HW 4,159 **DECLASSIFIED** [redacted] [redacted]

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DATE 5-4-49

SUBJECT Technical Division - Chemical Development Laboratory and Semi-Works - Section I - Report for Month Ending April 20, 1949 (49-5-79)

TO M. D. Peterson

FROM F. L. Steahly per W. K. Bister

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To: M. D. Peterson

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Date: May 4, 1949

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TECHNICAL DIVISION - CHEMICAL DEVELOPMENT

LABORATORY AND SEMI-WORKS - SECTION I

REPORT FOR MONTH ENDING APRIL 20, 1949

This report is prepared solely for use in the Technical Division.

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1.0 Introduction

The Redox development program on the first cycle and second uranium cycle for the recovery and decontamination of uranium and plutonium has been completed in the Semi-Works. The Laboratory is continuing work on the plutonium, ruthenium, and the solvent treatment phases of the process.

The first cold run in the ORNL Semi-Works is underway for the development of the uranyl ammonium phosphate process for the recovery of the uranium from the Hanford metal waste tanks. The laboratory development of an alternate precipitation procedure for the supernatant and total waste was completed, and no further work is planned other than necessary assistance to the semi-works operation.

The development of an alternate solvent extraction process for the recovery of uranium from the metal waste tanks at Hanford and ORNL has continued in the laboratory. Data were obtained on the effect of varying the solvent composition and the acidity, and a preliminary flowsheet run was made in batch counter-current equipment.

Two ion exchange processes have been developed by the laboratory. The first process replaces the final precipitation step and the second replaces both electrolysis and final precipitation in the RaLa process. Plans are being made to study the extraction and metathesis steps in the Semi-Works.

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A filtration study is continuing on the problem of crud removal from the solution of the fuel assemblies from the Nuclear Reactor Development Reactor. Data on filtration rates and uranium hold up were obtained.

In connection with the development of chemical processes for reducing the volume of the radioactive waste, two studies are in progress. The sodium nitrate crystallization process for separating this inactive salt from the bulk of the activity was investigated on a laboratory scale and plans were made for semi-works scale operation. The study of ion exchange for the reduction of activity from dilute solutions such as the condensate from the proposed radiochemical waste evaporator was continued to determine the capacity of the ion exchange bed.

The study of the chemical stability of commercially available paints was completed. Abrasion tests are to be made and the total results will be coordinated with decontamination tests underway in the Biology Division.

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2.0 Summary

Redox

1. Pretreatment of the metal solution with acetone and sodium nitrite improved the ruthenium decontamination by a factor of two to four in semi-works tests.
2. The oxidation of plutonium from IV to VI proceeded at a satisfactory rate in either acid or basic metal solutions.

Hanford Metal Recovery - UAP Process

The diammonium phosphate procedure for uranyl ammonium phosphate precipitation was demonstrated on a 500 milliliter scale with simulated Hanford total metal waste and gave results comparable to the Hanford supernatant runs; namely 1% uranium loss and gross fission product decontamination of 10^3.

ORNL Metal Recovery - Solvent Extraction Process

A counter-current batch solvent extraction using 40% tributyl phosphate - 60% hexane as the solvent gave a uranium loss of 0.07% and a gross beta decontamination factor of 5000.

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3.0 Redox

3.1 Plutonium Oxidation - Reduction Studies in Acid Deficient Aluminum Nitrate Solutions

The work of the past month has been devoted to investigation of feed solutions used in the ORNL Redox process for the recovery of plutonium. This work was carried out using a Beckman spectrophotometer which permitted the study of the various plutonium valence states without modifying the solution chemically. One purpose of this work was to obtain some information which would be relevant in explaining some discrepancies in the pilot plant plutonium recovery data.

In carrying out the slug dissolving step, it is possible to attain a range of free HNO_3 concentrations from excess free acid to a deficiency of free acid depending upon the amount of uranium metal dissolved.

Therefore, this investigation will be divided into two parts, one dealing with solutions that contain free acid and the other with solutions [redacted] that are either neutral or acid deficient.

The Preparation of Synthetic Dissolver Solutions

Aluminum nitrate was used in place of uranyl nitrate. This was desirable because $Al(NO_3)_3$ solutions do not absorb light appreciably in the range 400-1000 millimicrons whereas uranyl nitrate is strongly colored. This substitution permitted full use of the spectral range of interest. Moreover, when the nitrate ion concentration is the same, it is felt that substitution of aluminum for uranyl ion has no effect.

Plutonium was added to the solution as either Plutonium IV or a mixture of Plutonium IV and Plutonium VI, which was spectrophotometrically free

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of any polymer and contained only traces of calcium and magnesium.

