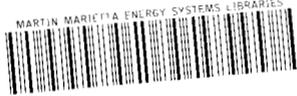


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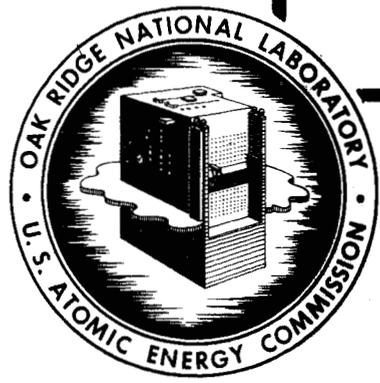
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LABORATORY RECORDS
1954



PROGRESS REPORT FOR MONTH
ENDING SEPTEMBER 30, 1949



OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION

OAK RIDGE, TENNESSEE

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CHEMICAL TECHNOLOGY DEPARTMENT

PROGRESS REPORT FOR MONTH ENDING SEPTEMBER 30, 1949

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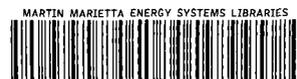
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1.0 Abstract

Chemical development is reported on the TBP Metal Recovery Process, the Redox Process, uranium fluorination, the RaLa Process, a homogeneous pile slurry study, a solvent extraction contactor study, the "23" Process, the Purex Process, and the metal solution step of the "25" Process.

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2.0 Introduction

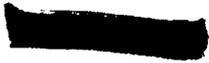
The TBP solvent extraction process development for uranium recovery from ORNL and Hanford metal waste was continued in the laboratory, investigating the feed preparation step, scouting the effect of uranium concentration on the solvent extraction, and starting the study of the effect of impurities in tributyl phosphate and Varsol. The Semi-Works investigated alternate methods of solid separations involved in feed preparation and the feasibility of pumping sludge from the ORNL waste tanks.

Laboratory effort was continued on the Redox Process to evaluate a crud problem and to determine the procedure to be used for the recovery of plutonium from the pilot plant IRP solution.

The scale of fluorination of metallic uranium was increased to simplify sample preparation, and work was started on distillation of uranium hexafluoride.

The RaLa Process improvement program was continued to determine the optimum filtration conditions prior to final demonstration of the process with the ion exchange procedure for final barium purification. Laboratory work was in progress on alternate ion exchange resins and the elimination of the metathesis step.

A homogeneous reactor study was started to determine the feasibility of using a slurry as the active element of a nuclear reactor.



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Introduction (continued)

A study was made to compare the Scheibel column with a mixer-settler as a contactor for laboratory solvent extraction studies.

The solvent extraction equipment for pilot plant development of the "23" Process has been completed and should be ready for use by November 15.

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3.0 Summary

TBP Metal Recovery

(1) The feed preparation step, by means of sulfuric acid precipitation followed by nitric acid dissolution, was the least expensive on the basis of the chemical cost; however, a study of overall equipment requirements for all procedures will be necessary before the final choice can be made.

(2) Satisfactory uranium recovery and decontamination was demonstrated in laboratory countercurrent batch solvent extraction equipment with Hanford supernatant that was directly acidified with nitric acid.

Purex Process

The recovery and decontamination of plutonium and uranium from pile irradiated uranium using a tributyl phosphate solvent extraction process has been demonstrated on a laboratory scale in batch countercurrent equipment. In one cycle countercurrent batch runs, losses for plutonium and uranium were less than 0.1%, with beta decontamination factors of greater than 7×10^3 through seven extraction and six scrub stages. The procedure consisted 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 was about one molar.

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4.0 TBP Metal Recovery Process

4.1 Feed Preparation - Laboratory Studies

Several methods of feed preparation were developed using Hanford metal waste supernatant from Tanks 103-T and 103-U and with simulated total waste. Total waste is defined as the waste solution resulting from an average mixture of metal waste supernatant and sludge as they occur in the Hanford waste.

The object of this work was to furnish a basis for the economic evaluation of the alternate procedures; the factors being uranium loss, final uranium concentration, quantity of chemicals required, and operability (see Table 4.1-1).

While the probable chemical cost would be the least for the method using the sulfuric acid precipitation followed by nitric acid dissolution of the precipitate, data will be necessary on equipment costs, effect on solvent extraction, ultimate waste processing, and perhaps on the method of sludge removal from the Hanford storage tank before a definite decision can be made.

Direct Acidification

By the addition of sufficient nitric acid to the Hanford supernatant, a 4.5 M HNO_3 feed solution for the tributyl phosphate solvent extraction was prepared containing 22 to 30 grams of uranium per liter. This required approximately 570 milliliters of 70% HNO_3 per liter of supernatant (Hanford 103-U).

Direct Acidification (continued)

Similarly, when the total waste was acidified, 400 milliliters of 70% HNO_3 per liter of total waste was required yielding a 3 M HNO_3 solution containing 50 to 60 grams of uranium per liter.

There was no uranium loss with this procedure; however, the chemical requirement and waste volume would be expected to be the greatest of the procedures investigated.

Sodium Hydroxide Precipitation

The uranium may be precipitated from the metal waste supernatant or total waste as the diuranate by the addition of 46 to 51 grams of sodium hydroxide per liter waste with a 0.2% uranium loss. The precipitate is separated from the solution and washed with hot water, reducing the phosphate content and the nitric acid requirement. The uranium loss during washing is approximately 0.02 to 0.05 grams per liter of water. The precipitate is then dissolved in 2.5 liters of 60% HNO_3 per kilogram of uranium in the Hanford 103-U supernatant, or 3.2 liters of 60% HNO_3 for total waste. The final uranium concentrations in the feed were 110 and 130 grams per liter for the supernatant and total waste, respectively.

This procedure reduces the chemical requirements, based on direct acidification, by a factor of two for the total wastes and a factor of ten for the supernatant. However, equipment for a precipitation cycle

Sodium Hydroxide Precipitation (continued)

are required and the precipitate formed is difficult to filter or centrifuge.

Acid Precipitation

Uranyl phosphate may be precipitated from Hanford metal waste supernatant or total waste by the addition of either nitric or sulfuric acid to a pH of 4.0 to 5.5 with a uranium loss of 0.02% for total waste and 0.1% for supernatant. These precipitates had good characteristics for filtration or centrifugation.

The precipitation with nitric acid required four to five liters of 70% HNO_3 per kilogram of uranium in the supernatant and 2.5 liters for total waste. Washing this precipitate was not investigated.

The precipitation with sulfuric acid required approximately two liters of 98% H_2SO_4 per kilogram of uranium in the supernatant and 0.9 liters for the total waste. This precipitate was then washed with 0.05 M mono sodium phosphate to reduce the sulfuric acid and phosphate concentration with no appreciable uranium loss. Washing with water, dilute phosphoric acid, trisodium phosphate, or dilute sodium hydroxide was not successful because of either high uranium loss or physical change in the precipitate.

Acid Precipitation (continued)

The uranium precipitate from either acid precipitation process was dissolved in approximately two liters of 70% HNO_3 per kilogram of uranium to give a final solution containing 120 to 140 grams of uranium per liter for both supernatant and total waste.

4.2 Feed Preparation - Semi-Works

Nitric Acid Precipitation Study

Tests with Hanford 103-U uranium waste supernatant on a 100 milliliter scale indicated that by nitric acid precipitation the uranium precipitate settled sufficiently to prepare feed solutions containing approximately 70 grams of uranium per liter.

