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LABORATORY RECORDS 1954

PROGRESS REPORT FOR MONTH ENDING OCTOBER 31, 1949

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TECHNICAL DIVISION

CHEMICAL TECHNOLOGY DEPARTMENT

# PROGRESS REPORT FOR MONTH ENDING OCTOBER 31, 1949


F. L. Steahly, Department Head
F. R. Bruce, Laboratory Chief
J. O. Davis, Semi-Works Chief

Edited by:

W. K. Eister


[redacted]

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## 1.0 Abstract

Chemical development is reported on the TBP Uranium Metal Recovery Process, the Redox Process, the Purex Process, the RaLa Process, the "25" Process, the "23" Process, the Thorium Recovery Process, uranium metal fluorination, and a homogeneous reactor slurry study.

2.0 Introduction

The development of the TBP Process for uranium recovery from the Hanford Bismuth Phosphate Metal Waste is now a major problem in the laboratory and Semi-Works sections. The semi-works study was started this month with the object of developing this process on feeds of varying uranium concentration. With the information obtained, it will be possible for Hanford to balance the economics of feed preparation with the processing costs and design the optimum process for their waste. It is felt that before a satisfactory procedure can be developed, it will be necessary for Hanford to undertake an intensive study of feed preparation, including the removal of the waste from the storage. The laboratory section emphasized the study of solvent stability and the development of conditions for processing feeds of varying uranium concentration.

The work on nitrite-acetone feed preparation for the ANL acid Redox Process was resumed in the laboratory section to bring this work to a satisfactory conclusion.

The Purex Process development for recovery and decontamination of uranium and plutonium by solvent extraction with tributyl phosphate from a nitric acid system was continued in the laboratory section to determine the optimum conditions for separation of the uranium and plutonium in Column 1B.

As yet, the chemistry of the revised purification steps of the RaLa Process has not been fixed. The application of Versene (a water soluble

Introduction (continued)

chelating agent) to eliminate the metathesis step was studied and shows promise. A new filter was installed outside the precipitation tank in a fashion similar to that planned for the plant.

The work on the metal solution crud removal step was completed prior to the Uranium 235-aluminum alloy runs in the Pilot Plant, and final tests were completed on the batch solvent extraction equipment for purification and concentration of the Uranium-235 product.

The Thorium Recovery Process development emphasized studies on the specific fission products giving trouble in decontamination.

The volatilization development now has two phases: first, the reaction of uranium metal with fluorine to yield volatile uranium hexafluoride, and second, the distillation of the uranium hexafluoride to achieve decontamination. During this period, the scale of the fluorination was increased to facilitate the sample preparation, and distillation equipment was fabricated.

3.0 Summary

TBP Process

(1) The extractive properties of tributyl phosphate were not altered by refluxing with five molar nitric acid for five hours. The only appreciable effect when refluxed with 16 molar nitric acid was the increase in the plutonium extraction by a factor of 50.

(2) The satisfactory recovery and decontamination of uranium from a feed solution containing only 20 grams of uranium per liter was demonstrated in small scale countercurrent batch equipment. The feed was prepared by direct acidification of Hanford 103 U supernatant.

(3) Uranium was satisfactorily extracted from aqueous feeds containing 0.6 molar phosphate ion, and it was indicated that the absolute amount of phosphate ion was controlling rather than the phosphate to uranium ratio.

(4) Uranium was satisfactorily extracted from solutions containing two molar sulfate ion.

Redox

Further studies on hexone pretreatment and the nitrite-acetone pretreatment of the feed indicate that acid Redox Process can obtain $10^5$ uranium decontamination in one cycle.

Purex

Uranium decontamination factor of $6.8 \times 10^4$ in a one cycle batch countercurrent solvent extraction.

"25" Process

(1) The solvent extraction process for concentration of the Uranium 235 product from the pilot plant was demonstrated in the full scale equipment to give a loss of approximately 0.001%.

(2) It was demonstrated that if the filtration was not successful the crud from the U-235 aluminum alloy slugs to be used in the Pilot Plant would be concentrated in the extraction column and would not effect to operation of process.

## 4.0 TBP Metal Recovery Process

### 4.1 Feed Preparation

Evaporation of Hanford Supernatant

Two semi-works evaporation trials, undertaken as a means of concentrating Hanford supernatant for the TBP process, were limited by precipitation. In the first trial, the unacidified Hanford supernatant, was evaporated 25% by volume before precipitation occurred. Acidification of the pot liquor to 1.8 N nitric acid restored the solution to the original volume which analyzed 38 g U/l. In the second trial, the supernatant was first acidified and then evaporated to 50% of the original volume of supernatant before precipitation started. Analysis of the concentrate was 75 g U/l and 2.8 N nitric acid. Further work on evaporation of Hanford supernatant does not seem warranted at this time.

Dissolution of Uranium in Hanford Waste by Versene

A Laboratory scouting experiment showed that Versene might possibly be used to complex and dissolve the uranium in the Hanford waste tanks at a pH of 6-7. Three 10 ml samples of synthetic Hanford waste (slurry + supernatant) were diluted to approximately 500 ml, made 0.12 M in Versene, and adjusted to a pH of 5. At this point 0.5 grams of uranium per liter were in solution. At lower Versene concentrations, less uranium dissolved. It was not determined whether the large dilution (50X) was necessary.

The Versene could be easily recovered for recycle by acidifying and filtering out the precipitated "Versenic" acid at pH 1.0. Versene costs

Dissolution of Uranium in Hanford Waste by Versene (continued)

about $0.60/lb.

Radioactivity Adsorption on Filter Aid

Diatomaceous earth pick up radiochemical ions as evidenced by a Semi-Works test. A portion of Hanford 103-U supernatant was filtered through Celite 545 filter aid on a 700x60 stainless steel screen. Samples of the supernatant taken before and after filtration indicated that about 40% of the activity was retained by the filter aid. No selective adsorption of specific fission products was observed.