The Behavior of Plutonium in Synthetic Feed Solutions Containing Free Acid

Depending on conditions prevailing in the feed solutions during the slug dissolving step, there are three possible conditions for the plutonium:

1. If oxidizing conditions prevail during the dissolving, all the plutonium may be converted to Plutonium VI. In this case, when the free acid is reduced to ORNL Redox specifications, 0.2 normal acid deficient, it has been shown that the Plutonium VI is stable.
2. If reducing conditions prevail during the dissolving, all the plutonium may be present as Plutonium IV.
3. However, the plutonium will probably be distributed in all valence states depending upon the acidity and temperature of the feed. The equilibrium prevailing will, in general, be governed by the following equations:

$$3\,Pu^{+4} + 2\,H_2O = 2\,Pu^{+3} + PuO_2^{++} + 4\,H^+$$

$$Pu^{+4} + PuO_2^{+} = PuO_2^{++} + Pu^{+3}$$

The problem in cases 2 and 3 becomes the study of the behavior of Plutonium IV under conditions simulating the manipulations necessary to produce a satisfactory ORNL Redox feed.

The problem was investigated in a free acid concentration of 0.2 N HNO_3. In general the procedure was to carry out all steps such as oxidation or preparation of "equilibrium mixtures" at 0.2 N free HNO_3 and then adjust to 0.2 normal basic and attempt to account for all the plutonium as Plutonium VI.

[redacted]

The first series of experiments were carried out in the following manner:

I	II
$Al(NO_3)_3$ - 1.3 M HNO_3 - 0.2 M Pu (total) - 0.000625 M	$Al(NO_3)_3$ - 1.3 M HNO_3 - 0.2 M Pu (total) - 0.000625 M $Na_2Cr_2O_7$ - 0.1 M
A. After standing 24 hours at 25°C, the plutonium was found to be: Pu IV - 64.5% Pu VI - 28.2%	A. After standing 24 hours at room temperature the plutonium was found to be: Pu VI - 92.3%
B. The solution was made 0.1 M in $Na_2Cr_2O_7$ and heated for 6 hours at 85°C then allowed to cool 18 hrs. [redacted] Analysis indicated that the plutonium was 97% Plutonium VI.	B. The solution was adjusted to pH 1.6 and heated at 85°C for 6 hours and allowed to cool 18 hours. Analysis indicated that plutonium was 98% Plutonium VI.

The good agreement between I and II in the amounts of Plutonium VI present indicates that substantially all the plutonium had been oxidized.

When this experiment was begun it was not anticipated that the oxidation in II would proceed as far as it did. It had been hoped to prepare a more equal mixture of Plutonium IV and Plutonium VI, then adjust to an acid deficient

[redacted]

condition and attempt to secure 100% oxidation under the condition described. However, in the case of II the low Plutonium IV concentration decreases the possibility of polymerizing Plutonium IV.

Another difficulty is created by the addition of $Na_2Cr_2O_7$ to these solutions because $Na_2Cr_2O_7$ makes it impossible to analyze for Plutonium IV or plutonium polymer since it absorbs light so strongly in the region below 600 millimicrons.

In general, plutonium material balances obtained spectrophotometrically agree within 2-3% with analysis by counting.

Another series of experiments were carried out with the "equilibrium mixtures" of Plutonium IV and Plutonium VI. A solution of the composition

$Al(NO_3)_3$ - 1.3 M

HNO_3 - 0.2 N

Pu (total) - 0.000734 M

was heated at 85°C for 6 hours and allowed to stand at room temperature for 44 hours. The total plutonium analyzed

Pu VI - 89.6%

Pu IV - 10.4%

It was spectrophotometrically free of polymer.

Another solution of similar composition was heated at 85°C for 2 hours and allowed to stand for 43 hours. Analysis for plutonium indicated:

Pu VI - 65.2%

Pu IV - 44.6%

It is interesting to note that the same quilibrium concentrations of Plutonium IV and Plutonium VI were not attained in the two cases but varied with the length of heating. Other studies on the equilibrium between Plutonium IV and Plutonium VI, which were carried out in perchlorate or lower nitrate ion concentration systems, indicated that the equilibrium was dependent mainly upon the acidity.

Results that were obtained in these experiments may be explained by attributing the increased oxidation to the nitrate ion or the fact that solutions did not stand long enough to attain true equilibrium. However, it may be pointed out that the presence of high nitrate ion concentration appears to increase the amount of Plutonium VI produced.

Two experiments were carried out on the "equilibrium mixture" of Plutonium IV and Plutonium VI. The equilibrium mixtures were prepared by heating at 85°C for eight hours and allowing the solution to stand several days before using. Unfortunately they were not analyzed before the experiment.

