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ORNL 323 PART 11

CHEMISTRY-SEPARATION PROCESSES FOR URANIUM

LABORATORY RECORDS 1954

TECHNICAL DIVISION

M.D. PETERSON, DIRECTOR

PART 11

TO

REPORT FOR QUARTER ENDING FEBRUARY 28, 1949

EDITED BY

E.C. MILLER

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Part II

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PART II
TO
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edited by

E. C. Miller

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Table of Contents

		Page
I.	Summary	9
II.	Redox Process Development	11
	A. Pilot Plant	11
	1. First Cycle Feed Preparation	11
	a. Source of Irradiated Uranium	11
	b. Coating Removal	13
	c. Metal Solution	13
	d. Acid Adjustment	13
	e. Time of Ageing	13
	f. Feed Filtration	15
	2. First Cycle Column Operation	15
	3. Second Cycle Feed Preparation	20
	4. Second Cycle Column Operation	20
	5. Analytical Developments	23
	B. Laboratory and Semi-Works	26
	1. Comparison of Redox First Cycle Flowsheets	26
	a. Laboratory Batch Runs	26
	b. Laboratory Column Runs	26
	c. Semi-Works Column Runs	29
	2. Comparison of Redox Second Uranium Cycle Processes	33
	a. Laboratory Batch Runs	33
	b. Semi-Works Column Runs	34

[redacted]

[redacted]

[redacted]

[redacted]

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Table of Contents (continued)

		Page
	3. Plutonium Studies	38
	a. Plutonium Valence State Distribution Coefficients	38
	b. The Absorption Spectra of the Plutonium Valence States Under Acid Deficient Redox Conditions	39
	c. The Behavior of Plutonium VI During Extraction with Hexone - Laboratory	39
	d. The Oxidation of Plutonium V by Sodium Dichromate	40
	4. Ruthenium Studies - Laboratory	41
III.	UAP Process Investigation for Hanford Metal Waste Recovery	43
	A. Design of UAP Semi-Works	43
	1. Extent of Proposed Investigation	43
	2. Equipment Flowsheet for UAP Semi-Works	44
	3. Equipment Location and Service Piping	46
	4. Job Progress	46
	B. Hanford Metal Recovery -UAP Process - Laboratory	46
IV.	Radiochemical Liquid Waste Disposal	52
	A. Liquid Waste Survey	52
	B. Evaporators for Active Liquid Wastes	52
	1. Results of Pilot Model Evaporator Tests	52
	a. Specifications of Pilot Model Evaporator	55
	b. Heat Transfer Coefficients	55
	c. Decontamination	55
	2. Design of Plant Scale Evaporator	57
	a. Design Information	59
	b. Flowsheet	60
	c. Equipment	60
	d. Instrumentation	63
	e. Building	64

Table of Contents (continued)

		Page
	C. Alterations to the Waste Disposal System	64
	D. Aluminum Nitrate Decontamination - Laboratory	65
	1. Crystallization Process	65
	2. Ion Exchange Process	68
	E. Sodium Nitrate Decontamination by Crystallization-Laboratory	71
	F. Evaporation Studies - Laboratory and Semi-Works	71
V.	25 Separations Design and Development	72
	A. Design Progress	72
	B. Pilot Plant Development	72
VI.	23 Separations Semi-Works Design	72
VII.	Unit Process Development	72
	A. Dynamic Ion Exchange Column Study	72
VIII.	Equipment Development	76
	A. Pilot Plant Samplers	76
IX.	RaLa Process Design Studies	76
X.	Personnel	77

Table of Figures

		Page
1.	Variations in Concentrations, 1AP Stream, First Cycle	19
2.	Redox Second Cycle - ORNL #1 Flowsheet	21
3.	Redox Second Cycle - ORNL #2 Flowsheet	22
4.	UAP Semi-Works Flowsheet	45
5.	UAP Semi-Works Cell Arrangement	47
6.	Liquid Waste Evaporator Flowsheet	61
7.	Radiochemical Waste Evaporator	62
8.	Aluminum Decontamination Flowsheet - Ion Exchange	69

List of Tables

		Page
I.	Overall Decontamination and Losses	12
II.	Pilot Plant Redox Dissolver Data	14
III.	First Cycle Run Objectives and Losses	16
IV.	First Cycle Column Decontamination Factors	17
V.	Second Cycle Columns Run Objectives and Conditions	24
VI.	Second Cycle Columns Decontamination Data	25
VII.	Decontamination Factors Obtained Comparing First Cycle Flowsheets	27
VIII.	Plutonium Recovery in Redox 1A Column	28
IX.	Flooding Rates for Redox First Cycle	30
X.	Semi-Works First Cycle Redox Runs	32
XI.	Comparison of Uranium Second Cycle Flowsheet Results of Counter-Current Batch Runs	35
XII.	Comparison of Pilot Plant and Laboratory Counter-Current Batch Results	36
XIII.	Semi-Works Redox Second Uranium Cycle Runs	37
XIV.	Distribution Coefficients of the Plutonium Valence States	38
XV.	The Change in Plutonium VI Concentration in the Aqueous Raffinate	40
XVI.	Oxidation of Plutonium V to Plutonium VI by Sodium Dichromate in Acid Deficient Aluminum Nitrate Solution	41
XVII.	Correlation of Ru Distribution Coefficients with Amount of Oxidizable Ruthenium in Samples During Slug Dissolution	42
XVIII.	Comparison of the Fraction of Oxidizable Ruthenium Present in the Pilot Plant IDF with the Ruthenium Decontamination	42

List of Tables (continued)

		Page
XIX.	Precipitation of Uranyl Ammonium Phosphate with Ammonium Nitrate (K-25 Procedure)	48-49
XX.	Precipitation of Uranyl Ammonium Phosphate with Dibasic Ammonium Phosphate	50
XXI.	Effects of the Ammonium Phosphates and Phosphoric Acid on First Cycle Uranyl Ammonium Phosphate Precipitation Yield	51
XXII.	Ionic Composition of Pilot Evaporator Feeds	53
XXIII.	Radiochemical Analyses of Pilot Evaporator Feeds	54
XXIV.	Heat Transfer Coefficients for Pilot Plant Evaporator	56
XXV.	Comparison of Activities in Feed Solution and in Product Condensate	58
XXVI.	Recovery and Decontamination of Aluminum Nitrate by Crystallization From 85% HNO_3	66
XXVII.	Individual Fission Product Decontamination After Recrystallization of Aluminum Nitrate from 80% HNO_3	67
XXVIII.	Plutonium Decontamination by the Break-Through Method	70
XXIX.	Batch Tests for Determination of Expected Equilibrium Distribution Coefficients at the Top and Bottom of a Dynamic Resin Column	74
XXX.	Distribution Coefficients of Fission Products Between Liquid and Resin	75
XXXI.	Technical Division Personnel	77-78

I. Summary

Work in the field of chemical process development is presented in this section of the report, ORNL-323, Part II. For purposes of distribution, the reactor development phases of the work are being published separately, as ORNL-323, Part I.

Redox Chemical Process Development

The Laboratory has continued its participation in the development of the Redox solvent extraction process for the separation and decontamination of plutonium and uranium from Hanford metal. The completion data of the Pilot Plant program has been extended to June 15, 1949. Final pilot plant runs will be made at full Hanford activity.

The first cycle acid deficient Redox process gave gross fission product decontamination factors of 10^3 to 10^4 in laboratory and semi-works tests. In the pilot plant tests of the acid ANL Redox process, decontamination was 10^2 to 10^3.

The second cycle acid deficient Redox flowsheet in pilot plant tests gave a decontamination factor of approximately 100, as compared with 3 to 10 for the acid process.

Under the ORNL flowsheet first cycle conditions, a double salt (ammonium uranyl chromate) precipitated. Its formation was prevented by neutralizing all feed solutions with sodium hydroxide instead of ammonium hydroxide.

