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ORNL-580

CHEMISTRY-SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM

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CHEMICAL TECHNOLOGY DEPARTMENT
PROGRESS REPORT FOR MONTH
ENDING DECEMBER 31, 1949

LABORATORY RECORDS

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CHEMICAL TECHNOLOGY DEPARTMENT

PROGRESS REPORT FOR MONTH ENDING DECEMBER 31, 1949

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CARBIDE AND CARBON CHEMICALS DIVISION
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Contents

	Page Number
1.0 Abstract	4
2.0 Introduction	5
3.0 Summary	6
4.0 TBP Process for Metal Recovery	8
4.1 Plutonium Study	8
4.2 Volume Reduction of TBP Wastes by Evaporation	11
4.3 Pilot Plant Development	12
Re-use of the Solvent	12
Effect of Column Flow Rate	12
Future Program	12
5.0 Purex Process - Flooding Rates	14
6.0 "25" Process - Pilot Plant Program	14
7.0 "23" Process - Pilot Plant Start-Up	14
8.0 RaLa Process	16
8.1 Sulfate Precipitation and Metathesis - Filtration Step	16
8.2 Purification of Barium by Ion Exchange	16
9.0 Thorex Process	17
9.1 Effect of Thorium Age	17
9.2 Flooding Rates	18
10.0 Dry Fluoride	18
11.0 Homogeneous Reactor Slurry Study	19

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1.0 Abstract

Chemical development is reported on the TBP Process, Purex Process, 25 Process, 23 Process, RaLa Process, Thorex Process, uranium fluorination, and the homogeneous reactor slurry study.

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2.0 Introduction

The development of the TBP Process for the recovery of uranium from the uranium-containing waste at Hanford and ORNL continued to be the major problem in the Laboratory and Semi-Works. Studies of the plutonium distribution and waste reduction by evaporation were carried out by the Laboratory. The effect of re-using the solvent and varying the flow rates was studied by the Semi-Works.

The application of tributylphosphate, the Purex Process, to the recovery and decontamination of uranium and plutonium from a natural uranium nuclear reactor is in the laboratory stage of development. Satisfactory operation of the process was previously demonstrated in batch countercurrent equipment, and the operability in a packed column was tested during this period.

The Pilot Plant successfully completed the final development of the 25 Process through the first and second cycles and processing through the isolation cycle is in progress.

The start-up tests of the pilot plant equipment for the 23 Process are now in progress. Uranium-233 is to be separated from irradiated thorium by hexone extraction.

The RaLa Process improvement studies developed filtration rates for the precipitation steps. Ion exchange runs were made with large amounts of activity, demonstrating the overall feasibility of the process.

Introduction (continued)

The continuation of this program for the application of the process to other sources of metal is anticipated.

The application of tributylphosphate extraction to thorium recovery has now been named the Thorex Process. It was studied by the Laboratory during this period to determine the effect of the age of the feed and the operability of the process in packed columns.

The Dry Fluoride development of fluorination of hot metal showed that plutonium hexafluoride did not quantitatively follow the uranium and this is not being studied.

Studies were continued to develop a stable uranium slurry for a homogeneous type nuclear reactor.

3.0 Summary

TBP Process

(1) Plutonium can be recovered from the metal waste along with the uranium.

(2) The satisfactory re-use of the solvent without treatment after each use was demonstrated in the semi-works tests.

Purex Process

The flooding rates in a 1-1/2 inch diameter packed column were determined to be satisfactory.

Summary (continued)

25 Process

The 25 Process has been satisfactorily demonstrated on full chemical scale through the first and second cycles at 20% of the expected activity level.

RaLa Process

The purification of the barium by ion exchange has been satisfactorily demonstrated at high activity levels.

Thorium Recovery

(1) The thorium decontamination decreased rapidly as the age of the waste decreased.

(2) The flooding rates in a 1-1/2 inch diameter packed column were determined to be satisfactory.

Dry Fluoride

(1) Increasing the fluorination temperature was found to be effective in increasing the volatilization of the plutonium.

(2) All fission products exhibited the same decontamination indicating that none formed volatile fluorides.