ORNL Sludge Pumping Tests

A thick, heavy sludge was pumped in a preliminary trial from ORNL Tank W-10, using a hose extension on the suction of the air-motor driven pump in order to reach into the sludge layer a few feet from the pump. A six-foot section of two-inch hose was attached to the pump suction and the pump lowered into Tank W-10 so that the hose lay on the tank bottom. The material passing through the sight glass in the pump lines appeared to be quite concentrated, but a representative sample was not obtained.

Another trial is planned using a ten-foot section of four-inch hose. A sufficient quantity of sludge will be pumped to permit sampling for determining the solids concentration.

4.2 Solvent Study

The stability of tributyl phosphate to nitric acid was studied

Solvent Study (continued)

in laboratory tests by digesting with varying concentrations of nitric acid and temperatures. At room temperature and expected process nitric concentrations, the stability was very satisfactory; however at 70° to 100°C, brown fumes indicated some decomposition. No diluent was present in these tests.

It was found that these decomposition products increased the distribution coefficient (organic/aqueous) of plutonium IV from 1 to 49 and fission products from 0.0006 to 0.01, but had little effect on the uranium (see Table 4.2-1).

An attempt to find a contaminant responsible for the increased plutonium distribution coefficient was not successful. Isobutraldehyde was the only impurity showing a marked effect, and it decreased plutonium extraction by a factor of 50 (see Table 4.2-2). This study will be continued.

Table 4.2-1

Effect of Refluxing TBP with $HNO_3$ on Subsequent Plutonium, Uranium, and Fission Product Distribution Coefficients

Aqueous Phase: Dissolver Solution 100 mg/ml U, 3.0 N $HNO_3$
$Pu^{IV}$, $10^6$ β c/m/ml

Organic Phase: 15% TBP, refluxed for 5 hrs., 85% Varsol, 0.55 M $HNO_3$

| $HNO_3$ Conc. used in refluxing (M) | Distribution Coefficients in Extraction*(O/A) | | | | Solvent Reducing Normality Prior to Extraction |
|---|---|---|---|---|---|
| | Pu α | U | Gross β | $HNO_3$ | |
| - | 0.99 | 5.35 | 0.0061 | 0.031 | 0.197 |
| - | 0.95 | 5.48 | 0.0011 | 0.028 | 0.244 |
| 3 | 0.74 | 4.78 | 0.0084 | 0.026 | 0.28 |
| 5 | 0.56 | 6.96 | 0.0092 | 0.026 | 0.14 |
| 7 | 4.33 | 4.22 | 0.0095 | 0.022 | 0.18 |
| 9 | 7.04 | 3.31 | 0.0089 | 0.016 | 0.15 |
| 11 | 10.3 | 5.13 | 0.013 | 0.016 | 0.21 |
| 13 | 20.77 | 5.19 | 0.010 | 0.011 | 0.21 |
| 16 | 49.80 | 8.26 | 0.011 | 0.014 | 0.15 |

* Values given represent average of duplicate analyses.

Table 4.2-2

Effect of Impurities on Extraction of $Pu^{IV}$ with Tributyl Phosphate

Organic Phase: 15% tributyl phosphate
85% Varsol, 0.2 molar in various impurities.
Aqueous Feed: 4.0 M $HNO_3$, $Pu^{IV}$ tracer
Temperature: 20°C ± 0.2

| Impurity added to solvent | $Pu^{IV}$ Distribution Coefficient (Org/Aq) |
|---|---|
| n-butyric acid | 7.52 |
| iso-butyric acid | 7.58 |
| n-butyraldehyde | 7.76 |
| iso-butyraldehyde | 0.19 |
| n-butyl alcohol | 7.80 |
| iso-butyl alcohol | 8.14 |
| butyl nitrate | 9.9 |
| "control" | 11.3 |

4.3 Fission Product Decontamination Study

Results based on gross counting of tracer ruthenium indicated distribution coefficients (organic/aqueous) of less than $10^{-4}$ in the acid range of 1-5 normal. In the same range of acidity, zirconium distribution coefficients varied from 0.03 to 0.6. However, there was appreciable variation of these values depending on the grade of tributyl phosphate used (see Table 4.3-1). A solvent clean-up procedure will be investigated which may improve overall decontamination from zirconium. The addition of uranium to the aqueous feed depressed the one-stage extraction of zirconium by factors greater than 10 when the organic phase was 80% saturated in uranium (see Table 4.3-2).

Table 4.3-1

Effect of $HNO_3$ on Ru and Zr Extraction

by

Tributyl Phosphate

Feed: 0-5N $HNO_3$, Tracer

Solvent: 15% $Bu_3PO_4$-85% Varsol

Equal volume equilibrations at 20°C for five minutes.

| $HNO_3$ N | Zr Dist. Coeff. (gross β) (Organic/Aqueous) | Ruthenium Dist. Coeff. (Organic/Aqueous) (1) | (2) |
|---|---|---|---|
| 0.0 | 0.080 | 0.00053 | - |
| 0.1 | 0.083 | 0.00041 | - |
| 0.5 | 0.057 | 0.00073 | - |
| 1.0 | 0.074 | 0.00077 | - |
| 2.0 | 0.105 | 0.00083 | - |
| 3.0 | 0.16 | 0.00055 | 0.75 |
| 5.0 | 0.72 | 0.00084 | 0.31 |

1. Ruthenium tracer in nitric acid, probably tetravalent.
2. These feeds contained 0.02M periodic acid, ruthenium was probably in the octavalent state.