A correlation of pilot plant and semi-works data indicates that the oxidizable form of ruthenium is responsible for the low ruthenium decontamination in solvent extraction. The non-oxidizable ruthenium is scrubbed out under acid deficient conditions.

Low cerium decontamination factors resulted during the shutdown operation in the pilot plant runs. This was corrected by stopping the solvent and scrub feed four hours after the metal feed runs out.

The zirconium decontamination in the pilot plant was improved by increasing the hexone purity.

Hanford Metal Recovery (UAP Process)

A 50 gallon semi-works plant has been designed to test the precipitation steps of the uranyl ammonium phosphate process for the recovery of Hanford waste metal, using the K-25 flowsheet. Construction has been started by the J. A. Jones Construction Company. The proposed completion date is April 11, 1949.

The K-25 UAP ammonium nitrate process has been tested on a 500 milliliter scale in the laboratory using full Hanford level activity, and K-25 results were confirmed. The substitution of monobasic or dibasic ammonium phosphate for ammonium nitrate gave lower losses (1% instead of 12%, without recycle) with comparable decontamination (300). This may eliminate the recommended recycle steps.

Radiochemical Liquid Waste Disposal

A survey of the radiochemical waste problems at ORNL has been completed and will be issued as ORNL-328. Plans are now being formed for extensive modification and improvement of the ORNL waste collection, treatment, and storage systems.

A pilot evaporator, to concentrate radioactive liquid waste, has been assembled and tested to obtain design data and to investigate scale formation. A volumetric reduction of 20 to 1 is feasible. Results are reported in ORNL-224.

As a result of the pilot evaporator runs, a plant scale evaporator has been designed to handle 50,000 gallons of radiochemical waste per week with a condensate decontamination of 10^3. Construction is in progress and operation is planned for the latter part of April.

Laboratory tests have demonstrated the feasibility of further reducing the volume of radiochemical wastes after evaporation, by removing sodium nitrate by crystallization. The ion-exchange process for aluminum nitrate decontamination has been improved to effect decontamination of plutonium as well as beta and gamma activity by a factor of 10^3. The two cycle crystallization process for aluminum nitrate decontamination gave an aluminum yield of 95% and beta and gamma decontamination factors of 10^4 and 700, respectively.

II. Redox Chemical Process Development

A. Pilot Plant

The pilot plant data for the Redox first cycle and the second uranium cycle, presented in Table I, show that the losses of both plutonium and uranium are well within the allowable limits as specified in the Argonne Redox Flowsheet of June 1, 1948. The uranium two cycle decontamination values are less than those reported using an acid flowsheet (ANL) in both cycles, and about the same as those using the combination of an acid first cycle and an acid deficient (ORNL) second cycle. This non-reproducibility of decontamination, using the acid flowsheet, between sites, is due mainly to the differences in ruthenium decontamination.

The uranium losses shown indicate that the uranium can be separated from the plutonium in the Redox process with an overall recovery of 99.9%. The loss data presented are high due to the pilot plant columns being run batchwise instead of continuous, although every effort was made to include only the data from the equilibrium portion of the run. The adequate uranium decontamination of 3.5×10^5 appears to be reasonable well proven to be possible in three cycles (one U/Pu separation and two uranium recovery cycles), with an acid first cycle, if the subsequent two uranium recovery cycles are acid deficient. Three acid cycles will not yield adequate uranium gamma decontamination.

The plutonium losses obtained definitely prove an overall process recovery of 99.8%. Of the two losses in the first cycle, the larger by a factor of approximately 5, is in the separation column (1B), so that the losses in the subsequent cycles of extraction and stripping without the U/Pu separation column, should be very low. The gross decontamination of plutonium is within the approximate limits stated in the ANL flowsheets, especially in the later runs. The cause of the low gross decontamination of the plutonium streams of the first seven runs was due to insufficient decontamination from cerium and zirconium. The decontamination of cerium and zirconium was increased in later runs by improving the purity of the hexone.

1. First Cycle Feed Preparation

a. Source of Irradiated Uranium

Of the twenty active Redox runs made in the ORNL Pilot Plant, the first eleven were made using approximately 1000 day irradiated and 150-300 day cooled ORNL Reactor slugs. The remaining nine runs were made using 70% by weight ORNL slugs and 30% by weight HW production slugs.

[redacted]

TABLE I

ORNL Pilot Plant Redox Data

Overall Decontamination and Losses

(ANL Flowsheet Used in all First Cycle Runs)

Run	Plutonium (1 cycle)				Approx. Second Cycle Flowsheet	Uranium (2 cycles)		
	β DF	γ DF	UDF	Total % Losses		β DF x 10^5	γ DF x 10^5	Losses %
4	200	60	10^6	0.7	ANL	0.1	.07	.007
5	270	220	10^6	0.2	ANL	0.3	.2	.01
6	500	670	10^6	0.3	ORNL #1	3.4	2.8	.2
7	260	210	10^7	1.9	ORNL #1	2.7	1.1	.6
8	210	430	10^8	0.4	ORNL #1	0.7	0.7	.1
9	7500	3100	10^6	0.1	ORNL #1	4.3	0.9	.01
10	190	360	10^6	0.8	---	---	---	---
11	1800	880	10^6	0.2	---	---	---	---
12	2100	1500	10^6	0.2	ANL	0.004	0.003	.01
13	2700	2000	10^7	0.1	ORNL #1	0.4	0.3	.004
14	1900	750	10^6	0.2	ORNL #1	1.1	0.6	.03
15	780	90	10^6	0.3	ANL	0.004	0.003	.04
16	590	170	10^6	0.1	ORNL #1	0.3	0.2	.2
17	---	---	---	---	ORNL #2	1.6	1.2	.02
18	170	50	10^6	0.1	ANL	0.04	0.002	.01
19	450	80	10^7	0.1	ORNL #1	0.7	0.4	.1
20	---	---	---	---	ORNL #2	1.2	0.8	.1
21	420	110	10^6	0.05	ORNL #1	1.3	0.9	.02
22	960	270	10^6	0.1	ANL	0.01	.01	.03
23	---	---	---	---	ORNL #1	0.36	0.3	.03
24	---	---	---	---	ORNL #2	0.83	0.4	.04
25	1200	280	10^6	0.05	ANL	.002	.001	.01
26	---	---	---	---	ORNL #1	1.0	0.5	.02

[redacted]

b. Coating Removal

The jackets of the slugs are removed by the usual sodium hydroxide-sodium nitrate method. This operation has been smooth and without incident.

c. Metal Solution

This operation has been variable during the past period, due to the necessity for changes in operation, unusual occurrences, and investigation of the non-reproducibility of column data. The data taken during column operation indicate that the method of preparation of the feed may be the cause for the differences between extraction decontamination obtained in the ORNL pilot plant and in ANL results. Ruthenium was used as a basis of comparison between the various runs. The variables investigated during dissolving include concentration of acid, ratio of dissolved to undissolved uranium metal (heel), and digesting the dissolved uranium for an extended period of time under reducing conditions. The resulting data showed only minor trends (see Table II). These trends indicated that decontamination was slightly better when 55% HNO_3 was used during dissolution and when the dissolver metal heel was greater than 100%. Further investigation of these specific variables will not be warranted on a pilot plant scale until more laboratory studies are completed. Comparison of the ruthenium decontaminations of this process with those obtained in 25 work, indicate the advisability of going to the acid deficient system developed by the ORNL laboratory and semi-works development section.

d. Acid Adjustment

If the dissolver solution comes out of the dissolver too acid, it is neutralized by the addition of ammonium hydroxide to the first cycle mix tank. The ammonium hydroxide has been added in varying quantities and under varying conditions, in some cases going 0.05N basic and back-acidifying to 0.3N acid, but still no apparent effect on decontamination results. In run 9, the excess acidity was reduced by the hydrolysis of urea, which also destroys the nitric oxide present in the feed solution. In run 18, a duplication of the conditions of run 9 was attempted, to reproduce the high ruthenium decontamination. This run shows that urea hydrolysis increased the ruthenium decontamination markedly but still insufficiently.

e. Time of Ageing

A time study made on the length of time required for the preparation of each step during feed preparation and time between steps, showed that the time of ageing of various solutions for each step of preparation had no marked effect on the fission product decontamination.

