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ORNL 392
CHEMISTRY-SEPARATION PROCESSES FOR PLUTONIUM

LABORATORY RECORDS

TECHNICAL DIVISION

INTRA-DIVISIONAL MEMO-CHEMICAL DEVELOPMENT LABORATORY AND SEMI-WORKS REPORT FOR MONTH ENDING JULY 31, 1949

F.L. STEAHLY
W.K. EISTER

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TECHNICAL DIVISION

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F. L. Steahly per W. K. Eister

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To: M. D. Peterson

From: F. L. Steahly per W. K. Eister

1.0 Introduction

The chemical process development problems for this period included solvent extraction, precipitation, ion exchange, and metal solution.

Solvent extraction development problems were: the Redox process for uranium and plutonium decontamination, which was completed; the TBP process for uranium recovery from ORNL and Hanford metal waste, and preliminary work on decontamination of irradiated thorium from breeder reactor blanket material.

Precipitation processes being investigated were the UAP process for the recovery of uranium from the Hanford metal waste as developed by K-25, and the RaLa process for the separation of radioactive barium from pile metal.

Also in connection with the RaLa process, the development of an alternate procedure for the purification of barium by ion exchange was continued.

The metal dissolution problems studies were: the dissolution of uranium-aluminum alloy by reaction with nitric acid for the pilot plant development of the "25" process, and the dissolution of uranium by reaction of fluorine to give volatile uranium hexafluoride.

2.0 Summary

Redox

(1) The optimum nitric acid concentration for the oxidation of Plutonium IV in two molar uranyl nitrate solution with 0.1 molar sodium dichromate at 85°C was 0.1 molar.

(2) The critical dependence of plutonium yield on the final acidity of the dissolver solution was indicated by a correlation of pilot plant and laboratory data. The optimum final acid concentration appeared to be 0.1 molar nitric acid.

Metal Recovery - UAP

The uranyl ammonium phosphate precipitation process was successfully demonstrated on a 50 gallon scale by the Semi-Works using Hanford supernatant solution with inactive chemicals added to simulate the "total" waste.

(1) The overall uranium loss averaged 0.6%.

(2) The beta and gamma decontamination factors averaged 1300 and 830 for 103T (4 years old) waste; 470 and 270 for 103U (3 years old) waste, respectively.

Metal Recovery - TBP

(1) Washing the used solvent (tributyl phosphate-hexane) with sodium carbonate or sodium hydroxide solution was found to be beneficial.

(2) The uranium extraction HETS was less than two feet as indicated by the correlation of batch and column data.

(3) A higher-boiling petroleum fraction may be substituted for hexane as the tributyl phosphate diluent giving a flash point even higher

than that for methyl isobutyl ketone.

"25"

Adequate fission product decontamination was obtained when ferrous sulfamate was eliminated from the first solvent extraction cycle and added in the second cycle only. The presence of mercuric nitrate, added as a catalyst during dissolving of the uranium-aluminum assemblies, in the metal solution prevented the addition of ferrous sulfamate because of precipitation.

3.0 Redox

3.1 Plutonium Equilibrium Study

The work of the past month was devoted to the study of the oxidation of Plutonium IV under feed make up conditions for the ORNL Redox process and to the investigation of the behavior of Plutonium IV and Plutonium VI under conditions prevailing in the region of the feed plate of the first cycle extraction column.

The optimum region for the oxidation of Plutonium IV by 0.1 M $Na_2Cr_2O_7$ in 2.0 M UNH at 85°C was about 0.1 N free HNO_3.

The rate of oxidation of Plutonium IV under conditions approximating the feed plate of the extraction section was not rapid enough to secure quantitative oxidation in the time the feed remained in this region. Since this region is probably the most favorable one in the column for oxidation, it is very likely that any Plutonium IV entering the column will be lost.

Studies of conditions prevailing during extraction of plutonium by hexone indicate that the system is sufficiently oxidizing to prevent reduction of Plutonium VI to Plutonium IV.

3.2 Plutonium Loss Study

Further data was obtained which indicated the Redox first cycle plutonium loss was a function of the final dissolving acidity with the optimum final acidity approximately 0.01 M nitric acid.

For pilot plant Run 53, the first dissolving yielded a final solution three molar in nitric acid. This was due to a plugged slug chute. This

solution was oxidized with dichromate at this acidity by heating at 85°C for about 24 hours. Samples of this solution were neutralized to 0.2 N basic in one case (a) by direct base addition to the feed to allow diuranate precipitation and supposed conditions for polymer formation, and in another case (b) by base addition to the scrub solution to prevent local diuranate precipitation, before performing the usual exhaustive batch extraction procedure. In both cases, about 50% of the plutonium was found to be inextractable. This feed was subsequently neutralized to 0.7 N HNO_3 and heated again for eight hours at 85°C, and a sample presented to the laboratory for plutonium loss determinations. 40% of the plutonium was still found to be inextractable under basic flowsheet conditions. This feed was not run through the columns, due to these abnormal conditions.