Table 4.3-2

Effect of Uranium on Zr and Ru Extraction by Tributyl Phosphate

Feed: 5.2N $HNO_3$, 20-200 mg/ml U, tracer

Solvent: 15% $Bu_3PO_4$-85% Varsol

Equal volume equilibrations at 20°C for five minutes.

| Solvent Saturation in Uranium (%) | Zr Dist. Coeff. (Gross β) (Organic/Aqueous) | Solvent Sat. in Uranium (%) | Ru Dist. Coeff. (Gross β) (Organic/Aqueous) |
|---|---|---|---|
| 0 | 0.7 | - | - |
| 31 | 0.30 | 36 | 0.00122 |
| 53 | 0.088 | 63 | 0.00158 |
| 69 | 0.030 | 80 | 0.00081 |
| 78 | 0.028 | 85 | 0.00064 |
| 80 | 0.031 | 91 | 0.00069 |
| 80 | 0.024 | 90 | 0.00049 |

4.4 Extraction From Low Concentration Uranium Solutions

Countercurrent batch studies of metal solutions have shown that the process is feasible with uranium concentrations in the feed as low as 20.3 g/l, giving a beta decontamination factor of $1.4 \times 10^4$. Since low uranium losses (approximately 0.1%) were obtained, direct acidification is indicated to be a simple and feasible means of feed preparation. To accomplish these results, the organic mixture was reduced to 10% tributyl phosphate - 90% Varsol, the scrub 1.0 M in $HNO_3$, and the metal feed was 4.1 M $HNO_3$. The amount of uranium refluxed in the scrub section was about 35% (see Table 4.4-1).

[redacted]



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Table 4.4-1

Tributyl Phosphate Uranium Extraction From Solutions of Low Uranium Concentrations

Source of Feed Processed: Hanford Waste 103 U Supernatant
Organic Flow Rate calculated to give Ca. 70% saturation at feed plate.

Organic: Feed: Scrub: Strip ratio is 3 : 2 : 1 : 3 in all runs.

| Run # | U g/L | $HNO_3$-M | β c/m/mg U | $HNO_3$-M | β c/m/mg U | Overall | 1 AW | 1 BW | % U * | $\%(C_4H_9)_3PO_4$ | Ext.** | Scrub** | Strip** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H-2 | 23.8 | 4.45 | $3.18 \times 10^5$ | 0.0 | 8.60 | $3.7 \times 10^4$ | 0.21% | 0.21% | - | 13% | 6 | 4 | 4 |
| H-3 | 23.4 | 4.48 | $3.53 \times 10^5$ | 0.0 | 17.50 | $2.1 \times 10^4$ | 0.62% | 0.09% | 72.0% | 13% | 7 | 4 | 4 |
| H-4 | 24.5 | 5.00 | $3.38 \times 10^5$ | 0.0 | did not strip | | 0.10% | - | 68.0% | 13% 0.1M $HNO_3$ | 6 | 4 | 0 |
| H-7 | 24.0 | 4.65 | $2.94 \times 10^5$ | 0.0 | 36.30 | $8.2 \times 10^3$ | 0.17 | 0.23 | 70.70% | 12% | 6 | 4 | 4 |
| H-5 | 26.3 | 5.00 | $2.86 \times 10^5$ | 0.2 | 34.30 | $9.2 \times 10^3$ | 0.06 | 0.07 | 54.0% | 13% | 6 | 4 | 4 |
| H-6 | 21.2 | 4.50 | $3.86 \times 10^5$ | 0.3 | 34.00 | $1.27 \times 10^4$ | 0.30 | 5.00 | 55.0% | 13% 0.1M $HNO_3$ | 6 | 4 | 4 |
| H-1 | 26.0 | 2.75 | $3.83 \times 10^5$ | 3.0 | 7.90 | $5.18 \times 10^4$ | 8.5% | None % | - | 6 1/2% | 5 | 4 | 5 |
| H-8 | 20.3 | 4.05 | $3.84 \times 10^5$ | 1.00 | 26.81 | $1.43 \times 10^4$ | 0.12 | 0.005 | 35.50% | 10% | 6 | 4 | 4 |

$$* \text{ Reflux} = \frac{\text{vol. x conc. U in Aqueous of 1st Scrub stage}}{\text{vol. x conc. U in Organic in 1st Ext'n stage}} \times 100\%$$

** Number of stages.

[redacted]

4.5 Semi-Works Process Development

The Semi-Works TBP metal recovery process equipment has been satisfactory tested and is now ready for engineering development runs using "hot" feed. The first runs, in which "cold" UNH was used for the feed, were made to test the equipment and to make necessary adjustments to accommodate very low ($\sim$ 20g/l) uranium feed concentrations, which are obtained by direct acidification of Hanford supernatant. Principal alterations were in the interface controller instrument assembly, to permit higher air pressure on the jack leg systems to off set the lower effective specific gravity in the column system due to the lower uranium feed concentration.

The Semi-Works runs will be made with Hanford supernate and sludge to develop the optimum process conditions for feed uranium concentrations of 20 to about 100 grams per liter.

4.6 Effect of Phosphate Ion Concentration

Since phosphates and sulfates impair the extraction of uranium, and are present in waste metal feed solutions, a series of countercurrent batch extraction studies was made with tributyl phosphate-Varsol solvent mixtures to determine the effect of these constituents on the uranium distribution coefficients and completeness of extraction. These studies were made using synthetic feeds 0.525 M uranium, and varying the molarity of the phosphate ion in the feeds from 0.5 M to 1.0 M and the sulfate ion from 1.0 M to 2.0 M.

Effect of Phosphate Ion Concentration (continued)

Nitric acid was the only salting agent present, except for one run with 1 N $NaNO_3$ added to feed.

From the data obtained, it is concluded that uranium can be extracted with a loss of approximately 0.05%, from waste metal solutions containing as much as 0.6 M phosphate ion. In the presence of this much phosphate, 5.0 M nitric acid is required in the aqueous feed. At lower phosphate concentrations, less nitric acid is necessary to achieve the desired recovery. It is anticipated that average feeds prepared from Hanford metal waste contain about 0.3 M phosphate. Satisfactory recovery of uranium from such a solution requires about 4.0 M nitric acid as a salting agent (see Table 4.6-1). In actual feed solutions, however, sodium nitrate will be present and, consequently, less nitric acid salting agent will be required. These data infer the absolute amount of phosphates in the feed is more controlling over uranium losses than the uranium to phosphate ratio in the aqueous feed.

A similar series of tributyl phosphate solvent extraction runs were made with synthetic feeds containing from 1.0 M to 2.0 M sulfate ion, and nitric acid only as a salting agent. Feeds 2.0 M in sulfates were extracted with a uranium loss of 0.03% by employing 3.0 M nitric acid as a salting agent. In general, the effect of sulfates on extraction is small and no difficulty is anticipated in waste metal recovery (see Table 4.6-2).