[redacted]

TABLE II

ORNL PILOT PLANT REDOX DISSOLVER DATA

All column runs made at Argonne National Laboratory
Redox Chemical flowsheet conditions of 6/1/48

Run	Material Source	% HNO_3 in diss.	Calculated % Heel (1) A	B	First Cycle Ru decont. factor for U
4	ORNL	55	195	240	17
5	ORNL	55	75	75	10
6	ORNL	55	245	150	65
7	ORNL	55	190	120	90
8	ORNL	55 (2,3)	160	55	15
9	ORNL	55	110	13	380
10	ORNL	60	170	70	12
11	ORNL	60	140	40	10
12	ORNL	60	135	30	8
13	ORNL	60 (2)	120	12	6
15	ORNL	60 (2)	100	neg.	4
16	ORNL-HEW	60	125	30	8
18	ORNL-HEW	60 (3)	155	30	33
19 (4)	ORNL-HEW	60	105	6	8
21 (5)	ORNL-HEW	60	130	neg.	10
22 (6)	ORNL-HEW	60	120	30	12
	ORNL-HEW	60	180	70	
25	ORNL-HEW	60	35	65	5
27	ORNL-HEW	60	210	230	4
28	ORNL-HEW	60	135	135	9
30	ORNL-HEW	60	310	--	14

1. Two uranium dissolvings required for each run. "A" and "B" denote the first and second dissolving respectively.
2. Excessive dilution during one of the dissolvings required evaporation at the end of dissolution and would have lowered the acid concentration value.
3. The excess acid of Run 9 was reduced by the hydrolysis of urea and an attempt was made to reproduce these conditions in Run 18.
4. An otherwise normal dissolving was held in contact with a uranium metal heel for an additional 24 hours.
5. ANL dissolving procedure involving adding the acid in thru separate portions after each preceding one had been essentially used up.
6. Four batches of metal were dissolved up for this high flowrate run.

[redacted]

f. Feed Filtration

Solution clarification is accomplished by drawing the two molar UNH solution through sintered stainless steel. The previous sintered stainless steel element used in the 25 Process Development work was a plate type, lying at the bottom of the filter tank. At the start of the Redox work this unit was replaced with a vertical star-shaped filter element that had an area of approximately four square feet.

Operation with this filter has been moderately satisfactory, considering that it is the first unit of this shape and is used in equipment for which it was not designed. One objection is the extremely slow filtering rate that occurs as the upper portion of the unit becomes exposed, when filtering the last portion of a batch of material in an attempt to leave only a very small heel. Cleaning of the element is accomplished by alternate washes of NaOH and HNO_3. One element was removed after processing approximately 1300 gallons of IAF solution. This rather short life was felt to be partially caused by permitting the element to become dry between runs, allowing solids to accumulate in the interstices of the filter, which were impossible to remove by the usual cleaning solutions.

2. First Cycle Column Operation

There has been no indication of column fouling in any of the first cycle columns although 1600 gallons of active solution have been processed through the first cycle equipment. A leak which developed in column IA was indicated by a drop in liquid level while standing between two of the 30% HEW level runs, and was found to be caused by loose bolts in one of the column flanges. The columns were easily decontaminated using the usual mild decontaminating agents and steam, and the flange bolts were tightened by direct maintenance methods.

The run objectives and data in Tables III and IV show that normal operation would give a uranium recovery of 99.9% plus through the first cycle three column operation. In runs 7 and 8 it was noted that the uranium losses in the extraction column increased forty fold toward the end of each run. This was found to be caused by dilution of the aluminum nitrate in the extraction section as indicated by a drop in specific gravity of the extraction column raffinate. By checking volumetric material balances it is felt that water entered the feed displacement tank via the displacement fluid stream, mixing by diffusion with only that portion of the feed material entering the column during the latter part of the run. No further difficulty has been encountered with high uranium losses since an apparent water heel was removed from the displacement fluid tank.

[redacted]

TABLE III

ORNL Pilot Plant Redox Data

First Cycle Run Objectives and Losses

Run[1]	Object	U Losses %		Pu Losses %	
		IAW	ICW	IAW	IBU
4	Prepare second cycle feed	.005	.0005	.2	.5
5	Prepare second cycle feed	.003	.0015	.1	.1
6	Prepare second cycle feed	.008	.003	.04	.24
7	Prepare second cycle feed	0.1	.002	.13	1.75
8	Prepare second cycle feed	0.1	.0008	.2	.2
9	Prepare second cycle feed	.004	.0008	.05	.07
10	Prepare second cycle feed	.006	.0008	.3	.5
11	Test if the mixed salting agent of NH_4NO_3-$Al(NO_3)_3$ was the cause of the high decontamination of Run 9R.	.001	.002	.1	.1
12	Determine range of reproducibility in the first cycle columns using a common column feed material.	.0004	<.001	.06	.1
13		.0004	.001	.07	.06
14		.0004	.03	.08	.1
15	Duplicate of 12, 13, and 14 including the dissolver step	.02	.002	.16	.1
16	Duplicate of 15 using a 30% mixture of HEW slugs with ORNL slugs.	.19[2]	.003	<.01[3]	.1
18	Attempted duplication of 9R by neutralizing excess HNO_3 with urea.	.007	.001	<.01	.1
19	Determine effect of holding dissolved UNH in contact with metal heel for 24 hours at 90° C.	.09[2]	.003	<.01	.1
21	Test ANL dissolving procedure	.002	.01	<.01	.05
22	Test increased flow rates	.03	--	<.01	.1
25	Determine effect of low (30%) heel at end of dissolving.	.008	.006	<.01	.04
27	Determine effect of 200% heel.	nil	.0003	<.01	.03
28	Determine the effect of 150% heel.	.004	.0005	<.01	.03
30	Determine the effect of 250% heel.	.0004	.001	<.01	.04

1. No first cycle runs 17, 20, 23, 24, 26, or 29 were made to enable the same sequence of numbers be used in both first and second cycle.
2. Losses increased 20-50 fold in only the middle of run for unknown reasons.
3. Revised plutonium analysis used for determining losses starting with run 16.

[redacted]

Table IV

ORNL Pilot Plant Redox Data

First Cycle Column Decontamination Factors

(Specific fission product decontamination are for betas)
(June, 1948, ANL Flowsheet Conditions Throughout)

Run	Plutonium Decontamination					Uranium Decontamination			
	β	γ	Ce (x10^3)	Ru	Zr	β	γ	Ru	Zr
4	200	60	.2	90	50	340	140	17	140
5	270	220	.2	80	140	230	180	10	440
6	500	670	.2	330	650	1000	800	60	2800
7	260	210	.2	220	150	1160	500	90	620
8	210	430	.2	145	320	190	190	15	1750
9	7500	3100	.2	2200	180	7900	1700	680	330
10	190	360	.2	115	100	200	100	12	190
11	1800	880	26	110	460	170	150	10	460
12	2140	1450	4	180	1000	160	125	7	5700
13	2700	2040	5	170	2200	120	90	6	850
14	1930	750	7.7	130	440	110	80	5	1570
15	780	90	7(1)	150	110	80	55	4	240
16	590	170	15	220	40	120	110	8	70
18	170	50	5	380	6	280	120	35	25
19	450	80	19	200	30	150	100	8	90
21	420	110	21	90	60	130	90	10	190
22	960	270	8	240	140	180	120	12	650
25	1200	280	80	70	220	110	50	5	640
27	2000	1000	760	80	1400(2)	100	40	4	3000
28	2700	1300	2700	110	3600	100	50	9	18000
30	3300	1500	1400	180	2900	340	150	14	8900

