a Three-Column Type Flowsheet for Simultaneous Extraction of Plutonium and Americium

Feed: gross  $\alpha$ ,  $3 \times 10^7$  c/m/ml; Am  $\alpha$ ,  $2.71 \times 10^5$  c/m/ml; acid, 0.19 N

Extractant: 30% TBP in Amsco

Scrub: 3 M  $\text{NH}_4\text{NO}_3$

Partition: 3 M  $\text{HNO}_3$

Strip: 0.1 N hydroxylamine sulfate

Flow ratio: feed, 10; extraction, 5; scrub, 1; partition, 1; strip, 2

Stage	$\alpha$ Activity (c/m/ml)		DC	EF
	Aqueous Phase	Organic Phase		
Ex-4	$2.85 \times 10^4$	$4.80 \times 10^5$	20.4	10.2
Ex-3	$2.38 \times 10^5$	$1.74 \times 10^6$	7.3	3.7
Ex-2	$9.92 \times 10^5$	$3.10 \times 10^6$	3.1	1.6
Ex-1	$1.87 \times 10^6$	$6.07 \times 10^7$	32.5	16.3
Sc-1	$1.69 \times 10^7$	$5.08 \times 10^7$	3.0	15.0
Sc-2	$8.81 \times 10^6$	$5.00 \times 10^7$	5.7	28.5
Sc-3	$5.97 \times 10^6$	$5.54 \times 10^7$	9.3	46.5
P-1	$1.42 \times 10^7$	$5.25 \times 10^7$	0.27	0.14
P-2	$1.10 \times 10^7$	$5.42 \times 10^7$	0.20	0.10
P-3	$8.92 \times 10^6$	$5.77 \times 10^7$	0.15	0.08
P-4	$4.3 \times 10^6$	$4.80 \times 10^7$	0.09	0.04
St-1	$1.71 \times 10^8$	$4.72 \times 10^7$	3.6	1.44
St-2	$2.72 \times 10^8$	$4.62 \times 10^7$	5.9	2.36
St-3	$1.06 \times 10^8$	$4.21 \times 10^5$	250	100
St-4	$2.8 \times 10^6$	$5.50 \times 10^3$	510	204

BP (americium product):  $4.17 \times 10^5$  Am  $\alpha$  c/m/ml;  $1.77 \times 10^7$  Pu  $\alpha$  c/m/ml

CP (plutonium product):  $6.64 \times 10^4$  Am  $\alpha$  c/m/ml;  $1.62 \times 10^8$  Pu  $\alpha$  c/m/ml

### Appendix 3

#### EXTRACTION OF PLUTONIUM IN THE AMEX PROCESS

As has been pointed out (see Sect. 3.3), plutonium that remains in the Amex feed after the plutonium extraction cycle is also largely unextracted in the americium extraction cycle. A suggested explanation of this fact is that under the neutral or slightly alkaline conditions in the Amex feed, the Pu(IV) is partially in a hydrolyzed and perhaps polymerized state. Approximately one third of the plutonium was recovered with the americium while the other two thirds remained in the aqueous waste. Since the americium will eventually have to be separated from the plutonium and since the amount of plutonium lost is a negligible percentage of the total, this is not only allowable but also desirable. However, if an appreciable amount of plutonium were not extracted in the plutonium cycle, a method of recovering this plutonium in the Amex process would be advantageous.

A series of exhaustive batch extractions showed that the addition of 0.1  $M$   $Na_2Cr_2O_7$  to the Amex feed solution before neutralization increased the extractability of the plutonium (see Table 9). Digestion of this feed at boiling with total reflux for 3 hr further increased the extractability of the plutonium. In one run over 98% of the plutonium present was extracted with the americium in three stages.

Table 9

Distribution Coefficient (O/A) for Amex Feeds Having Various Treatments

Feed: Pu  $\alpha$ ,  $4 \times 10^6$  c/m/ml; Am  $\alpha$ ,  $2 \times 10^5$  c/m/ml

Run 1: neutralized feed without dichromate

2: feed to which 0.1 M  $\text{Na}_2\text{Cr}_2\text{O}_7$  was added before neutralization

3: feed to which 0.1 M  $\text{Na}_2\text{Cr}_2\text{O}_7$  was added, before neutralization;  
after neutralization, digested by boiling at total reflux for  
3 hr

Run No.	Plutonium Distribution Coefficient		
	Stage 1	Stage 2	Stage 3
1	0.047	0.014	0.013
2	10	0.28	0.021
3	47	0.58	0.04