The uranium was precipitated by the addition of 60% nitric acid to the agitated supernatant at 90°C until a pH of 5 to 6.5 was obtained. The precipitate was settled at 70°C for one hour. The slurry then occupied approximately half of the total solution volume resulting in a 70 gram uranium solution after decantation and acidification. After settling for 100 hours at room temperature, the slurry was one-third of the total solution volume. The settling rate was decreased by either too much acid addition or too little agitation or too much agitation. The uranium loss in the supernatant was 0.1% (0.05 mg U/ml).

This procedure will be used where necessary to prepare the feeds for the Semi-Works runs.

Filtration of ORNL Metal Waste Slurry

Filtration tests were conducted by the Oliver United Filters, Inc. in the ORNL Semi-Works on the caustic precipitated uranium from the ORNL metal waste storage tank (W10). Preliminary results of these tests

Filtration of ORNL Metal Waste Slurry (continued)

indicated that a precoat rotary filter would be applicable in the preparation of the feed for the recovery of the uranium from the ORNL metal waste.

The filtration tests evaluated the effect of temperature, vacuum, and cycle time (see Table 4.2-1).

The data indicate quite clearly that as the cake forming time is decreased, the flow rate rises rather sharply. Tests #6 and #7 show that the data are quite reproducible. Tests #3 and #4 show that the effect of a 5°F temperature change was not significant.

The five minute cycle (Test #8) yielded a cyclical filtrate flow rate of 4.9 ml/cm² - hr. or based on active filtering area 12.4 ml/cm² - hr. From data reported previously, it is indicated that this flow rate might be increased by starting at a low pressure and going to the maximum sometime before the end of the cake forming period.

The filter cake was quite loose and watery immediately after removal from the slurry, but upon drying for a period equivalent to the cake forming time, it became leathery and was easily peeled off.

The solids from the slurry apparently do not penetrate the precoat very far. It was estimated that a cut or shaving of 0.006 cm would expose essentially fresh surface. For example, in Test #8, thirty eight cubic centimeters of filtrate indicates a deposit of 12-1/2 cu. cm. of

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Filtration of ORNL Metal Waste Slurry (continued)

solids from the 25% solids feed slurry on an area of 93 sq. cm. The cake thus formed is approximately 0.14 cm thick. These data indicate roughly one volume of filter aid would be required per twenty volumes of solids. This ratio contrasts with the approximately 1:1 volume ratio of solids to filter aid required when filtration is carried out without precoat but with filter aid added directly to the slurry. Assuming (a) 2.5 cms of removable precoat could be applied, (b) a shaving rate of 0.006 cm/rev, and (c) a drum velocity of 12 r.p.h., a precoat rotary filter unit could be operated for 35 hours on one precoat. The precoating operation requires one to two hours.

Optimum operating conditions based on this data would be a flow rate of 12.4 ml/cm² - hr. for 2 min. filtration of 25% solids slurry at a temperature of 120° F and a vacuum of 58 cm Hg using HYflo Super Cel precoat, but no filter aid in the slurry has been obtained.

Advantages of Precoat Operation over operation without precoat but with filter aid in the slurry are:

1. About 1/20 as much filter aid required, thereby greatly decreasing waste disposal problem. One ton of filter aid would be required to process 100,000 gallons of ORNL sludge.
2. Operation less affected by changes in slurry composition.

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Filtration of ORNL Metal Waste Slurry (continued)

3. Capable of operating on a shorter time cycle thereby taking advantage of high initial flow rates.
4. Delivers a clear filtrate.

Disadvantages are:

1. Higher initial cost.
2. Semi-continuous operation.

Centrifugation of ORNL Metal Waste Slurry

Preliminary tests indicated that separation of the caustic precipitated uranium from the ORNL metal waste by centrifugation in a 12 inch solid bowl centrifuge would not be feasible for the Semi-Works scale of operation. Clear centrifugates were not obtained with a feed rate of 250 milliliters per minute to the centrifuge developing 1500

Table 4.2-1

Constant Pressure Filtration of W-10 Sludge Using 1.6 cm Precoat of Hyflo Super-Cel on Rayon Cloth. No Filter Aid Added to Slurry

Filter Area: 93 sq cm

Test	Conditions of Filtration			Filtering Time (min.)			Filtrate	
	Percent Solids	Temp. °F	Vacuum cm. Hg.	Cake Forming	Cake Drying	Cycle*	Volume (ml)	Flow Rate** (ml/cm ² - hr)
1	25	110	43	4.5	7	11	47	2.8
2	25	106	43	5	10	125	57	2.9
3	25	104	46	5	5	12.5	57	2.9
4	25	99	46	5	5	12.5	58	3.0
5	25	126	58	3	4	7.5	52	4.5
6	25	120	58	3	3	7.5	48	4.2
7	25	120	58	3	3	7.5	46	4.0
8	25	120	58	2	2	5	38	4.9

* Based upon 40% submergence of rotary drum; i.e., cake forming time represents 40% of total cycle time.

** Based upon time for cycle rather than cake forming time. To find flow rate for active filtering area multiply by 2.5.

Note: Data taken 8/18-19/49 by Kenny, Jealous, and Freeh.

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4.3 Countercurrent Batch Runs

Uranium was recovered from 103-U supernatant containing 42 g/l of uranium with a beta decontamination factor of 1.26×10^4 and a LAW loss of 1.0%. This was accomplished by using 13% tributyl phosphate and maintaining the required saturation at the feed plate (70%) by using 1.84 M nitric acid as scrub to increase the reflux of uranium (see Table 4.3-1).

Uranium was extracted with tributyl phosphate from feed solutions containing only 24 g/l of uranium by using a solvent to aqueous flow ratio of 1:1 and maintaining a 70% uranium saturated organic at the feed plate. This degree of saturation, again, was accomplished by decreasing the acidity of the aqueous scrub, so as to maintain a higher uranium reflux from the scrub section.

The feeds were prepared and extracted in countercurrent batch equipment as described below, and varied from 24 to 79.5 g/l of uranium.

In the first run (F-1), 13% tributyl phosphate - 87% Varsol was used as organic solvent, and distilled water as scrub. A uranium distribution coefficient of 1.1 was maintained at the feed plate and an acceptable beta decontamination factor of 2.1×10^4 was obtained. However, more than seven extraction stages were necessary for complete extraction using a 3:2:1 organic:feed:scrub ratio.

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Counter Current Batch Runs (continued)

Feed F-3 - 1560 ml of Hanford waste supernatant was precipitated with excess 50% caustic and allowed to settle for 20 hours and decanted. The decanted liquor analyzed 0.08 mg/ml in uranium and beta activity 5.45×10^6 c/m/ml. The solids were washed with an equal volume of distilled water then centrifuged and decanted. The decanted liquor from this wash analyzed 0.024 mg/ml in uranium and beta activity 9.93×10^5 c/m/ml. The solids were dissolved in 70% nitric acid to 3.1 M excess. This required 3.4 ml 70% HNO_3 per gram of uranium. The resulting feed contained 79.5 g/l uranium and 1.5×10^5 beta activity c/m/mg of uranium.