A second dissolving was then made with the acidity on completion of dissolving being 0.07 N HNO_3 deficient. The acidity of the dissolver solution was adjusted to 0.2 N HNO_3 and a sample was presented to the laboratory for plutonium loss studies. It was found that 80-85% of the plutonium was extractable using "basic" flowsheet conditions without the normal oxidation procedure. Another 10% was found to be extractable from this raffinate using 0.5 N HNO_3 in the hexone. After the normal oxidation procedure at the Pilot Plant, the final feed was determined to contain 0.00 to 0.02% inextractable plutonium by TTA analysis; however, 1.5% of some alpha activity was inextractable, as indicated by LaF_3 analyses. Column results for plutonium losses were 0.75-1.0% by LaF_3 and 0.35% by TTA in this run. Exhaustive extraction of the first column raffinates indicated no further plutonium recovery was possible with neutral hexone; however, with hexone containing 0.5 N HNO_3, the loss value was decreased to

0.05-0.10%. This latter effect is characteristic of all checks that have been made on pilot plant first column raffinates from the 100% Hanford level runs.

3.3 Pilot Plant Crud Problems

Last month it was reported that the crud which formed in the organic line between the D and E columns in the Redox process was predominantly $Fe(NO_3)_3$, and an effort was being made to determine the source of the ferric iron. An ever-increasing quantity of crud formation pointed to the possibility of air oxidation of the ferrous sulfamate in the bulk storage tank, so a determination of ferric ion in this reagent was made and found to be in the order of 0.5-1.0%. This would correspond to about 40-50 mg Fe^{+3} per liter in process feeds and scrubs. It is not felt that this amount is significant in crud formation.

In the course of the analytical determinations, it was observed that the colorimetric method utilizing orthophenanthroline and hydroxylamine-hydrochloride (recommended by Sandell) gave inconsistent results, indicating 35-50% Fe^{+3}. However, the volumetric procedure utilizing ceric oxidation and Jones reduction and the colorimetric procedure utilizing ammonium thiocyanate gave consistent results of the order reported above.

No further investigation on this problem is contemplated.

4.0 Metal Recovery

4.1 UAP Process

The Uranyl Ammonium Phosphate Process, for recovery and decontamination of uranium from Hanford metal waste, was demonstrated in ten radioactive simulated total waste runs on a semi-works scale (approximately 150 liters of feed). The simulated total waste feed was prepared by spiking the 103-T or 103-U supernate solution with uranium, sodium, phosphate, sulfate, and nitrate ions to simulate ionically the total waste (combination of dissolved sludge and supernate). Fission product concentrations were approximately 95% of that in supernate.

The source of feed had a definite effect on the decontamination factor but recycling had no noticeable effect upon the factor over a series of seven runs.

The average gross β and γ fission product decontamination factors were: 1300 and 830 for a series of three simulated 103-T total waste runs, somewhat higher than the 470 β and 270 γ obtained from a series of six simulated 103-U total waste runs. Recycle material from the previous run was added to each run except the first 103-T and last three 103-U simulated total waste runs. The data from Run 22 were invalid because of the addition of insufficient phosphate ion for precipitation resulting from an error in feed preparation, hence these data were excluded from the average (see Table 4.1-1).

The uranium loss was consistently less than one percent, averaging 0.55%.

The process operability was comparable to previous "cold" synthetic runs described in ORNL-287, with the exception that the first cycle filtration time

was approximately doubled. A study of the filtration cycle is being conducted, but conclusive information will not be obtained until an investigation of the filter medium is made upon completing the present series of runs.

Two more radioactive test runs are planned to complete the present program. It is indicated from the consistency of the results that additional investigations, on semi-works scale, are unnecessary.

Table 4.1-1

Uranyl Ammonium Phosphate Process - ORNL Semi-Works Uranium and Decontamination Data

Feed: Hanford supernate from Tanks 103-T and 103-U spiked with inactive chemicals to give a solution composition as follows:

0.26 M U^{+4}	0.33 M PO_4^{-3}	0.11 M CO_3^{-2}
3.91 M Na^{+}	0.28 M SO_4^{-2}	0.71 M NO_3^{-}

Run Number	Grams U in Starting Feed Solution	First Cycle				Second Cycle				Recycle	Overall			Final β Activity
		% Loss to Recycle	% Loss in Washes	Gross β D.F.	Gross γ D.F.	% Loss to Recycle	% Loss in washes	Gross β D.F.	Gross γ D.F.	% Loss in Effluent	% Loss	Gross β D.F. ($x10^{-3}$)	Gross γ D.F. ($x10^{-2}$)	
19*	10,588	6.69	0.04	79	41	2.3	0.09	17.7	19.8	0.907	1.03	1.4	8.11	2.29
20	10,750	8.13	0.06	83	54	3.2	0.04	16.9	13.6	0.331	0.43	1.4	7.34	3.07
21	10,954	7.77	0.07	68	46	5.83	0.12	11.7	20.5	0.166	0.36	1.2	9.52	3.13
Ave. 103T Runs		7.73	0.056	77	47	3.78	0.086	17.4	18.0	0.495	0.64	1.33	8.32	2.83
22	11,033	16.83	0.18	71	45	7.16	0.22	5.3	3.7	0.34	0.74	0.380	1.68	8.50
23	10,859	5.53	0.03	58	41	4.68	0.13	7.9	6.0	0.24	0.40	0.46	2.46	6.06
24	11,298	10.5	0.03	55	41	4.5	0.22	8.7	7.6	0.23	0.48	0.477	3.12	5.33
25	11,214	7.24	0.02	40	53	8.0	0.10	11.7	5.8	0.10	0.22	0.473	3.07	5.07
26*	8,527	9.24	0.09	47.6	47.4	5.3	0.31	9.4	7.8	0.36	0.76	0.477	3.68	6.47
27*	10,600	7.46	0.06	61	49	8.7	0.24	8.6	4.3	0.25	0.55	0.525	2.11	4.51
28*	9,743	4.89	0.06		16	9.3	0.17		12.2	0.27	0.50	0.432	1.95	5.74
Ave. 103U		7.53	0.05		41.2	6.6	0.195		7.3	0.24	0.49	0.473	2.73	5.53
Average All Runs		7.49	0.067			5.76	0.157				0.541			

* No recycle material added.