TABLE 4.6-1

The Effect of Phosphate Ion Concentration in Aqueous Feed on the Extractibility of Uranium in the TBP Process

Feed (2 volumes): 0.525 M U
Scrub (1 volume): 3 M $HNO_3$
Solvent (6 volumes): 15% TBP-85% Varsol
Counter-current batch extraction

| Run No. | Conc. $PO_4^{\equiv}$ | | Conc. $HNO_3$ M | | % U | Stages | |
|---|---|---|---|---|---|---|---|
| | Feed | Extraction Section | Feed | Extraction Section | Losses | Ext. | Scrub |
| 1 | 1.0 M | 0.67 M | 6.13 | 5.09 | 2.00 | 6 | 4 |
| 2 | 1.0 M | 0.67 M | 5.13 | 4.45 | 4.30 | 8 | 0 |
| 3* | 1.0 M | 0.67 M | 5.00 | 4.43 | 0.13 | 7 | 4 |
| 4 | 0.8 M | 0.53 M | 5.95 | 4.97 | 0.23 | 6 | 4 |
| 5 | 0.6 M | 0.40 M | 5.00 | 4.33 | 0.057 | 6 | 4 |
| 6 | 0.5 M | 0.33 M | 5.25 | 4.50 | 0.040 | 6 | 4 |
| 7 | 0.50 M | 0.33 M | 3.00 | 3.00 | 0.22 | 6 | 4 |

* 1.0 M $NaNO_3$ used as salting agent in addition to $HNO_3$.

[redacted]



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TABLE 4.6-2

THE EFFECT OF SULFATE ION CONCENTRATION IN AQUEOUS FEED ON THE EXTRACTABILITY OF URANIUM IN THE TBP PROCESS - SIX EXTRACTION AND FOUR SCRUB STAGES IN EACH RUN

| Run No. | Conc. $SO_4^{=}$ M | | Conc. $HNO_3$ M | | | Conc. U-M | % $(C_4Hq.)_3 PO_4$ | Ratio | | %U Loss |
|---|---|---|---|---|---|---|---|---|---|---|
| | Feed | Extraction Section | Feed | Extraction Section | Scrub | | | Feed | Org. | |
| 1 | 1.0 M | 0.67 | 4.55 | 4.05 | 3.15 | 0.525 | 15 | 1 | 2 | 0.006 |
| 2 | 1.0 | 0.67 | 2.95 | 3.0 | 3.15 | 0.525 | 15 | 1 | 2 | 0.012 |
| 3 | 2.0 | 1.34 | 5.10 | 4.45 | 3.15 | 0.525 | 15 | 1 | 2 | 0.005 |
| 4 | 2.0 | 1.34 | 2.90 | 2.93 | 3.00 | 0.525 | 15 | 1 | 2 | 0.030 |
| 5 | 2.0 | 1.34 | 2.80 | 2.67 | 3.00 | 0.10 | 12.5 | 1 | 1 | 0.200 |

[redacted]

## 5.0 Redox Process - ANL Flowsheet Feed Preparation Study

Since the acid Redox flowsheet affords an insurance against significant plutonium losses and an economy in the aluminum nitrate salting agent, further investigations have been made into the use of a nitrite-acetone pretreatment which allows significant improvement in ruthenium decontamination.

### The Effect of Methyl Isobutyl Carbinol on Decontamination

The concentration of methyl isobutyl carbinol in hexone was varied to indicate the magnitude of the effect on overall decontamination following the nitrite-acetone feed pretreatment. It was observed in batch experiments that through four scrub stages, beta decontamination was decreased by rather large factors with increasing MIBC content (see Table 5.0-1). Since the MIBC content was not determined analytically below 0.02%, the extremely low values are reported empirically as a function of increasing purification attained by successive hexone treatments with 1.5 N $HNO_3$ and 0.1 M $Na_2Cr_2O_7$, followed by water washes and sodium hydroxide washes. This procedure was developed and reported by an MIT practice group in Report K-427. The data indicate that quantitative removal of reducing substances is very important to overall beta decontamination.

Table 5.0-1

The Effect of Solvent Treatment and MIBC Content on Beta Decontamination in the ANL First Cycle Following the Nitrite-Acetone Pretreatment

Feed: 2M UNH, 0.3M $HNO_3$, 0.1M $Na_2Cr_2O_7$, $6x10^7$ β/m/ml

Scrub: 1.3M $Al(NO_3)_3$, 0.3N $HNO_3$, 0.01M $Na_2Cr_2O_7$

Solvent: Hexone, 0.3N $HNO_3$

Procedure: An aqueous solution containing one volume of feed and one volume of scrub was contacted with two volumes of solvent; this solvent was then scrubbed four times with equal volume passes of scrub and finally stripped with an equal volume of $H_2O$.

| Solvent Treatment | β DF (Scrub) | β DF (Overall) |
|---|---|---|
| Fresh Solvent, 0.02% MIBC (feed not pretreated) | $6x10^1$ | $2.0x10^2$ |
| Treated X6 with $HNO_3$-$Na_2Cr_2O_7$ Procedure | $1.3x10^4$ | $4.0x10^4$ |
| Treated X4 with " " " | $6.0x10^3$ | $1.0x10^4$ |
| Treated X2 with " " " | $3.3x10^3$ | $4.3x10^3$ |
| Solvent, 0.025M MIBC | $6.0x10^2$ | $6.1x10^2$ |
| Solvent, 0.05M MIBC | $1.6x10^2$ | $2.4x10^2$ |

The Effect of Acidity and the $NaNO_2$

The nitrite-acetone pretreatment was previously found to be considerably acid dependent. Optimum conditions for the pretreatment were as follows: the feed containing 2M UNH, 0.3N $HNO_3$ was made 0.05M $NaNO_2$ and 1% acetone and then heated at 90°C for about two hours, after which the feed was adjusted to 0.3N $HNO_3$ and 0.1M $Na_2Cr_2O_7$. It has been found that some beneficial effect is possible by making the nitrite addition in basic solution, adjusting to 0.3N $HNO_3$ and 1% acetone, and proceeding as usual (see Table 5.0-2).