Table 4.3-1

Tributyl Phosphate Uranium Extraction from Solutions of Low Uranium Concentration

Source of Uranium Processed: Hanford Waste 103-U Supernatant

F-1 Acidified Supernatant

F-2 Supernatant precipitated with 50% NaOH, settled, decanted and solids dissolved in 70% HNO₃

F-3 Supernatant precipitated with 50% NaOH, settled, decanted, centrifuged, decanted, washed, decanted, and solids dissolved in 70% HNO₃

Organic Flow rate calculated to give ca. 70%. Saturation at feed plate
Feed:Scrub Ratio is 2:1 in all runs.

Run No.	Extract Feed			Scrub HNO ₃ (M)	% TBP in Solvent	No. of Stages			% Scrub Uranium Reflux	% U Loss		Gross β D.F.	Final Product Specific β Activity c/m/mg U
	U g/l	HNO ₃ (M)	Gross β c/m/mg U			Ext.	Scrub	Strip		Ext.	Strip		
F-1	24.0	4.5	3.5x10 ⁵	0.0	13	7	4	4	31.4	0.62	0.09	2.1x10 ⁴	17.5
F-2	42.0	2.8	2.5x10 ⁵	1.8	13	6	4	4	35.0	0.06	0.18	1.3x10 ⁴	20.5
F-3	79.5	3.1	1.5x10 ⁵	2.5	15	6	4	4	32.6	0.06	0.03	1.3x10 ⁴	11.7

4.4 Solvent Study

A study of the chemistry of Varsol and tributyl phosphate has been initiated. Varsol is a straight run fraction of petroleum consisting of approximately 7% aromatics, 32% naphthenes, and 61% paraffins. Several methods have been used in determining these constituents but the results do not agree well. Fractional distillation does not give any appreciable separation of these groups. It has been determined that Varsol does not contain any unsaturates, and by the method of analysis used, it does not contain a detectable concentration of reducing agents.

Tributyl phosphate as received from Commercial Solvents Corporation is essentially the pure ester containing a small amount of butyl alcohol. There are apparently no unsaturates (by ASTM method for Br number) present although the reducing normality of various samples, as determined by titration with cold, strongly acid dichromate, was as high as 0.19. Two washes with 1/5 volumes of 0.1 M $\text{Cr}_2\text{O}_7^{=}$ - 0.1 M HNO_3 , followed by two washes with 1/5 volumes of 0.1 M Na_2CO_3 or 0.1 M NaOH were sufficient to decrease the reducing normality to less than 0.005. There was no evidence of saponification with sodium hydroxide concentrations of the order of one molar at temperatures up to 60°C.

The major portion of the reducing normality in tributyl phosphate (probably butyl alcohol) is eliminated in the first 10% fraction of

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Solvent Study (continued)

vacuum distillation. It is planned to test the effectiveness of steam sparging and other washing procedures in removing this reducing normality. By the A.S.T.M. procedure for determination of bromine number, no evidence was found that there are olefins present in tributyl phosphate.

Further work is also planned to determine the effect of other diluents such as "Gulf BT" and "AMSCO #360" on the extraction process in comparison with Varsol.

4.5 Semi-Works Process Equipment Installation

The installation of equipment for the Semi-Works demonstration of the TBP Process for metal waste recovery is nearly complete. Two samplers and one feed control rotameter remain to be installed on the columns. The final product evaporator is expected to be in place by September 19. An unexpected delay of two weeks in the delivery of agitators will not interfere with the testing of the system and the calibration of equipment. Upon the arrival and installation of the agitators, the system will be ready for tests with synthetic process solutions. A detailed report and flowsheet of the semi-works TBP equipment installation is being prepared and will be published in the near future.

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Semi-Works Process Equipment Installation (continued)

The strip column (1B) was redesigned when the low flooding rate was obtained. The diameter of this column is now 2-1/2 inches instead of 1-1/2 inches as previously reported.

4.6 Laboratory Column Study

The solvent extraction process for the recovery of uranium from the ORNL waste metal tanks consists of the following operations: removal of the uranium from the tanks as an alkaline sludge, dissolution of this sludge in 60% HNO_3 and solvent extraction with $(\text{C}_4\text{H}_9)_3\text{PO}_4$ diluted with Varsol.

The solvent extraction of uranium from the sludge solution has been studied in laboratory batch experiments, countercurrent batch extractor, and glass columns. The column studies have been limited to testing the process operability, determination of flooding rates, determination of an approximate HETS and a short scrub study was made. The following sections present the data and conclusion from these studies.

Process Demonstration

Seven runs were made in the one inch column at ORNL flowsheet conditions to demonstrate the performance and operability of the process.

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Process Demonstration (continued)

The feeds for these seven runs were nitric acid solutions of ORNL, W-10 sludge. The conditions and results of these runs are presented in Table 4.6-1, Run 18 - Run 24.

The beta fission product activity of the recovered uranium from all these runs was less than 10% the activity of natural uranium, and with six feet of scrub section, the activity of the product was not significantly different from the background of freshly extracted uranium. In Run 21, the uranium concentration in the solvent at the feed plate was only 30% of saturation. This low uranium concentration caused a significant drop in decontamination; however, the activity of the product was still less than 10% the activity of natural uranium.

The IAW uranium loss was about 0.1% from the 10 feet of extraction used. A longer extraction section would not significantly reduce this loss as approximately this amount of uranium has been found to be inextractable from ORNL sludge solutions.

The IBW uranium loss was about 0.2% from the 9 packed feet of strip column. This loss can be reduced to any desired value by additional column height or increased flow of IBX.

Run 24 demonstrated the recovery of uranium from a solution of ORNL sludge which contained only 66 g/l of uranium. This was accomplished

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Process Demonstration (continued)

by reducing the organic to aqueous flow ratio to 1.5:1 and reducing the concentration of $(C_4H_5)_3PO_4$ in the solvent mixture to 12%.

Run 25 demonstrates the recovery of uranium from HW supernatant. The IAF for this run was prepared by precipitating the uranium from HW supernatant by the addition of an excess of NaOH. The sludge thus formed was then centrifuged and the cake redissolved in 70% HNO_3 to an excess of 4.5 N in the final IAF.

The uranium recovered from this feed contained 7 beta fission products counts per minute per mg of uranium and the total uranium loss was 0.2%.

Table 4.6-1

Summary of Waste Metal Recovery Column Runs

Columns: 1" diameter pyrex glass pipe, packed with 1/4"x1/4" Raschig Rings

1A: Extraction length - 10 ft. - Scrub length as given in table

1B: 9 ft. packed section

Feeds: 1AF: Solution of ORNL sludge with 70% HNO₃ to about 3 N excess acid

1AS: 3 N HNO₃

1AX: (C₄H₉)₃PO₄ diluted with Varsol to concentration indicated

1BX: water

Flowratios: 1AF: 1AS: 1AX: 1BX = 2:1:ca6:ca6

Run Number	Length of Scrub Section ft.	(C ₄ H ₉) ₃ PO ₄ Concentration Percent	Beta Activity c/m/mg U		β D.F.	Uranium Loss %		Percent Saturation at feed
			1AF	1BP		1AW	1BW	
18	4	15	2.3x10 ⁴	4	6x10 ³	0.07	0.2	60
19	4	15	2.6x10 ⁴	4	6x10 ³	0.07	0.2	66
20	4	15	2.6x10 ⁴	6	4x10 ³	0.08	0.2	60
21	6	15	2.7x10 ⁴	4	7x10 ³	0.11	0.2	30
22	6	15	2.7x10 ⁴	< 1	>1x10 ⁴	0.06	0.2	50
23	6	15	2.7x10 ⁴	< 1	>1x10 ⁴	0.13	0.1	66
24	6	12	2.2x10 ⁴	<1	>1x10 ⁴	0.05	0.2	47
25*	6	12	1.2x10 ⁵	7	1.7x10 ⁴	0.11	0.09	66

* The metal feed solution for Run 25 was prepared from HW supernatant by precipitation of the Uranium with an excess of NaOH, centrifugation and dissolution of the precipitate in 70% HNO₃ to about 5 N excess acid. The resulting solution contained 68 g/l of uranium.