Homogeneous Reactor Slurry Study

Attempts to form a stable colloidal uranium oxide-water slurry have not been successful. The use of stabilizing agents is being investigated.

4.0 TBP Process for Metal Recovery

4.1 Plutonium Study

The laboratory study of plutonium extraction with tributylphosphate indicated that the plutonium can be recovered from the metal waste along with the uranium.

The solvent extraction equilibration time was less than five minutes and increasing the equilibration time to 18 hours showed no effect. At low acidities (0.5 M), plutonium distribution coefficients were equal for the IV and VI states. At higher acidities (3.0 M), the plutonium IV distribution coefficient was approximately twice that of the plutonium VI (3.54 vs 1.4) (see Table 4.1-1).

Increasing the tributylphosphate concentration from 2 to 15% increased the distribution coefficient for plutonium IV from 0.04 to 1.9, while the plutonium VI increased from 0.04 to 0.9 (see Table 4.1-2).

As the uranium concentration increased, the plutonium distribution coefficients decreased rapidly (from 2.26 at 20 grams of uranium per liter to 0.23 at 100 grams of uranium per liter). It is anticipated that the metal recovery process will be carried out at about 60 grams of uranium per liter where the plutonium distribution is about 1.0 (see Table 4.1-3).

Table 4.1-1

Effect of HNO_3 on Pu^{IV} Extraction with Tributylphosphate

Organic Phase: 15.4% TBP (0.565 M)*

Aqueous Phase: Pu tracer, HNO_3

Temperature: 20°C

Initial HNO_3 Conc.	Pu Dist. Coeff. (Org/Aq)			HNO_3 Distribution	
(M)	Pu^{III}	Pu^{IV}	Pu^{VI}	Org.Phase	Aq.Phase
0.11	0.003	0.005	0.01	0.002	0.098
0.30	-	0.06	0.05	0.010	0.300
0.50	0.01	0.13	-	0.026	0.475
0.82	-	0.40	-	0.055	0.770
1.1	0.03	0.83	0.51	0.090	1.02
1.60	-	1.54	-	0.140	1.46
2.03	-	1.75	1.01	0.188	1.84
2.3	-	2.85	-	0.220	2.11
3.1	-	3.54	1.4	0.290	2.81
3.9	-	6.02	-	0.365	3.54

* Solvent was pre-washed with 1.0 NaOH, followed by 4 washes with H_2O.

[redacted]

Table 4.1-2

Effect of TBP Concentration on Plutonium Extraction

Aqueous Phase: 1.85 M HNO_3, Pu tracer

Organic Phase: TBP-Gulf-BT Mixtures

Temperature: 20°C

TBP Conc. (Vol. %)	Pu Distribution Coefficient (Org/Aq) Pu^{IV}	Pu^{VI}
2.05	0.04	0.044
5.13	0.31	0.21
10.27	1.45	0.577
15.40	1.90	0.95

Table 4.1-3

Effect of Uranium Concentration on Plutonium Extraction

Aqueous Phase: Pu tracer, 3.0 M HNO_3 U

Organic Phase: 15% TBP-85% Varsol

Temperature: 20°C

Aq. Uranium Concentration mg/ml	Distribution Coefficients (Org/Aq) Pu^{IV}	Pu^{VI}
20	2.26	0.91
40	1.13	0.56
80	0.34	0.16
100	0.23	0.11
200	0.11	0.04

[redacted]

4.2 Volume Reduction of TBP Wastes by Evaporation

Using the TBP wastes from countercurrent batch runs, the amount of volume reduction by alkaline evaporation (pH 8 to 9) of the process wastes was determined for four flowsheets involving four methods of feed preparation. The final solutions had a 15°C freezing point. The final waste volume is expressed as the percent of the original total waste volumes after neutralization and subsequent evaporation of the process wastes. The results are summarized as follows:

	Feed Preparation Method	Final Waste Volume
(1)	Direct acidification of total waste to 3.0 N HNO_3	125 to 135%
(2)	Direct acidification of total waste to 2.0 N HNO_3, and concentration by evaporation	110 to 120%
(3)	NaOH precipitation of total waste and dissolution of the precipitate to 3.0 N HNO_3	85 to 95%
(4)	HNO_3 precipitation of total waste and dissolution of the precipitate to 3.0 N HNO_3	85 to 95%

4.3 Semi-Works Development

Re-use of the Solvent

The semi-works data indicated that treatment of the solvent after each use would not be necessary. This will significantly reduce the waste volume from this step. After cycling the solvent five times, a small increase in the beta activity and plutonium in the final product was noted. Washing the solvent with sodium hydroxide reduced the product uranium to its original purity (see Table 4.3-1, Run HS-13).

