[redacted]

ORNL 721
Chemistry-Separation
Processes for Plutonium
and Uranium 7A

AEC RESEARCH AND DEVELOPMENT REPORT

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360766 6

LABORATORY RECORDS 1994

Classification Cancelled
Or Changed To
By Authority Of AEC 9.13.71
By E. Goldberg Date 11.5.71

CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT FOR MONTH OF APRIL, 1950

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS DIVISION
...D CARBON CORPORATION
UCC
...OFFICE BOX P
...GE, TENNESSEE

CLASSIFICATION CANCELLED
David R. Hamrin 5/31/2013
ADD Signature Date
Single review of CCRP-declassified documents was authorized by DOE Office of Declassification memo of August 22, 1994.

[redacted]

[redacted]

Report Number: ORNL-721

This document consists of 35 pages.
Copy 7 of 100 Series A.

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT FOR MONTH OF APRIL, 1950

F. L. Steahly, Director
F. R. Bruce, Chief, Chemical Laboratory Section
F. L. Culler, Chief, Process Design Section
J. O. Davis, Chief, Unit Operations Section
D. G. Reid, Chief, Pilot Plants Section

Edited by:

W. K. Eister

DATE ISSUED

JUN 27 1950

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS DIVISION
Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

[redacted]

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0360766 6

[redacted]

ORNL 721
Chemistry-Separation
Processes for Plutonium & Uranium

INTERNAL DISTRIBUTION:

1. G. T. Felbeck (C&CCC)
2-3. 706-A Library
4. 706-B Library
5. Biology Library
6. Health Physics Library
7-8. Training School Library
9. Metallurgy Library
10-13. Central Files
14. C. E. Larson
15. A. M. Weinberg
16. E. J. Murphy
17. C. E. Center
18. J. A. Swartout
19. A. Hollaender
20. J. H. Gillette
21. D. C. Reid
22-23. F. L. Steahly
24. J. A. Lane
25. R. N. Lyon
26. W. D. Lavers (Y-12)
27. W. B. Humes (K-25)
28. Morton J. Skinner
29. D. W. Cardwell
30. F. R. Bruce
31. F. L. Culler
32. J. O. Davis
33. W. K. Eister

EXTERNAL DISTRIBUTION:

34-39. Argonne National Laboratory
40. Armed Forces Special Weapons Project
41-47. Atomic Energy Commission, Washington
48-51. Brookhaven National Laboratory
52-53. Carbide and Carbon Chemicals Division (K-25)
54. Chicago Operations Office
55-61. General Electric Company, Richland
62-63. Hanford Operations Office
64-65. Idaho Operations Office
66. Iowa State College
67. Kellex Corporation
68-71. Knolls Atomic Power Laboratory
72-74. Los Alamos
75-77. Mound Laboratory
78-81. New York Operations Office
82. Patent Branch, Washington
83-97. Technical Information Division, ORE
98-100. University of California Radiation Laboratory

[redacted]

Table of Contents

		Page Number
1.0	Abstract	5
2.0	Introduction	6
3.0	Summary	7
4.0	TBP Process	8
4.1	Dissolution of Hanford Metal Waste Sludge	8
4.2	Hanford Sludge Demonstration Runs	8
4.3	ORNL Waste Demonstration Runs	9
5.0	Purex Process	12
5.1	Radiation Stability of the Solvent	12
5.2	Batch Countercurrent Test of 30% TBP - 70% Gulf-BT Solvent	12
5.3	Distribution Coefficients for the TBP-Carbon Tetrachloride Solvent	17
5.4	Freezing Points of Metal Solution Feeds	17
5.5	Effect of Sulfuric Acid in the Strip Column	21
5.6	Plutonium Reducing Agent Study	21
5.7	Batch Countercurrent Test of a Static Uranium-Plutonium Partition Column	21
5.8	Column Test of the 15% TBP - 85% Varsol Flowsheet	22
5.9	Column Flooding Rates 30% TBP - 70% Varsol Flowsheet	28

[redacted]

Table of Contents (continued)