1. Revised column IA shutdown procedure initiated in Run 15 to avoid carry over of Ce.

2. Special high purity hexone used starting with Run 27.

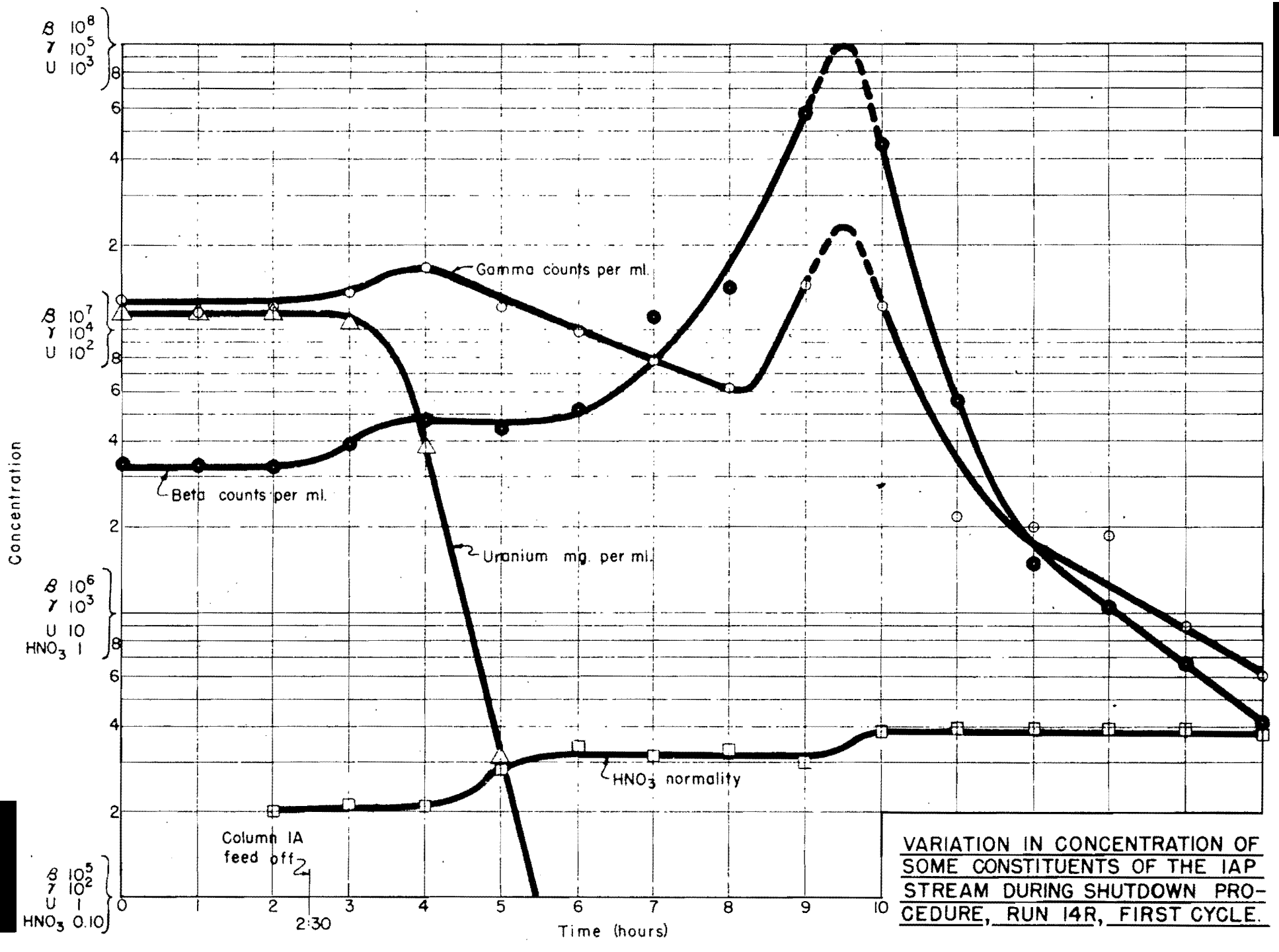
[redacted]

The plutonium in the first column is recovered better than 99.9%. The losses of the extraction column during the first runs are much higher than those reported in the last nine runs due to the presence of americium. (See page 23). The plutonium losses from the IB separation column are considered to be essentially correct, although there is a small amount of masking of the determination by uranium alphas.

The decontamination of uranium from ruthenium has been the major process problem during the past period. The data in Table VI show that the ruthenium form, soluble under the highly salted conditions of the 1A extraction column, partitions in the highly salted 1B uranium-plutonium separation column, and is removed from the solvent in the 1C stripping column. This is contrary to the action of zirconium, which is reduced by a factor of three in the 1B column. This shows that the reducing action of the ferrous sulfamate in the 1B column did not materially affect the ruthenium decontamination. This was subsequently shown to be true in the second cycle process.

The cerium decontamination for plutonium, was low during the first seven runs, 4 through 10. This was due to excessive carry-over of the cerium during the shutdown procedure, and was satisfactorily corrected by modifying column shutdown procedures. In runs 11 through 13, the variation of cerium content of the progressive 1BP samples of a single run was studied and shown to vary markedly, in that the cerium content of the 1BP stream decreased during the middle of the runs and increased again at the end. In run 14 all of the 1A and 1B column scrub and extract feed pumps were permitted to operate for a period of fifteen hours after expiration of the uranium feed. The 1A column U/Pu bearing hexone stream was sampled each hour and analyzed, with the resultant data plotted in Figure 1. The specific fission product analyses at six and seven hours after uranium feed cutoff (hours 9 and 10 in Figure 1), showed that, although the uranium content of the 1AP stream was negligible, the gross beta activity actually increased by a factor of 300, due to the increase in cerium activity by a factor of approximately 5000, and the zirconium by 100, while the columbium activity remained essentially the same and the ruthenium activity dropped by a factor of 4. This phenomenon was partially explained by recent laboratory data which showed that under acid conditions the distribution coefficient for cerium in favor of the hexone phase was approximately 3 at .01M sodium dichromate, possible only during shutdown, as compared with a distribution coefficient of 0.2 at 0.1M sodium dichromate. No further trouble has been experienced with cerium breakthrough since the new column procedures have been put into effect. These involve shutting down the solvent (1AX) pump two hours after uranium feed expiration, to avoid carryover of and contaminating the 1B column with cerium.

The zirconium decontamination has been found to be markedly reduced by small amounts of impurities in the hexone. The decontamination factors for zirconium were only moderately satisfactory during the first ten runs,



VARIATION IN CONCENTRATION OF SOME CONSTITUENTS OF THE IAP STREAM DURING SHUTDOWN PROCEDURE, RUN 14R, FIRST CYCLE.

Drawing # 7045 FIGURE 1

in that they were quite variable. No effort was expended to improve the decontamination for specific fission products because of its being a relatively minor activity in the product streams, until a marked decrease in decontamination in runs 16 through 21. This increase of zirconium in both the plutonium and uranium streams was due to a relatively large increase in the methyl isobutyl carbinol content of the process hexone, caused by blending in an unusually large percentage of ordinary raw hexone as process makeup, although it was contacted with an acid dichromate wash and distilled before use. In runs 27 and 28 using only hexone reclaimed from the process that had been contacted with an additional acid dichromate wash before recovery by steam distillation, the zirconium decontamination was improved by a factor of 10, and also appeared to increase cerium decontamination. The use of only special commercial hexone prepared by the Shell Chemical Company (SS Solvent) in run 30, after it had been contacted with dichromate and distilled, showed no marked effect on decontamination.