All future runs will be made with used solvent with only enough new solvent added when necessary to replace losses.

Effect of Column Flow Rate

The runs have generally been made at 25 percent of flooding. One run was made at 70 percent of flooding with no difficulty except that the uranium losses were high caused by a low solvent flow rate (see Table 4.3-1, Run XHS-1).

Future Program

Work is now in progress to determine the effect of eliminating the scrub section. The major advantage is the reduction of the nitric acid requirement.

As soon as Hanford metal waste sludge is available, it will be used to develop the process which to date has used Hanford supernatant with inactive chemicals added to simulate the average waste.

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Table 4.3-1

Semi-Works TBP Process Development

Equipment: 1-1/2" SS extraction column packed with 1/4" x 3/8" SS split rings
extraction section 17.5'
2-1/2" SS strip column packed with 1/4" x 3/8" split rings
strip section 18.0'

Materials: Hanford 103 U supernatant
Tributyl phosphate in hydrocarbon diluent (Gulf BT - high flash point solvent naptha)

Run #	AF			AS		AX		BX	Product BP			U Losses	
	U g/l	H^+ N	Flow rate cc/m	H^+ N	Flow rate cc/m	TBP %	Flow rate cc/m	Flow rate cc/m	β c/mg/U	Pu α c/mg/U	γ mv/mg U	Extraction %	Strip %
HS-11	61.2	2.95	60	3.1	30	13	108	120	4.4	0.66	0.002	0.14	0.03
HS-12	58	2.98	60	3.1	30	13	108	120	7.1	0.97	0.003	0.11	0.045
XHS-1	37++	2.95	150	3.0	30	13	150*	150	6.9	0.56	0.004	0.6*	0.044
HS-13A				2.7		12.6	80	80	3.4	0.75	0.001	**	0.059
B				2.7		12.6	100	100	6.0	0.90	0.001	0.08	0.095
C	45.0	3.1	60	3.1	30	12.8	100	100	4.6	0.64	-	0.10	0.108
D				3.0		12.4	100	100	6.3	0.80	-	0.11	0.071
E				3.0		12.4	100	100	12.0	1.10	-	0.12	0.089
F				3.15		12.4	100	100	3.5	0.96	0.002	0.10	0.147

++ 0.05 M in ferrous sulfamate
* AX should have been about 170 to keep the extraction loss down
** High and erratic losses because of insufficient solvent to extract the uranium

	Metal Feed Composition (AF)		
	Total NO_3^- (M)	$PO_4^{\equiv}$ (M)	$SO_4^{=}$ (M)
HS-11	4.2	0.28	0.13
HS-12	4.6	0.13	0.44
XHS-1	4.0		
HS-13			

[redacted]

5.0 Purex Process - Flooding Rates

The flooding rates for the Purex Process first cycle were determined in a 1-1/2 inch diameter glass column packed with 1/4 inch by 1/4 inch stainless steel split rings. The limiting flow rate is in the IB column and is about 30 percent that of the Redox Process (see Table 5.0-1).

6.0 25 Process - Pilot Plant Program

The 25 Process has been demonstrated at 25 percent of the expected activity of the MTR fuel units using Hanford irradiated Uranium-235-aluminum alloy. The processing in the first and second solvent extraction cycle has been completed with a uranium loss of 0.2% (0.15% occurred in the filtration step which can be eliminated by further study) and a fission product decontamination factor of 10^6. The processing through the isolation step is now in progress.

7.0 23 Process - Pilot Plant Start-Up

The chemical and mechanical equipment tests necessary for the start-up of new process equipment are in progress and it is expected that the first development runs will be started in January.

Table 5.0-1

Flooding Rates of Purex Process First Cycle Columns

Column: 12 ft. of 1-1/2" glass pipe, packed with 1/4"x1/4" stainless steel split rings.