6.0 RaLa Process 28

6.1 Barium Sulfate Precipitation Without Carrier 28

6.2 One Column Versene Process 30

6.3 Elimination of Organic Color in the Product 30

7.0 25 Process - Final Product Concentration

8.0 Thorex Process - Batch Countercurrent Run Using Tributyl Phosphate - Carbon Tetrachloride Solvent 32

9.0 Fluoride Process Study - Fluorination Scale-up Test 32

10.0 Homogeneous Reactor Slurry Studies 34

11.0 Falling Film Evaporator 36

12.0 Pulse Solvent Extraction Column 36

13.0 Steam Jet Test 36

1.0 Abstract

The progress during the month of March on the following chemical technology problems is reported: the TBP Process for the recovery of uranium from the ORNL and Hanford Metal Waste; the Purex Process for the separation of uranium, plutonium and fission products from Hanford irradiated metal; the RaLa Process for separation of barium from metal solution; 25 Process for the recovery of fissionable uranium from the spent MTR fuel units; 23 Process for the separation of Uranium 233 from thorium; the Thorex Process for the recovery of thorium from the 23 Process Waste; a Fluoride Process study with object of separation of uranium, plutonium, and specific fission products; the Homogeneous Reactor Slurry Study to prepare a stable uranium slurry for use as the fuel in a homogeneous type reactor; a falling-film evaporator study aimed at the elimination of the foaming problem in the vaporation concentration of radioactive waste solutions; a preliminary study of a pulse solvent extraction column; and a test of a steam jet as a vacuum source.

2.0 Introduction

The major responsibilities of the Chemical Technology Division during this period were:

(1) Design and start-up of the chemical process facility at Arco for the recovery of fissionable material from the MTR and the EBR.

(2) Development of the TBP Process through the laboratory and "hot" pilot plant phases for the recovery of uranium from the Hanford metal waste.

(3) Improvement of the chemical process and facilities for the RaLa Process that is now in operation at ORNL.

(4) Development of the Purex Process for the separation of uranium, plutonium, and fission products from Hanford. The possible advantage of this process over others developed to date is that a volatile salting agent is used. It may be removed from the waste by evaporation and re-used in the process.

In addition to these problems, there are other problems related to the development of the homogeneous reactor, concentration and control of radioactive wastes, fluorination of irradiated uranium metal, chemical processing of irradiated thorium, and chemical engineering equipment studies.

3.0 Summary

TBP Process

(1) The uranium was successfully recovered from Hanford metal sludge in the pilot plant using a one-cycle solvent extraction process. The product purity was not comparable to the supernatant runs due to entrainment in the extraction column.

(2) Plutonium and uranium recovery from ORNL metal waste was demonstrated in the pilot plant extraction column.

Purex Process

(1) The amount of non-volatile reducing agent, ferrous sulfamate, required can be significantly reduced by the addition of hydroxylamine-hydrochloride.

(2) The strip uranium loss may be significantly reduced by using a 0.001 molar sulfuric acid strip solution.

RaLa Process

The separation of barium sulfate without lead sulfate carrier from metal solution was not successful using centrifugation.

4.0 TBP Process

4.1 Dissolution of Hanford Metal Waste Sludge

Sludge from the Hanford metal waste tank 101U was successfully dissolved by the addition of nitric acid to the sludge. The final solution had a volume of 110 liters and contained approximately 15.2 kilograms of uranium with a uranium concentration of 138 grams per liter and a nitric acid concentration of 4.3 molar. Complete solution of the sludge was effected by the addition of 48 liters of 70% nitric acid, and 34 liters of water. On another basis, 11.8 moles of nitric acid were required per mole of uranium. The final solution was clear (see Table 4.1).

At no time during the dissolving was there any evidence of excessive gasing. The rate of acid addition varied from 50 cc per minute for the first two liters to 4000 cc per minute for the last 23 liters.

4.2 Hanford Sludge Demonstration Runs

Pilot plant runs in packed countercurrent columns are now in progress demonstrating the TBP Process with the feed prepared from Hanford Metal Waste sludge. The first run has been completed with an overall uranium loss of 0.03% and a beta decontamination factor of 1.5×10^5 over the extraction column. The overall decontamination factor was markedly less because of aqueous entrainment in the extraction column. The final product contained 170 β counts and 0.02 γ millivolts per milligram of uranium.

Hanford Sludge Demonstration Runs (continued)

The feed for this run was prepared by adding the metal sludge to solution 170 liters of acidified 103 U supernatant yielding a final solution containing 67.5 grams of uranium per liter and 4.3 molar nitric acid. 80% of the uranium in the first run was derived from Hanford sludge. The second run is to be made with a higher proportion of the uranium derived from the supernatant.

