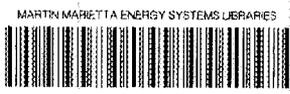


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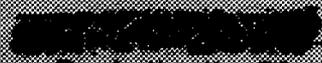
PUREX PROCESS FOR PLUTONIUM AND URANIUM RECOVERY



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PUREX PROCESS FOR PLUTONIUM AND URANIUM RECOVERY

by

W. B. Lanham and T. C. Runion

DATE ISSUED

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To: F. L. Steahly

Date: October 4, 1949

From: W. B. Lanham and T. C. Runion

Subject: Purex Process for Plutonium and Uranium Recovery

Laboratory data have been obtained which indicate that the recovery of plutonium and uranium, and decontamination from fission products, is feasible in a solvent extraction process using tributyl phosphate. Since nitric acid, rather than solid aluminum nitrate, is used as a salting agent, subsequent waste disposal problems are greatly simplified. By distilling off the nitric acid for reuse, the fission products are made readily available in a "packaged" form.

In laboratory countercurrent batch runs, losses for plutonium and uranium were less than 0.1%, with beta decontamination factors of greater than 7×10^3 in a single extraction. These data compare favorably with those previously obtained with the Redox Process. The procedure consists of extracting plutonium IV and uranium with 15% tributyl phosphate - 85% "Varsol", using 5.0 N nitric as a salting agent. The optimum uranium concentration in the feed is about one molar.

Since the preliminary results are very promising, further laboratory development is being actively pursued, and as soon as possible the process will be tested on a larger scale.

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To distinguish this process from Redox and from the process for the recovery of uranium from metal waste using the same solvent, the name Purex has been applied (Plutonium, Uranium, Reduction, Extraction).

The equipment necessary for this process will be very similar to that required for Redox and the construction of the Redox plant should in no way depend on the final demonstration of the Purex Process.

Laboratory Countercurrent Batch Demonstration

Although further development will be required to determine the optimum process conditions, a tentative flowsheet for the first extraction is as follows:

Feed Solutions

Metal feed: 1.0 M $UO_2(NO_3)_2$, 6.0 N HNO_3 , Pu^{IV}

Organic feed: 15% tributyl phosphate, 85% "Varsol", 0.15 N HNO_3

Scrub feed: 3.5 N HNO_3

Flow Ratios

Metal/Organic/Scrub = 3/15/2

A series of runs was made in a laboratory countercurrent batch extractor with a nitric acid concentration in the extraction section of about 5 N. The solvent to total aqueous flow ratio was maintained at 3 to 1 to obtain a satisfactory plutonium extraction factor at the feed plate. To insure that the

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plutonium tracer used in these studies was all in the tetravalent state, the nitrous acid oxidation procedure developed by J. R. Thomas and H. W. Crandall (CN-3733) was employed. Uranium slug dissolver solution, diluted with acid to the necessary uranium and HNO_3 concentrations, was the source of the feeds for the various runs. It was found in these runs that the factors which contributed to increased separation of plutonium and uranium from fission products were (1) lowered acid concentration in the scrub solution, from 5 N to 3.5 N (Run 2), (2) a high percentage uranium concentration of the solvent at the feed plate (Runs 3, 4, and 5) and, (3) a solvent mixture low in reducing impurities (Run 6). The conditions and the results obtained from the laboratory runs are given in Table I.

Plutonium Distribution Studies

The Purex Process was based on laboratory batch studies showing the effect of nitric acid and uranium concentration on the distribution coefficients of various valence states of plutonium.

The extraction of plutonium IV by 15% tributyl phosphate in Varsol from 1.0 M HNO_3 was greater than plutonium VI by a factor of ca. 10, and greater than plutonium III by a factor of almost 100 (see Tables 2, 3, 4). However, plutonium III was oxidized to plutonium IV at NO_3^- concentrations greater than 3.0 N. Also, in the initial experiments, untreated, commercial grade tributyl phosphate was used in the solvent mixture and considerable reduction of plutonium ^{IV} was caused by the presence of butyl alcohol and other reducing impurities. Washing with 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ -0.1 M HNO_3 , followed by washes with sodium carbonate and water, lowered the reducing normality of the tributyl

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phosphate from 0.19 to 0.06. The reducing normality of a final 50% cut of a fractional vacuum distillation was 0.005. These solvent pretreatment procedures successively improved the extraction of both plutonium IV and plutonium VI (see Tables 2 and 3). In all cases, however, the extraction of plutonium IV was higher than that of plutonium VI by factors of 3-10.