4.2 TBP Process

4.21 Column Extraction Experiments

4.211 Solvent Reuse

Five laboratory column runs were made in which the effect of repeated use of tributyl phosphate-hexane solvent mixture on uranium losses and fission product decontamination was investigated. No appreciable change was noted in the uranium losses. The gross beta decontamination factor dropped from 9×10^3 for the initial use to 2×10^3 for the fifth successive use of the same solvent; however, part of this decrease could have been caused by lower uranium concentration in the solvent at the feed plate.

This solvent, which had been used in five successive column runs without treatment, was then transferred to the laboratory and tested in the countercurrent batch extractor. One portion was used without treatment; one portion was given three 1/10 volume washes with 1 M Na_2CO_3 and a 1/10 volume with 0.5 M HNO_3, and the third portion was treated with 1 M NaOH instead of Na_2CO_3. The comparison of these three portions in the countercurrent batch extractor showed significantly lower uranium losses for those runs employing the treated solvent (see Table 4.2-1). A caustic wash is therefore recommended for the treatment of used solvent in the TBP process.

4.212 Scrub Study

It was found that increased scrub length markedly increased decontamination from fission products. The gross beta decontamination factors obtained for various scrub section lengths were 0 feet -580,

4 feet - $8x10^3$, and 10 feet - $1.6x10^4$.

4.213 Extraction HETS

Two lengths of extraction section were used. With an extraction section of 4 feet, the IAW uranium loss was 1.4%. This loss was less than the uranium loss (3.8%) observed in a counter-current batch extractor run made with identical feeds and conditions using 3 extraction stages. Thus it was concluded that the first four feet of the column was equivalent to more than three stages, and the HETS for the one-inch column packed with 1/4 x 1/4 Raschig rings was less than 1.5 feet. The IAW uranium loss observed when an extraction section of 10 feet was used was 0.06%. No conclusions as to HETS can be drawn from this value as this amount of uranium has been found to be inextractable with both column and counter-current batch extractor.

Column runs are now being made to determine the possibility of substituting a petroleum cut, "varsol", or carbon tetrachloride for hexane as a diluent for tributyl-phosphate.

Table 4.2-1

Effect on Yield and Decontamination of Washing Used Solvent

Countercurrent Batch Extraction Tests

Feed: 133 g U/l, 4.5×10^4 β c/m/mg U, 5.3 γ mv/mg U, 71 Pu α c/m/mg U

Solvent: Used for five column runs without treatment, treated before batch runs as noted.

Solvent Treatment	β D.F.	γ D.F.	Uranium Loss %		
			Pu D.F.	AW	BW
None	1.5×10^4	4.4×10^3	11	0.15	0.95
Carbonate Washed	1.3×10^4	7.6×10^3	9	0.09	0.01
Caustic Washed	2.8×10^4	8.7×10^3	10	0.06	0.01

4.22 Alternate Tributyl Phosphate Diluents

Considerable effort has been spent searching for a less hazardous substitute for hexane as a tributyl phosphate diluent. Varsol appears to be quite satisfactory, since countercurrent batch results indicate decontamination and yield comparable to those with hexane. Varsol is now being studied in the laboratory columns. Carbon tetrachloride was chosen as a typical representative of the heavier than water, non-inflammable solvents and was tested as far as the countercurrent batch extractor as a diluent. It also compared favorably with hexane.

4.23 Feed Preparation

Semi-Works development of uranium feed preparation for the TBP solvent extraction process includes recovery of the uranium from underground retention tanks, and preparing a clarified acid solution of the uranium to be fed to the extraction columns. A centrifugal sump pump lowered into the sludge in Tank W-10 in the ORNL Tank Farm has effectively delivered a slurry of up to 35% solids by volume to the dissolver located above ground. After decanting the supernatart and lighter layer of slurry from the dissolver, the heavier slurry was dissolved in nitric acid. The acid solution was then clarified by filtering through a 700x60 mesh stainless steel screen precoated with Cellite 545 diatomaceous earth filter aid.

It will be necessary to concentrate the uranium pumped from the retention tanks. High-spot scouting indicates that (1) either filtration or centrifugation of the uranium slurry or (2) dissolving the pumped slurry followed by

evaporation of the acid solution is a reasonably effective means of preparing column feed.

Attempts to sample the sludge to determine stratification in Tank W-10 through the available tank nozzles have not yet been successful. Air spargers installed in the tank nozzles for use in precipitation operations may have created depressions around the spargers.

4.24 Semi-Works Equipment Design

Work has been initiated on the design and installation of equipment for demonstrating the recovery of uranium by continuous column extraction with tributyl phosphate from Hanford and ORNL metal wastes. An equipment flowsheet has been selected and design drawings for column installation and tank layouts are in progress. The procurement of the necessary tanks, pumps, agitators, valves, and accessory equipment has been started. Equipment, wherever possible, will be obtained from salvage or Y-12; sundry items such as explosion proof motor-driven agitators and special valves will have to be purchased. A small jungle hut to store equipment and parts for this job will be erected south of 706-HB.