Table 5.0-2

ANL First Cycle Feed Pretreatment

Effect of Acidity During Nitrite Addition on Beta Decontamination

Feed: 2M UNH, 0.3N $HNO_3$, 0.1M $Na_2Cr_2O_7$, $6 \times 10^7$ β/m/ml
Scrub: 1.3M $Al(NO_3)_3$, 0.3N $HNO_3$, 0.01M $Na_2Cr_2O_7$
Organic: Hexone ( <.02% MIBC), 0.3N $HNO_3$
Procedure: Same as that given in Table I.

| Feed Acidity During $NaNO_2$ Addition | βD.F. (Scrub) | βD.F. (Overall) |
|---|---|---|
| + 0.3N $HNO_3$ | $3.0 \times 10^3$ | $6.0 \times 10^3$ |
| + 0.1N $HNO_3$ | $5.0 \times 10^3$ | $1.5 \times 10^4$ |
| - 0.1N $HNO_3$ | $8.5 \times 10^3$ | $3.0 \times 10^4$ |
| - 0.2N $HNO_3$ | $1.0 \times 10^4$ | $7.5 \times 10^4$ |
| - 0.3N $HNO_3$ | $1.2 \times 10^4$ | $1.0 \times 10^5$ |

[redacted]

The Effect of Other Factors

Addition of potassium-iodide to feed solutions prior to the nitrite-acetone pretreatment was observed to lower decontamination factors. Scavenging of pretreated feeds with manganese dioxide was observed to increase decontamination. Heating feeds at 85° with 1% isopropyl alcohol prior to the regular nitrite acetone pretreatment was observed to improve decontamination. In general, this information may indicate that the pretreatment is less effective in the presence of $Ru^{+3}$ and that $RuO_2$ may be removed by carrying on $MnO_2$ (see Table 5.0-3).

Table 5.0-3

Summary of Other Factors which affect the Nitrite-Acetone Pretreatment

(Same solutions and procedure as given in Table II)

| Variations in Feed Pretreatment | β D.F. (Scrub) | β D.F. (Overall) |
|---|---|---|
| Feed heated at 85° with 0.01M Kl prior to usual pretreatment | $7.0 \times 10^2$ | $1.5 \times 10^3$ |
| Feed heated at 85°C with 1% isopropyl alcohol prior to usual pretreatment | $8.0 \times 10^3$ | $4.0 \times 10^4$ |
| Feed pretreated by usual procedure, prior to $MnO_2$ scavenging. | $2.0 \times 10^3$ | $3.3 \times 10^3$ |
| Feed pretreated by usual procedure and scavenged with $MnO_2$ | $6.0 \times 10^3$ | $1.0 \times 10^5$ |

Batch Countercurrent Test

A countercurrent run was made to determine the effect of improved hexone on beta decontamination. Previously a pilot plant run (48R), utilizing the nitrite-acetone pretreatment and hexone with <0.02% MIBC, had been checked by this countercurrent procedure with the following comparison: Overall beta decontamination by (a) laboratory countercurrent with eight scrub stages, D.F. $1.29 \times 10^3$ and (b) pilot plant run, D.F. $1.45 \times 10^3$. In a similar run, with the exception that only six scrub stages and purified hexone was used, an overall beta D.F. of $2.3 \times 10^4$ was obtained. With the beta distribution coefficient (O/A) observed in the scrub section it was estimated that a D.F. of $10^5$ could be attained in ten scrub stages (see Table 5.0-4).

Table 5.0-4

Data From Counter-current Run Utilizing Purified Hexone

Feed: 2M UNH, 0.3N $HNO_3$, 0.1M $Na_2Cr_2O_7$, $6 \times 10^7$ β/m/ml
Scrub: 1.3M $Al(NO_3)_3$, 0.0N $HNO_3$, 0.01M $Na_2Cr_2O_7$
Organic: Hexone (treated x 3 with $HNO_3$ - $Na_2Cr_2O_7$), 0.5N $HNO_3$
F/S/O Ratio: 1/1/2
Stages: 8 Ext., 6 scrub
Vol. Changes: 2.5

| Stage | Feed Plate | 2nd Scrub | 4th Scrub | 6th Scrub |
|---|---|---|---|---|
| Beta D.C. (O/A) | 0.003 | 0.032 | 0.14 | 0.18 |
| Beta D.F. | $3.5 \times 10^2$ | $1.8 \times 10^3$ | $8.5 \times 10^3$ | $2.3 \times 10^4$ |

## 6.0 Purex Process

The results of preliminary tests for the development of the Purex process were reported in the last monthly report, and a tentative flowsheet was suggested for the separation of plutonium and uranium from the bulk of the fission products in the first extraction (Column IA). Subsequent batch work indicated that it was feasible to separate plutonium and uranium in a second extraction (Column IB) by stripping out the plutonium with an aqueous solution of a reducing agent.

One hot countercurrent batch run has been made in remotely controlled apparatus in which a complete first cycle was simulated. Separation of plutonium and uranium from fission products in the first extraction (Column IA) was good. The losses of plutonium and uranium were 0.05 percent and the gross beta decontamination factor was $2.6 \times 10^4$ (see Table 6.0-1).

Separation of plutonium and uranium in Column IB was not satisfactory and is being studied further. Recovery of uranium through the complete cycle was greater than 99.8 percent with an overall decontamination factor of $6.8 \times 10^4$.

[redacted]





Table 6.0-1

Results of Hot Counter-Current Batch Extraction Simulating a Complete First Cycle of Purex Process

Conditions:

**Column 1A**

Feed(IAF): 0.65M $UO_2(NO_3)_2$
6.0N $HNO_3$
Pu$\alpha$=Ca $10^6$ c/m/ml
$\beta$=Ca. $5x10^7$

Scrub(IAS): 3.5N $HNO_3$

Organic(IAX): 15% treated TBP
85% Varsol
0.15N $HNO_3$

Flowratio: AF/AS/AX=3/2/10
Five scrub stages and six extractions

**Column 1B**

Feed(IBF): product of 1A column

Scrub(IBS). Same as IAX

Strip(IBX): 2.0N $HNO_3$
0.04M $NH_3OH \cdot HCl$

Flowratio: BF/BS/BX=10/1.7/2.5
Five strip and four scrub stages

**Column 1C**

Feed(ICF): organic product from column 1B.

