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ORNL 287
CHEMISTRY-SEPARATION PROCESSES FOR PLUTONIUM

LABORATORY RECORDS 1954

TECHNICAL DIVISION

INTRA-DIVISIONAL MEMO-CHEMICAL DEVELOPMENT LABORATORY AND SEMI-WORKS FOR MONTH ENDING JUNE 30, 1949

F.L. STEAHLY PER 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 laboratory development of the Redox Process for recovery and decontamination of plutonium and uranium is complete with the exception of studies of ruthenium and plutonium chemistry.

"Cold" UAP semi-works scale runs using simulated Hanford supernatant solution and total waste have been completed satisfactorily. A series of 12 runs are now in progress using actual Hanford waste supernatant solution with uranium salts added to simulate the total waste. These experiments should be completed within the next report period.

The laboratory development of the TBP Solvent Extraction Process for the recovery of uranium from Hanford waste emphasized studies on plutonium and fission product extraction factors, and evaluated other diluents than hexane for the extracting solvent, tributyl phosphate. The Semi-Works has made preliminary tests on pumping the metal waste sludge from an ORNL storage tank, and plans are in progress for the installation of solvent extraction equipment for the recovery of the ORNL metal waste.

A metal solution study was started to determine the procedure for dissolving the "25" aluminum alloy slugs that are to be used for the final pilot plant development of the "25" Process. The "25" Solvent Extraction Process is being developed for the recovery and decontamination of "25" from the spent MTR fuel assemblies.

The RaLa Process is being reinvestigated to increase the process efficiency. The barium-lead sulfate precipitation and metathesis steps are being tested on one-half plant scale to evaluate the effectiveness of filtration or centrifugation to replace the present decantation. An ion exchange study is also in progress in the laboratory aimed at the elimination of the present electrolysis, evaporation, nitrate precipitation, and HCl-ether precipitation steps used to purify and concentrate the barium.

2.0 Summary

Redox

(1) Increasing the number of scrub stages from 4 to 8 in counter-current batch tests did not significantly improve decontamination.

(2) Crud formation in the pilot plant organic product stream from the second cycle uranium extraction column was found to be due to oxidized iron. The origin of this iron is not known at present.

Metal Recovery - UAP Process

The semi-works runs with simulated Hanford total waste indicated a total uranium loss of 1% with about 10% of the uranium going through the recycle.

Metal Recovery - TBP Process

(1) The recovery of uranium from Hanford sludge by a single cycle batch counter-current run demonstrated a 99.3% uranium yield and a beta decontamination factor of 3×10^5. The beta activity of the final product was approximately 10% of natural uranium background.

(2) Plutonium is decontaminated by a factor of about 5.

(3) Decontamination factors for zirconium and cerium were 3×10^3 and greater than 10^6, respectively.

(4) n-Heptane and n-Octane compared favorably with hexane as a diluent for tributyl phosphate in batch counter-current tests. On the basis of cost and volatility, n-heptane seems to be preferred.

3.0 Redox

3.1 Decontamination Studies in Redox First Cycle

Using the counter-current batch extractor, it was found that increasing the number of scrub stages in column 1A from four to eight, had no effect on decontamination under ANL flowsheet conditions. Using ORNL #1 flowsheet conditions, decontamination was increased by approximately a factor of two and, using ORNL #2 flowsheet conditions, the increase was less than a factor of two (Table 3.1-1).

Four first cycle runs were made using pilot plant Redox feeds as a source of activity. The decontamination factors obtained in the laboratory extractor were in good agreement, in most cases, with results obtained in pilot plant Column 1A, for the same feed (Table 3.1-2).

Table 3.1-1

The Effect on Decontamination of Increasing the Number of Scrub Stages in Column 1A of the Redox Process

Runs made in laboratory counter-current batch extractor using six extraction stages, and scrub stages as indicated below. Beta activity in feeds = ca. 10^7 c/m/ml.

No. of Scrub Stages	Flowsheet Conditions	Decontamination Factors							
		Extraction Section				Overall			
		Gross Beta	Gross Gamma	Zr Beta	Ru Beta	Gross Beta	Gross Gamma	Zr Beta	Ru Beta
	ANL								
4	1AS-1.3M $Al(NO_3)_3$ 1AF-2M $UO_2(NO_3)_2$, 0.3N HNO_3, 0.1M $Na_2Cr_2O_7$ 1AX-hexone, 0.5N HNO_3	-	-	-	-	40	27	-	2.4
8	Flowratio AS/AF/AX = 1/1/4	-	-	-	-	39	30	-	2.3
	ORNL #1								
4	1AS-2M $Al(NO_3)_3$, 0.2N acid deficient, 0.01M $Na_2Cr_2O_7$	170	75	250	53	$6.1x10^3$	-	350	990
4	1AF-2M $UO_2(NO_3)_2$, 0.1M $Na_2Cr_2O_7$, 0.2N acid deficient	-	-	-	-	$3.6x10^3$	-	520	350
8	1AX-neutral hexone	-	-	-	-	$1.1x10^4$	-	390	670
8	Flowratio AS/AF/AX = 1/1/4	130	46	400	67	$8.6x10^3$	-	600	$1.5x10^3$
	ORNL #2								
4	1AS-1.3M $Al(NO_3)_3$, 0.01M $Na_2Cr_2O_7$, 0.2N acid deficient	200	66	520	56	$1.3x10^4$	-	$2.6x10^3$	$1.0x10^3$
4	1AF-1.2M $Al(NO_3)_3$, 0.9M $UO_2(NO_3)_2$, 0.1M $Na_2Cr_2O_7$ 0.2N acid deficient	170	70	690	38	$1.3x10^4$	-	$1.5x10^3$	$1.7x10^3$
8	1AX-neutral hexone	150	90	790	34	$1.5x10^4$	-	-	$1.8x10^3$
8	Flowratio AS/AF/AX = 1/2/3	180	66	470	41	$1.7x10^4$	-	$2.9x10^3$	$1.9x10^3$

Table 3.1-2

Comparison of Decontamination Factors Obtained in Counter-Current Batch Extractor and in Pilot Plant Column 1A, Using Redox Process First Cycle Conditions

Pilot Plant column 1A-25 foot extraction, 14 foot scrub sections
Counter-current batch extractor - 6 extraction and 8 scrub stages.

Laboratory Run Number	Pilot Plant Run Number	Flowsheet used	Decontamination Factors			
			Laboratory		Pilot Plant	
			β	Ru	β	Ru
C-70	R-34	ORNL #2	$3x10^4$	$3.9x10^3$	$1.4x10^4$	$2.1x10^3$
C-79	R-39	ORNL #1	$9x10^3$	760	$5.2x10^3$	370
C-82	R-41	ORNL #1	$5.1x10^3$	630	$5.7x10^3$	460
C-98	R-37	ORNL #1	$1.4x10^4$	$1.4x10^3$	$1.2x10^4$	$1.4x10^3$

3.2 Plutonium Equilibrium Studies

The equilibrium valence state of plutonium is critical in the ORNL Redox (acid deficient) Process because only Plutonium VI is sufficiently extractable to obtain the desired recovery. Therefore, equilibrium studies are being made using spectrophotometric analytical procedures.