3. Second Cycle Feed Preparation

The feed for the second (U recovery and decontamination) cycle is prepared by concentrating and neutralizing the uranium product solution (1CU) from the first cycle stripping column. The neutralization is done by adding ammonia slowly with agitation over a period of 45 minutes before boil-down. This direct neutralization replaced the previous time consuming and erratic neutralization by hydrolysis of urea.

The comparison of the three second uranium cycle flowsheets was made by combining the product from two first cycle runs. The entire batch was first made to fulfill the ANL second cycle flowsheet specifications, and one-third of the mixture was transferred to the feed tank and processed through the columns. The remaining material was made to conform to the specifications of the feed for the ORNL #1 chemical flowsheet after which a portion was transferred to the feed tank for column processing. The remaining material was made to ORNL #2 flowsheet conditions and processed.

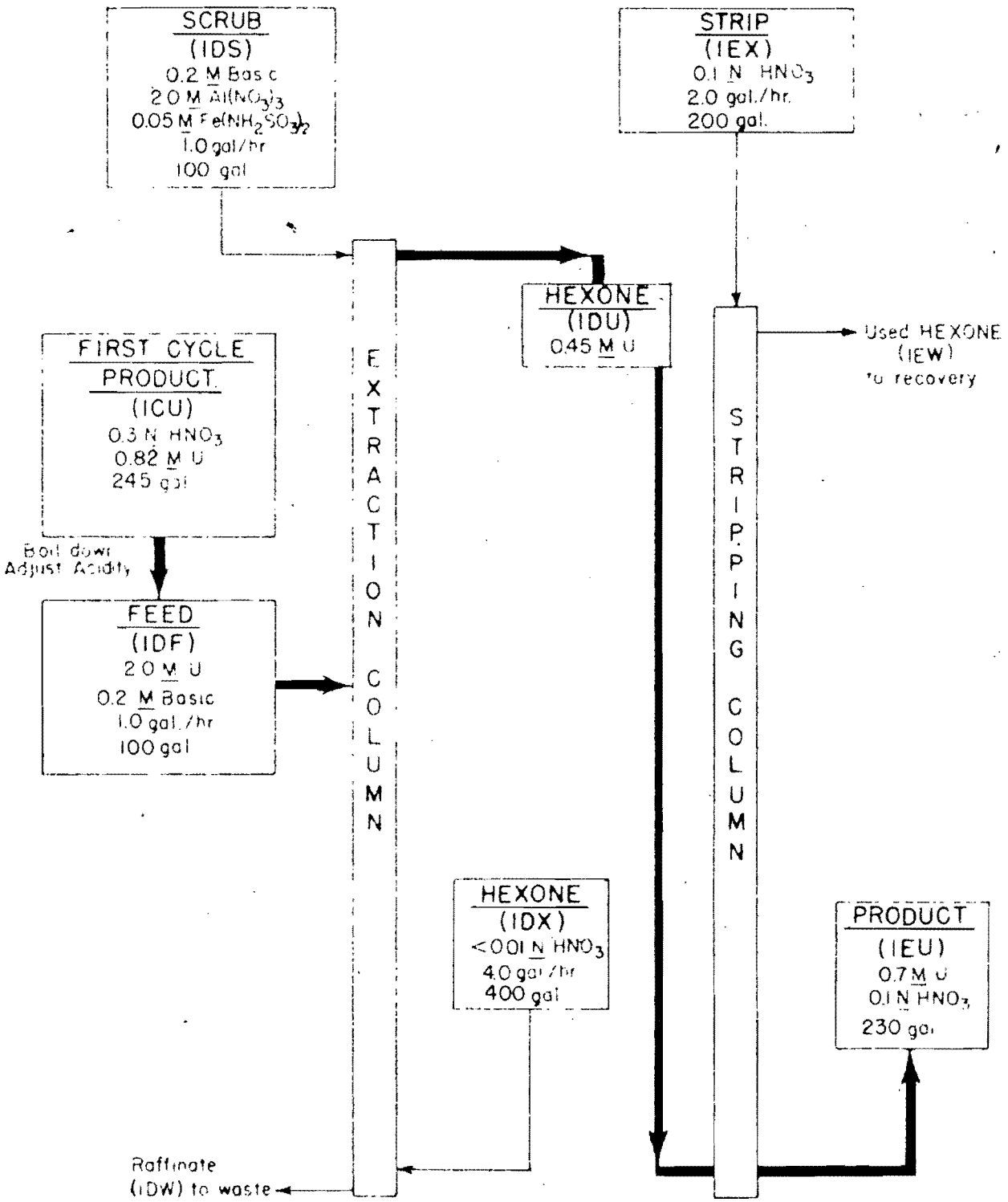
The ORNL #1 and ORNL #2 Second Cycle Chemical flowsheets are given in Figures 2 and 3.

4. Second Cycle Column Operation

The main objective of operating the second cycle columns has been to determine the chemical flowsheet to be used for recovering and decontaminating the first cycle uranium product, and to determine the number of cycles required to give an overall gamma decontamination of 4×10^5. Although the variations in the first cycle have tended to yield second cycle data giving only qualitative comparisons of fission product decontamination, the differences between flowsheets have been sufficient to eliminate the June, 1948 ANL second cycle flowsheet.