Flow Ratio (O:A)	Column	Flooding Rate* (gals/hr.ft^2 total throughput)
	1A	
1:1	1AF = 3N HNO_3 78 mg U/ml	700
3:1	1AX = 15% TBP; 85% Varsol	800
	1B	
4:1	BF = Organic product from 1A Column	360
2:1	IBX = 1 M HNO_3	380
4:1	BF = 15% TBP; 85% Varsol	660
2:1	1BX = 1 N HNO_3	
	1C	
1:1	1CF = Organic product from 1B Column	500
	1CX = Demineralized water	
1:1	1CF = 15% TBP; 85% Varsol	
	1CX = Demineralized water	660

* Results quoted are for duplicate runs.

8.0 RaLa Process

8.1 Sulfate Precipitation and Metathesis - Filtration Rates

The sulfate precipitation and metathesis steps operated satisfactorily using filtration for the removal of crud from the metal solution as well as for the separation of the lead-barium sulfate precipitate and the metathesis precipitate.

The crud was removed by filtering through celite 545 filter aid (0.25 g/in. for the precoat and 5 g/liter in the feed) on a "G" porosity sinter stainless steel filter plate. The sulfate and metathesis precipitates were filtered on the sintered stainless plate without filter aid.

The filtration rates were as follows:

Filtration Step	Volume/Unit Area gallons/ft^2	Rate gallons/hr.x ft^2
Crud Removal	107	35
Sulfate Precipitate	134	70
Metathesis Precipitate	54	300

8.2 Purification of Barium by Ion Exchange

Acetate-Citrate Process

The isolation of barium by the Acetate-Citrate ion exchange process has been demonstrated to be satisfactory at high levels of activity, and the development on this process is considered complete.

Purification of Barium by Ion Exchange (continued)

Versene Process

The development of the Versene ion exchange process is in progress in both the laboratory and pilot plant scale. The major advantage of this process is the elimination of the metathesis step, reducing the processing time from about 40 to 30 hours.

9.0 Thorex Process

9.1 Effect of Thorium Age

The decontamination of thorium from the 23 Process waste by tributylphosphate extraction increased significantly with increasing age of the waste. The beta decontamination for three to six month waste was 20, while 550 and 10^4 was obtained for 15 month waste and two year waste, respectively.

When processing 15 month waste, it was found that increasing the number of scrub stages from four to six increased the beta decontamination to 10^3. The ruthenium and zirconium were the limiting activities in decontamination.

The application of the sodium nitrite-acetone feed pretreatment procedure was effective in increasing the ruthenium decontamination; however, the formation of a white precipitate in extraction was noted.

Effect of Thorium Age (continued)

An incomplete analysis of this precipitate indicated the presence of th ium, nitrogen, and sodium.

9.2 Flooding Rates

The operation of the process in 1-1/2 inch diameter columns packed with 1/4 inch diameter by 1/4 inch split rings has been successfully demonstrated. It was necessary to reduce the tributylphosphate concentration by the addition of more diluent (Varsol) from 50% to about 25% before stripping in order to obtain a more satisfactory specific gravity differential.

10.0 Dry Fluoride

The amount of plutonium held in the reactor was reduced from about 45 percent to 27 percent by increasing the reactor temperature and decreasing the surface area of the reactor. The decontamination across the fluorination step was decreased by a factor of two, from 20 to 10.

Specific decontamination factors for all fission products analyzed were comparable, ranging from 15 to 30.

11.0 Homogeneous Reactor Slurry Study

Studies are in progress to prepare a stable slurry of uranium for use in a homogeneous type nuclear reactor. Approximately 40 grams of uranium per liter is required.

Uranium trioxide-(UO_3)-water and uranium peroxide-($UO_4 \cdot 2H_2O$)-water slurries prepared in a colloid mill had thixotropic characteristics; however, these were not stable after being heated to 250°C for an hour. The other oxides were also studied.

The effect of colloid stabilizing agents is now being studied. Representative of these is bentonite, a mixture hydrated oxides of aluminum, iron and silicon. Others such as sodium hydroxide, sucrose and stearic acid failed in preliminary tests.