4.3 ORNL Waste Demonstration Runs

Satisfactory operation of the extraction and the strip column was demonstrated using metal solution feed prepared from the ORNL metal waste. An overall uranium loss of 0.02% was obtained with a decontamination factor of 500. Approximately 0.1 percent of the plutonium was lost. The final uranium product contained approximately 22 counts of beta activity per milligram of uranium (see Table 4.3). This work will be resumed following the Hanford sludge runs.

Table 4.1

Dissolution of Hanford Metal Waste Sludge

First pilot plant sample from Hanford Tank 101U

Reagent	Volume, Liters	Rate of Addition ml/min	Visual Observation of Degree of Solution
70% HNO_3	1.5	50	
"	205	100	
"	11	250	Incomplete
"	10	1000	Incomplete
"	23	4000	
Water	34	4000	Complete

Final Solution: Volume 110 liters
Uranium 138 grams/liter
HNO_3 4.3 M

Acid Requirement: 11.3 moles HNO_3/mole U

[redacted]

Table 4.3

TBP Process - Pilot Plant Development with ORNL Metal Waste

		Run 0-1	Run 0-2
Feed: (AF)	Waste from ORNL Tank W-10		
	Uranium (g/l)	102	93
	HNO_3 (M)	3.9	4.6
	Ferrous Sulfamate (M)	0.0005	0.005
	$NaNO_2$ (M)	0.01	0.01
	Flowrate (ml/min)	60	
AX:	TBP (%)	15	
	Gulf BT (T)	85	
	HNO_3 (M)	0.1	
	Flowrate (ml/min)	170	150

No scrub in either run

Column: Extraction: 1-1/2" diameter packed 1/4" x 3/8" rings
Packed height (ft) 22.5 21.5

Run No.	% U Loss	% Pu Yield	β Decontamination Factor
0-1	0.01	77	420
0-2	0.01	99	645

Extraction Product Activity

	β c/m/mg U	Pu α c/m/mg U
0-1	27	260
0-2	22	357

5.0 Purex Process

5.1 Radiation Stability of the Solvent

The solvent for the Purex Process, tributyl phosphate, in the presence and the absence of the diluent, Gulf BT, was exposed to radiation equivalent to ten times that expected from beta radiation in the Purex column "A" operation employing Hanford solution. On the basis of uranium, plutonium, and beta extraction distribution coefficients, it was demonstrated that the solvent was not significantly affected. However, it was noticed that the irradiated solvent appeared cloudy immediately after irradiation and that on standing, a few drops of immiscible liquid appeared. This was probably water. The presence or absence of this second phase did not affect the distribution coefficient.

The solvent was irradiated using the ORNL van de Graaf generator which produced 20 microamperes of 1.3 million volt electrons. One second of this radiation was estimated to be equivalent to 33.8 curies of activity in the column for 100 seconds (see Tables 5.1-1, 2).

5.2 Batch Countercurrent Tests of 30% TBP - 70% Gulf BT Solvent

The chemical feasibility of increasing the TBP concentration from 15% to 30%, thereby increasing the uranium processed per volume of solution through the column, was satisfactorily demonstrated in a laboratory batch countercurrent run. The uranium throughput was increased by a factor

Batch Countercurrent Tests of 30% TBP - 70% Gulf BT Solvent (continued)

of 2.4 over that of the 15% TBP flowsheet. The beta decontamination factors for uranium and plutonium were 1.42×10^4 and 2.7×10^4, respectively. The losses of uranium and plutonium were 0.002% and 0.79%, respectively. The uranium decontamination of plutonium was 780. All of these results were comparable to those previously received using the 15% TBP solvent (see Table 5.2).