FIGURE 2

Drawing # 7046



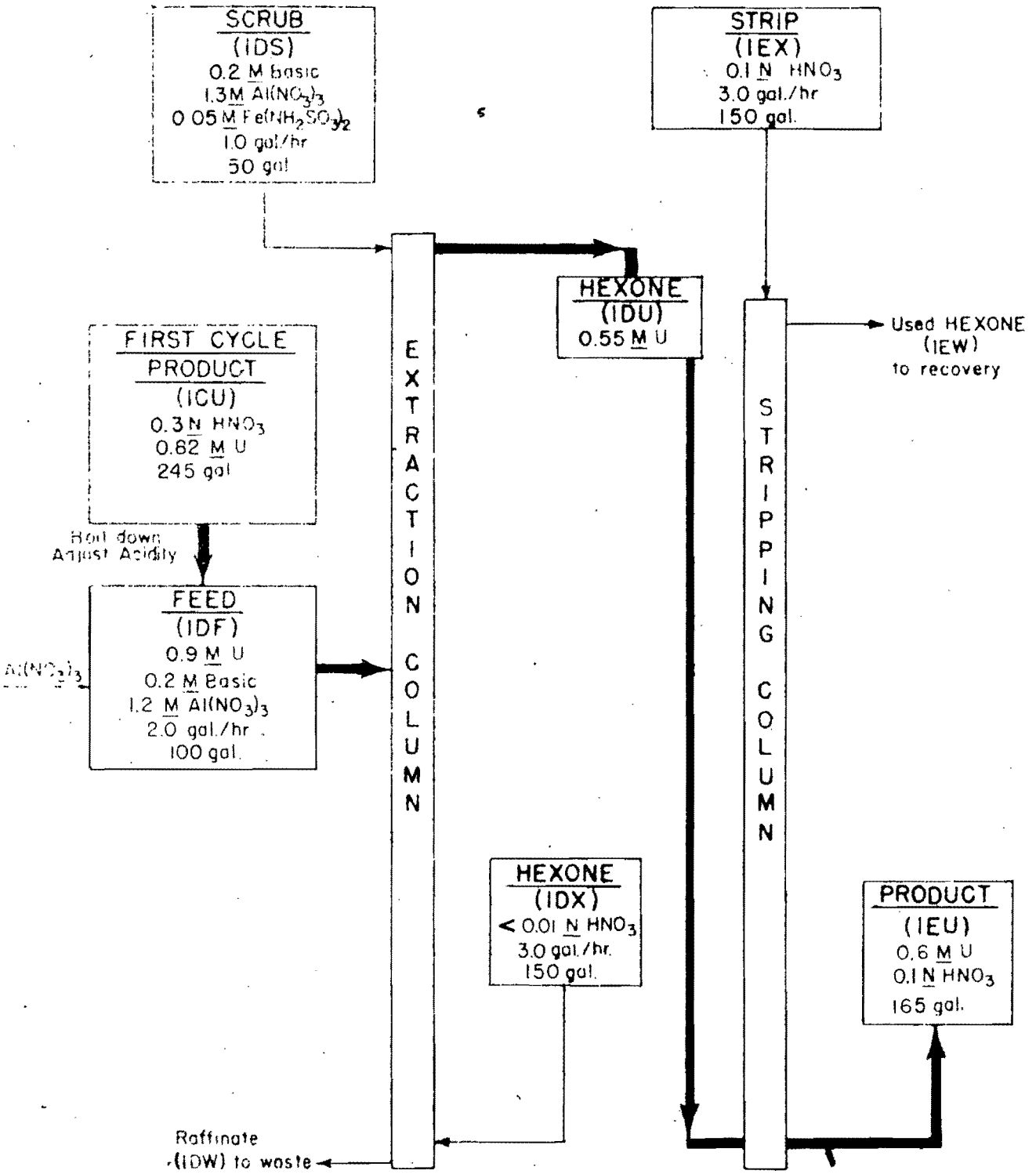
REDOX SECOND CYCLE

ORNL #1 CHEMICAL FLOWSHEET

2-15-49

FIGURE 3

Drawing # 7047



REDOX SECOND CYCLE

ORNL #2 CHEMICAL FLOWSHEET

2-15-49

[redacted]

The object and data of the runs to date, summarized in Tables V and VI, show that fission product decontamination factors of 2, 200, and 500 can be expected when processing the 1CU stream from the ANL first cycle process through a second cycle ANL, ORNL #1 and ORNL #2, respectively, with ruthenium being the limiting and major activity of both feed and product. The uranium losses are approximately the same for each of the flowsheets, as is plutonium decontamination if ferrous sulfamate is included in the ANL flowsheet. In comparative sets of runs, it was found that due to the presence of ferrous sulfamate the plutonium decontamination increased by a factor of 10 to 100 while the fission product (ruthenium) decontamination was essentially unaffected. The process requirement for plutonium decontamination is the only reason for inclusion of ferrous sulfamate in the second cycle flowsheet. As yet a definite decision on which of the acid deficient flowsheets to develop in detail has not been made, but should be reached in the coming period when pilot plant data for a two cycle acid deficient system become available.

5. Analytical Developments

The oxalate potentiometric method for the determination of HNO_3 has been scaled down to a micro technique using 10 lambda aliquots for analyses. The results of a control study submitted with the regular samples, show that the probable error of the HNO_3 determination in the 1AF solution is less than 0.02 normality units.

The spectrophotometric method and phthalic anhydride method for the analyses of methyl isobutyl carbinol in hexone, have been discontinued in favor of the colorimetric method. The latter method is being critically studied.

Comparison of the TTA extraction method with the lanthanum fluoride method for measuring plutonium in the 1A stream, has shown the TTA method to be preferable. The lanthanum fluoride precipitate was found to carry americium, an alpha emitter, which if counted as plutonium, would indicate losses far above those actually obtained.

The use of the ANL flowsheet in the Redox first cycle, results in the activity in both the ICU and IEU streams being 90 to 99.9% ruthenium, regardless of whether the ANL or ORNL flowsheet is used in the second cycle. For this reason, relatively little attention has been given to the decontamination of zirconium, columbium and cerium in the uranium streams. Furthermore, both the relative and gross amounts of these fission products activities in the IEU stream are in a range which is so low that the accuracy of the measurements is questionable. It is expected that the importance of accurate fission product analyses will be accentuated when the ORNL Redox flowsheets are used in the first cycle, for under these conditions it is expected that the ruthenium, zirconium and columbium decontaminations may be of the same order of magnitude. A special study is now being made of the accuracy which may be expected of the

[redacted]

TABLE V

ORNL Pilot Plant Redox Data

Second Cycle Columns Run Objectives and Conditions

(ANL conditions in all first cycle runs)

Run	Object	Condition	Total U Losses %	First Cycle Run # Used for Feed
4	Test ANL Flowsheet	ANL	.002	4
5	Test ANL Flowsheet	ANL	.007	5
6	Test ORNL #1 Flowsheet	ORNL #1	.16	6
7	Test ORNL #1 flowsheet with scrub .05 M in ferrous sulfamate.	ORNL #1	.47	7
8	Test ORNL #1 flowsheet with both scrub and feed 0.5 M ferrous sulfamate.	ORNL #1	.01	8
9	Repeat of Run 7	ORNL #1	.004	9
10	Intended to be original ORNL #2 runs but flowsheet was	--	--	--
11	found to be inoperable.	--	--	--
12	Three runs using a common feed to compare the three	ANL	.01	Mixture
13	different flowsheets without ferrous sulfamate	ORNL #1	.003	of 12
14		ORNL #2	.004	and 13
15	Three runs using a common feed to compare the three	ANL	.02	Mixture
16	flowsheets with scrub 0.5 M in ferrous sulfamate.	ORNL #1	.02	of 15
17		ORNL #2	.004	and 16
18	Three runs using a common feed to compare the three	ANL	.13	Mixture
19	flowsheets with both scrub and feed 0.5 M in	ORNL #1	.008	of 18
20	ferrous sulfamate.	ORNL #2	.01	and 19
21A	Determine improvement if feed was made .05 M in	ORNL #1	.01	21
21B	ferrous sulfamate in addition to the scrub.			
22	Three runs duplicating 15, 16, and 17 the present	ANL	.002	
23	flowsheet.	ORNL #1	.004	22
24		ORNL #2	.01	
25	Compare the ANL & ORNL #1 second cycle flowsheet using	ANL	.004	
26	the product of a first cycle run that was known to have had a low heel in both dissolvings.	ORNL #1	.01	25

[redacted]

TABLE VI

ORNL Pilot Plant Redox

Second Cycle Columns Decontamination Data

(See Table IV for Run, Objectives, and Actual Conditions)

Run	Approx. Flowsheet	Free Acidity N			U Losses %		Decontamination			
		Feed	Scrub	Hexone	Ext.	Strip	Pu	β	Ruβ	γ
4	ANL	0.25	0	0.5	.002	.0002	3.5	30	25	50
5	ANL	0.35	0	0.5	.0003	.007	15	110	125	90
6	ORNL #1	0.07	-0.38	0	.16	.0003	35	190	350	160
7	ORNL #1	-0.7	-0.43	0	.47	.0015	515	230	220	225
8	ORNL #1	-0.85	-0.6	0	.004	.005	15	390	350	390
9	ORNL #1	0.06	-0.4	0	.002	.002	70	55	35	56
12	ANL	0.34	--	0.5	.01	.005	1	2.6	2.5	2.6
13	ORNL #1	0.0	-0.4	0	.002	.001	1.3	310	320	310
14	ORNL #2	-0.14	-0.13	0	.002	.002	3.1	790	860	800
15	ANL	0.33	0.4	0.5	.0006	.02	30	4.4	4	5
16	ORNL #1	0.5	-0.33	0	.007	.02	24	330	360	280
17	ORNL #2	-0.27	-0.18	0	.003	.001	17	980	1200	980
18	ANL	0.2	-0.05	0.5	.13	.001	60	19	13	30
19	ORNL #1	0.01	-0.4	0	.002	.006	90	310	250	390
20	ORNL #2	-0.2	-0.18	0	.002	.01	53	570	540	700
21A	ORNL #1	0.02	0.5	0	.003	.004	20	1000	900	1000
21B	ORNL #1	0.02	0.4	0	.008	.02	30	720	700	800
22	ANL	0.32	--	0.5	.001	.001	700	8	8	8
23	ORNL #1	0.02	-0.35	0	.003	.001	600	200	300	200
24	ORNL #2	-0.17	-0.2	0	.006	.004	250	460	600	460
25	ANL	0.39	-0.08	0.5	.004	.0001	40	2	2	2
26	ORNL #1	0.05	-0.43	0	.014	.001	20	1000	800	1000

[redacted]

columbium, ruthenium, zirconium, cerium and plutonium analyses in very low ranges. Gamma counting in the second cycle has already been eliminated for those runs in which the ORNL second cycle flowsheets are used, because of the low number of residual counts. The use of the ion chamber for measuring gamma radiation in pilot plant process streams of both cycles has proven to be very successful, and it is contemplated that in the future at least 90% of the gamma determinations in both cycles will be by means of the ion chamber.