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Flooding Rates for IA and IB Columns

The flooding rate for the IA columns was found to be 1000 gal/hr/ft² total through put. The flooding rate for the IB column was found to be 500 gal/hr/ft² total through put.

Flooding rates were determined in a 1-1/2 inch pyrex glass pipe column packed with 1/4" x 3/8" Raschig rings. The column was 10 feet in length containing about 9 feet of packed section. No scrub section was used, and the IAF and IAS were mixed before entering the column.

The flooding rate was the rate of flow at which the packing no longer broke up the dispersed phase, or a second interface formed at the bottom of the column. For the IA column flooding was found to occur essentially at the same total through put for two flow ratios; solvent:aqueous phase = 1:1 and solvent:aqueous = 2:1. Only one flow ratio was tested for the IB column, solvent:aqueous phase = 1.

H.E.T.S. Determination

Average H.E.T.S. values for a 1-1/2 inch column 9 feet in length packed with 1/4" x 3/8" Raschig rings were: 75% of flooding - 3.6 feet, 50% of flooding - 3.0 feet and 25% of flooding - 2.5 feet. These values were determined from conventional XY diagrams.

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H.E.T.S. Determination (continued)

H.E.T.S. determinations were made by the following method. Runs were made in a 1-1/2 inch column, 9 feet in height, packed with 1/4" x 3/8" Raschig rings and having four samples set into the column in such a way as to permit sampling of the aqueous phase at four intermediate points in the column. Four such runs were made, one using ORNL sludge solution and three using a synthetic feed of approximately ORNL sludge solution composition.

With synthetic feed a run was made at 25% of flooding, 50% and 75% of flooding. The column was operated for more than three complete changes of the aqueous phase, and duplicate samples were taken for uranium analysis of the feed solution, of the aqueous phase at the four intermediate heights along the column and of the aqueous raffinate. The run with ORNL sludge solution was made at about 60% of flooding and the same procedure followed. The uranium concentration data from these four runs are presented in Table 4.6-2.

In connection with the column runs, the same solutions were processed in a four tube countercurrent batch extractor using the same flow ratio as was used in the column. The tubes were sampled after three complete changes and the uranium in both phases determined. The resulting data are given in Table 4.6-3.

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S E C R E T

H.E.T.S. Determination (continued)

The H.E.T.S. values were found graphically by a second method by plotting the concentration of uranium in the aqueous phase of each tube of the four stage countercurrent batch extractor made with identical conditions, determining where these concentrations intercept the uranium concentration line of the column, and scaling off the H.E.T.S. from these intercepts. The H.E.T.S. for all four runs as determined by this method are given in Table 4.6-4.

S E C R E T

Table 4.6-2

Uranium Concentration Data for H.E.T.S. Determination

Column: 1-1/2" glass pipe, packed to a height of 9 feet with 1/4" x 3/8" Raschig rings

Aqueous Feed: Run 1: Mixture of one part 3.0 HNO_3 and two parts HNO_3 solution of sludge from W-10, ORNL; 120 g/l - \bar{U} , 3.0 \underline{N} acid

Run 2, 3, and 4: Mixture of one part 3.0 \underline{N} HNO_3 and two parts synthetic ORNL sludge solution; 1.0 \underline{M} NaNO_3 , 0.7 \underline{M} NaHPO_4 , 0.8 \underline{M} Na_2SO_4 , 0.6 \underline{M} UNH

Solvent: 85% Varsol, 15% $(\text{C}_4\text{H}_9)_3\text{PO}_4$

Run Code Number	Feed Solution	Uranium Concentration g/l					
		Distance below feed point					
		1.3 Ft.	2.8 Ft.	4.3 Ft.	6.8 Ft.	9.0 Ft.	IAP
1	72	22	7.0	2.4	0.40	0.12	31
2	95	23	8.5	2.5	0.35	0.22	44
3	95	19	4.8	1.1	0.16	0.07	43
4	95	20	4.0	1.4	0.15	0.05	35

Table 4.6-3

Continuous Countercurrent Batch Extractor Runs for Comparison with Column Runs

To Determine H.E.T.S.

Feeds: Run 1: Same as feed for column Run 1, Table III
 Run 2: Same as feed for column Runs 2, 3, and 4, Table III

Solvent: 15% (C₄H₉)₃PO₄ - 85% Varsol

Extractor: Four tubes

Flowrates: Run 1 Feed = 36 cc/batch, solvent = 67 cc/batch.
 Run 2 Feed = 36 cc/batch, solvent = 82 cc/batch.

Run Number	Uranium Concentration (g/l)							
	First Tube		Second Tube		Third Tube		Fourth Tube	
	Aq. Phase	Org. Phase	Aq. Phase	Org. Phase	Aq. Phase	Org. Phase	Aq. Phase	Org. Phase
1	17	38	3.3	9.2	0.13	0.44	0.06	0.02
2	27	42	2.5	12	0.12	0.53	0.02	0.03

Table 4.6-4

H.E.T.S. For Tributyl Phosphate Extraction of Uranium

Column: 1-1/2 inch Pyrex glass pipe, packed with 1/4" x 3/8" Raschig rings, about 9 feet of packing.

Solvent: 85% Varsol, 15% $(C_4H_9)_3PO_4$

Feed: Run #1: Mixture of one part of 3.0 N HNO_3 and two parts of HNO_3 solution of sludge from ORNL - W-10, 120 g/l - U, and 3.0 N acid.

Run #2, 3, 4: Mixture of one part of 3.0 N HNO_3 and two parts synthetic ORNL sludge solution; 3.0 N HNO_3 , 1.0 N $NaNO_3$, 0.7 M Na_2HPO_4 , 0.8 M Na_2SO_4 and 0.6 M UNH.

Run Code Number	Percent of flooding rate	Length of first stage (feet)	Length of second stage (feet)	Length of third stage (feet)
1	60%	2.0	2.5	4.5
2	75%	1.6	2.8	Less than 3 complete stages
3	50%	1.3	2.7	4.0
4	25%	1.3	2.7	3.6

The Effect of Scrub Section Length on Decontamination

Increased length of scrub section gave a marked improvement in the beta decontamination factor. The decontamination factor was 6×10^2 with no scrub section, 8×10^3 with four feet of scrub section and 1×10^4 with ten feet of packed scrub section (see Table 4.6-5).