In these experiments, plutonium III was prepared by reduction with 0.02 N hydroxylamine in 0.5 M HNO_3 and plutonium ^{VI} was prepared by oxidation with 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$, 0.1 M HNO_3 , at 85° for 4.5 hours. To establish plutonium IV, the procedure outlined by Crandall and Thomas in "The Chelate Process" (CN-3733) was used. In this method, all plutonium is reduced to the three state and then reoxidized to plutonium IV with NaNO_2 .

It was found highly desirable in the development of a process for tributyl phosphate solvent extraction of uranium from waste metal (ORNL 260) to maintain the solvent at the feed plate near saturation in uranium to obtain maximum separation from fission products. Based on this consideration, plutonium IV was the only valence state about which a process could be designed (Table V). If the solvent were 90 percent saturated in uranium, the plutonium IV distribution coefficients were 0.37, 0.51, and 0.75 using aqueous feeds 4, 5, and 6 normal in HNO_3 , respectively. Under these conditions, the uranium distribution coefficients were 1.4, 1.45, and 1.6, respectively.

Separation of Uranium and Plutonium

The separation of uranium from plutonium was demonstrated batchwise in a manner similar to that employed in the Redox Process. That is, the plutonium in the solvent (Pu^{IV}) was easily stripped (as Pu^{III}) into a nitric acid solution

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containing ferrous sulfamate, the uranium remaining in the solvent.

In one series of experiments, the reducing agent concentration was held constant at 0.03 N and the acid concentration varied from 0 to 6 N. The plutonium and uranium distribution coefficients were determined and the separation factors were calculated as functions of HNO_3 concentration (Table VI). The values varied from 13 at 0 N HNO_3 to 78 at 4 N HNO_3 . In another series of experiments, in which the concentration of ferrous sulfamate was varied from 0.01 to 0.4 N, the concentration of reducing agent showed no effect on the separation of uranium and plutonium. Other reducing agents (hydrazine, hydroxylamine) are being investigated as a substitute for ferrous sulfamate.

The distribution of fission products during this separation has not as yet been accurately determined.

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Table I

Results of Laboratory Countercurrent Batch Extraction Runs for the Recovery of Plutonium
and Uranium

Seven extraction and six scrub stages.
Three minute equilibrations in each stage.

Pu α in all feeds = 8×10^5 c/m/ml
Gross beta concentration of all feeds = 3×10^6 c/m/ml

Run Number	Conditions						Flow Ratio M/Sc/Sol. cc	Pu Loss %	U Loss %	Gross β Decontami- nation Factor	Saturation of Solvent at feed Plate in Uranium %
	Metal Feed		Scrub Feed HNO ₃ M	Solvent* Feed							
	HNO ₃ M	UO ₂ (NO ₃) ₂ M		HNO ₃ M	TBP %						
1	5.0	0.8	5	0.15	15	6/4/30	0.09	0.001	180	64	
2	6.0	0.8	3.5	0.15	15	6/4/30	0.03	0.001	400	60	
3	6.0	0.8	3.5	0.15	12	6/4/30	0.08	0.001	1.6×10^3	78	
4	6.0	0.8	3.5	0.15	12	6/4/25	0.10	0.05	1.7×10^3	97	
5	6.0	1.0	3.5	0.15	15	6/4/30	0.05	0.001	1.5×10^3	87	
6**	6.0	0.9	3.5	0.15	15	6/4/30	0.06	0.15	7.5×10^3	72	

* Tributyl phosphate (TBP) diluted with commercial "Varsol"

** The solvent used in this run was given the $\text{Cr}_2\text{O}_7^{2-} - \text{CO}_3^{2-} - \text{H}_2\text{O}$ wash described in the report.