6. Program

With the completion of the testing of the first cycle Argonne flowsheet, the program for the coming quarter consists of testing both ORNL first cycle flowsheets at the present 30% HW level. The uranium product from these acid deficient flowsheets will then be processed through the three second cycle flowsheets for comparison. It is expected that, by the end of the coming period, a recommended choice of the combined first and second cycle flowsheets can be presented, after which the optimum flowsheets will be tested at 30% HW activity level.

In the subsequent period, it is planned that both the first cycle ANL, second cycle ORNL and the two cycle ORNL optimum flowsheets will be tested at full Hanford level for process verification. The fissionable material separated during these investigations will then be concentrated and returned to production channels.

B. Laboratory and Semi-Works

1. Comparison of Redox First Cycle Flowsheets

a. Laboratory Batch Runs

Experiments carried out on a counter-current batch extraction apparatus indicate that fission product decontamination is higher by a factor of 2 to 3 for the ORNL #2 flowsheet compared with the ORNL #1 flowsheet (See Table VII for details).

b. Laboratory Column Runs

The uranium and plutonium recoveries were found to be comparable under column 1A conditions for the ANL (July, 1948) and ORNL #2 Redox first cycle processes (see Table VIII). These tests were made in one inch diameter glass columns packed with 3/16 inch Fenske packing.

[redacted]

Table VII

Decontamination Factors Obtained Using Two Acid Deficient First Cycle Redox Process Flowsheets in Counter-Current Batch Extraction Apparatus

Six extraction stages and four scrub stages
Oxidation of acid deficient feed: Heating for 6 hours at 85 - 90°C

Run Number	Conditions	Acid Deficiency of 1AF N	Decontamination Factors β	γ	Ru
	ORNL # 1				
C-26	1AS-2 M $Al(NO_3)_3$, 0.2 N acid deficient	0.13	1.2×10^3	580	650
C-29	1AF-2 M $UO_2(NO_3)_2$, 0.1 M $Na_2Cr_2O_7$				
	1AX-hexone, neutral	0.2	3.4×10^3	930	740
	Flowratio - AX/AF/AS= 4/1/1				
	ORNL # 2				
C-25	1AS-1.2 M $Al(NO_3)_3$, 0.2 N acid deficient	0.18	6.8×10^3	1.6×10^3	2.1×10^3
C-28	1AF-1.2 M $Al(NO_3)_3$, 0.9 M $UO_2(NO_3)_2$, 0.1 M $Na_2Cr_2O_7$	0.2	2.2×10^3		1.7×10^3
C-27	1AX-hexone, neutral	0.2	4.5×10^3	1.8×10^3	1.6×10^3
	Flowratio - AX/AF/AS=3/2/1				

[redacted]

Table VIII

Plutonium Recovery in Redox 1A Column

Column: 1 inch Pyrex glass pipe packed with 3/16 inch Fenske packing
10 ft. of extraction section
1/2 ft. of scrub section for Runs F-1, F-2, F-4
3-1/2 ft. of scrub section for Runs F-5, F-7, F-14, F-16, F-17

	1 AF (Metal Feed)*			1AS (Scrub)		1 AX (hexone)		Total				
Run No.	UNH M	$Al(NO_3)_3$ M	HNO_3 M	$Al(NO_3)_3$ M	HNO_3 M	HNO_3 M	Flow Ratio AX:AF:AS	Through-put Gal/hr/ft^2	Reflux %U	Reflux %Pu	Loss %U	Loss %Pu
F-1	2.0	0	0.3	1.3	0.04	0.5	4:1:1	175	--	--	0.2	0.1
F-2	0	1.3	-0.3	1.3	-0.3	0	3:2:1	115	--	--	--	0.1
F-4	1.1	1.3	-0.2	1.3	-0.4	0	3:2:1	120	--	--	0.3	1.1
F-5	1.3	1.2	-0.2	1.3	-0.4	0	3:2:1	120	25	43	0.01	1.8
F-7	1.0	1.2	-0.1	1.3	-0.3	0	6:2:1	130	12	20	0.01	0.04
F-14	0.9	1.2	-0.2	1.3	-0.3	0	3:2:1	90	22	54	0.2	2.2
F-16	0.9	1.2	-0.2	1.3**	-0.3	0	3:2:1	90	20	20	0.3	0.2
F-17	0.9	1.2	-0.3	1.3***	-0.3	0	3:2:1	120	9	14	0.1	0.1

* All metal feeds were 0.1 M $Na_2Cr_2O_7$ and were heated to 85°C for six hours
** The scrub for Run F-16 was 0.1 M $Na_2Cr_2O_7$
*** The scrub for Run F-17 was 0.01 M $Na_2Cr_2O_7$

A control run (F-1) was made using the ANL flowsheet in which the uranium loss was 0.2% and the plutonium loss was 0.1%. No uranium was present in the initial acid deficient runs, and the plutonium losses were about 0.1%. When uranium was added to the feed, the plutonium losses increased by a factor of 10 (1 to 2%) while the uranium losses were quite low (0.01% to 0.3%). This adverse effect on plutonium extraction in the presence of uranium was confirmed in batch equilibrations. These plutonium losses of 1 to 2% have been reduced to 0.2% in acid deficient runs, either by doubling the solvent flowrate (Run F-7), or by adding 0.01M sodium dichromate to the scrub solution (Run F-17). Plutonium losses could also be reduced by lengthening the extraction column or by decreasing the flow rates, to keep the feed in the column longer. Of these four methods, the addition of sodium dichromate to the scrub is thought to be the best from the viewpoint of decontamination and ease of operation.

In several runs under ORNL #2 conditions, a yellow precipitate was noted in the 1A column. Analyses showed that it consisted of a double salt $(NH_4)_2CrO_4 \cdot 2UO_2CrO_4 \cdot 6H_2O$ due to the presence of ammonium ion in the aqueous phase at about pH 2. By using sodium hydroxide for neutralization of the feed and scrub, the precipitate was eliminated.

Flooding rates were determined for the 1A column using the ANL flowsheet, ORNL #1 flowsheet, and ORNL #2 flowsheet (see Table IX). The amount of uranium that can be put through the 1A column is as follows:

ANL flowsheet	175 kg/(hr)(ft^2)
ORNL #1 flowsheet	200 kg/(hr)(ft^2)
ORNL #2 flowsheet	140 kg/(hr)(ft^2)

The flooding rate for the 1B column using ORNL #1 flowsheet was 30% greater (based on uranium throughput) than that for the 1A column. The 1B column was a one-inch glass pipe packed with 3/16 inch Fenske packing. The extraction section (top of column) was 4 feet, and the scrub section (bottom of column) was 6 feet. Both plutonium and uranium losses were 0.1%.

c. Semi-Works Column Runs

Plutonium and uranium losses of less than 0.1%, and beta decontamination factors of 1800 for the ORNL #1 flowsheet and 14000 for the ORNL #2 flowsheet, were obtained with oxidized 0.2 normal acid deficient feeds. No ANL Redox first cycle runs were made because of large numbers previously made by the Pilot Plant, which indicated beta decontamination of 100 to 200. The tests were made in two columns, 1A and 1C, without a 1B column for the separation of the plutonium from the uranium.