Table 4.6-5

The Effect of Scrub Section Length on Decontamination of

Uranium from Metal Waste

- Column: One inch glass pipe
Scrub Section as noted in Table
Strip Section 10 feet
- Feed: ORNL Waste sludge solution from W-10. 3 N HNO₃
flow rate 15 cc/min.
- Solvent: 85% Hexane - 15% tributyl phosphate, flow rate
45 cc/min.
- Scrub: 3 N HNO₃ flow rate 7.5 cc/min.
- Strip: Demineralized water, flow rate 45 cc/min.

Scrub Section Length (feet)	Extraction Section Length (feet)	Overall Beta Decontamination Factor	IAW U Loss %
0	10	6×10^2	0.05
4	10	8×10^3	0.07
10	4	1×10^4	1.4

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5.0 Redox

5.1 Pilot Plant Crud Problem

Suspended matter has previously been observed in the methyl cyclohexane displacement medium which has been used in the Pilot Plant. This substance was suspected as a possible source of particulate matter which may have contributed to plutonium losses in the basic Redox Process. In order to observe the characteristics of this material, a four gallon sample of wash water was obtained during a clean-up of the MCH storage or catch tank, B9, along with about three liters of MCH present in the tank.

Semi-quantitative analysis indicated that the material was made up of some organic substance with varying amounts of uranium oxides present either in occlusion or in combination. The uranium was soluble in nitric acid, but a residual amount of insoluble organic and siliceous material remained. Carbon and hydrogen analyses were made on the substance, but no definite composition was established. Observations and analyses are recorded in Table 5.1-1. No nitrates were found in any of the samples.

[REDACTED]

Pilot Plant Crud Problem (continued)

It is recommended that the MCH be periodically washed, filtered, or purified to preclude the presence of this crud in the column streams.

No additional laboratory studies on this problem are anticipated.

Table 5.1-1

Approximate Composition of Cruds Found in the
Pilot Plant Methycyclohexane Tanks

Crud No.	Source	Description	Wt. Composition(%) and Estimated Mole Ratios					Mol. Wt. (Est.)
			Uranium	Carbon	Hydrogen	Water	Unknown	
1	Organic Phase	Finely divided white suspension	21% (3)	8.87% (25)	2.24% (76)	3.3% (9)	64.6% (*)	3400
2	Inter-phase	Grey-white emulsion	54% (9)	5.17% (17)	1.31% (52)	9.1% (20)	30.4% (**)	3960
3	Aqueous Phase	Greenish-yellow amorphous ppt.	82% -	0.78% -	-	-	17% (***)	-

Spect. Analysis (in order of abundance).

* (Residue after uranium solution) Si, β , Cr, Fe

** U, Ca, Cr, Al, Fe, Mg

*** U, Ca, Fe, Al, Mg, Mn

5.2 Plutonium Recovery from Pilot Plant IBP Solutions

Results of one cycle countercurrent batch runs on IBP plutonium indicate that gamma decontamination in E-2 and F-2 solutions is sufficient in one cycle to meet specifications as set out by Hanford, i.e. 10^7 d/m/gm plutonium. The product from E-2 contained 1.3×10^6 d/m/gm plutonium and the product from F-2 contained 6.3×10^6 d/m/gm plutonium.

Beta decontamination, however, was insufficient in two cycles to meet the specification of 10^8 d/m/gm plutonium. The product from E-2 contained 1.5×10^8 d/m/gm plutonium and the product from F-2 contained 3.0×10^8 d/m/gm plutonium. Thus, present information indicates that three cycles will be necessary for adequate beta decontamination. However, three cycles are planned by the Pilot Plant, in any event, since an additional decontamination from uranium is necessary.

To prepare the second cycle feed, the organic effluent from a first plutonium cycle countercurrent run was stripped and then adjusted to 1.2 M $\text{Al}(\text{NO}_3)_3$. Having insufficient solution for a countercurrent system, batch methods were employed to observe overall beta decontamination through the second cycle in both E-2 and F-2 solutions. Low beta decontamination factors of approximately 2.0 and 5.0 were observed with E-2 solutions and F-2 solutions, respectively. Beta activity measurements of the products from this cycle indicated that the E-2 product was below specifications by a factor of 1.5 and the F-2 product by a factor of 3.0.

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Plutonium Recovery from Pilot Plant IBP Solutions (continued)

A subsequent countercurrent check was made in the case of the F-2 solution. A first cycle plutonium run was carried out using volumes of sufficient quantity to provide an effluent after equilibrium for a second cycle feed closely simulating actual column conditions. Decontamination factors were found to check closely with those obtained in single batch experiments (see Table 5.2-1).

[REDACTED]

Table 5.2-1

Plutonium Losses and Decontamination Factors Through Two Cycles -

Countercurrent Batch Extraction

(Plutonium Solutions from Tank F-2)

Conditions:	<u>First Cycle</u>	<u>Second Cycle</u>
Feed	1.0 M Al(NO ₃) ₃ 0.08 M Na ₂ Cr ₂ O ₇ 0.23 N HNO ₃	1.2 M Al(NO ₃) ₃ 0.1 M Na ₂ Cr ₂ O ₇ 0.5 N HNO ₃
Scrub	1.3 M Al(NO ₃) ₃ 0.01 M Na ₂ Cr ₂ O ₇ 0.3 N HNO ₃	1.2 M Al(NO ₃) ₃ 0.0 M Na ₂ Cr ₂ O ₇ 0.0 N HNO ₃
Organic:	Hexone, neutral	Hexone, neutral
Flow Ratio:	F/S/O=1/1/2	F/S/O=1/1/2
Stages:	8 Ext. 6 Scrub	8 Ext. 6 Scrub
Vol. Changes	4.0	2.5

	Pu Dist.Coeff. (Org/Aq)	Pu Loss (%)	Overall Decon. - Factor		Beta Activity per g Pu	
			β	γ	Feed	Product
First Cycle	5.7	0.002	27	ca.300	1.64x10 ¹¹ ^{cpm/gm}	1.3x10 ⁹ ^{cpm/gm}
Second Cycle	9.1	0.0003	2.5	-	9.3x10 ⁸ "	3x10 ⁸ "

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6.0 Dry Fluoride

6.1 Reaction of Uranium Metal with Elemental Fluorine

Experiments were carried out in which metallic uranium was completely reacted with elemental fluorine to form uranium hexafluoride. In these experiments with uranium samples weighing from 15 to 48 gms, the fluorine flow rates were about 70 to 250 ml/min (ca. 25°C and 1 atm) and temperature range was of the order of 300° - 550°C during the major portion of the reaction period. The temperature measurements are assumed to be fairly reliable since the metallic uranium sample rested on a thermocouple well inside of the reactor.

During the first experiments, difficulty in temperature control was encountered in carrying out the reaction between metallic uranium and elemental fluorine. Recent experiments have indicated that starting the reaction at a temperature of 300°C with a fluorine flow rate of about 70 ml/min produced in 3 or 4 minutes a reaction which sustained a temperature of 300 - 350°C. Increasing the fluorine flow rate 30 - 40 ml/min rapidly increased the reaction temperature. A maximum reaction temperature of about 550°C was found at a flow rate of 175 ml/min under the conditions used, while higher flow rates up to 250 ml/min failed to increase the observed reactor temperature.