Table 5.1-1

Effect of High Energy Electron Radiation on Tributyl Phosphate

Aqueous Phase: 78 g/l U (as UNH)
3.7 M HNO_3
6.17×10^5 Pu-α cts/min/ml at 52% geometry
1.78×10^5 β cts/min/ml at 11% geometry
Used 50 ml

Organic Phase: Tributyl phosphate with or without Gulf Solvent BT diluent. Always used 15 ml of tributyl phosphate

Irradiation: One second of 20 microamperes of 1.3 million volt electrons

Treatment	Volume Diluent-ml	Distribution Coefficients		
		U	Pu	Beta
Non-Irradiated	None	23.4	6.0	0.086
	15 ml	13.8	2.8	0.027
	85 ml	3.4	0.5	0.004
Irradiated-Shaken*	None	28.1	7.3	0.102
	15 ml	12.8	2.2	0.026
	85 ml	3.6	0.6	0.005
Irradiated-Centrifuged*	None	25.5	6.0	0.099
	15 ml	13.0	3.1	0.024
	85 ml	2.7	0.4	0.003

* The irradiated tributyl phosphate appeared cloudy immediately after irradiation. On standing, a few droplets of an immiscible liquid appeared. In one series of tests this second phase was mixed into the major liquid by shaking; in another series it was separated by centrifugation.

Table 5.1-2

Effect of High Energy Electrons on Tributyl Phosphate in Gulf BT

Aqueous Phase: 50 ml as in Table I

Organic Phase: 30 ml equivolume solution of tributyl phosphate in Gulf Solvent BT.

Irradiation: One second of 20 microamperes of 1.3 million volt electrons.

Treatment	Distribution Coefficients		
	U	Pu	Beta
Non-Irradiated	11.5	3.43	0.026
Irradiated	13.9	3.25	0.034

Table 5.2

Countercurrent Batch Extraction Simulating Entire First Cycle of Purex Process Using 30 Percent TBP-70 Percent Varsol Solvent

Conditions	Run Characteristics: Column A	Column B	Column C
Stages:	6 Extraction, 4 Scrub	5 Extraction, 4 Scrub	7 Strip
Flowratio:	F/S/X=3/2/10	F/S/X=3/1/1	F/S=3/2
Feed:	315 g/l U, 3M HNO_3, Pu α, 1.39×10^6 c/m/ml Gross β-1.46×10^8 c/m/ml	Column A Product	Column B Product
Scrub:	3 M HNO_3	30 percent TBP - 70 percent Varsol	
Extractant:	30 percent TBP - 70 percent Varsol	2 M HNO_3, 0.03 M Fe^{++} 0.001 M H_2SO_4	

Process Phase	% Loss		β Decontamination	
	U	Pu	U	Pu
Extraction	0.0016	0.41	199	199
Scrub			26.5	26.5
Partition	0.0004	0.38	1.27	5.15
Strip	0.0001		2.12	
Total	0.002	0.79	1.4×10^4	2.72×10^4

[redacted]

5.3 Distribution Coefficients for the TBP Carbon Tetrachloride Solvent

The extraction of uranium, plutonium, and gross beta activity has been determined using tributyl phosphate diluted with carbon tetrachloride, over the range of TBP concentration from 30 to 50 percent of nitric acid concentration from 3 to 6 molar in the feed, and of uranium concentration from 40 to 595 grams per liter (see Table 5.3-1 and 2).

It was found that in order to maintain a satisfactory distribution coefficient for plutonium, the nitric acid concentration would have to be increased from approximately 3 molar to 6 molar. The plutonium distribution coefficients were about a factor of 3 lower in the carbon tetrachloride system than they were in the corresponding Varsol system.

5.4 Freezing Point of Metal Solution Feed

The freezing point of the metal solution feed as a function of the uranium concentration and the nitric acid concentration was determined over the range of 2-3 molar nitric acid and 325-428 grams uranium per liter. At 3 molar nitric acid, it was found that the maximum uranium concentration would be approximately 325 grams per liter (see Table 5.4) to maintain freezing point below 0°C.

Table 5.3-1

Nitric Acid Concentration Dependence of Plutonium Distribution

Conditions:

Aqueous Feed: Uranium and Nitric Acid as indicated, Pu (IV) α - 10^5 c/m/ml.

Solvent: 50 percent TBP - 50 percent CCl_4

Equilibration times were 10 minutes using two volumes of solvent to one volume of feed at room temperature.

Uranium Concentration in Feed (g/l)	Nitric Acid Molarity	Plutonium Distribution Coefficient
435	4.0	1.33
	5.0	2.56
	6.0	5.30
475	3.0	0.88
	4.0	1.14
	5.0	1.31
	6.0	2.56

Table 5.3-2

Plutonium (IV) and Gross Beta Distribution Coefficients as Functions of Percent Uranium Saturation of Solvent

Conditions:

Aqueous Feed: 3 M HNO_3, β = Ca. 10^6 c/m/ml, Pu (IV) $\alpha = 10^5$ c/m/ml, uranium as indicated.