The equilibrium of the Plutonium IV and VI states in the extraction feed, 2.0 M UNH - 0.2 M acid deficient without sodium dichromate present, was 93% Plutonium IV and 7% Plutonium VI at 23°C (Table 3.2-1). This experiment was repeated at 85°C and the equilibrium concentrations were 13.7% Plutonium IV and 86.3% Plutonium VI at the end of two hours. However, after four hours at 85°C and then ageing at 23°C for 18 hours, the equilibrium shifted to 88.4% Plutonium IV and 11.6% Plutonium VI. These results indicate the presence of reducing conditions during digestion at elevated temperatures (Table 3.2-2).

The oxidation of Plutonium IV by sodium dichromate was slow at 23°C, approximately 20% Plutonium IV remaining after 24 hours (Table 3.2-3). Previous work had shown that Plutonium IV is quantitatively converted to VI by heating the solution at 85°C for six hours.

It was demonstrated that, in a 0.2 M HNO_3 solution, plutonium polymer could be broken by making the solution 0.005 M NaF. This forms a plutonium fluoride complex which is not oxidized by sodium dichromate. However, by making the solution 0.05 M in boric acid, the plutonium was then completely oxidized by 0.1 M $Na_2Cr_2O_7$ at 85°C for six hours.

Table 3.2-1

Plutonium Valence State Equilibrium in the Simulated ORNL Redox Feed at 23°C

Solution Composition: UNH - 2.0 M
HNO_3 - 0.2 N HNO_3
Pu (total) - 0.000523 M
Temp. - 23°C

Time (Hours)	% Pu IV (A)	% Pu VI (A)
0.5	99.2	0.8
2.25	94.3	5.7
4.16	93.7	6.3
27	93.7	6.3
46	92.5	7.5

(A) These results are based on calculation for Plutonium IV using the 660 millimicron band.

Table 3.2-2

Plutonium Valence State Equilibrium in Simulated ORNL Redox

Feed at 85°C

Solution Composition: UNH - 2.0 M
HNO_3 - 0.2 M
Pu (total) - 0.00050 M

Heating Time (Hours)	Cooling Time to 23°C	% Pu IV (A)	% Pu VI (A)
1	30 mins.	15.6	84.4
2	30 mins.	13.7	86.3
4		88.4 (B)	11.6 (B)
7.3	30 mins.	79.3	20.7
7.3	-	97.0 (B)	3.0 (B)

(A) These values are based on the determination of Plutonium VI using the 837 millimicron band.

(B) These values were obtained when the samples had been allowed to stand about 18 hours at 23°C.

Table 3.2-3

Oxidation of Plutonium IV by $Na_2Cr_2O_7$ in a Simulated ORNL Redox Feed at 23°C

Solution Composition: UNH - 2.0 M
HNO_3 - 0.2 M
Pu (total) 0.000508 M
$Na_2Cr_2O_7$ - 0.1 M

Time (Hours)	% Pu IV (A)	% Pu VI (A)
0.17	89.6	11.4
0.42	85.4	14.6
1.0	81.3	18.7
1.3	76.6	23.4
2.8	66.6	33.4
3.4	61.1	38.9
24.0	20.1	79.9

3.3 Plutonium Loss Studies

Laboratory work has been carried out in conjunction with ORNL Pilot Plant Redox tests in an effort to determine causes for losses encountered at the beginning of full Hanford level runs. Due to the high level activity, small-scale batch work was instituted on an emergency basis to investigate as many variables as possible. Data are thus fragmentary and not intended as exhaustive information. Conclusions that may be drawn are thus tentative and must await further development.

A slow growth of unextractable plutonium has been observed in feeds containing 2 M UNH, 0.1 M $Na_2Cr_2O_7$ and 0.2 M HNO_3 deficiency. Possibly a self-reduction and oxidation equilibrium is indicated as a cause for this effect (Tables 3.3-1 and 3.3-2).

There has been reason to suspect that some deleterious action could occur in the filter-transfer-storage phase. Adipic acid, a decomposition product of methyl cyclohexane, was observed to increase losses (Table 3.3-3).

Effects of other possibly deleterious substances introduced in hexone and scrub solutions were scouted briefly. Organic acids, iron, and sulfate ion were considered possible offenders. None of these materials in reasonable amounts affected plutonium extraction.

Reduction in extraction and scrub sections with long contact times was examined insofar as feasible by batch methods. No effect was observed. High radiation level was also observed to have no effect.

Increasing HNO_3 concentration was sufficient to extract the plutonium unextracted under the basic conditions (Table 3.3-4).

Table 3.3-1

Increased Plutonium Loss Due to Ageing of the Extraction Feed

Feed Composition: 2 M UNH
(from Pilot Plant runs) 0.2 M acid deficient
0.1 M $Na_2Cr_2O_7$
Activity level: 30% full Hanford level
Extraction procedure: One volume of scrub (2.0 M $Al(NO_3)_3$, 0.2 N acid deficient, 0.01 M $Na_2Cr_2O_7$) added to one volume of feed and batch extracted 12 times with equal volume batches of hexone.

Pilot Plant Run Number	Ageing Time Weeks	% Plutonium Loss (a)		
		Original	Final	Diff
48 (b)	1	1.2	1.7	0.5
46	2	0.8	1.38	0.54
39	5	0.23	0.63	0.40
37	6	0.32	1.16	0.84

(a) LaF_3 procedure for analysis

(b) Full Hanford activity level

Table 3.3-2

Effect of Acid Conditions During Ageing on Plutonium Loss

Feed Composition: (from Pilot Plant Run 50R)
2 M UNH
0.2 N acid deficient
0.01 M $Na_2Cr_2O_7$

Activity level: Full Hanford level
Extraction procedure: one volume of scrub (2.0 M $Al(NO_3)_3$, 0.2 N acid deficient, 0.01 M $Na_2Cr_2O_7$) added to one volume of feed and batch extracted 12 times with equal volume batches of hexone.

Two samples of the feed solution were taken; the first after oxidation under 0.2 M acid conditions, and the second after neutralization with NaOH to 0.2 N acid deficient. The acid feed was neutralized after ageing to 0.2 N acid deficient immediately before extraction.

Ageing Time (Days)	Plutonium Loss (a)	
	0.2 N acid	0.2 N acid deficient
0	0.01	0.05
3	-	0.12
5	0.06	0.17
7	0.08	-

(a) TTA procedure used for analysis

Table 3.3-3

Effect of Adipic Acid on Plutonium Loss

Feed Composition: Varying amounts of adipic acid added
Activity level: Full Hanford level
Extraction Procedure: One volume of scrub (2.0 M $Al(NO_3)_3$, 0.2 N acid deficient, 0.01 M $Na_2Cr_2O_7$) added to one volume of feed and batch extracted 12 times with equal volume batches of hexone.

Adipic Acid M	% Plutonium Loss (a)
0.0	0.73
0.01	0.83
0.02	2.8

(a) LaF_3 procedure used for analysis

Table 3.3-4

Effect of Nitric Acid Concentration on Plutonium Loss from Extraction

Raffinate (1AW)

Feed Composition: (1AW from Pilot Plant Run 50R)
1.0 M $Al(NO_3)_3$
0.05 M $Na_2Cr_2O_7$
0.2 M acid deficient
Activity level: Full Hanford level
Extraction procedure: 6 equal volume passes with the indicated amounts of HNO_3 added to the hexone.