The semi-works installation of the TBP solvent extraction process will consist of two stainless steel 1-1/2 inch diameter columns packed with 1/4x7/8" Raschig rings; an extraction-scrub column with 12' 6" of packed extraction section and 9' 10" of packed scrub section, and a strip column with 18' of packed section, and the necessary feed and effluent tanks and process control instrument. Both columns and all tanks holding radioactive solutions

are to be installed in Bank A, Cell B, while the tanks handling cold solutions as well as all solvent recovery and make-up equipment will be installed in Cell C of Bank A in 706-HB. The installation and erection of the equipment will be done by the ORNL mechanical and maintenance departments.

5.0 "25" Process Development

5.1 Effect of Sodium Nitrate on the Aluminum Nitrate Determination

Since it was anticipated that sodium hydroxide would be used in neutralization of feed and scrub of "25" process solutions, it was desired to check the term, 0.33c, in the formula:

$$Al(NO_3)_3 \text{ conc. (M)} = 6.592\,x - .0083y + 0.00322t - 0.33c - 6.672$$

Where x = observed sp g, y = U conc., t = temp., and c = $NaNO_3$ conc. Several points were checked and the value found to be the true correction for $NaNO_3$ in the formula.

5.2 Effect of Mercuric Nitrate

Use of 1% $Hg(NO_3)_2$ catalyst in the dissolving of aluminum assemblies was found to present a problem due to the formation of a milky white crud when the basic feeds containing 0.002 M Hg were adjusted to 0.05 M ferrous sulfamate. Sulfamate was known to form basic salts with mercury and silver. The finely dispersed crud was observed to settle from solution in about 8-12 hours, but passed through a 10 micron filter disc. It dissolved in free nitric acid and was considerably more soluble in feeds neutralized with ammonium hydroxide rather than sodium hydroxide. After contacting feeds containing the crud for several minutes with hexone, a light-brown precipitate

collected at the interface.

Consideration of methods for controlling this problem has led to the decision to eliminate ferrous sulfamate from the first cycle and to utilize it in the second cycle where no mercury is present; thus, plutonium reduction and separation would be effected and the improved factor for ruthenium decontamination due to sulfamate would be retained. Studies of other reducing agents, to replace ferrous sulfamate, in the relatively short time available did not seem feasible.

Countercurrent batch experiments (see Table 5.1-1) have indicated that the first cycle β decontamination factors will be reduced by a factor of ten by leaving out ferrous sulfamate; however, if sulfamate is introduced into the second cycle, β decontamination will be well within the range of specifications. These batch experiments indicated also that insignificant amounts of mercury are extracted in the first cycle since no cruds were observable with addition of ferrous sulfamate to the second cycle feed. Demonstration of decontamination factors thru two cycles was limited since final products were very close to background.

Table 5.1-1

Uranium Loss and Beta Decontamination Factors Observed in Counter-Current Extractions Demonstrating Effect of Ferrous Sulfamate and/or Mercuric Nitrate in First Cycle of "25" Process

Conditions:

Feed: 1.6 M $Al(NO_3)_3$
14 mg U/ml
0.2 N HNO_3 def.
1.27×10^7 β/m/ml
7.4×10^3 γ/m/ml
0.002 M Hg^{++} and/or
0.05 M $Fe(SO_3NH_2)_2$
Flow ratio: F/S/O = 4/1/5

Scrub: 0.75 M $Al(NO_3)_3$
0.2 N HNO_3 def.
(0.05M $Fe(SO_3NH_2)_2$ in No.'s (2), (3)
Flow ratio: s/o = 1/5

Organic: s.s. Hexone neutral
Number of Stages:
Ext. 6
Scrub 8
Volume Changes:
2.5

Values Determined	(1) Feed Contained 0.002 M Hg^{+2}	(2) Feed Contained 0.05M $Fe(SO_3NH_2)_2$	(3)* Feed Contained 0.002M Hg^{+2}+0.05M $Fe(SO_3NH_2)_2$
U D.C. (O/A) Feed Plate	5.1	4.6	5.15
U Loss (5 stages)	0.1%	0.27%	0.4%
β D.F. (Feed Plate)	1.5×10^3	5.9×10^2	7.1×10^2
β D.F. (Overall)	3.4×10^3	3.4×10^4	5.1×10^4

* White crud ($Hg(OH)(SO_3NH_2)$?) in this feed was observed to change to brown after extended contact with hexone and to collect at interface.

5.3 "25" Alloy Slug Dissolution

The ORNL Pilot Plant has requested development of a safe, reliable process for dissolving aluminum alloy slugs containing 4% U-235 which have been irradiated at Hanford in preparation for the final demonstration of the "25" solvent extraction process for purification of uranium. Nitric acid catalyzed with mercuric nitrate is the dissolving agent; the dissolving must be quantitative, and the final solution concentration should be not less than 1.8 M in aluminum nitrate.

5.31 Dissolver Runs

Approximately 18 dissolving runs have been made, 6 in glass, 12 in a steel dissolver. Data of the first fifteen runs are given in the June 20 CPD report, the last three in Table 5.3-1. Conclusions drawn from these runs are:

1. The initial reaction is smooth and easily controlled using 1-2% mercuric nitrate catalyst based on the weight of aluminum to be dissolved when the starting solution is neutral or slightly acid, and acid is added at a rate which approximately balances the rate of dissolving.
2. Dissolving rate approaches zero as the concentration of aluminum nitrate in the disslover solution approaches 2.0 M. This effect increases as the concentration of excess nitric acid in the dissolver solution increases. Therefore, near the end of dissolving, additional acid added is not consumed and in turn causes a further decrease in dissolving rate.