[redacted]

III	IV
$Al(NO_3)_3$ - 1.3 M	$Al(NO_3)_3$ - 1.3 M
HNO_3 - 0.2 M	HNO_3 - 0.2 M
Pu (total) - 0.000614 M	Pu (total) - 0.000638 M
Add:	Adjust to pH 1-8 and add:
$Na_2Cr_2O_7$ to 0.1 M conc.-heat for six hours at 85°C and let stand at room temperature for 18 hours.	$Na_2Cr_2O_7$ to 0.1 M conc. heat for six hours at 85°C and let stand at room temperature for 18 hours.
Analysis for plutonium:	Analysis for plutonium:
Pu VI - 93.4%	Pu VI - 90.5%

[redacted]

In the experiments described in this section, it has been pointed out that the presence of $Na_2Cr_2O_7$ interferred with determination of the other plutonium valence species. In order to overcome this deficiency it would be necessary to choose another oxidizing agent of equal oxidizing power which was colorless. These experiments will probably be repeated and extended by using either sodium or potassium bromate as the oxidant since the oxidizing strength of these reagents are almost equivalent to dichromate and they themselves as well as their products of reaction are colorless.

The Behavior of Plutonium in Synthetic Feed Solutions which are Basic or Neutral

Because of the polymerization and disproportionation that Plutonium IV undergoes when it is in solutions of low free acid concentration, it is not advisable to attempt the preparation of such solutions. Moreover, in attempting to approximate the neutral or basic feed solutions which are prepared by dissolving sufficient metal to lower the acidity, the acidity changes at a more uniform rate as more metal goes in the solution. Thus, if we assume that the plutonium goes into solution as Plutonium IV, we may expect that as the acidity is decreased the Plutonium IV will disproportionate and that the equilibrium between the valence states will adjust itself as the free acidity and temperature of the feed changes.

One way to approximate this condition in the laboratory is to start with a solution of Plutonium IV in HNO_3 containing urea. When a solution of this composition is heated at reflux, the urea is hydrolyzed to NH_3 and CO_2 at a convenient rate so that it is possible to reduce the acidity slowly.

A synthetic feed of the following composition was prepared:

$Al(NO_3)_3$ - 1.3 M

HNO_3 - 2.0 M

Pu (total) - 0.000682 M

Urea - 5.2 grs

After 27 hours reflux the solution analyzed:

Acidity - pH 0.21 (0.11 M)

Pu V - 6.0%

Pu VI - 96.4%

More urea was added to this solution and the reflux was extended for another 24 hours. At the end of this period the analysis was

Acidity - pH 1.6 (0.02 M basic)

Pu VI - 100%

In both analyses spectrophotometric examination failed to indicate the presence of any other valence species or plutonium polymer.

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3.2 Effect Oxidation Temperature on ORNL #1 Decontamination

Table 3.2-1

The Effect on Decontamination of Heating Metal Feed Solutions

ORNL #1 flowsheet conditions used in all runs. Runs made in laboratory counter-current batch extraction consisting of 6 extraction and 4 scrub stages

Run No.	Oxidation		Extraction D. F.			Overall D. F.		
	Time Hrs.	Temp. °C	β	γ	Ru	β	γ	Ru
C-72	24	25	$1.7\text{x}10^2$	80	32	$3.6\text{x}10^3$	$4.5\text{x}10^3$	$3.1\text{x}10^2$
C-73	6	85-90	$1.45\text{x}10^2$	80	36	$3.14\text{x}10^3$	$4.5\text{x}10^3$	$2.255\text{x}10^2$
C-74	24	85-90	$1.6\text{x}10^2$	70	35	$4.13\text{x}10^3$	$4.5\text{x}10^3$	$2.6\text{x}10^2$

* It was not possible to calculate an accurate overall γ D.F. because of low activity level.

No effect was noted on the solvent extraction decontamination [redacted] when the oxidation digestion temperature and time for the ORNL #1 flowsheet was varied from 24 hours at room temperature to 24 hours at 85-90°C (see Table 3.2-1).

3.3 Ruthenium Study

A pretreatment of Redox feeds utilizing acetone reduction of ruthenium compounds, to increase decontamination especially in acid systems was described in a preliminary report last month. Ruthenium D.F.'s of $2\text{x}10^2$ and overall D.F.'s as high as $1.3\text{x}10^4$ have been demonstrated in laboratory counter-current runs, under ANL first cycle conditions. Further studies have been made to determine the effect on ruthenium decontamination of (a) the nitric acid concentration during the pretreatment (b the inclusion of $NaNO_2$,

[redacted]

(c) the method of slug dissolution and (d) the apparent qualities of hexone.

Optimum conditions for the nitrite-acetone treatment in ANL first cycle feed appear to be the following: prior to addition of the sodium dichromate, i.e. At 2 M UNH, 0.3 N HNO_3, add 0.025 M $NaNO_2$ and 0.5%/volume acetone (0.07 M); heat to 90-100°C for about four hours then adjust conditions to 2.0 M UNH, 0.3 HNO_3, and 0.1 $Na_2Cr_2O_7$. Specifications for nitric acid concentration during the treatment have been set at 0.35 ± 0.05 N HNO_3.