Type of Extraction	Hexone Acidity M	Aqueous Acidity M	% Plutonium Loss	
			LaF_3	TTA
Pilot Plant*	0	-0.2	1.2	1.0
Laboratory Batch*	0	-0.2	0.5	0.05
Laboratory Batch	0	-0.2	1.2	0.9
	0.1	0.05	0.9	0.4
	0.2	0.10	0.8	0.3
	0.3	0.15	0.78	0.26
	0.4	0.20	0.7	0.2
	0.5	0.25	0.55	0.06

* These extractions made with 1AF
** Aquesous acidity at equilibrium estimated from known distribution coefficients

3.4 Pilot Plant Crud Problem

The Pilot Plant has experienced the difficulty of crud formation in the 1/2" I.D. line between the D and E columns (second cycle) while operating the Redox tests. This line carries the DX stream to the E column. It is observed that this crud is either formed or transported in the organic phase, is insoluble in the hexone, and adheres to the stainless steel tubing. Plugging of the line has occurred at rather frequent intervals requiring a water flushing procedure to clear the system.

This crud is an amorphous, brown precipitate which has an approximate composition of $Fe(NO_3)_3 \cdot Al(NO_3)_3$ and is soluble in H_2O. Filtered samples were found to contain entrapped UNH which could be washed out with repeated hexone washes.

4.0 Metal Recovery

4.1 UAP Process

The Uranyl Ammonium Phosphate (UAP) Process proposed by the K-25 research and development groups, for recovery and decontamination of uranium from Hanford metal waste, is essentially a two cycle precipitation-filtration process using nitric acid to dissolve solids and ammonium nitrate to precipitate uranyl ammonium phosphate. A recycle step recovers 10% to 15% of the uranium remaining in the filtrates by precipitation with sodium hydroxide. The Semi-Works development at ORNL will be concerned with uranium recovery, decontamination, and process operability. Approximately 13 kg of uranium are processed in each semi-works run. Runs programmed are:

7 - Synthetic Hanford 103 T Tank supernate runs. (no fission product activity)

11 - Synthetic Hanford 103 T Tank total waste runs. (no fission product activity)

10 - Hanford supernate runs spiked with U, Na, PO_4, SO_4, and NO_3 ions to simulate the Hanford total waste, 3 (103 T - aged 3 years), 7 (103 U - aged 2 years).

2 - Hanford supernate runs, 1 (103 T), 1 (103 U).

The cold runs have now been completed and the final equipment alterations before starting the hot runs are in progress.

4.11 Uranium Data

The overall process losses have been continually reduced, and were less than one percent in the latest runs (Table 4.1-1). Higher losses (ca. 3%) and erratic material balances in early runs are attributed to mechanical difficulties plus a few process uncertainties which have been overcome. In all cases, the uranium data are based on the weight of uranium in the feed.

The recycle step received (for recovery and use with subsequent feed solutions) the filtrate and the first wash solution during Runs 1 - 12; after Run 12, the first two washes were recycled with the filtrate. Approximately 4% to 6% of the total uranium was sent to recycle from each precipitation step in most runs; higher values were sometimes caused by increased solubility of the uranyl ammonium phosphate because too much nitric acid had been added.

The discarded first and second cycle filtration wash solutions and the discarded solutions from the centrifuge in the recycle step are the sources of uranium loss.

The losses in the discarded wash solutions (last three or four washes) have been reduced from approximately 0.3% per cycle in the earlier runs to about 0.05 - 0.2% per cycle in the last three runs. This has been due to change in the wash procedure, decreasing the filter vacuum, and sending the first two washes instead of only the first to recycle.

The centrifugation losses in the recycle step have been continually reduced from approximately 5% to less than 0.5%, which is satisfactory. This has been due to better control of the feed rate to the centrifuge.

The material balances for the first cycle were generally high because of the undetermined hold up of material in the second cycle precipitation vessel from the previous run entering into the calculations.

The material balances over the recycle step were in error because complete dissolution of the centrifuge cake was not obtained. This situation was corrected in Runs 12 - 14 by heating the nitric acid used for dissolution. An excellent material balance (101%) was demonstrated in Run 14.

4.12 Process Operability

4.121 Metal Waste Dissolution

The first cycle feed solution was acidified with 60% nitric as follows:

Approximately 40 liters of acid are required for the supernate and 48 for total waste runs.

(1) First fifth of the acid was added in three minutes.

(2) Next three-fifths in twenty minutes in order to control the rate of gas evolution.

(3) Solution was heated to 85°C and acid added in liter portions, or smaller, until complete solution was reached, checking for completeness of solution after each addition by withdrawing a sample to a sight glass in the sampler system. Complete solution could be reached with precision by this means, so predetermination of acid requirement on laboratory scale was found to be unnecessary.

4.122 First and Second Cycle Precipitation

Precipitation methods produced crystals that were readily filterable. The same methods and amounts of precipitating agent were used for both first and second cycles.

Supernatant feed runs were precipitated at 85°C with slow agitation by adding approximately 3 moles of ammonium nitrate per mole of uranium. The ammonium nitrate was added as a solution that was 50% ammonium nitrate by weight and 0.7 N with respect to nitric acid. The precipitating agent was added over a 15 minute period as soon as possible after the acidification step, and the resulting solution cooled to 25°C at the rate of 1°C per minute, then digested for one hour.

For total waste feed runs, approximately 2 moles of ammonium nitrate per mole of uranium, in a 59% ammonium nitrate solution $(0.7\ N\ HNO_3)_3$, were added over a 2 minutes time. Otherwise, the precipitation methods were the same as for supernatant feed runs.

4.123 First and Second Cycle Filtration

The filtration of the uranyl ammonium phosphate crystals appeared to produce satisfactory filtrates in a reasonable time cycle (10 - 33 minutes) with a filtration vacuum of approximately 8 inches of mercury, and 2,515 sq. cm. filtration area. Cake depth was approximately 4 inches. The filter medium was a 60x700 mesh Dutch twill stainless steel cloth. Filtration constants appear to be generally well below the minimum value quoted for Hanford operation.

4.124 First and Second Cycle Filter Cake Wash

The filter cake was washed five times with one-tenth volume, based on original feed volume, of 0.01 M NH_4NO_3 solution. All washes were added through the precipitator and jetted to the filter to facilitate the complete transfer of precipitate to the filter. The cake was slurried on the filter with the first wash solution. In the subsequent four washes, the cake was washed by displacement. The vacuum for all washes was 2 inches of mercury, and 2 to 6 minutes per wash was required to pull the wash through the cake.

4.125 First Cycle Filter Cake Dissolution

Redissolving the uranyl ammonium phosphate product from the first cycle filter for subsequent reprecipitation in the second cycle was satisfactorily demonstrated using the following method: (assuming a 95% first cycle yield.)