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Reaction of Uranium Metal with Elemental Fluorine (continued)

It was observed during the latter part of the reaction period that a rapid rise in the reactor temperature (ranging from 25 - 200°C) occurred in a time of 10 - 15 seconds and then rapidly fell off to the normal, slowly declining, operating temperature. This occurrence took place 4 or 5 times during a period of 15 - 20 minutes. The reactor temperature then fell more rapidly to a point at which any reaction failed to take place, since essentially all of the metal has been converted into a fluoride. On termination of the experiment at this point, some non-volatile lower fluorides of uranium still remained in the reactor. In order to convert these lower fluorides to the volatile hexavalent state, it was necessary to carry out the reaction with fluorine for an additional time of 1/2 - 3/4 hour while maintaining the reactor temperature at 450 - 500°C.

Condensation of the volatile hexafluoride product, in a single copper U tube, cooled in a dry ice tri-chloro-ethylene mixture gave recovery values of about 95%, and it appears that no trouble is to be expected in collecting the volatile uranium product.

Further experiments are to be carried out using larger samples of metallic uranium. The samples will be 1/4 inch by 1 inch diameter wafers cut from a 4 inch by 1 inch slug. The reason for this change is due to

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Reaction of Uranium Metal with Elemental Fluorine (continued)

the increased cost of machining slugs of irradiated material into smaller sizes. This change in sample size necessitates the construction of a larger reactor tube and cold trap system, which is now underway.

6.2 Distillation of Uranium Hexafluoride

Equipment consisting of a still-pot, still-head, and condenser is being fabricated for the batch distillation of 100 gram quantities of uranium hexafluoride. The method of controlling pressure at 40 psi has not yet been determined; however, a controller which will vent the system if the pressure falls too low may be satisfactory.

The batch distillation equipment can be used for fractional distillation by inserting a column between the still-pot and the still-head.

Design of the equipment will continue through the next period.

7.0 RaLa Process

7.1 Purification of Ba¹⁴⁰ by Ion Exchange - Laboratory

Preliminary results reported in the quarterly report ending August 10, 1949 showed that approximately 99% of the iron, chromium, nickel, and lead present in the RaLa Process could be removed by making the solution 1.0 M in sodium acetate, pH 5.5 to 6.0, and passing through an A-2 or IR4B anion resin column. The results from 5 recheck runs using

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Purification of Ba¹⁴⁰ by Ion Exchange - Laboratory (continued)

IR⁴B resin show the impurity removal to be no better than 80 to 90% with barium yields ranging from 15% to 85%. The rechecks on A2 resin showed even lower impurity removal. Since every effort was made to duplicate the conditions of the earlier runs, the conclusion reached is that in these runs an abnormal phenomenon such as colloidal physical adsorption or filtration of precipitated impurities must have taken place. Impurity removal by anion exchange will be abandoned for the present as adequate removal is being obtained in the cation exchange process.

Comparison of IRC 50 and Dowex 50

In an effort to determine the optimum conditions for separation of barium and strontium, a large number of distribution coefficients have been run for the systems sodium citrate-Dowex 50 resins, and sodium citrate - IRC 50 resin. Determinations were made at 0.1, 0.3, and 0.5 M sodium citrate and at pH's of 6.0, 7.8, and 9.0. Some of the analyses are being rechecked, and the results will be reported next month.

Comparison of Nalcite and Dowex 50

The distribution coefficients were compared for barium and strontium between the newer Dowex resin, Nalcite, and Dowex 50, in 0.5 M sodium citrate at pH 9.0. The barium distribution coefficients were 2.75 and 1.95,

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Comparison of Nalcite and Dowex 50 (continued)

respectively, while the strontium distribution coefficients were 0.52 and 0.92. Thus, the separation factor for barium and strontium using Nalcite is 5.28 while that for Dowex 50 is 2.14. The capacity of the air dry hydrogen form of the two resins was 4.15 m.e./gm for Dowex 50 and 4.37 m.e./gm for Nalcite.

Investigation of Versene

Versene (ethylene di-amine-tetra-acetic acid) is a strong complexing (chelation) agent. The complexes are so strong that such compounds as barium and lead sulfate are easily dissolved. As the system is very dependent on pH, it is proposed to adjust the pH of the solution to the point where the Ba and Pb sulfates will not precipitate, but where the Ba will be adsorbed on the resin and thus separated from the sulfate.

7.2 Sulfate Precipitation and Metathesis Development - Semi-Works

During the last period it was concluded that filtration would be used for separation of the sulfate and metathesis steps, and since then, equipment revisions have been in progress. A filter similar to that to be used in the full scale operation is being designed and will be tested in the Semi-Works.

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7.3 Purification of Ba¹⁴⁰ by Ion Exchange - Semi-Works

The ion exchange development for the final purification of barium is not complete but to date, iron, nickel, chromium, strontium, and lead separations have been effective with low barium losses in the wastes. Full scale lead and sodium removal have not been demonstrated yet. Radiochemical analytical results have been erratic making some difficulty in interpreting operations.

Runs 13 and 14 were poorly metathesized and, consequently, the bulk of the barium was in the form of sulfate. This explains the heavy column breakthrough and high waste losses. It can be observed from Table 7.3-1 that barium losses in the wastes are sufficiently low. The reason for the low barium yield for Runs 15 and 16 is not certain but could be analytical error or channeling in the resin, since elution curves indicate that elutions were complete.

Runs 15 and 16 were centrifugation runs and only about 1 gram of lead remained. This amount of lead was reduced to 0.04 g and <0.03 g, respectively, in the barium product. Iron, nickel, and chromium analyzed very low and the bulk of the iron was removed either in the Na Ac in the feed or the pH 3 citric acid. The ratio of strontium to barium beta counts has varied from 0.008, 0.04 to 0.14. In Run 15, about 1/3 of the total beta counts were reported as strontium. However, over 200% of the

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Purification of Ba¹⁴⁰ by Ion Exchange - Semi-Works (continued)

strontium was found in the pH 9 sodium citrate elution, indication considerable error in the strontium analytical results. Observation of the elution activity has always shown a very definite and complete elution for strontium.

Future runs on the ion exchange column will be made with the full scale amount of lead in the feed.

Table 7.3-1

Barium Losses and Material Balances for the Ion Exchange Procedure

Column: 3" x 3"

Resin: 100 - 200 mesh Dowex 50

- Procedure:
1. Adsorb metathesized product
 2. Elute Pb with 0.5 NaOH
 3. Elute Fe, Ni, Cr with 0.5 M citric acid at pH 3
 4. Elute Sr with 0.1 M Na citrate at pH 9
 5. Elute Ba with 6 N HNO₃

Run	Feed Waste	NaOH Waste	Barium Losses Citric Acid Waste (pH 3)	% Sodium Citrate Waste (pH 9)	Yield (%)	Material Balance (%)
Test run	0.71	0.09	0.09	0.11	81.0	81.9
12	0.52	0.01	0.03	2.2	171.0	173.76
13*	36.0	-	7.3	-	70.1	113.4
14*	11.1	-	4.6	11.5	44.9	72.1
15	0.068	0.004	0.24	3.23	64.0	67.54
16	0.006	0.004	0.35	0.19	56.0	56.55

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8.0 Homogeneous Pile Studies

The renewed interest in the development of a homogeneous reactor at ORNL has led the Technical Division to undertake some of the problems associated with this program.

At the present time, the specifications for the pile are such that a maximum of 40 grams of enriched uranium per liter of water may be necessary. The pile, as now envisioned, would operate at about 250°C and 1000 pounds pressure in a suitable container of low neutron cross-section. Uranium-233 will probably be formed by breeding in a thorium blanket.