Strip(ICX): distilled water

Flowratio: CF/CX=1/1
Six strip stages.

| | Column 1A | Column 1B | Column 1C | Overall |
|---|---|---|---|---|
| Pu Loss (%) | 0.05 | 29 | - | ~ 30 |
| U Loss (%) | 0.04 | ~ 0.05 | 0.1 | ~ 0.2 |
| $\beta$ D. F. for U | $2.6x10^4$ | 1.2 | 2.2 | $6.8x10^4$ |
| $\beta$ D. F. for Pu | $2.6x10^4$ | 1.7 | - | $4.4x10^4$ |

[redacted]

## 7.0 RaLa Process

### 7.1 Dissolution of Barium and Lead Sulfate with Versene

Versene (ethylene diamine 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. The equilibria in this system have been considered by Schwarzenbach in Heh. Chemica Acta 30, 1798 (1947) and 21, 1029, (1948) and from this work the amount of free barium present can be calculated for any pH and Versene concentration. It is found that at a pH of 6.5 to 7, the percent barium complexed is low while the Sr and especially the Pb are still in the complex form. If the equilibrium constants for Pb were known, it would be possible to calculate the minimum amount of Versene needed to dissolve barium and lead sulfate at pH 6.5 from the fact that the amount of free barium should not exceed the $K_{s.p.}$ of $BaSO_4$.

Empirical experiments in the laboratory have shown that 7.1 to $7.9 \times 10^{-3}$ moles of Versene is the minimum amount necessary to dissolve 1 gram of lead and 10 milligrams of barium as the sulfates, and 10 milligrams each of iron, chromium, nickel (1/100 RaLa scale) at a pH of 6.5 in 50-60 milliliters of solution.

Feeds of this composition at pH's of 6.5 and 7.0 have been passed through 10 and 20 ml of Dowex 50 resin (sodium form) and 10 ml of IRC 50 resin (sodium form, buffered to pH 6.8 with sodium acetate). Under these conditions, it

Dissolution of Barium and Lead Sulfate with Versene (continued)

has been found that up to 60% of the barium is adsorbed on the resin while all the sulfate and the bulk of the other cations pass through the column. Larger amounts of resin will be tried in order to increase the barium yield (see Table 7.1-1).

Table 7.1-1

Recovery of $Ba^{140}$ By Ion Exchange From A Solution of Ba and $PbSO_4$ In Versene

Conditions:

Column: Runs 2-6: 10 ml Dowex - 50 Resin, 100-200 mesh
" 8-10: 20 ml " " " "
Run 9: 5 ml (Air dry, $H^+$-form) IRC-"50" resin, 60-80 mesh

Activation: For all runs except Run 9: Resin initially converted to $Na^+$-form with conc. $NaNO_3$ and $H_2O$ washed.
Run 9: Resin initially converted to $Na^+$-form with 1.0M NaOH(up-flow), and buffered (down-flow) with 1.0M Na-acetate, pH 6.8.

Feed: 10 mg, each, of Ba, Cr, Ni and Fe; 1 gm. Pb; 1 mg Sr + 10 ml Ba "tracer"
Volume: 60-60 ml.

Flowrate: 0.55 ml/$cm^2$/min.

| Run No. | Feed pH | Moles Versene Present in Feed | Ba Yield % | Ba Material Balance (%) |
|---|---|---|---|---|
| 2 | 7.0 | 0.0079 | 29.28 | 76.28 |
| 3 | 6.5 | 0.0079 | 60.27 | 88.66 |
| 4 | 6.0 | 0.0079 | (disregarded-feed cloudy) | |
| 5 | 7.12 | 0.0071 | 11.7 | 101.08 |
| 6 | 6.5 | 0.0075 | 35.0 | 70.8 |
| 8 | 7.0 | 0.0079 | 22.65 | 86.01 |
| 9 | 6.5 | 0.0075 | 16.2 | 78.2 |
| 10 | 6.5 | 0.0075 | 56 | 100 |

7.2 Semi-Works Development

Little progress has been made during this period because of equipment breakdown and filter plugging. Recently acquired UNH has contained sufficient graphite to cut filtration rates through a 4 inch "G" micrometallic filter from 1 to 2 liters per minute to 0.2 liters per minute and less. The graphite has been detected after another Alsop filtration and has been found in the barium product solutions. All UNH used in the future is to be derived from canned slugs. A 6 inch micromettalic filter is being installed outside the precipitator to simulate the proposed installation in 706-D.

In the ion exchange equipment, 350 milliliters or 3 inches of resin was not sufficient to give the desired barium and Sr separation with the full quantity of Pb present, 85 grams. The resin bed has been extended to 7 inches or 800 milliliters of resin to provide more capacity and more plates for separations. Sodium removal, which has been neglected until now because of corrosion, will be demonstrated on future runs using sulfuric acid rather than hydrochloric acid.

## 8.0 "25" Process

### 8.1 Testing of Final Concentration Equipment

A batch extraction apparatus has been designed and constructed for the purification and concentration of Uranium 235 from the "25" Pilot Plant development. Preliminary testing has been completed using UNH in the feed salted with 2.5 M $Al(NO_3)_3$, and the extraction accomplished with diisopropyl ether. Two runs were made at uranium concentrations in the feed of 12.5 and 76 g/l. Results of these runs indicate a uranium loss of 0.0004% in extraction and a loss of 0.0006% in stripping with a total loss of 0.001%. On a weight basis, this represents a uranium loss of 0.66 mg in extraction and 1 mg in stripping for a combined loss of 1.66 mg uranium.

The operation of the apparatus was satisfactory and is to be transferred to Building 706-HB for operation by the Pilot Plant Section. This equipment will also be used for concentration and purification of Uranium 233.