(1) Calculate the amounts of reagents required from the following

relations:

Nitric acid (60%): 2.15 ml per gram of uranium in the starting solution.

Phosphoric acid (85%): 5 ml per liter of starting solution.

Water: 17 ml per gram of uranium in the starting solution.

(2) Add the calculated amounts of acids and one third of the water to the filter vessels through the precipitation vessel, heat to 85°C, agitate 20 minutes, and drain to 2nd cycle precipitation vessel.

(3) Add the remaining two thirds portion of water to the filter vessel through the precipitation vessel, heat to 85°C with agitation, and drain to the 2nd cycle precipitation vessel.

4.126 Second Cycle Filter Cake Removal

Back-washing and slurrying with approximately 100 liters of water appeared to be satisfactory. A displacement method of weighing the final product is being investigated. It involves determining the increase in weight of a given volume caused by the presence of the product, determining the specific gravity of the product with a pycnometer, and calculating the weight of product from the relation: Wt. of Product = Wt. increase x Sp. Gr. ÷ (Sp. G. - 1).

4.127 Recycle Precipitation

The uranium in the filtrates and wash solutions was precipitated as uranyl ammonium phosphate by raising the pH to 2.0 with 35%

sodium hydroxide solution. The pH recirculating system connected to the tank was probably accurate to about 0.5 of a unit. These values were checked on a portable unit, and adjusted to the high side so that the range was probably from 2.0 to 2.5 pH units for most runs.

4.128 Recycle Decantation

The precipitated solution was allowed to settle and the uranium stripped supernatant solution decanted off, so the remaining slurry could be centrifuged.

This method would probably be satisfactory if the longer settling time could be tolerated, and if the centrifuge could be fed at a considerably lower rate than is now possible (2 liters/minute). The losses in the decantation step using a three hour settling period were slightly higher than expected (1 to 2%). Decantation was discontinued on Run 7 in favor of complete centrifugation of all the recycle solution.

4.129 Recycle Centrifugation

The uranium slurry, from the filtrate and wash solutions, is now being centrifuged satisfactorily by feeding the Byrd solid bowl type (12 inch diameter) centrifuge at a rate of approximately 2 liters per minute while running at a speed of 3300 RPM. Later runs using these conditions have shown that the losses are reduced to less than one percent of the total uranium processed when the above conditions are employed. The cake was removed satisfactorily using hot 60% nitric acid solution.

Table 4.1-1

Uranium Data (Uranyl Ammonium Phosphate Process - ORNL Semi-Works Runs)

Feed: (Synthetic total Hanford Waste)

0.26 M U 0.33 M PO_4^{-3} 0.109 M CO_3^{-2}
3.91 M Na^+ 0.28 M SO_4^{-2} 0.71 M NO_3^{-1}

Run No.	Grams U in Starting Feed Solution	First Cycle			Second Cycle		Recycle		Overall
		% Loss to Recycle	% Loss in Washes	Material Bal. %	% Loss to Recycle	% Loss in Washes	% Loss in Effluent	Material Balance	% Loss
8	11,400	5.41	0.114	102	---	---	---	---	---
9	13,900	5.78	0.375	91	9.6	0.158	1.56	75.5	2.09
10	12,900	5.43	0.146	109.3	12.9	0.056	2.95	64.5	3.15
11	13,560	8.25	0.201	126.0	8.5	0.27	0.981	66.6	1.44
12	15,140	6.26	0.13	121.0	5.33	0.122	1.68	141	1.93
13	8,872	7.94	0.10	---	3.30	0.202	0.436	123	0.74
14	12,520	4.02	0.12	92.0	4.50	0.054	0.36	101	0.53

4.2 TBP Process

4.21 Plutonium and Fission Product Studies

A study of the variables affecting the solvent extraction of fission products by tributyl phosphate has been initiated.

The extraction coefficient for Ce^{III} (0.001) was the same at all concentrations of acid and $NaNO_3$.

In the absence of uranium and sodium nitrate, the distribution coefficient, organic to aqueous, for zirconium varied from 0.004 to 0.2 when the nitric acid concentration was increased from 0.2 to 3 molar. In a 3 M HNO_3 and 4 M $NaNO_3$ solution, the zirconium distribution coefficient was 0.7. However, with the organic phase saturated with uranium, batch counter-current tests indicated a zirconium distribution coefficient of 0.002.

Plutonium IV extraction was affected in the same manner as zirconium by salt concentration with values increasing from 2 to 17 at $NaNO_3$ concentrations from 0 to 4 N and 3 N HNO_3; however, with varying HNO_3 concentration, the Plutonium IV extraction coefficient increased from 0.05 at 0.2 N HNO_3 to 5.4 at 6 N HNO_3 and decreased at higher acidity to a value of 1.4 at 16 N HNO_3.

Reducing agents have been shown to have little effect on plutonium extraction in the presence of small amounts of sulfate. Oxidizing agents decreased the extraction by less than a factor of 4, possibly due to their reaction with impurities in the solvent rather than the oxidation state of the plutonium.

Saturation of the solvent with uranium decreased plutonium distribution coefficients from approximately 2 at 3 N HNO_3, 1 N $NaNO_3$, and 20% saturation of the solvent with uranium to 0.25 and 0.06 for reducing or neutral and oxidizing solutions, respectively, at 70% saturation.

An investigation of the need for solvent treatment is now being made. Preliminary data have shown no need for solvent treatment.

4.22 Counter-Current Batch Extraction Experiments

The laboratory demonstration of the tributyl phosphate extraction of uranium from metal waste has been extended to include Hanford waste sludge and a simulated Hanford current waste, spiked with Hanford 90 day activity. The uranium from the Hanford sludge was recovered with a 0.7% uranium loss and decontaminated to 7% the beta activity of natural uranium. Uranium from the simulated current waste was recovered with a 0.4% uranium loss and decontaminated to 3% the beta activity of natural uranium. The results of these runs are compared with the results of similar extractions of uranium from Hanford supernatant and ORNL sludge in Table 4.2-1.

Specific fission product analyses were made on the product solutions from solvent extraction ob both Hanford sludge and the solution spiked with 90 day activity. In the case of Hanford sludge, ruthenium was the major activity found with the product uranium. Zirconium was the major activity found in the product solution from the 90 day waste. In both cases, the ruthenium decontamination factor was of the order of 2×10^4, and on the simulated current waste, the zirconium decontamination factor was 3×10^3.

Two longer chain hydrocarbons, n-heptane and n-octane were tested in counter-current batch extraction experiments and were found to work equally as well as hexane. The lower volatility of heptane and octane reduces the hazard associated with hexane as a diluent for tributyl phosphate. Further investigations are being made.