Effect of HNO_3 Concentration During Feed Pretreatment Using Acetone

To feeds containing 2 M UNH at varying nitric acid concentrations, 1.0% acetone/volume was added and heated at 100°C for two hours. The solutions were adjusted to 0.3 M HNO_3 and made 0.1 M $Na_2Cr_2O_7$. The feeds were then mixed with equal volumes of scrub, 1.3 M $Al(NO_3)_3$ 0.3 N HNO_3 and 0.1 M $Na_2Cr_2O_7$, and extracted with two volumes of hexone containing 0.3 N HNO_3. This extract was scrubbed with four successive equal volume passes of the above scrub solution. The data obtained gave information concerning distribution coefficients on batch extraction and scrubbing. Overall D.F.'s were calculated by specific activity measurement of the feed and the final scrub. Although this data cannot be directly correlated with column conditions, it allows comparison of treated and untreated feeds.

The information obtained indicated that the optimum HNO_3 concentration for the acetone treatment is in the range of 0.3 to 0.4 N (see Table 3.3-1).

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Table 3.3-1

Effect of HNO_3 on the Acetone Pretreatment of ANL First Cycle Feeds Containing S.W. Dissolver Solutions

Feed: 2.0 M UNH
0.3 M HNO_3
0.1 M $Na_2Cr_2O_7$
1.9×10^7 c/m/ml

Scrub: 1.3 M $Al(NO_3)_3$
0.3 M HNO_3
0.1 M $Na_2Cr_2O_7$

Ext. Ratio: F/S/O=1/1/2

Organic: Hexone (SD)
0.3 N HNO_3

Scrub Ratio: S/O=1/1

All feeds were treated with 1% acetone

N. HNO_3 during Acet. Treatment	c/m/ml Final Scrub	D.F.
Control-No Acetone	28,000	55
-0.45 N	17,000	97
-0.25 N	15,000	105
0.00 N	12,500	128
+0.10 N	[redacted] 6400	247
+0.20 N	1000	1560
+0.25 N	600	3800
+0.30 N	170	9,000
+0.40 N	280	6,000
+0.50 N	456	3500
+1.00 N	570	2700
+2.00 N	8630	200

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The Nitrite-Acetone Pretreatment

It was indicated previously that the inclusion of 0.025-0.05 N $NaNO_2$ in the pretreatment of feed solutions was essentially unimportant in the effectiveness of the acetone effect on ruthenium distribution. At that time only two different samples of semi-works dissolver solution has been investigated. Tests made since with pilot plant dissolver solutions (which were made with excess metal) indicate that $NaNO_2$ may be necessary. Although no explanation of this behavior is possible at this time, it appears the acetone treatment will be more generally effective if the ruthenium in the feed is first converted to the nitrite, insuring perhaps a more quantitative form of the element.

The optimum nitric acid concentration during pretreatment utilizing nitrite-acetone is essentially similar to that using acetone alone.

Using dissolver solution from Run 42-R pilot plant run, D.F.'s calculated after four batch scrubs were 350 for control, 450 for the acetone treatment, and 1000 for the nitrite-acetone treatment, indicating in general that results are much lower than those obtained with semi-works dissolver solution. The increased D.F. found with use of $NaNO_2$ appears to be significant, however. Similar results were obtained with run 46-R solution.

It appears that the effect of excess metal or the consequent conditions of low nitric acid concentration toward completion of dissolving affects the chemical forms of the ruthenium present in the F.P. solution. Further studies will be made to determine if $NaNO_2$ addition to the pilot plant material will suffice to produce added ruthenium decontamination.

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The Effect of Hexone Treatment

When work was first begun on the acetone pretreatment of feeds, it seemed apparent that the hexone used was of especially good quality, since on obtaining a new supply from semi-works storage, D.F.'s obtained from identical feeds were observed to have decreased significantly, i.e., from $9x10^3$ to $1.5x10^3$. Analysis of the two different hexones revealed that each had a reducing normality of 0.002. Scouting experiments were then begun to ascertain if these differences were real.

A sample of pilot plant hexone was observed to give decontamination factors of only $4.5x10^2$. After steam distillation, this decontamination factor was increased to $1.3x10^3$. This latter material, previously contacted with macro amounts of $Ru(NO_3)_4$ at 0.3 N HNO_3 and after thorough water washing, gave a decontamination factor of 2.4x103. Similar treatment with macro amounts of columbium gave a decontamination factor of $2.6x10^3$, and with zirconium a decontamination factor of $5.3x10^3$. [redacted] It was found that if the hexone were contacted with 0.1 M $Na_2Cr_2O_7$, 0.6 N HNO_3 washed with 0.3 N NaOH, and then thoroughly H_2O washed, the decontamination factor after zirconium treatment was increased to $1.8x10^4$. A counter-current run was made using ANL first cycle conditions and utilizing zirconium treated hexone. With eight scrub stages, the following results were obtained: for ruthenium, decontamination factor on extraction was 86 and overall was 156; for total β, decontamination factor on extraction was $6.52x10^2$ and overall was $1.3x10^4$; no γ was detectable in the final product solution. A previous run utilizing untreated hexone gave an overall β decontamination factor of 670 by comparison.