### 8.2 Metal Solution Crud Problem

The "25" solvent extraction feed preparation studies, necessary for the special Pilot Plant "25" metal runs, have been completed. Investigation of the aluminum-uranium slug dissolving operation have been previously reported. Results from unit operations investigations of; (a) filtration, and (b) column operation with unfiltered dissolver solution (slurries containing silicon solids), are reported here.

Filtration

The first filtration test using the G-porosity (10 μ ave.) Micro Metallic sintered stainless steel disk filtration medium (same type as in pilot plant filter) indicated that approximately 32 sq. ft. of filtration area would be required to filter 60 gallons of slurry (approximately 0.14% crud) before the filter disk became blocked with solids (at max. vac.). The second filtration test using Celite 545 filter aid with the same filtration medium, indicated that 60 gallons of slurry could be filtered in about 7-1/4 hours through a one sq. ft. filter at 150°F with 10" Hg. vacuum. A precoat of 1.38 oz. filter aid/sq. ft. of filter area was used, and 0.668 oz./gal. of filter aid was added to the slurry. The clear filtrate as observed by the unaided eye was free from solids and analysis indicated that the silicon content was negligible. Uranium was removed from the filter cake (about 4" thick) by displacement washing with the solutions shown in Table 1. A slight crack in the cake was observed during the $Al(NO_3)_3$ washings. The third filtration test employed the 700 x 60 mesh stainless steel cloth instead of the sintered disk medium, with all other conditions remaining the same as in test 2. The time requirement for an equivalent filtration operation using this screen would be about 4 hours. The amount of wash solutions were changed slightly for this test as shown in Table 8.2-1, which also shows the uranium distribution. It is indicated that both of these methods of filtration using filter aid are satisfactory for the pilot plant "25" metal runs.

Table 8.2-1

Semi-Works Feed Preparation Studies For The "25"

Pilot Plant Program-Uranium Distribution

Evaluation of Filter Cake Washing Operations

All washing by displacement at 150°C, 10 in. Hg. P

| Uranium Contained in | ** Test No. 2 | | | Test No. 3 | | |
|---|---|---|---|---|---|---|
| | % U | *% Vol. | equal No. passes | % U | *% Vol. | equal No. passes |
| Slurry | 100 | | — | 100 | | |
| Filtrate | 98.47 | 100 | | 97.91 | 100 | |
| 1.6 M $Al(NO_3)_3$ washes | 1.41 | 15.5 | 10 | 2.02 | 27.6 | 10 |
| Conc. $HNO_3$ washes | 0.061 | 12.4 | 8 | 0.0705 | 13.8 | 5 |
| Water washes | 0.034 | 7.75 | 1 | 0.000 | 13.8 | 1 |
| Washed and Dried Cake | 0.022% | — | — | 0.0000066 | — | — |

* Total Volume of all passes.

** Cake cracked before washing.

[redacted]

Column Operation with Unfiltered Metal Solution

Satisfactory column operation was obtained for a period of 155 hours using pilot plant aqueous feed solutions containing "crud" concentrations of 2 to 5 grams per liter (as silicon). Both aqueous and organic (hexone) phases were recirculated. The solvent did not appear to pick up crud. A three-inch glass column packed 42" high with 1/4" x 3/8" Raschig Rings, with the aqueous feed being injected into the continuous phase in the packed section, was used for the test. The column was operated continuously for 90 hours with a "crud" concentration of approximately 2 grams/liter, and then intermittently for approximately 65 hours with about 5 grams/liter of "crud". The flow rates during the first period (90 hours) were approximately 240 ml./min. for each phase (rate used in pilot plant), and were raised to more than 400 ml./min. (129 gal/hr./sq. ft. of unpacked column) for each phase for the last 65 hours of operation without any indication of flooding. The column was drained and cleaned. About 62 grams of (dry) solids were removed from the packing and column walls, out of a total of 150 grams (as silicon metal) added to the solution.

From observing the appearance and filtration characteristics of the crud in the various tests, it appears that two forms of crud originating in Si-Al alloy can be distinguished. One is a fine, flocculent, brownish precipitate which plugs filters quickly, settles very slowly, adheres to glass surfaces, and accomulates at a column interface where it eventually forms large clumps. This type of precipitate has been encountered in solutions from dissolving

Column Operation with Unfiltered Metal Solution (continued)

assemblies or slugs containing Al-Si bonding material, and in some solutions from dissolving unfabricated Al-Si alloy.

The second type of crud consists of large, blue-black particles which are somewhat gritty to the touch and can be filtered or settled out rather easily. This latter type of crud has been most noticeable in the crud suspensions prepared from unfabricated Al-Si alloy. The origins of these distinct types of crud, which may correspond to allotropic forms of silicon metal, should be explored by metallurgical specialists.

9.0 "23" Process-Thorium Recovery

An extraction process using tributyl phosphate as the solvent for the recovery and decontamination of thorium from 23 raffinates has been developed. Results of countercurrent batch extraction runs on two year cooled thorium slugs indicate a thorium recovery of greater than 99.98% and a beta decontamination factor of greater than $10^5$. Beta activity of recovered thorium has been shown to be about 56% of reagent grade thorium.

In the recovery and decontamination of irradiated thorium of short cooling (3-6 months) with tributyl phosphate as the solvent and nitric acid as the salting agent, zirconium and ruthenium are the principal fission products extracted. Decontamination factors of about 2 are the best obtained to date.

In an effort to increase the decontamination factor of zirconium, six complexing agents have been tried in countercurrent batch extractions with none showing promise. The complexing agents investigated were: Oxalic acid, salicylic acid, molybdic acid, oxanilic acid, potassium ethyl xanthate, and ethylbenzoyl pyruvate.

In all previous work using tributyl phosphate as the solvent for thorium extraction, the solvent was diluted with hexane to obtain the desired mechanical characteristics. However, hexane being very inflammable is not a desirable diluent from an industrial point of view. To eliminate this hazard, Varsol was investigated as the diluent for the tributyl phosphate. Results of two countercurrent batch extraction runs indicate that Varsol is the equivalent of hexane as a diluent.