Table 4.2-1

Tributyl Phosphate Extraction of Uranium from Metal Waste -

Counter-Current Batch Runs

Feed: 3.0 to 4.5 N HNO_3 solution of waste as indicated
Solvent: 85% hexane - 15% tributyl phosphate
Scrub: 3.0 N HNO_3
Strip: Water
Equipment: Counter-current batch extractor; 5 stages of extraction, 4 stages of scrub, 5 stages of strip
Flow ratio: Solvent:Feed:Scrub:Strip = 10:3:2:10

Source of Uranium Processed	Uranium Loss %	Beta Activity of Product β c/m/mg U	γ Activity of Product Mv/mg U	Beta Decontamination Factor
ORNL Sludge	0.1	2	0.001	1.5×10^4
HW Supernatant	0.1	2	0.001	3×10^4
HW Sludge	0.7	5	0.002	3×10^5
Simulated HW current waste (90 day activity)	0.4	2	0.001	2×10^4
Activity of natural U		70	0.005	

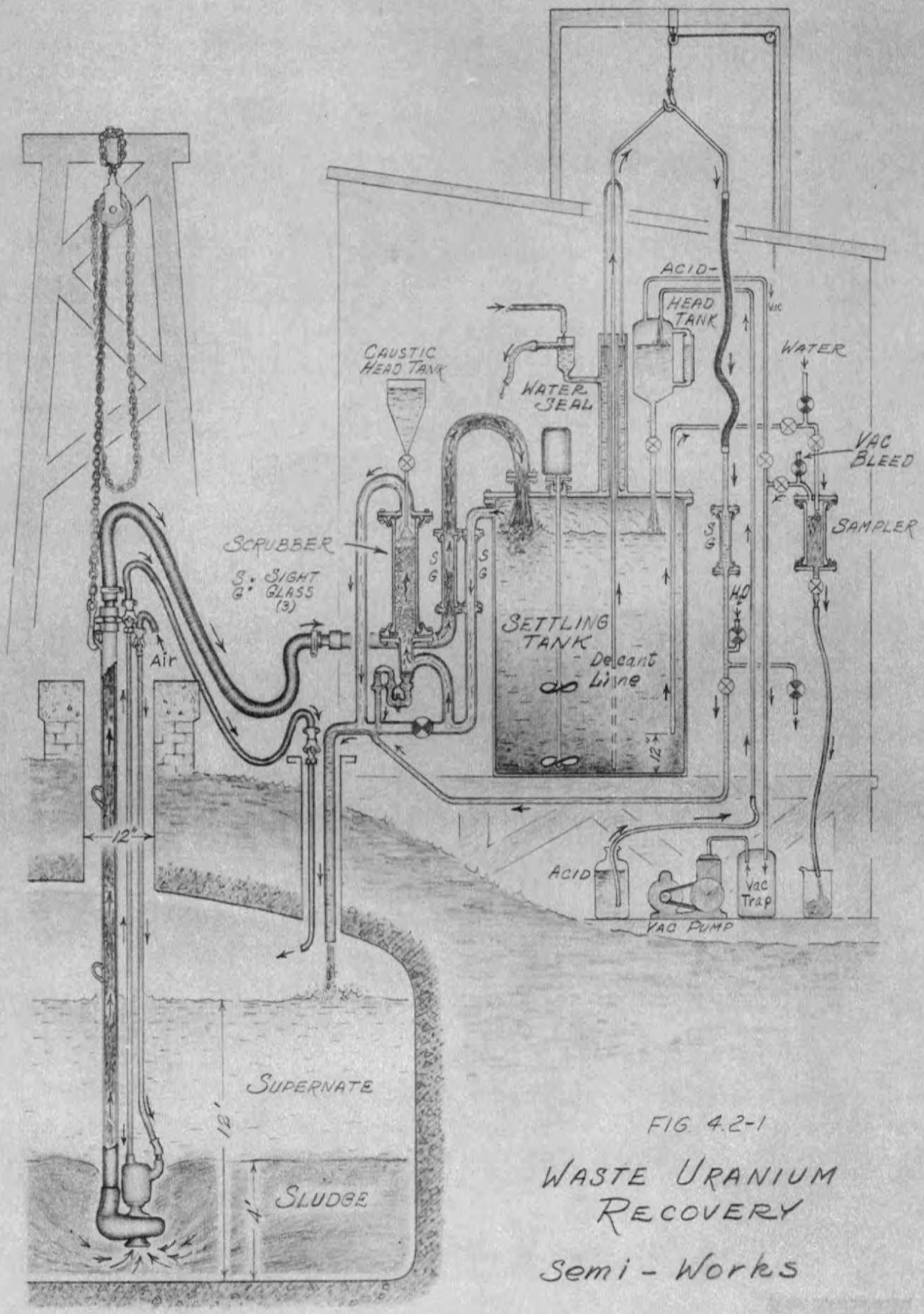


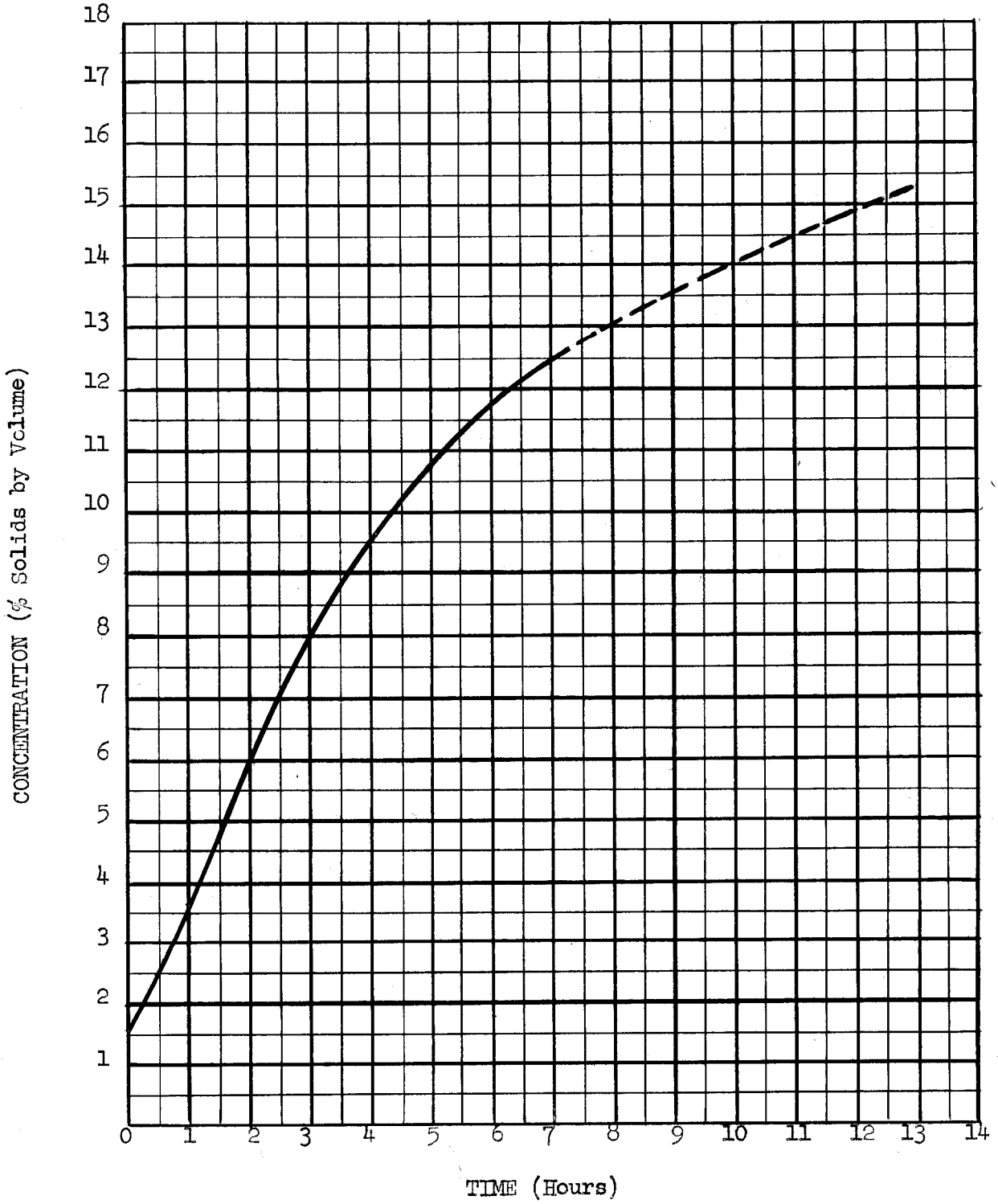
FIG. 4.2-1

WASTE URANIUM RECOVERY

Semi - Works

J. W. Landry
6-10-49

Figure 4.2-2



TYPICAL SEDIMENTATION TEST CURVE

Concentration (% Solids by Volume) vs. Time (Hours)
Conditions: 100 cc of slurry (1.6% solids by volume) Tank W-10, ORNL Tank Farm. Height of column of slurry: 20 cm.

6-10-49
A. C. J.

4.23 Feed Preparation

The Semi-Works development of uranium feed preparation for the TBP solvent extraction process includes selection of a means of pumping uranium sludge, concentrating and dissolving the sludge, and clarifying the acid solution of sludge. A centrifugal sump pump driven by an air motor was assembled for lowering in a 12" nozzle at Tank W-10 in the ORNL Tank Farm. A 1000 liter vertical tank was installed nearby for settling, decanting, and dissolving slurry pumped from Tank W-10 in the ORNL Tank Farm (see Fig. 4.2-1). Two pumping operations and one settling, decanting, and dissolving operation have been carried out in this installation.

Preliminary scouting of filtration and centrifugation has been made. Evaporation of dissolved slurry will be scouted also.

Results:

(1) The pumping operations demonstrate that soft, slimy sludges up to 35% or more solids content by volume can be pumped to a height of at least 30 feet. Slurry was pumped at the rate of 2000 liters/hour.

(2) Gravity sedimentation is very slow, scouting data indicating a range from 5-8 cm/hr during the first hour or so to about 0.4 cm/hr twenty-four hours after settling started. This settling rate data corresponds to concentration rates based on percent solids by volume of 2 to 3% increase per hour initially down to 0.1% or less per hour after the first twenty-four hours (see Figure 4.2-2).

(3) The specific gravity of (a) compacted solids is 1.68, and (b) supernatant is 1.13. The particle size as determined by an electron microscope is less than 0.5 micron. Assuming the viscosity of supernatant is 10 cps at room temperature, and applying Stokes Law, calculated settling rates agree reasonably well with observed values.

(4) Sludge neutralization and dissolving is limited by the evolution of carbon dioxide gas. With excellent agitation and mixing, a reasonable rate of dissolution is about 35 liters of [redacted] sludge/sq.ft./hr.

(5) Filtration of the acid solution of sludge using a 700x60 mesh screen appeared to be satisfactory. 200 liters of clear solution was obtained by vacuum filtration of the acid solution. The final solution was about 0.3 M in uranium and 1.5 N in nitric acid.