3. Optimum Conditions for dissolving are (approximately):

   a. 1.5-2.0% $Hg(NO_3)_2$ catalyst, water heel adjusted to give final solution 1.6-1.8 M.

   b. Reaction started at about 80°C, temp. gradually increased to 100°C during the first five hours, and held at 100-105°C for the remainder of the time.

   c. Nitric acid, 3.5 moles per mole aluminum, added over a period of fifteen hours, approximately 10% of the total during first hour, decreasing to 5%/hour during the last hour.

   d. At end of acid addition, dissolver should be sampled, and heating resumed if necessary to complete the dissolving.

5.32 Dissolving Rate Determinations

A series of small-scale dissolvings at fixed conditions of temperature solution acidity and aluminum nitrate concentration were undertaken to evaluate accurately the separate effects of these variables. Dissolving rates in 1.8 M $Al(NO_3)_3$ solutions of 95, 100, and 105°C were determined for 0.5 N acid deficient, "neutral", 0.5 N acid excess, and 1.0 M acid excess. The extremely low dissolving rates (10 mg/sq. cm/hr.) in the "neutral" solution were especially noteworthy, and had not been anticipated. Figure 5.3-2 is a cross-plot of Figure 5.3-1 data versus temperature. The dissolving rates determined in 1.8 M $Al(NO_3)_3$ are all lower than predicted from the correlation obtained from the dissolver runs.

In 1.4 M $Al(NO_3)_3$ solution dissolving rates increased from approximately 500 mg/sq. cm/hr. at neutral and 0.5 acid deficient to approximately

1000 mg/sq. cm/hr. at 1.0 N acid excess (Figure 5.3-3). The dissolving rate increased approximately 40% when the temperature was increased from 95 to 105°C.

A few tests at 2% catalyst gave dissolving rates near 1000 mg/sq. cm/hr, but the high rates caused temperature rise and decrease in acidity during the test and hence gave inaccurate results.

Further tests are being carried out in 1.0 M $Al(NO_3)_3$, and at higher acidities. Following this, several runs will be made under closely simulated pilot plant conditions, using 4% uranium slugs, with the recommended conditions for final testing of the process.

Table 5.3-1

Aluminum Slug Dissolvings - Semi-Works (June, 1949)

70% HNO_3 added steadily during run to disslover containing 1.36 in. diameter x 8 in. long cylinderical aluminum slugs in a water heel containing 1% mercuric nitrate catalyst, based on the weight of aluminum.

Run Hour	Concentration - Normality Units					
	Run 16		Run 17		* Run 18	
	Al	Acid	Al	Acid	Al	Acid
1	0.5	-0.3	0.6	0.1	0.6	-0.2
2	1.1	0.0	1.1	-0.2	1.0	0.1
3	1.6	-0.2	1.3	0.6	1.3	0.6
4	1.8	-0.6	1.5	1.2	1.3	1.1
5	2.1	-0.2	1.6	1.8	1.4	1.6
6	2.1	-0.7	1.4	2.4	1.4	2.0
7	2.0	+0.1	1.5	2.4		
8	2.1	+0.2	1.6	2.3		
9	(not all acid added)		1.6	2.2	(run discontinued because of acid build-up)	
10			1.6	2.1		
11			1.6	2.1		
% of slug remaining	11%		13%		28%	

*Temperature held at 95°C throughout run, other runs started at 85°C, increased to 100°C at end of second hour, and were held at 100-103°C thereafter.

[redacted]