Solvents: TBP as indicated diluted with CCl_4.

Equilibration times were 10 minutes using two volumes of solvent to one volume of feed at room temperature.

Percent TBP in Solvent	Uranium Concentration in Feed (g/l)	Distribution Coefficients			Percent Uranium Saturation in Solvent
		Gross β $\times 10^{-3}$	Plutonium	Uranium	
30	40	-	2.84	27.4	11
	119	-	0.93	21.8	30
	159	-	0.96	19.7	41
	198	-	0.60	17.1	51
	238	2.22	0.42	12.8	57
	278	2.09	0.30	10.4	64
	318	1.88	0.36	7.6	71
	357	1.23	0.19	4.8	79
40	357	3.73	0.44	11.4	63
	397	2.79	0.31	9.9	69
	435	2.22	0.29	7.2	75
	475	2.10	0.33	5.7	81
50	475	5.32	0.88	12.4	67
	515	3.98	0.71	10.5	72
	555	2.99	0.60	8.6	77
	595	2.52	0.49	6.7	81

Table 5.4

Freezing Point of Uranium Solutions in Nitric Acid

Nitric Acid Molarity	Uranium Concentration (g/l)	Freezing Point °C
3.0	428	18
	405	17
	381	14
	357	11
	325	0
2.5	428	17
	405	3
	381	2
	357	below 0
2.0	428	11
	405	1
	381	below 0
	357	below 0

5.5 The Effect of Sulfuric Acid on the Strip Column

The use of 0.001 molar sulfuric acid instead of water reduced the uranium loss in the strip column by a factor of 10^3. Formic and acetic acid were considered for the purpose of reducing the aqueous volume required to strip the uranium, but these were not effective.

5.6 Plutonium Reducing Agent Studies

Laboratory tests have indicated that the non-volatile reducing agent concentrations in the partition column may be lowered from 0.05 molar to 0.01 molar ferrous sulfamate by the addition of 0.03 molar hydroxylamine hydrochloride. The degree and rate of plutonium reduction was determined by measuring its distribution coefficient (see Table 5.6-1 and 2).

5.7 Batch Countercurrent Tests of a Static Uranium - Plutonium Partition Column

The operation of a static uranium-plutonium partition column was investigated by batch countercurrent techniques to determine if this method may be effective in decreasing the volume of the plutonium product solution from the first cycle. In this particular experiment, 8 volumes of feed from the extraction column were passed through 4 batch stages containing 1/5 volume of 1.0 M nitric acid - 0.05 M ferrous sulfamate. It was found that the final plutonium concentration in the first stage was

Batch Countercurrent Tests of a Static Uranium-Plutonium Partition Column (continued)

37 fold that of the feed and the plutonium loss from the fourth stage was 0.02% with a decontamination factor of 14 (see Table 5.7). Further work is to be done investigating reduced flows in countercurrent columns.

5.8 Column Test of the 15% TBP Flowsheet

The Purex Process with a 15% tributyl phosphate - 85% Gulf BT solvent was demonstrated in laboratory scale column with a hot feed. The uranium losses for extraction, partition, and stripping were 0.004, 0.005, and 0.3 percent, respectively. The addition of 0.001 molar sulfuric acid to the strip solution would significantly decrease the uranium loss reported. The decontamination across the extraction column varied from 1.4×10^3 to 9.5×10^3 as the length of the scrub section was increased from 4 to 10 feet. The plutonium loss in the first column was approximately 0.3 percent. The results of plutonium in the partition column were not significant because of uncontrolled operating conditions (see Table 5.8-1 and 2).

The "hot" feed for these runs was pumped using the displacement method. The displacement fluid was Gulf BT which was found to compare favorably with methyl cycle hexane.

Table 5.6-1

Distribution Coefficient of Plutonium after Extraction of 1B Column Feed with Ferrous Sulfamate-Hydroxylamine-Hydrochloride Solutions of Varying Concentrations

Conditions:
Organic Feed (BF): 30% TBP diluted with Varsol, Pu γ, 2.25×10^5 c/m/ml
Aqueous Extractant (BX): 1 M HNO_3, ferrous sulfamate and hydroxylamine-hydrochloride as indicated.