(6) Centrifugation of a 16% solids slurry in a Sharples super centrifuge at about 1800 rpm and 600 ml/min feed rate provided a colorless filtrate. A centrifugal force of 6000 g is developed in the Sharples unit at this speed.

Conclusions:

(1) Centrifugal pumping is adequate for handling slimy sludge of the type found in Tank W-10 of the ORNL Tank Farm. An electrically driven pumping unit is, of course, preferable to an air driven unit.

(2) Gravity sedimentation is very slow. Hence thickening, which is continuous gravity sedimentation, would involve considerable (two to three weeks) material hold-up.

4.24 Waste Disposal

The waste disposal process for the ORNL waste uranium recovery process has been developed. The acid raffinate from the column is evaporated and subsequently neutralized with the basic supernate. This mixture is then further volume reduced. During the evaporation of the acid solution, 25% of the nitric acid is recovered for reuse. Beta and gamma decontamination factors of 10^5 and gamma to background, respectively, are obtained for the distillate from the volume reduction of the neutralized solution. The resulting slurry volume (pH 9) is 22.5% of the original combined acid raffinate and basic supernatant.

5.0 "25" Alloy Slug Solution

The controlled dissolution of uranium-aluminum alloy slugs was demonstrated on a 50 and 500 gram scale in preparation for the final stage of the pilot plant development of the "25" Process using Hanford irradiated Uranium 235-aluminum alloy slugs.

Several qualitative observations have been made in the course of this study:

(1) Dissolving rate is proportional to surface area.

(2) Increasing catalyst concentration causes somewhat more than a proportional increase in the reaction rate.

(3) As solution becomes more concentrated in $Al(NO_3)_3$, the dissolving rate decreases and appears to approach zero as the solution approaches saturation with respect to $Al(NO_3)_3$.

(4) Acid deficient solutions dissolve the slugs much more rapidly than solutions containing excess acid. An unfortunate result of this is that the dissolving is non-self-regulating: Acid deficient solutions tend to become more acid deficient, and acidic solutions become more acidic with a fixed temperature - acid addition schedule (see Figure 5.0-1).

Optimum conditions to date are:

(1) 2% catalyst added to initial water heel

(2) 4 moles 70% HNO_3 per mole Al added evenly over 6 hour period.

(3) Temperature gradually raised from 80°C at start to 100°C during first 3 hours, and held at 100°C for 5 hours.

(4) Reaction is smooth and easily controlled in conventional water-jacketed steel dissolvers. Spasmodic reaction was encountered only at 0.1% catalyst.

Major problems to be solved are:

(1) What is composition of crud formed when slug is dissolved on the basic side, and how should it be disposed of?

(2) How reliable is the recommended procedure? (A series of check runs will be made.)

(3) How do dissolving on the acid deficient side and high mercuric nitrate concentration affect the chemistry of the 25 process?