Drawing # 7361

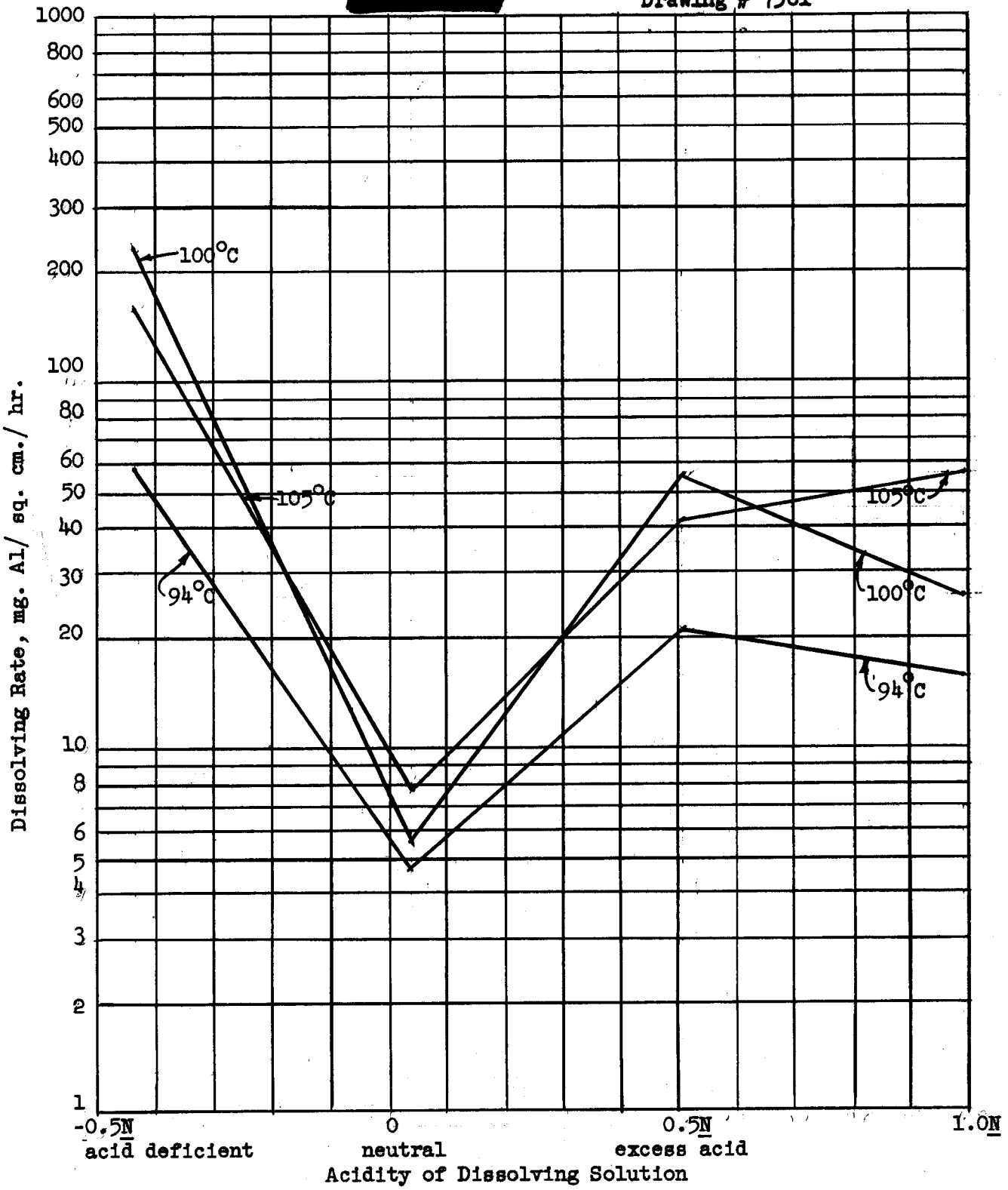


FIGURE 5.3-1
Aluminum Dissolving Rate
(multiple batch tests, Semi-Works)
Effect of Solution Acidity

Conditions: 200 ml. 1.8 M $Al(NO_3)_3$ solution
0.11 g. Hg. $(NO_3)_2$ catalyst
6.8 g. Al, 10.5 sq. cm. surface.
10-15 minutes dissolving time.

[redacted]

[redacted]