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Table 2

Effect of HNO₃ Concentration and Solvent Pretreatment on Pu^{IV}Distribution Coefficients

Aqueous Phase: Pu^{IV} tracer in HNO₃
 Organic Phase: Equal volume 15% tributyl
 phosphate - 85% "Varsol"
 Temperature: 20°C ± 0.2

HNO ₃ Concentration (M)	Pu ^{IV} Distribution Coefficient (Org/Aq)		
	<u>1*</u>	<u>2*</u>	<u>3*</u>
0.01	0.434	-	2.19
0.5	3.45	-	8.74
1.0	2.49	0.65	9.39
3.0	4.4	7.03	11.83
5.0	-	13.12	12.36
8.0	15.18	17.03	17.13

- 1* Commercial tributyl phosphate was used in solvent. Reducing normality of the mixture was 0.03.
- 2* Tributyl phosphate was washed with 0.1 M HNO₃ - 0.1 M Cr₂O₇⁼, followed by washes with 1.0 M Na₂CO₃, and water. Reducing normality of the solvent mixture was 0.02.
- 3* Tributyl phosphate used was last 50% cut of a vacuum distillation. Reducing normality of solvent mixture was 0.0025.

Table 3

Effect of HNO₃ and Solvent Pretreatment on Pu^{VI} Distribution Coefficients

Aqueous Phase: Pu^{VI} tracer in HNO₃
Organic Phase: Equal volume 15% tributyl phosphate -
85% Varsol
Temperature: 20°C ± 0.2

HNO ₃ Concentration in Aqueous Feed (M)	Pu ^{VI} Distribution Coefficients (Org/Aq)			
	<u>1*</u>	<u>2*</u>	<u>3*</u>	<u>4*</u>
0.01	0.006	0.004	0.02	1.99
0.50	0.171	0.141	0.26	0.73
1.0	0.400	0.372	0.51	0.66
3.0	1.66	1.55	1.54	1.94
5.0	-	-	2.47	2.42
8.0	1.94	2.03	1.50	2.29

- 1* See Note 1, Table 2
- 2*) See Note 2, Table 2
- 3*) See Note 2, Table 2
- 4* See Note 3, Table 2

Table 4

Effect of HNO₃ on Plutonium III Distribution Coefficients

HNO ₃ Concentration in Aqueous Feed (M)	Pu ^{III} Distribution Coeff. (Org/Aq)
0.01	0.003
0.5	0.03
1.0	0.03
3.0	0.16

Note: At higher nitrate concentrations, Pu^{III} was apparently oxidized to Pu^{IV} very rapidly.

Table 5

Effect of Uranium Concentration on Plutonium Extraction

Aqueous Phase: Pu tracer, 3.0 M HNO₃, UO₂(NO₃)₂
 Organic Phase: 15% tributyl phosphate - 85% "Varsol"
 Temperature: 20°C ± 0.2

Aqueous Uranium Concentration (mg/ml)	Distribution Coefficients (Org/Aq)*	
	Pu ^{IV}	Pu ^{VI}
20	2.26	0.9,91
40	1.13	0.56
80	0.34	0.16
100	0.23	0.11
200	0.11	0.04

* The tributyl phosphate used in these experiments was not pretreated (reducing normality equals 0.19) and these figures, as previously indicated, are probably low.

Table VI

Effect of HNO₃ Concentration in Stripping on Plutonium and UraniumDistribution Coefficients and Separation Factors

Conditions:

Solvent Feed: Solvent product from countercurrent batch extraction 15% TBP in Varsol, U=42 mg/ml, P_{ux} = 2.6x10⁵ c/m/ml, 0.15 N HNO₃

Aqueous Strip Feed: 0.03 N ferrous sulfamate, varying acidity

Equal volume equilibrations for five minutes at 20°C

HNO ₃ Concentration of Strip Solution (M)	Distribution Coefficients (Org/Aq)		Separation Factor (U D.C.) (Pu D.C.)
	Pa U	β Pu	
0	0.55	0.04	13
1	1.9	0.08	23
2	4.0	0.09	46
3	5.8	0.09	62
4	7.6	0.10	78
5	7.2	0.09	79
6	6.9	0.10	66