Two possible ways of achieving a satisfactory pile media involve a homogeneous water solution of a uranium salt such as UO_2SO_4 or $UO_2(NO_3)_2$ or slurry of some oxide or other compound of uranium in water which will have the fluid properties of a solution.

The Chemistry Division of ORNL is investigating the properties of UO_2SO_4 systems. Members of the Chemical Technology Department of the Technical Division have undertaken the slurry development phase of the program. Among the factors to be considered in the slurry problem are:

- (1) methods of dispersing the solid in water
- (2) measurement of the stability of the dispersion
- (3) effects of radiation on the slurry
- (4) the investigation of other uranium compounds beside the oxides as a slurry component.

Homogeneous Pile Studies (continued)

Work on this program will be initiated with the preparation of the oxide slurries using a colloid mill recently obtained for this purpose.

9.0 Solvent Extraction Contactor Development

The problem of obtaining reliable solvent extraction data by simple, rapid operation on the laboratory scale has become increasingly important as extraction has become more useful in processes for treating reactor products. To make unnecessary the use of batteries of separatory funnels for simulating columns (i.e. countercurrent batch), it is desirable to have small scale equipment for continuous countercurrent extraction. As the objective in development of such equipment, the following specifications have been outlined:

The column, or other apparatus should:

- (1) be not over four feet high (if vertical) or six feet long (if horizontal), to permit installation under a laboratory hood;
- (2) provide ten theoretical stages;
- (3) be susceptible to remote control;
- (4) require only 500-1000 ml of "hot" feed per run, i.e., the volume of the apparatus should be small to minimize the volume of "hot" solution required to attain equilibrium.
- (5) be adaptable to sampling of stages by remote control.

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Solvent Extraction Contactor Development (continued)

Survey of the literature shows that the only types of extraction equipment capable of providing a high number of theoretical stages in a short column or compact space are those designed for mechanical mixing of the solutions within the apparatus. These types of equipment include the pulse column, mixer-settlers, spinner columns, and the Scheibel column.

A one inch Scheibel column (Figure 2), having 14 actual stages, was tested under the conditions of ORNL Redox Flowsheet No. 1, with composite feed and scrub solutions. The highest average stage efficiency was about 50% corresponding to a uranium loss of less than 0.1%, and the volume of aqueous solution required was about 2-1/2 liters per run.

A 15 stage Scheibel column, 9/16" i.d., was constructed with side arms for sampling at the mixing section of each even-numbered stage. In two runs with this column, the average stage efficiencies were 51% and 69% (for details see Table I). With one exception, the analyses of stage samples showed good agreement with an equilibrium curve determined by batch-wise equilibration.

The runs with the small Scheibel column required about 2 to 2-1/2 hours including 40 minutes for stage sampling after steady-state operation had been obtained. About 1600 cc of solution (equivalent to 800 cc of IA feed) were used for each run. Five aqueous thru puts (200 cc each) assured steady-state operation.

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Solvent Extraction Contactor Development (continued)

A six-stage Leaders-Mitchell mixer-settler (Figure 1) was constructed so that the aqueous phase transfer from each settler to the next mixer is made through a three-way stop cock which may be used for sampling.

In four runs with this apparatus, the stage efficiencies were 83% to 100%. The analyses of samples taken from the stages agree well with the equilibrium curve determined by batchwise equilibrations. Samples of the organic phase in each stage were taken most easily from the settler by means of an aspirator.

Runs with the mixer settler required about 2-1/2 to 3 hours and approximately five thru puts of aqueous solution. The flow rates were limited to about 5 cc/min of aqueous and 10 cc/min of hexone. At higher rates the efficiency fell off slightly and there was a tendency toward flooding, i.e., both phases sometimes came out both ends of the apparatus.

Both the Scheibel column and the tube-type mixer-settler show considerable promise for laboratory scale extraction work.

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10.0 "23" Process

10.1 Pilot Plant Equipment Installation

The "23" Pilot Plant (706-HB) construction has been completed. The equipment has been tested hydraulically and with acid. Preparation of operating instructions and equipment calibration has begun.

Present plans are to begin cold runs about November 1.

10.2 Thorium Recovery

The recovery and decontamination of thorium may be accomplished using tributyl phosphate as the solvent and nitric acid as the salting agent with a thorium loss of less than 0.02% and a decontamination factor of greater than 1.7×10^3 . Six countercurrent batch runs have been made varying feed, solvent, and scrub acidity in an effort to increase the decontamination of thorium from zirconium. The best results were achieved if the 55% tributyl phosphate were made 1 M in HNO_3 and the scrub 6 M HNO_3 ; however, a zirconium decontamination factor of only 2 was obtained with an overall β decontamination factor of 650. Reducing the acid concentration in the system gave no better decontamination and resulted in lower thorium distribution coefficients.

Stripping of thorium from the solvent was accomplished with an organic-distilled water flow ratio of 1 to 1.5. The thorium loss in this step was 0.003% through six stripping stages.

Thorium Recovery (continued)

In the first of two countercurrent batch stripping runs, an organic-distilled water ratio of 1:1.5 was used. The strip distribution coefficient (org/aq) increased from 0.675 in the first stage to 10.85 in the sixth stage with a thorium loss of 0.003%. This rapid change was due to the removal of HNO_3 from the solvent, since it is known that thorium will not strip at high acid concentrations. In the second stripping study, equal volumes of solvent and water were used. After six strip stages, the thorium distribution coefficient was less than one, resulting in a thorium loss of about 8%. These results indicate that a HNO_3 - thorium tributyl phosphate equilibrium had been reached. It is concluded that an organic-aqueous flow ratio of at least 1:1.5 will be necessary to strip thorium from tributyl phosphate with a HNO_3 concentration of 1 M in the thorium-organic extract.

In some stripping studies, a white crud was observed at the interface as the stripping reached equilibrium. Spectrographic analysis of this material indicated that it contained principally thorium and phosphorus. To eliminate this crud formation, the tributyl phosphate was washed with two half volumes of 0.5 M Na_2CO_3 followed by a half volume distilled H_2O wash. No further crud formation has been observed in batch or countercurrent batch stripping runs after treating the solvent by this procedure.

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Thorium Recovery (continued)

A series of experiments were run to determine the beta activity of reagent grade thorium, reagent grade thorium extracted with tributyl phosphate, and thorium decontaminated and recovered from 23 raffinates that had cooled about two years. Results of these experiments indicate that the beta activity of the thorium recovered from 23 raffinates is about 56% of the background activity of reagent thorium extracted with tributyl phosphate and about 15% of the β background activity of reagent thorium.

11.0 Purex Process

11.1 Plutonium Distribution Coefficients

Batch studies showing the effect of HNO_3 in the range of 0.1 - 8.0 M on the various valence states of plutonium were carried out. 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 approximately 10, and greater than plutonium III by a factor of almost 100 (see Tables 11.1-1, 2, and 3). 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 VI 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

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Plutonium Distribution Coefficients (continued)

reducing normality of the tributyl 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 Table 1, and 2). 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 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°C 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 .

The effect of uranium in depressing the extraction of plutonium is shown in Table 11.1-4. In the presence of 1.0 M uranium, only plutonium IV maintained a distribution coefficient sufficiently high to provide a basis for a solvent extraction procedure.