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These results, though inconclusive, indicate that hexone quality can be improved. Work will be continued to ascertain, if possible, the effect of the various impurities or decomposition products of hexone on specific fission product decontamination.

3.4 Development of Acetone Feed Treatment Procedure - Semi-Works

The acetone metal feed digestion procedure, in semi-works runs, improved the gross beta decontamination factor of the ANL Redox first cycle process by a factor of four, from 120 to 470, and of the ORNL #1 process by a factor of two to three, from 2000 to 4000. While the acetone treatment significantly improved the acid ANL Redox process, it was yet a factor of five lower in decontamination than the acid deficient ORNL process (see Table 3.4-1).

Comparing the results of using the acetone treatment in both flowsheets, it may be observed that the ORNL #1 flowsheet will yield:

(a) gross decontamination factors which are 10 times higher,

(b) ruthenium decontamination factors which appear to be about four times higher, and

(c) columbium and zirconium decontamination factors which appear to be 60 to 100 times higher than values obtained from the acid flowsheet.

The decontamination enhancement from incorporating the acetone pretreatment was not as pronounced in the semi-works runs as indicated in laboratory scale runs. However, the scrub section on the semi-works columns is only 4 feet high, and it may be that with additional scrub length a more pronounced

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advantage would be demonstrated.

It appears from the four runs that the acetone treatment without sodium nitrite may be best. In any case, no operational difficulties were encountered in semi-works runs by incorporating the acetone pretreatment in the run procedure. Plutonium and uranium losses were unaffected by use of the acetone pretreatment.

With the completion of these runs the semi-works Redox program was terminated.

<u>Procedure for Acetone Pretreatment of the Metal Feed</u>

The cold UNH solution was transferred to the oxidizer tank in Cell #2 and spiked with the solution from the dissolution of two X slugs. The acidity was adjusted to 0.3 N H^+ with HNO_3. One percent by volume of acetone was added to the feed solution in the oxidizer. In one run, R-35, 0.5 M sodium nitrite was also added to the feed. The mixture was heated to 92°C by a steam jacket on oxidizer and held there for two hours. The heat was turned off and sufficient sodium dichromate was added to the feed to make it 0.05 M $Na_2Cr_2O_7$ and the temperature of the solution was maintained at 85°C for six hours to complete the oxidation of plutonium to the VI state. After the oxidation, the feed was adjusted to 0.3 N H^+ for the acid flowsheet runs and to 0.2 N acid deficient for the ORNL #1 flowsheet runs. Sodium hydroxide was used to adjust the solution to the acid deficient state.

The runs were then made in the usual manner with samples of the effluent streams taken every four hours as in previous runs.

The feed preparation for R-36, an ORNL flowsheet run, was somewhat unorthodox in that the feed was inadvertently diluted on being transferred to the oxidizer. It was necessary to transfer the diluted feed to another tank and to reduce the volume by boiling until it was 2 M in uranium. This required an additional heating period of about eight hours. The feed was then transferred back to the oxidizer and the acetone digestion and plutonium oxidation were then carried out in the usual manner. No adverse effects were observed due to additional heating.

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Table 3.4-1

Semi-Works First Cycle Redox Development Runs

Equipment: 1-1/2 D. columns packed with 1/4" x 3/8" split rings extraction 13.5 feet, scrub 4 feet, and strip 11 feet.

Conditions common to all runs:
Oxidant: $Na_2Cr_2O_7$: 0.05 M in 1 AF; 0.01 M in 1AS
Flow Ratio: 1 Feed; 1 Scrub; 4 Extractant
Hexone: Pretreated Special Shell
Activity: 2 X slugs dissolving per run

	1AF		1AS		1AX	Extraction Losses		Overall Decontamination Factors				
Run No.	U (M)	H^+ (N)	Al (M)	H^+ (N)	H^+ (N)	% U	% Pu	Grβ	I.Cγ	Ruβ	Cbβ	Zrβ
ANL Flowsheet:												
35ᵃ	2.0	0.28	1.3	-0.05	0.5	0.07	0.012	40	90	270	160	60
37ᵇ	1.9	0.25	1.3	0.04	0.5	0.60	0.01	470	160	650	440	50
						[redacted]						
ORNL #1 Flowsheet:												
34ᶜ	1.8	-0.4	2.0	-0.25	0.0	0.29	0.50	6150	1940	1120	25000	5180
36ᵃ	2.0	-0.15	2.0	-0.21	0.0	0.46	0.09	4340	1880	440	2300*	630*
ANL Flowsheet (without oxidation):												
2	2	0.25	1.3	0.06	0.5	0.25		120	60	8	370	100
ORNL #1 Flowsheet:												
24/25	1.9	-0.2	2.0	-0.2	0.0	0.1	0.04	2000	900	130	-	-