Contact times were 1 minute using four volumes of feed to one volume of extractant.

Concentration of Reducing Agents		Distribution Coefficient (Org/Aq)
$NH_2OH.HCl$ M	$Fe(NH_2SO_3)_2$ M	
0.03	0.01	0.0060
	0.005	0.0066
	0.001	0.0552
	0.0005	0.0923
	0.0001	0.1726
	0.0	0.7430
0.02	0.001	0.0598

Table 5.6-2

Rate of Plutonium Extraction from 1B Column Feed by Ferrous Sulfamate-Hydroxylamine-Hydrochloride Solutions of Varying Concentrations

Conditions:

Organic Feed (BF): 30% TBP diluted with Varsol, Pu γ = 1.60×10^5 c/m/ml

Aqueous Extractant (BX): 1 M HNO_3, ferrous sulfamate and hydroxylamine-hydrochloride as indicated.

Total contact times were 5 minutes using four volumes of feed to one volume of extractant.

Concentrations of Reducing Agents		Plutonium Concentration in Organic Phase ($c/m/ml \times 10^4$)					
Hydroxylamine Hydrochloride M	Ferrous Sulfamate M	0 Sec.	10 Sec.	30 Sec.	60 Sec.	120 Sec.	300 Sec
0.03	0.01	16.0	13.6	1.23	0.138	0.108	0.152
-	0.005	16.0	8.30	0.509	0.223	0.132	0.117
0.02	0.01	16.0	14.0	1.38	0.158	0.117	0.113
-	0.005	16.0	11.0	0.802	0.154	1.17	1.17
0.01	0.01	16.0	10.2	0.357	0.163	0.103	-
-	0.005	16.0	15.1	1.50	0.314	0.197	0.131

[redacted]

Table 5.7

Results of Simulated "Static" Type 1B Column Run

Conditions:

Four stages representing four short columns.

Feeds: BF = solvent product from 1A column; 30% TBP, 70% "Varsol"; BX = 0.05 M ferrous sulfamate, 2.5 M HNO_3, 24 g U/l

Flowratio: BF/BX = 5/1

	Composition of Solutions in the System at the End of the Run							
	Stage 1		Stage 2		Stage 3		Stage 4	
	Solvent Phase	Aqueous Phase	Solvent Phase	Aqueous Phase	Solvent Phase	Aqueous Phase	Solvent Phase	Aqueous Phase
Uranium (g/l)	88.8	22.0	92.0	21.8	92.0	22.8	92.0	21.6
HNO_3 (M)	-	3.0	-	2.9	-	2.7	-	2.6
Plutonium (cts/min/ml)	1×10^4	8.6×10^6	320.	3.1×10^5	32	4.6×10^3	30	900
Gross Beta (cts/min/ml)	3.2×10^4	9.5×10^4	2.8×10^4	1.1×10^5	2.0×10^4	1.6×10^5	1.3×10^4	9.9×10^4

Table 5.8-1

Decontamination and Loss Data for 1A Column

Column: 1 inch column packed with 1/4 x 1/4 inch split Raschig rings
Solvent: 15% TBP, 85% "Gulf BT"
Scrub: 3 M HNO_3
Feed: R10, 11, 14 135 g/l U, 2.9 M HNO_3 5.4×10^4 c/m/ml
Pu γ, 2.5×10^7 c/m/ml Gross β
R 15, 20 128 g/l U, 3.0 M HNO_3, 1.55×10^5 c/m/ml
Pu γ, 6.5×10^7 Gross β
Flowratio: AF/AS/AX = 3/2/10
Total Flow: 20% of flooding

Run	Feet of Scrub Section	Feet of Extraction Section	Percent Uranium Saturation	Percent Uranium Loss	Percent Plutonium Loss	Decontamination Factor
R10	4	16	71	0.004	0.102	1.45×10^3
R11			70	0.001	0.308	1.42×10^3
R14	6	14	50	0.002	0.35	1.88×10^3
R15			-	0.001	0.56	-
R20	10	10	58	0.019	0.33	9.54×10^3

[redacted]