Table 5.0-1

Aluminum Slug Dissolvings Semi-Works (May, 1949)

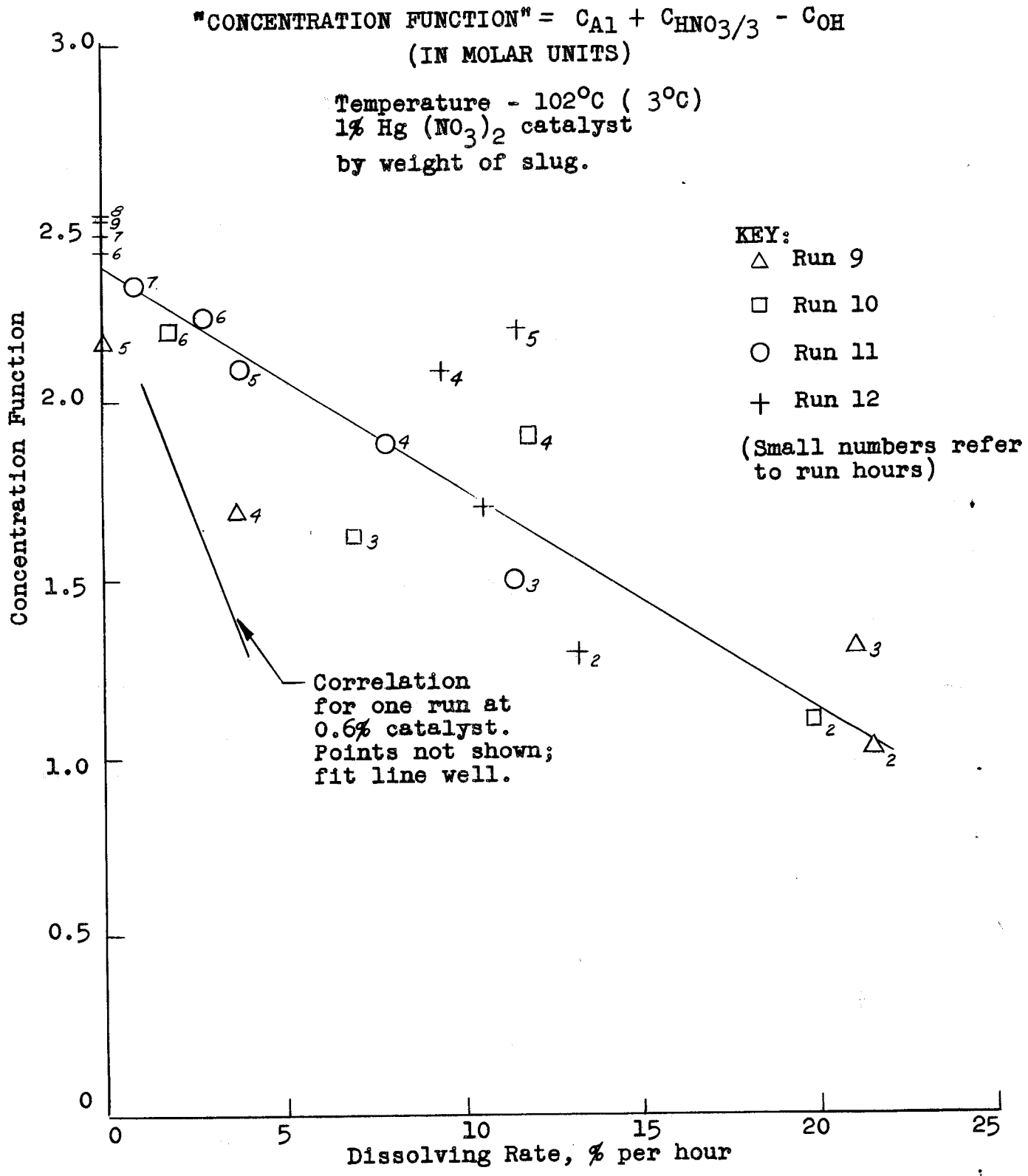
70% HNO_3 added evenly during run to dissolver containing 1.36 in. diameter cylindrical aluminum slugs in water heel containing more uric nitrate catalyst. Glass dissolver runs used 75 g Al (slug section 1" long); metal dissolver runs used 600 g Al (8" slug). Temperature erature controlled by water jacket.

Run No.	% Catalyst $Hg(NO_3)_2$ by Wt. Slug	Dissolver	DISSOLVING TEMPERATURE °C			Run Time Hr.	FINAL CONDITIONS		
			1st Quarter of Run	2nd Quarter of Run	Latter Half		Al M	HNO_3 M	% Slug Dissolved
1	0.1	Glass	70	70	77	8	0.34	5.4	16.7
2	0.4	Glass	50	50	80	9	1.32	1.4	49.6
3	0.4	Glass	78	102	104	10	1.0	3.85	54.8
4	0.6	Glass	76	96	104	9	1.38	2.87	71.0
5	0.6	Glass	74	91	90	12	1.17	3.2	71.2
6	0.6	Metal	73	91	100	9	0.93	3.1	49.4
7	0.6	Metal	86	98	102	6	1.20	0.91	50.0
8	0.6	Metal	91	102	102	11	1.17	3.9	27.6
9	1.0	Metal	77	100	100	6	1.66	2.0	88.6
10	1.0	Metal*	87	101	101	6	1.83	0.29	100
11	1.0	Metal	87	102	103	8	1.50	2.3	75.0
12	1.0	Metal*	87	103	102	10	1.26	3.65	71.2
13	1.0	Glass	Approx. 100° to 110°			6	2.0	-.5	100
14	2.0	Metal	83	102	105	6	2.0	0.16	100
15	2.0	Metal	93	102	100	7	1.86	1.15	96.3

* 96% Al - 4% U slugs

FIGURE 5.0-1

ALUMINUM SLUG DISSOLVING-SEMI-WORKS
EFFECT OF SOLUTION CONCENTRATION ON DISSOLVING RATE



6.0 Thorium Recovery

The investigation of thorium recovery and decontamination from 23 raffinates is being continued. A beta distribution coefficient (organic/aqueous) of 3.5×10^{-3} with a thorium distribution coefficient of 0.1 (equal volume pass) has been obtained using 15% tributyl phosphate - 85% hexane as the extractant. Stripping may be accomplished with water yielding an aqueous/organic distribution coefficient of 9. The reaction compound of thorium and tributyl phosphate has been shown to be three mols of tributyl phosphate per mole of thorium.

7.0 RaLa Process

7.1 Purification of Ba^{140} by Ion Exchange

A tentative flowsheet for the purification of $Barium^{140}$ by an ion exchange process subsequent to the present metathesis step was presented in the quarterly report ending May 10, 1949. An attempt has been made to develop an upflow resin column for use in this process so that if gas is formed as a result of water decomposition from radiation, the bubbles can escape and thus not block the column. An investigation of bed expansion as a function of resin mesh size and upflow rate was made. Resin sizes smaller than 200-240 mesh were found to be impractical. A resin bed was prepared for further study containing known percentages of resin mesh size varying from 40 to 240 mesh where the bed expansion was 25% for a flow rate of 0.56 cc/cm^2. The theory of such a column is that in upflow operations the large particles would remain at the bottom and each particle would assume a position relative to its size. Thus, the

bed would not "churn" and a chromatographic separation would be made possible. Duplicate runs made on upflow and downflow columns to separate barium and strontium under flowsheet conditions (citrate elution) showed the product barium obtained in the upflow column contained 14.4% of the strontium while the product barium from downflow operation contained only 0.13% of the strontium. Further work on upflow columns will be deferred until a definite process has been developed by downflow methods.

The formation of a barium nitrate complex as reported in the literature was confirmed as it was found that 6 N HNO_3 would remove barium from a resin column 3 times as fast as 6 N HCl.