Notes: Constituents used in Oresky 1AF feed pretreatment:
a. 0.1 M $NaNO_2$ and 1% by volume of acetone
b. 1% by volume of acetone
c. 0.5% by volume of acetone

* These factors are considered doubtful. No reasonable explanation has been found yet for the large discrepancy.

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4.0 Metal Recovery

4.1 Uranyl Ammonium Phosphate Precipitation Process Development

In the uranyl ammonium phosphate precipitation process, the use of diammonium phosphate instead of ammonium nitrate as the precipitant was demonstrated with the composite Hanford waste yielding in two precipitation cycles gross fission product decontamination factor of 1.5×10^3 with an 0.75% uranium loss. These runs were made in the laboratory on a 500 milliliter scale. The results were similar to the results obtained with the supernatant of the Hanford waste. K-25 demonstrated that when ammonium nitrate was used as the precipitant, the uranium loss was approximately 15% which will require a recycle step for adequate uranium recovery. K-25 has requested that the emphasis be placed on the ammonium nitrate procedure because the crystals obtained using diammonium phosphate were not retained on 700x60 filter screen. No further laboratory development at ORNL is planned.

The equipment for the Semi-Works demonstration of the uranyl ammonium phosphate process for recovery of the uranium from the Hanford metal waste tanks has been installed. The equipment is now being tested and calibrated. The completion date for this study will be August 1, 1949.

Since all previous uranyl ammonium phosphate work at ORNL was done on Hanford or synthetic supernatant, it was deemed advisable to investigate the behavior of feeds which approximated Hanford total waste. To simulate these solutions, Hanford supernatant was butted with additional uranium and non-uranium salts. These feeds are designated semi-hot total alkaline waste to conform with K-25's nomenclature. Concentration of the various ions are as follows: U 55.5 mg/ml, $CO_3^{=}$ 52.8 mg/ml, NO_3^{-} 46.5 mg/ml, $SO_4^{=}$ 23 mg/ml, $PO_4^{=}$ 23.5 mg/ml, and NO_2^{-} 2.3 mg/ml.

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To determine the optimum quantity of dibasic ammonium phosphate compatible with good uranium yield and fission product decontamination, several 25 ml scale runs were made. Results of these experiments indicate that 55 g $(NH_4)_2HPO_4$ per cycle is necessary. To further test this procedure, three 500 ml laboratory scale runs were made. Average results of these runs indicate a uranium loss through two cycles, including washing, of $<0.75\%$ with beta and gamma decontamination factors of 1.7×10^3 and 1.6×10^3.

Use of the reducing agents, ferrous ammonium sulfate and hydrazine hydrate, and the oxidizing agent, periodic acid, in concentrations of 0.05 M was investigated as an aid in improving the decontamination in uranyl ammonium phosphate precipitation from Hanford supernatant solutions with dibasic ammonium phosphate. Their use was also investigated in wash solutions for removal of the mother liquor from the precipitated uranyl ammonium phosphate. No significant improvement was shown.

On precipitating uranyl ammonium phosphate with ammonium nitrate (K-25 procedure) from Hanford supernatant, the uranium loss in the first cycle is about 3.5% and about 10% in the second cycle. This high loss necessitates a recycle process for the recovery of uranium from these filtrates. The recycle procedure consists of adjusting the acidity with NH_4OH or NaOH to pH 2.0, centrifuging, washing the precipitate and transferring a solution of the precipitate in HNO_3 to a subsequent first cycle precipitation.

Laboratory experiments to determine uranium losses in the recycle phase indicate 0.05 mg/ml at pH 2.0 with beta and gamma decontamination factors of 80 and 285, respectively. At pH 3.0 the beta and gamma decontamination factors are 7 and 65 with a uranium loss of 0.006 mg/ml. The uranium loss at pH 5.0

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is 0.005 mg/ml with beta and gamma D.F.'s dropping to 4 and 27. In all cases, the precipitates were extremely difficult to centrifuge in an International #1 centrifuge at 2000 rpm. Great care had to exercised to avoid disturbing the precipitate. On the basis of these recycle data, it is recommended that the pH of the recycle material be raised to 5.0. This will reduce the uranium loss by a factor of 10 without appreciable interference with decontamination when this material is returned to an initial precipitation cycle.