Table 5.8-2

Separation of Uranium and Plutonium in the 1B Column

Column: 1 inch glass column packed with 1/4"x1/4" Raschig rings.
1BF: Solvent product from 1A column.
1BX: 0.03 M $Fe(NH_2SO_3)_2$, HNO_3 M given in table
1BS: 15% TBP, 85% "Gulf BT"
Flowratio: BF/BS/BS = 4/1/1
Total Flow: 43% of flooding

Run	Feet of Scrub Section	Feet of Extraction Section	HNO_3 in BX	Percent Uranium Loss
R12	8-1/2	8-1/2	2	0.038
R13				0.033
R14			1.5	0.029
R15				0.028
R18	13	2	1.0	0.004
R19				0.006

[redacted]

5.9 Column Flooding Rate for the 30% TBP - 70% Varsol Flowsheet

The flooding rates for the Purex Process using the 30% tributyl phosphate, 70% Varsol-type solvent were determined for the extraction, partition and stripping column to be 610, 320, 310 gallons per hour per square foot cross section area, respectively. These rates are somewhat lower than those obtained for the 15% TBP solvent. When compared with the Redox flooding rates, the extraction flooding rate is similar; however, the rate in the partition column is a factor of 3 lower (see Table 5.9).

6.0 RaLa Process

6.1 Barium Sulfate Precipitation Without Carrier

The centrifugation studies aimed at the removal of barium sulfate from the metal solution without lead carrier were not successful, probably due to the fact that the barium sulfate solubility was a sizeable fraction of the small concentration of barium present in solution. In this study the separation was effected by centrifuging the solution at 2200 G's with a flowrate varying between 0.7 and 2.5 liters per minute, and the barium concentration varying from 4 to 16 milligrams per liter of metal solution. The barium losses varied from 12 to 99% in the five trials and could not be correlated with any of the controlled variables.

In subsequent runs, precipitation of barium sulfate using lead carrier was then performed by the standard procedure and the precipitate separated by centrifugation to prepare feed for resin column tests. The

Table 5.9

Flooding Rates in the 30% TBP in Varsol Flowsheet

Column: 10 feet of 1-1/2" glass pipe packed with 1/4"x1/4" stainless steel Raschig rings.

Flow Ratio (O/A)	System	Flooding Rate* (Gals/hr/sq ft Total Throughput)
	1A	
2:1	1AF = 3 N HNO_3 175 g U/l 1AX = 30% TBP, 70% Varsol	610**
	1B	
4:1	1BF = organic product from 1A column (54 g/U/1, density = 0.91) 1BX = 1 N HNO_3	320**
	1C	
1:2	1CF = organic product from 1B column (50 g U/1, density = 0.90) 1CX = Demineralized water	310**

* Result of duplicate runs in all cases.

** Flooding rates determined with same column and packing for 15% TBP-Varsol system and for Redox system were:

	1A	1B	1C
15% TBP	750	350	500
Redox	680	1000	-

[redacted]

Barium Sulfate Precipitation Without Carrier (continued)

barium losses were less than 1 percent. However, it was found that complete metathesis was not accomplished in the centrifuge bowl. This phase of the program has been discontinued.

6.2 One-Column Versene Process

The development of the one-column Versene Process for the purification of barium is nearing completion. The conditions have been satisfactorily demonstrated in the laboratory for the process when only a total of one gram of barium and strontium was present in the metal solution. This process required no metathesis as the sulfate precipitate was dissolved in Versene. When the amount of barium and strontium exceeds one gram, it is necessary to use the metathesis step in order to limit the amount of Versene that was required to dissolve the precipitate. Increasing the amount of Versene rapidly increases the size of the column required for this process, causing an undesirable increase in the volume of the solutions. Indications from pilot plant runs are that the metathesis step should be retained.

6.3 Elimination of Organic Colors in the Product

The fuming nitric acid precipitation procedure has been chosen for eliminating the organic colors from the product. This will be carried

Elimination of Organic Colors in the Product (continued)

out by taking the product solution from the ion exchange process and evaporating it down to a volume of two liters, adding two liters of 98% fuming nitric acid, thereby precipitating barium nitrate, filtering the solution, redissolving the barium nitrate in water and transferring that to the shipping column. Product evaluation by the customer will be necessary to evaluate the effectiveness of this procedure.