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Simultaneous Extraction of Plutonium and Uranium (continued)

the plutonium VI to plutonium IV. This procedure was developed by J. R. Thomas and H. W. Crandall. The resulting solution was spiked with slug dissolver solution and diluted with acid to the necessary uranium and HNO_3 concentrations for the feeds of the various runs. The conditions of the results obtained from the laboratory runs are given in Table 11.2-1.

In Run 1, the plutonium and uranium losses through seven extraction stages were less than 0.1% and the gross beta decontamination factor was 180. In the second run, the acid concentration of the scrub solution was reduced from 5 to 3.5 N and the acid concentration of the feed increased to 6 N. The plutonium and uranium losses from these runs were still low and the decontamination factor increased to 400. In both of these runs, the solvent at the feed plate was only about 60 - 65 percent saturated in uranium. In the third run, the TBP concentration of the solvent was reduced to 12 percent in order to increase to 88% the percent saturation in uranium of the solvent at the feed plate. The decontamination factor increased by a factor of 4. Reducing the solvent flow ratio in Run 4 further increased the degree of uranium saturation of the solvent at the feed plate to 95 percent without materially increasing decontamination. In Run 5, the uranium concentration of the feed was increased to 1.0 M and a decontamination factor of 1.5×10^3 , while plutonium and uranium losses

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Simultaneous Extraction of Plutonium and Uranium (continued)

were less than 0.05%. Pretreating the solvent mixture with $\text{Cr}_2\text{O}_7^{=}$, HNO_3 , $\text{CO}_3^{=}\text{-H}_2\text{O}$ washes (Run 6) further improved decontamination by a factor of 4.

These runs demonstrate clearly the feasibility of separating uranium and plutonium simultaneously from fission products. Determination of plutonium IV distribution coefficient at the feed plate revealed that it was higher than would be expected from batch studies (approximately 1). This should make it possible to reduce the solvent volume or to decrease the acid concentration of the feed, and still maintain a satisfactory plutonium extraction coefficient. Either change would be expected to result in reducing the cost of the process and probably improve decontamination. It is planned to investigate both possibilities.

11.3 Separation of Uranium and Plutonium

The separation of uranium and plutonium was scouted in batch tests. Since the distribution coefficient of plutonium III was very low, this seemed the logical state for the separation from uranium. Reduction of plutonium IV to plutonium III was accomplished by contacting equal volumes of a solvent product from the countercurrent batch runs and an aqueous solution containing ferrous sulfamate. In one set of experiments, the reducing agent concentration was held constant at 0.03 N and the acid

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Separation of Uranium and Plutonium (continued)

concentration varied from 0 to 6 N. The plutonium and uranium distribution coefficients were determined and from these, the separation factors as functions of HNO_3 concentration (Table 11.3-1). The values varied from 13 at 0 N HNO_3 to 78 at 4 N HNO_3 . In a second series of experiments, aliquots of the solvent product solution were contacted with equal volumes of 1 N HNO_3 in which the concentration of ferrous sulfamate was varied from 0.01 to 0.4 N. The concentration of reducing agent had no effect on the separation of uranium and plutonium. Other reducing agents (hydrazine, hydroxylamine) are being investigated as a substitute for ferrous sulfamate.

[REDACTED]

Table 11.1-1

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)		
	1*	2*	3*
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 11.1-2

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
Temperature: 20°C ± 0.2

HNO ₃ Concentration in Aqueous Feed (M)	Pu ^{VI} Distribution Coefficients (Org/Aq)			
	1*	2*	3*	4*
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 11.1-1
- 2* See Note 2, Table 11.1-1
- 3-4* See Note 3, Table 11.1-1

Table 11.1-3

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 11.1-4

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	0.91
40	1.13	0.57
60	0.34	0.16
100	0.23	0.11
200	0.11	0.04

Note:* 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 11.2-1

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	Solvent* Feed						
	HNO ₃ M	UO ₂ (NO ₃) ₂ M	HNO ₃ M	HNO ₃ M	TBP %					
1	5.0	0.8	5	0.15	15	7/4/30	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.

Table 11.3-1

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

Conditions:

Solvent Feed: Solvent product from countercurrent batch extraction 15% TBP in Varsol, U=42 mg/ml, Pu $\alpha = 2.6 \times 10^5$ c/m/ml, 0.15 N HNO₃

Aqueous Strip Feed: 0.03 N ferrous sulfamate, varying acidity

Equal volume equilibrations for 5 minutes at 20°C

HNO ₃ Concentration of Strip Solution (M)	Distribution Coefficients (Org/Aq)		Separation Factor (U D.C. / Pu D.C.)
	Pu	U	
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

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12.0 "25" Process - Aluminum Slug Dissolving Development - Crud Studies

A process for dissolving aluminum alloy slugs containing 4% uranium in nitric acid with mercury - catalyst has been recommended (memo 9/1/49, Central Files No. 49-9-33) in preparation for final pilot plant demonstration of the "25" solvent extraction for the purification of U-235. Large quantities of "crud" are produced in the dissolver solution from dissolving the Al-Si bonding agent which constitutes approximately 5% of the total slug weight. The amount of crud is estimated at 5 grams per liter of solution, and the flocculent precipitate occupies approximately 20 ml per liter of solution after settling for three days.

Removal of crud by filtration through a sintered stainless steel filter dish appears impractical from semi-works tests because 20 square feet of filter area would be required to pass one dissolver batch (60 gallons) before plugging, and a 4 square foot filter is the largest available in the Pilot Plant. Even when the precipitate was separated by decantation, it was indicated that 10 square feet of filter area would be required per batch. A "G" porosity Micrometallic dish as used in Pilot Plant gave satisfactory clarification. An F filter removed approximately half of the crud but still plugged quickly while coarser filters did not remove a significant proportion of the crud.

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"25" Process - Aluminum Slug Dissolving Development - Crud Studies (continued)

Earlier work on the "25" process feed preparation problem (in February - March, 1949) indicated that addition of diatomaceous earth filter aid such as Johns-Manville Celite improved removal of such crud greatly. Crud solution without filter aid would (typically) plug a sintered disk completely after 10-20 cc. of solution were passed per sq. cm. filter area, whereas, with filter aid 100 cc per sq. cm. would pass during the first hour, 40 cc the second hour, 30 cc the third hour, 25cc the fourth hour, etc.

Indications were that essentially all adsorbed uranium was removed by washing with hot, concentrated nitric acid. These earlier indications are being checked to determine the usefulness of this procedure for the immediate problem.

The only feasible alternative to the use of filter aid now in sight is simply letting the crud follow through the first extraction column. If successful, this would dispense with the crud problem completely, except for uranium which might be adsorbed on the crud so strongly that it would not be removed under extraction column conditions. However, decontamination could conceivably be reduced if crud particles carried over into the solvent stream, and plugging might occur in the column or auxiliary equipment.

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"25" Process - Aluminum Slug Dissolving Development - Crud Studies (continued)

These possibilities will be scouted with a small, continuous glass column contactor set up to simulate conditions in the pilot plant extraction column. Portions of hexone and aluminum nitrate solution containing crud will be circulated continuously in countercurrent through the column, for 4 - 10 days and the behavior of the crud observed.