4.2 Solvent Extraction Process Development

A solvent extraction process is being developed for recovery of the uranium from the metal waste tanks at ORNL and Hanford. The process, now in the preliminary laboratory stage, consists of dissolving the metal waste in nitric acid and solvent extracting with a mixed solvent, hexane and tributyl phosphate. It has not been necessary to remove the phosphate and sulfate ion before extraction nor to add additional salting agent.

During the month, batch tests were run in order to determine the optimum composition of hexane-tributyl phosphate mixture for the solvent. It is indicated that the mixture is between 70% and 80% hexane. An aqueous phase 3 N in HNO_3 would give a uranium distribution coefficient of about 2 and a beta distribution coefficient of about 0.0005. A study made to check the effect of nitric acid, showed an increase in both uranium distribution coefficient and separation from beta until the acid in the aqueous feeds exceeds 4 N.

Two counter-current runs were made using 60% hexane - 40% tributyl phosphate mixture as the organic feed. The aqueous feed in the first run was 4 N in nitric acid. Seven extraction stages and six scrub stages were used. It was found that the uranium distribution coefficient did not decrease on subsequent extractions; gross beta decontamination was 5000 and the uranium loss was 0.07%. The second run was made with the aqueous feed 3.2 N in nitric acid and the organic 0.91 N in nitric acid. Distilled water was used as scrub. A uranium loss of 0.3%, 3.4 decontamination for scrubbing and overall decontamination of 3400 were obtained.

5.0 Waste Disposal

5.1 Decontamination of $NaNO_3$ from ORNL

After the evaporation of radiochemical waste, further concentration of the concentrated evaporator liquor may be obtained by crystallizing out the sodium nitrate.

A total decontamination factor of 1.8×10^5 has been attained for three crystallizations from nitric acid with less than 100 cts/ml/min at 10% geometry in the final concentrated salt solution.

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Decontamination is also satisfactory by crystallizing in the presence of as little as 0.01 M acid but is not adapted to batch operation because of the high salt loss in the mother liquor. Decontamination factors of 10 to 300 have been obtained per crystallizations on laboratory and semi-works filters. The inconsistent decontaminations per cycle are believed to be due to poor mechanical separation of crystals and liquor and incomplete washings. At lease two and probably three crystallizations will be necessary to reduce the activity in the salt to a disposable level. Apparently no fission products

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are quantitatively carried by the salt but both ruthenium and columbium are in greater relative abundance than in the feed.

Crystallization of sodium nitrate has been successful from W-6 concentrate after separation of insoluble solids. The bulk of the aluminum and sulfate concentrates in the first mother liquor and the bulk of the chloride crystallizes with the nitrate. Major effort in the next period will be concentrated on operating procedure and equipment design for a semi-works demonstration of W-6 crystallization. Also further laboratory runs will be made to determine ion distribution in W-6 and Hanford type waste.

5.2 Condensate Decontamination by Ion Exchange

Simulated waste evaporator condensate runs have been continued on the 1-1/2" x 2' cation and anion exchange beds. Using W-6 waste diluted 10^4 times with demineralized water with added X-metal solution as a source of activity, 95% to 99% adsorption of activity has been maintained over 5000 [redacted] bed volumes of feed without signs of breakthru. To simplify equipment design, the reactivation solutions have been fed in the same direction as the feed without any apparent effect on decontamination. At 5000 gallons per day of condensate from the tank farm evaporator, a minimum diameter of about 8" would be required. The column length is not too critical but should be something in the order of 4 to 8 feet. An activity breakthru point has not yet been reached but from present data columns 8" x 6' will run two weeks without saturating the resin.

Since the evaporator condensate activity will be largely volatile iodine, runs were made with iodine tracer oxidized to I_2 with bromine. An earlier

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run on a laboratory scale gave a decontamination factor of 200 on IRA 400 amberlite anion resin. Ten millicuries of iodine tracer in the I_2 form in 200 l of solution was fed to the 1-1/2" x 2' Dowex 50 and A-2 resin columns with only a fraction of the activity adsorbing. The results were unexpected on the basis of the laboratory runs. Further laboratory tests will be made. The mechanism of I_2 adsorption is reaction with the benzene structure of the resins rather than ion exchange. The Dow resins are not of the phenolic type as are the Amberlites which may account for the discrepancy in adsorption results.

Future runs will be made with W-6 solution diluted 10^3 with demineralized water instead of 10^4 in order to determine an activity breakthru point.

6.0 Barium^{140} Separation Development - Ion Exchange Study

Two ion exchange processes are under development for the improvement of Barium^{140} yield.

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I Citrate - Acetate Process

This process would follow the present electrolysis and evaporation step replacing the ether hydrochloride extraction and would effect the separation of Pb, Fe, and other lesser impurities from the Barium^{140}. The steps in this process are as follows:

(1) Take the $Ba(NO_3)_2$ up in 0.5 M citric acid and pass through a Dowex 50 resin column where the cations are adsorbed.