## 10.0 Dry Fluoride

### 10.1 Reaction of Uranium Metal with Elemental Fluorine

A continuation of the work on converting metallic uranium into uranium hexafluoride was carried out. Samples of uranium weighing 70-75 gm were successfully treated with elemental fluorine, at temperature ranges of 300-550°C in a nickel reactor, to convert the metal to a volatile uranium hexafluoride, the conversion being essentially complete. The volatile hexafluoride was virtually all collected in copper cold traps, cooled in a mixture of dry ice and trichloroethylene.

In these experiments, it has been found that a film deposit occurs on the walls of the reactor which does not volatilize out of the reactor. This film, which is normally expected to be nickel fluoride, contains a small quantity of uranium which is removable by washing. In one experiment, the uranium remaining in the reactor was found to be 0.21% of the weight of the original sample.

There has been some indication of the occurrence of a small quantity of a lower valent uranium fluoride formation in the cold trap system. This material, a greenish solid, is water insoluble and occurs to only a slight extent. It is not known whether the occurrence of this material is caused by a reduction of the hexavalent product by the copper or brass cold trap or if it is due to a mechanical carry over of lower fluorides from the reactor.

Reaction of Uranium Metal with Elemental Fluorine

Fluorine consumption has been found to be 100% of the theoretical during the major portion of the reaction when conducting the reaction at reduced pressure or at atmospheric pressure. An excess of fluorine was used in converting the lower fluorides first formed into the hexavalent form when operating at atmospheric pressure. Also it has been demonstrated that the reaction may be carried out in a closed system in which 100% fluorine consumption is obtained. In a reaction of the later type, no loss of products of the reaction would be possible, barring possible equipment failure, such as leaks in the valves, etc.

Some trouble was encountered in which a teflon gasket, used on the reactor, was found to sublime when the system was evacuated at elevated temperature. Also, the teflon gasketing material forms a volatile product when in contact with nitrogen at elevated temperatures. These difficulties have been overcome by the use of a cooling coil on the gasketed end of the reactor.

It is thought that a run with irradiated samples will be made in the near future.

10.2 Distillation of Uranium Hexafluoride

Design and fabrication of distillation equipment has been continued. A 1 inch column 2 feet high has been built. This will be

Distillation of Uranium Hexafluoride (continued)

packed with Raschig rings cut from 1/4 inch copper tubing. A distillation head with reflux control is nearly complete. A nickel funnel is hung just below the condenser. By means of electromagnets, the funnel can be moved to either reflux all condensate to the column or discharge to the product catch tank.

The pressure controller for the distillation column has been ordered and will be delivered in two or three months. Until this arrives, distillation of alcohol mixtures will be made to test the operation of the equipment.

## 11.0 The Homogeneous Reactor Slurry Study

Ideally, the most satisfactory type of uranium trioxide - water suspension for use in a homogeneous pile would be mixture having true colloidal properties. That is, the particles of uranium trioxide would be dispersed to colloidal dimensions so that the settling rate would be very slow. In this way, the danger of having the uranium trioxide settle out during pile shutdown periods would be minimized.

The quickest approach to this problem is to attempt to process uranium trioxide in a colloid mill to reduce the particle size by mechanical methods. For this purpose, an Eppenbach colloid mill was obtained. This mill has an adjustable clearance between the rotor and stator, making it possible to obtain a range of particle sizes depending upon the clearance.

In the preliminary work to evaluate the mill, samples of uranium trioxide in water were milled for one half hour at five different mill clearances from a completely open mill setting to one which was almost closed.

It was hoped to correlate the fineness of milling with particle size, viscosity, and sedimentation measurements; however, at this time, the data on particle size are not yet available.

The viscosity data were obtained with a Stormer viscosimeter using 19.9 grams as the driving forces. The results are given as revolutions per second of the indicator.

The sedimentation data are presented in terms of settled volume of solids per total volume after a given period of time. The ideal uranium

The Homogeneous Reactor Slurry Study (continued)

trioxide-water slurry would be one whose settled volume to total volume ratio is 1, indicating no settling.

The results are listed in order of increasing fineness of milling.

The uranium trioxide was prepared by decomposing uranyl peroxide at 225°C. The resultant anhydrous uranium trioxide was brick-red in color.

Since the data on particle size are not yet available, it is not possible to correlate the results on viscosity and sedimentation quantitatively.

However, it appears that as the fineness of the milling is increased, both viscosity and sedimentation values pass through a minimum values which are associated with a very unstable uranium trioxide-water system.

The product produced by milling at the most open setting is interesting in view of its thixotropic characteristics. A thixotropic system is characterized by the property of having gel-like structure which liquefies under force. Such a system would show great resistance to settling out of the solid phase during shutdown periods in pile operation because when the circulating pumps are shut down, no forces act on the mixture and it would revert from a liquid to a gel-type substance.

Concerning the composition of this thixotropic uranium trioxide suspension, it appears to be a partially hydrated uranium trioxide. Completely hydrated uranium trioxide is yellow whereas the dehydrated oxide is brick-red; therefore, the dark green color would indicate incomplete hydration.

Table 1.0-1

Evaluation of Colloid Mill Performance on Uranium-Trioxide-Water Mixtures

Milling time - 30 minutes
Listed increasing fineness of milling

48 grs - uranium trioxide

1000 ml - water

| Milling Sample No. | Color of Milled Oxide | Viscosity rev./sec. | Sedimentation Data vol. solids / (Total Vol.) 1 hr. | 16-3/4 hrs. | 62 hrs. |
|---|---|---|---|---|---|
| 1 | dark green | .A | 0.98 | 0.98 | 0.92 |
| 2 | green-yellow | 3.9 | 0.97 | 0.66 | 0.63 |
| 3 | yellow | 5.4 | 0.56 | 0.31 | 0.34 |
| 4 | yellow | 4.3 | 0.98 | 0.79 | 0.60 |
| 5 | yellow | 4.7 | 0.98 | 0.78 | 0.60 |

Note A: This suspension has thixotropic characteristics.