Dowex 50 resin is stable in 0.5 M NaOH-0.1 M H_2O_2 solution. Traces of lead in a solution of 5 mg/ml Pb in 0.5 NaOH are oxidized to lead dioxide when the hydrogen peroxide concentration exceeds 0.001 M. Traces of H_2O_2 will be present under process conditions as a result of decomposition of H_2O by radiation.

It was found that if the maximum amounts of Fe, Ni, and Cr, expected to be present in the RaLa process, are precipitated as the hydroxide they will carry 2 to 5% of the barium. When Fe is present alone, 85 to 99% of the barium is carried, while if 5 mg/ml of Pb is present, only 2% is carried. Washing the $Fe(OH)_3$ with 0.5 M NH_4NO_3, pH 5.0 removes (recovers) the greater portion of the barium from the precipitate. This system will be investigated further.

Experiments using barium tracer have shown that the solubility of freshly precipitated $BaSO_4$ in 6-9 M NaOH is at least 42 mg/100 ml of solution. The barium remains in solution when the solution is diluted 10 times.

As $PbSO_4$ is also soluble in NaOH, the possibility is suggested that the $PbSO_4$-$BaSO_4$ precipitate obtained in the RaLa process could be dissolved in strong NaOH, diluted and passes onto an ion exchange column thus eliminating the metathesis, electrolyses, and ether hydrochloride steps.

7.2 Barium Precipitation Study

Precipitation equipment has been set up to carry out semi-works development on the barium separation from metal solution by coprecipitation with lead as the sulfate on half the full plant scale. The object of this investigation is to determine the increase in process efficiency using either filtration or centrifugation instead of the settling procedure that is now used in the plant.

The filtration tests with 700x60 mesh stainless steel cloth were not satisfactory. Using Type G Micrometallic sintered stainless steel, the results were only partially successful but further work with this filter is planned.

The lead-barium sulfate precipitate was satisfactorily centrifuged in a 12 inch solid bowl at 900 rpm (160 G) with feed rate of two to four liters per minute.

Hot flowsheet runs will be made during June with the filter and the centrifuge for separating $PbSO_4$ and $PbCO_3$ precipitates. Other experiments planned are:

(1) metathesis ($PbSO_4 \rightarrow PbCO_3$) in the centrifuge bowl without dilution.

(2) separation of Pb and Ba in the centrifuge bowl by solubilizing the Pb with caustic.

(3) Centrifugation of $BaSO_4$ precipitate without Pb carrier.

Ion exchange equipment for developing the final purification of barium will be set up.

8.0 Design Criteria of the Chemical Development Semi-Works for the New Research Facilities

The design criteria of the Chemical Development Semi-Works for the new research facilities, summarized in the following section, have been transmitted through the Building Steering Committee to the Austin Company.

The proposed Semi-Works structure is 135 ft. by 65 ft. with three floors at 12 feet, 24 feet, and 36 feet. Interior walls will be of masonry and removable steel partitions and cell walls will be poured concrete two feet thick. The volatile reagent room will contain an explosion relief hatch. Floors will be finished, reinforced concrete to carry a live load of 250 lbs./sq. foot, with a slope to drain of 38 inches/foot. Class III areas to be separated from Class IV areas by covered (steel grating) troughs sloping from east to west. A freight elevator of 2000 pounds capacity and a "hot" dumb waiter capable of carrying loads up to 200 pounds will be provided. Stairways will be at the east and west ends of the building.

There will be four types of drains: (1) sanitary, (2) process, to handle cooling water and waste from laboratory bench troughs; floor drains (excepting those in the cells) and basins for hand washing, (3) "hot" chemical waste - for usual laboratory radiochemical wastes such as from "hot" sinks, basins for dish washing, and special "hot" drains, and

(4) metal segregation - as name implies, wastes in (3) and (4) will run to special control tanks, thence to a precipitator, treatment plant, or settling basin.

Services:

Building will be supplied with the following services throughout:

(a) Steam - at 15 psi and 125 psi gauge (full supply line pressure).

(b) Air - at 100 psi - for control instrumentation.

(c) Water

1. Potable - (filtered) to drinking fountains, laboratory sinks, wash basins, showers, and toilets.

2. Process at line pressure for heat exchangers, decontamination, and cooling jackets.

(d) Vacuum estimated requirements - 100 CFM at 20 inch mercury vacuum, with an additional 100 CFM standby unit.

(e) Electrical

1. A. C. Outlets

Electricity supplied at 110 V and 440 V 3 phase grounded circuits through a single master switch, with an additional master switch for each floor. Buried 1 inch conduit will encircle the operating area and all service rooms with outlets spaced 10 feet apart on walls 5 feet from floor level.

2. D. C. Outlets

D. C. Outlets on each floor level for standard arc welding equipment.

3. Lights

Lights and fixtures inside the cells and the volatile reagent room will be NEMA-7, explosion proof and outside the cells NEMA-4, vapor proof. Illumination in the operating area (control board - see Sketch 1), staff shop, "hot" and cold laboratories, decontamination area and offices will be 50 foot candles. All other areas 35 foot candles. Lights will be fluorescent type flush with the ceiling excepting for cells. Lighting for each cell to be controlled by individual switches.

(f) Gas

Gas header will be brought to building and capped off.

(g) Emergency Services

Emergency electrical services to be provided for cell lights, Health Physics monitoring equipment, and the exhaust system and lights of the volatile reagent room.

The foregoing services will be available at each floor level, running horizontally near the ceiling and vertically on permanent cell walls. Both vertical and horizontal service lines will be covered by sheet metal dust guards wherever practical.

Ventilation

(a) Building

Entire building will be ventilated with controlled air. The Austin Company is to study overall ventilation picture and

recommend workable economical solution.

(b) Cells

Cells to be ventilated by individual dampered ducts on manifold to common blower and exhaust line. Ventilation will be 3000 CFM/cell, or total of 18,000 CFM.

(c) "Hot" Off-Gas System

Each cell to be provided with a 3 inch, 347 stainless steel vent line through which process gas is to be exhausted. Vent line to leave building via drain or service tunnel (for shielding), thence to stack.

(d) Volatile Reagent Room

This area to be ventilated with supplementary system using air from the outside, based on use of extremely toxic chemicals and inflammable solvents.

Cell Bank

Cell bank to be 54' x 12' in plan, and 21' high. Two center cells to be 8' x 8' inside dimensions with two pits 8' x 4' x 10' deep in north half of cells. Two end cells to be 14' x 8' inside dimensions with beam for support of 2 ft. thickness of stacked solid concrete block for segregation wall. Cell walls will be poured concrete 2 ft. thick. Entry from first and second floors to be made through 6' x 6' openings placed in south cell face. Removable cell tops to be provided of cast concrete 1 foot thick. Cell tops to be in two sections, and will be handled by a 5 ton crane. All cell floors to drain to "hot" chemical waste drain.

Service lines and valve extension handles to enter cell via 4" and 6"

diameter pipe sleeve holes provided in the operating cell faces sloped to the interior of the cells 0.25 inches/foot.

General

The foregoing criteria allow for considerable leeway in the final design of a new Semi-Works; however, the size of the building and cells and the location of attendent facilities thereof have been fixed in definite usuable proportions relative to the cell bank. Changes in these areas would have to be based on serious economic considerations or untenable construction features.