(2) Elute with 0.5 M ammonium citrate, pH 3, to remove Fe

(3) Elute with 1 M ammonium acetate pH 6.0 to remove Pb, Cr, Sr, Ni

(4) Elute the Barium^{140} in a small volume of 6 N HCl.

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A trial run using this procedure showed Dowex 50 resin to be unsuitable because of its slow diffusion rate. As a result, the elutions to remove impurities were cut short because of time limitations. The results showed a 90% yield of Ba, and removal of the following percentages of impurities: Pb, 16%; Fe, 82%; Cr, 77%; Ni, 100%. Qualitative runs using IR 105 resin have shown it to have a much faster diffusion rate than Dowex 50. Future runs will be made with IR 105 resin and higher molarity of eluting agents.

II Alkaline Process

This process would replace both the electrolysis and ether extraction steps in the present RaLa process. The present electrolysis procedure, while adequate in theory, actually leaves up to 1 gm of Pb with the Barium^{140}. The steps in the proposed ion exchange process are as follows:

(1) Add enough 0.5 M NaOH to hold the Pb in solution as the plumbate and pass through a Dowex 50 resin column. The barium is adsorbed on the resin while the plumbate anion passes through the column. [redacted]

(2) Remove impurities by citrate and acetate elution as in process I.

(3) Elute Barium^{140} in a small volume of 6 N HCl.

A tracer run using this procedure on 1/10 the ionic barium concentration of the present RaLa process has been made. 99.5% of the Pb was separated from the barium. Barium yield was ca. 67%. Refinement of technique and use of IR 105 resin should improve these figures.

7.0 "25" Development - Metal Solution Crud Removal

Filtration of the solution of a fuel assembly for the proposed Nuclear Reactor Development Reactor was most satisfactorily carried out using a

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700 x 60 mesh stainless steel cloth with 25 milligrams per square centimeter of Johns Manville Celite 545 filter aid precoat, and approximately five grams per liter of the filter aid slurried in the metal solution to be filtered. To recover uranium, the filter cake was washed with two 10% volumes of 3 molar nitric acid at 55°C removing 3.87% uranium. The filter cake was then washed with two 5% volumes of 70% nitric acid removing 0.1% uranium.

The uranium 235 from the spent fuel assemblies from the Nuclear Reactor Development Reactor is recovered by dissolving the assembly in nitric acid and solvent extracting the uranium. The solution of the assembly contains insoluble material, a silicon-aluminum alloy which would interfere with the solvent extraction process and must therefore be removed.

The "crud" (silicon-aluminum alloy) was examined under the optical microscope and a photomicrograph at 100X was made. The particles were irregularly shaped, varying from notched elongated needles to fragment [redacted] like plates, ranging in size from 10 microns to 500 microns.

Filtration tests using sintered stainless steel filter mediums with and without filter aid were not satisfactory.

8.0 Dry Fluoride Development

A small scale fluorinator has been built for use in studying the direct fluorination of cold uranium metal. The fluorinator consists of 3/4" nickel tube with a resistance heater wound around the outside. This assembly fits into a section of 3 inch black iron pipe which is used as a cooling water jacket.

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A chemical trap for removing fluorine from the off-gas is now being fabricated. About three feet of nickel capillary tubing needed for control of fluorine flow has been located.

As soon as the new laboratory space in the Semi-Works is ready for occupancy, it is planned to assemble the fluorination equipment in one of the stainless steel hoods located there. At the present rate of progress it will be about the middle of May or the first of June before any experimental work may be done. In the meantime, the survey of available information will continue.

9.0 Protective Coatings for Concrete Surfaces

The chemical resistance of 64 commercially available paints to hexone and three molar solutions of nitric acid, hydrochloric acid, sulfuric acid, and sodium hydroxide was determined. None of the paints successfully withstood the attack of all the reagents.

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One coating, a rubber like material, Research Sample J-653, resisted hexone satisfactorily but failed against 3 M NaOH and 3 M HNO_3 in 96 hours and 160 hours, respectively. Two other coatings, however, Deven Resin Solution K-5925 and Spraylat SC-1054, resisted hexone for twenty-four hours.

On the basis of these chemical tests, the following coatings are considered useful for protecting concrete surfaces from the chemical reagents tested: (1) Devan Resin Solution K-5925, (2) Research Sample J-653, (3) Amercoat -31, (4) Corrosite Plastic Coating, 8228, (5) Amercoat -55, (6) Bisonite M-100 and M-101, (7) Ucilon 400-9.

A final evaluation of the coatings will be made upon completion of

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decontamination and susceptibility tests by Bizzell of the Biology Division. The coatings selected must then be tested for wearing qualities to define their field of application.

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