7.0 25 Process - Final Product Concentration

The di-isopropyl ether batch solvent extraction procedure for the concentration and purification of Uranium 235 was successfully demonstrated on a feed resulting from the 25 pilot plant program. Approximately 2 kilograms of Uranium 235 was processed with an overall loss of 0.001 percent. The final analysis of the product indicated 30 parts per million of each of iron, aluminum, and chromium with 0.5 beta counts of ruthenium per minute per milligram of uranium at 10 percent geometry. This program has been completed. Permanent facilities are now available for purification and concentration of gross amounts of Uranium 233, Uranium 235 and plutonium.

8.0 Thorex Process - Batch Countercurrent Run Using Tributyl Phosphate - Carbon Tetrachloride Solvent

The Thorex Process using a solvent composed of 30% tributyl phosphate, 58% carbon tetrachloride, and 12% nitric acid was demonstrated in countercurrent batch extraction to give an overall loss of 0.02% thorium and a beta decontamination factor of 7×10^3. Feed for this run was scavenged with Filtrol preceding the run to increase the zirconium decontamination (see Table 8.0).

9.0 Fluoride Process Studies - Fluorination Scale-up Test

The scale of the hot fluorination studies was increased from approximately 60 grams of metal to 245 grams to evaluate this effect on the process results. Approximately 1.2 curies of beta activity were present. The uranium recovery and beta decontamination, 98% and 8×10^3, respectively, were essentially the same as those experienced in the smaller scale runs. The plutonium distribution through the equipment was also similar namely 30% in the reactor, 20% on the filter, 39% cold trap, and 8% in the uranium product.

A series of runs made to determine the effect of surface area on the plutonium removal were made. However, these runs were not conclusive. Evidently some variables as yet unknown were not being controlled.

Table 8.0

Thorex Process - Batch Countercurrent Run Using Tributyl Phosphate-Carbon Tetrachloride Solvent

Extraction (six stages)

Metal feed:	$Th(NO_3)_4$	0.5 M
4 Volumes:	$Al(NO_3)_3$	0.1 M
	NaF	0.02 M
	HNO_3	2.5 M
Extractant:	TBP 30%	
10 Volumes:	CCl_4 58%	
	HNO_3 12%	

Scrub (six stages)

Feed:	HNO_3 6 M	
1 Volume		

Strip

Feed:	Distilled H_2O
10 Volumes	

10.0 Homogeneous Reactor Slurry Studies

The study of uranium oxide slurries was continued using bentonite as the stabilizing agent and Calgon, sodium hexametaphosphate, as the iron complexing agent. Previous tests with bentonite stabilized uranium oxide slurries were unstable due to the release of iron from the bentonite at high temperatures. The Calgon was added to complex the iron and hold it in solution.

The addition of the Calgon was effective in holding the iron in solution; however, the slurries continued to be unstable after being heated to 250°C in a sealed quartz tube and then standing for 24 hours. A green material settled out of solution which indicated the formation of uranyl phosphate. The factors may have been insufficient bentonite, or the fact that Calgon acted to disperse the bentonite decreasing the viscosity.

This work is to be continued using a mixed slurry of uranium oxide and uranium phosphate.

Slurry Composition

	#1	#2
UO_3 (g)	48	48
Bentonite (g)	8.7	6.4
Calgon (g)	10.0	10.0
Water (g)	1000.	1000.

11.0 Falling-Film Evaporator

A falling-film evaporator is being studied for application to the waste concentration problem. Preliminary studies have indicated liquid film heat transfer coefficients of 1225 Btu/hr/sq ft/°F using a 2 to 33 percent sodium nitrate solution feed, with a decontamination factor of 10^3 to 10^4. This work was carried out by the MIT Practice School and the study will be continued.

12 0 Pulse Solvent Extraction Column

An experimental pulse-type solvent extraction column, 1/2" diameter by 30 inches high, has been set up to evaluate its use as laboratory tool.

13.0 Steam Jet Test

A 3/4" Schutte and Koerting steam-jet exhauster, Catalogue Figure 431-A was capable of developing 27 inches of mercury vacuum with 0.9 cfm of air evacuated and 4.4 gallons of water per minute required for the water jet condenser. As this evacuator was proposed for the RaLa Process, it was recommended that a surface condenser instead of a water jet condenser be used for condensing the vapors from the jet exhauster, to decrease the amount of contaminated water.