Drawing # 7360

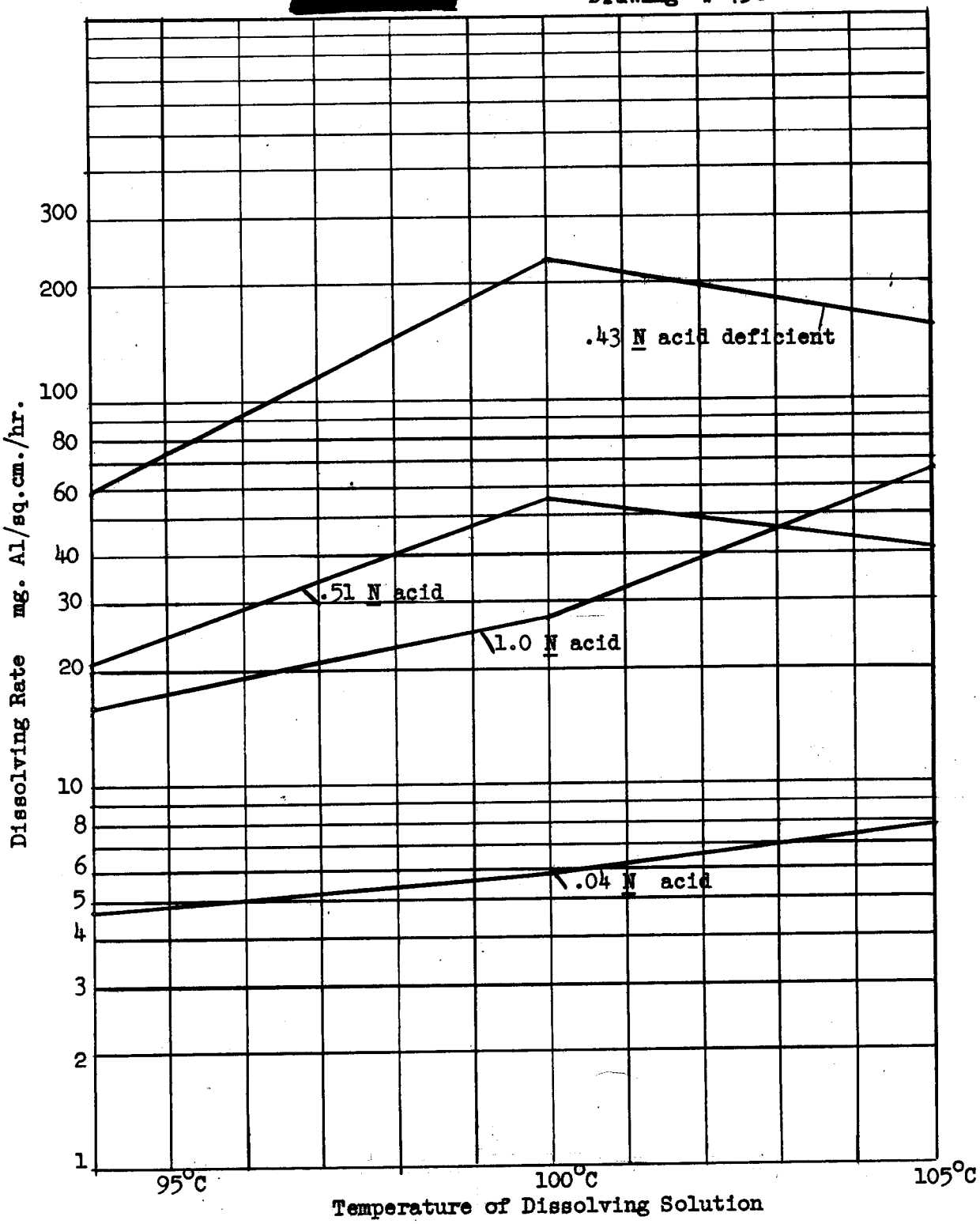


FIGURE 5.3-2

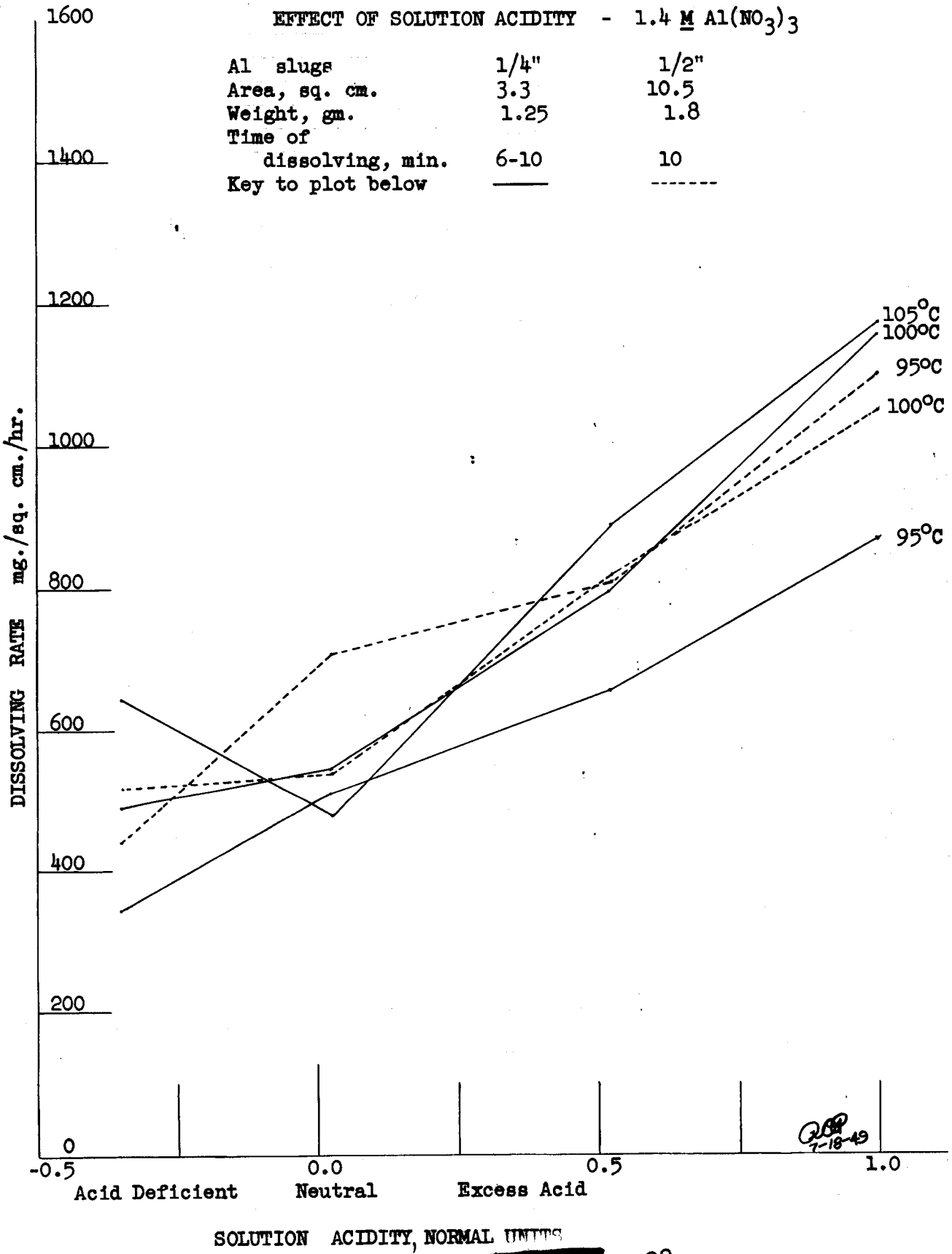
Aluminum Dissolving Rate
(multiple batch tests, Semi-Works)
Effect of Temperature
(conditions given on Figure 1)

[redacted]

Drawing # 7351

Figure 5.3-3

ALUMINUM SLUG DISSOLVING



[redacted]

6.0 Thorium Recovery

An extraction process using tributyl phosphate as the solvent for the recovery and decontamination of thorium from 23 raffinates is being developed. Preliminary laboratory data indicate that a thorium recovery of 99.5% with beta decontamination factors of about 10^3 should be possible.

The extraction of thorium with tributyl phosphate has been shown to be a rapidly reversible reaction with the optimum total nitrate concentration at 2 to 6 molar. Scrub data indicate that an aqueous/organic distribution coefficient of 0.24 with a beta decontamination factor of about 50 is obtained with a four molar nitric acid scrub of the tributyl phosphate-thorium complex. A series of countercurrent batch extraction runs are planned to determine thorium loss and decontamination, with nitric acid concentration and flow rates as the variables.

Five organic solvents, butyl analine, butyl sulfone, butyl benzene, butyl propionate, and butyl oxalate have been scounted for thorium extraction, with none showing promise.

A total of 256.6 mg of 23 from one, four inch Hanford bombarded thorium slug has been extracted and concentrated to 50 ml using diisopropyl ether as the extracting solvent. This separation was made to obtain actual 23 raffinates to be used in studying thorium recovery.

It has been found that tributyl phosphate-hexane may be used to extract protactinium to the extent of about 7 percent per equal volume pass.

7.0 RaLa Process

7.1 Purification of Ba^{140} by Ion Exchange

Two ion exchange processes have been developed in an effort to simplify the present RaLa process for Ba^{140} purification by the elimination of the electrolysis and ether-hydrochloride steps. In the "Alkaline-Citrate" process, the feed is basic. Iron, nickel, and chromium are precipitated as hydrous oxides and separated from the solution. The lead passes through the Dowex-"50" cation exchanger column as the plumbite while the barium and strontium are adsorbed on the resin. Strontium and sodium are selectively eluted, leaving the barium still held strongly on the column. The barium product is recovered by elution with 6 N nitric acid. In the "Acetate-Citrate" process, the feed is 0.5 M in sodium acetate. Part of the lead, along with 60-90% of the iron passes through the exchange bed. Selective elution of the remaining iron, nickel, lead, strontium, and sodium follows. The barium product is recovered in 6 N nitric acid. During the past month, major consideration has been given to refinements of the Alkaline process, especially as to adequate separation of strontium and sodium from the barium product.

In both the above processes, a large amount of sodium is associated with the product. It has been suggested that the weight of sodium in the final product should not exceed the weight of the barium. It was found that a 6 N hydrochloric acid wash of the column, prior to barium elution, resulted in about 25-fold reduction in the amount of sodium present in the barium product so that the final ratio of Na:Ba was approximately 3. The barium loss in this washing step was less than 0.01%.

The use of IRC-50 resin is being investigated as a means of reducing the volume of acid used for elution of barium product thus reducing evaporation volume.

Adequate separation of strontium from barium has been achieved by selective elution of strontium with sodium citrate at pH[7]. The barium loss in this wash is about 0.03%.

A study of the efficiencies of nitric acid and hydrochloric acids as elutriants for barium has been made, and 6 N nitric acid has been selected as the most satisfactory because of the relatively small volumes required.

The possibility of elimination of the metathesis step in the RaLa process by direct dissolution of the barium and lead sulfates in 6 M sodium hydroxide (CO_3= free) before ion exchange treatment has been investigated. Experiments have also been carried out dealing with the separation of barium and lead as the carbonates immediately after metathesis. Success of this method depends upon the relative solubilities of barium and lead carbonates in strong (4 M) potassium carbonate or in a 0.5 M potassium carbonate solution, 6 M in potassium hydroxide.

Attempts to minimize the carrying of barium by the hydrous oxides in the precipitation step of the "Alkaline" process by use of ammonium nitrate, pH[5], as a washing agent have reduced the barium losses to less than 1% (in the presence of "cold" barium and/or lead).

7.2 Barium Precipitation Study

Two "hot" filtration runs have been made using a "G" micrometallic filter for the separation of barium carried by lead sulfate and carbonate with

total losses of about 0.3% for all separations and washes thru the metathesis step. Using the same ratio of tank heels and metathesis solution as used in the 706-D operation, metathesis was only 17% complete with respect to barium. Reducing tank heel and increasing the potassium carbonate concentration resulted in complete metathesis in the next run.

One run has been made in the centrifuge, but at low speed (135 G's) because the high speed motor winding burned up while feeding the lead sulfate slurry in 50% UNH. A lead-barium separation was made in the centrifuge at low speed by forming plumbite ion with 3 M KOH and leaving barium carbonate. Barium losses were 1% to 2% in each lead solution effluent with a total lead separation of about 90%. This run is being repeated at high speed or 2200 G's.

Future runs will be made to determine:

1. The optimum filter media.
2. Plumbite ion and barium carbonate separation in the centrifuge bowl.
3. Forming plumbite from the lead sulfate instead of lead carbonate.
4. Centrifugation of barium sulfate without lead carrier or much less carrier.
5. Lead sulfate precipitation cold without digestion to reduce sulfuric corrosion in the precipitation.
6. If cold metathesis is as effective as hot.

Ion exchange equipment is nearly complete for testing the barium purification procedures.

8.0 Reaction of Uranium Metal with Elemental Fluorine

A study of direct fluorination of uranium metal is being made (1) to determine if the reaction can be controlled, (2) to determine the operation characteristics and limitations of a laboratory fluorinator, and (3) to give laboratory personnel experience in handling fluorine and uranium hexafluoride.

The equipment consisting of a fluorine cylinder, nitrogen cylinder, flowmeter, fluorinator, cold trap, chemical trap, and vacuum pump has been assembled and degreased. Several leaks have been found and are now being repaired. Temperature recording instruments are being prepared for installation.

A series of runs is planned in which various fluorine flow rates will be used. Since the reaction rate is very rapid, the result of increasing the fluorine flow should be an increase in the reaction chamber temperature.