[redacted]

Table IX

Flooding Rates for Redox First Cycle

Column: 10 feet of 1-1/2 inch Pyrex glass pipe packed with 1/4 x 3/8 inch Raschig Rings

Process	Column	TOTAL THROUGH-PUT $\frac{Gal.}{Hr. Ft.^2}$		URANIUM THROUGH-PUT $\frac{Kg}{Hr. Ft^2}$	
		Highest rate without flooding	Lowest flooding rate	Highest rate without flooding	Lowest flooding rate
ANL	1A*	580	680	174	204
ORNL #1	1A*	580	780	204	234
ORNL #2	1A*	520	650	140	175
ORNL #1	1B**	960	1080	260	290

* Scrub and feed were mixed before entering column

** Solvent carrying uranium and fresh hexone mixed before entering column.

[redacted]

The feeds for these runs were digested at 85° C for six hours with 0.1 molar sodium dichromate added to oxidize the plutonium to VI valence state. It was also found necessary to add 0.01 molar sodium dichromate to the scrub solution to prevent reduction of the plutonium in the scrub section.

The ORNL flowsheet in the 1A column was similar to the ANL, July 1948, flowsheet with the exception that the acidity was decreased from 0.3 normal to -0.2 normal (acid deficient), which necessitated the increase of the aluminum nitrate concentration in the scrub from 1.3 molar to 2.0 molar to hold the plutonium and uranium distribution coefficients constant. In the 1B column the aluminum nitrate strip feed was made 0.2 normal nitric acid to compensate for the low acid in the organic coming from 1A.

The ORNL #2 flowsheet differed from the ORNL #1 flowsheet in that the aluminum nitrate concentration in the scrub was decreased and the excess aluminum nitrate that was required was added one or two stages below the metal solution feed point, to allow greater reflux of fission products in the scrub section. In the semi-works test runs, the aluminum nitrate was added with the metal solution feed because it was not feasible to make the necessary changes in the semi-works equipment. The feed solution was then 1.3 molar aluminum nitrate - 0.9 molar uranyl nitrate - 0.2 normal acid deficient, and it was difficult to prevent precipitation of the feed under these conditions. The complete details of the chemical composition and flow ratios are shown in Table X along with analytical results.

[redacted]

Table X

Semi-Works First Cycle Redox Runs

Equipment: 1-1/2" diameter columns packed with 1/4"x3/8" split rings, 13.5 ft. extraction, 4.0 ft. scrub, 11.0 ft. strip

Run No.	Extraction Feed U M	Extraction Feed Al M	Extraction Feed H^+ N	Extraction Feed $Cr_2O_7^=$ M	Scrub Al M	Scrub H^+ N	Scrub $Cr_2O_7^=$ M	Ext. Flow Ratio F:S:E*	Extraction Loss % Pu	Extraction Loss % U	Overall D.F.'s (Log) Gross β	Overall D.F.'s (Log) I.C.γ	Overall D.F.'s (Log) Ru β
ORNL #1													
R-22									0.34	0.08	2340 (3.37)	760 (2.88)	130 (2.11)
R-23									0.25	1.10	1860 (3.27)	895 (2.95)	-- --
	1-9	-	-20	0.1	2.0	-.2	-	1:1:4					
R-24							0.01		0.04	0.13	1810 (3.26)	970 (2.98)	157 (2.19)
R-25							0.01		<0.01	0.10	1880 (3.27)	1090 (3.02)	101 (2.00)
ORNL #2													
R-20A								2:1:6	0.10	0.01	3620 (3.56)	1860 (3.27)	244 (2.38)
R-21								2:1:6	<0.01	0.01	7400 (3.82)	2880 (3.46)	467 (2.67)
	0.9	1.20	-20	0.1	1.3	-.20	--	2:1:6					
R-20B								2:1:3	0.50	0.30	3950 (3.60)	1500 (3.18)	200 (2.30)
R-27							0.01	2:1:3	0.04	0.12	14000 (4.15)	6500 (3.81)	890 (2.95)
R-28	1.06	1.10			1.5		0.01	2:1:3	0.02	0.12	16845 (4.23)	4955 (3.69)	890 (2.95)

Run 20A and B, one ORNL slug for activity, other runs used two slugs each

* F:S:E. Feed to scrub to Extractant (1 is equivalent to 38.5 gal/(hr.)(ft^2)

Neutral Hexone used as extractant in 1A. 0.10 N HNO_3 used as extractant in 1C column.

[redacted]

2. Comparison of Redox Second Uranium Cycle Processes

a. Laboratory Batch Runs - Second Uranium Cycle

In the last quarterly report, results were given for laboratory work which has been done in developing an acid deficient Redox second cycle uranium concentration process. Synthetic metal feeds were used throughout these studies, since no first cycle product was available at that time. The decontamination obtained with the acid deficient conditions indicated a marked improvement over acid conditions. From the results of this work, two acid deficient flowsheets were selected for further study in the Semi-Works and Pilot Plant. They are as follows:

ORNL Flowsheet #1

DF - 2.0 M $UO_2(NO_3)_2$, 0.2 N acid deficient

DS - 2.0 M $Al(NO_3)_3$, 0.2 N acid deficient

DX - neutral hexone

Flowratio: DX/DF/DS = 4/1/1

ORNL Flowsheet #2

DF - 1.2 M $Al(NO_3)_3$, 0.9 M $UO_2(NO_3)_2$, 0.2 N acid deficient

DS - 1.3 M $Al(NO_3)_3$, 0.2 N acid deficient

DX - neutral hexone

Flowratio: DX/DF/DS ≐ 3/2/1

A third flowsheet was considered also, in which the aluminum nitrate concentration of the scrub solution was reduced to allow a greater reflux of uranium in the scrub.

During this quarter, a composite of the 1CU product from Pilot Plant runs R13 and 14 was used to make up metal feeds for a series of runs to reevaluate these three acid deficient flowsheets as compared with the present Redox flowsheet. Also, portions of several pilot plant second cycle metal feeds have been used for laboratory runs to establish the correlation between results obtained in the pilot plant vertical packed column and the laboratory counter-current batch extraction apparatus.

The 1CU products from pilot plant runs R13 and 14 were combined and the resulting composite used to make metal feed solutions reported in this section. Radiochemical analysis showed that about 80-90 percent of the beta activity in the composite was due to ruthenium.

Three acid deficient flowsheets and the present Redox flowsheets have been compared in the counter-current batch extraction apparatus. Results of these runs are given in Table XI. A very clear advantage in decontamination for the acid deficient flowsheets is shown as compared to the acid flowsheet. The ORNL flowsheet gives better decontamination than the acid flowsheet by a factor of approximately 100 (for this particular 1CU product), the ORNL #2 flowsheet is superior to the ORNL #1 flowsheet by a factor of approximately 4, and the ORNL #2 and ORNL #3 flowsheets give about equal decontamination.

These acid deficient conditions have been obtained at the expense of additional aluminum nitrate in the system per unit of uranium processed. The ratios of aluminum nitrate to uranium processed for the four flowsheets are as follows:

Flowsheet	Moles of $Al(NO_3)_3$ per mole of uranium processed
ANL (July, 1948)	0.65
ORNL #1	1.00
ORNL #2	2.06
ORNL #3	2.1

Portions of metal feed solutions, used in pilot plant second cycle runs, were used to make parallel runs in the laboratory counter-current batch extraction apparatus. Decontamination factors obtained were compared with the results obtained from the corresponding pilot plant runs and were found to be in very good agreement (see Table XII).

b. Semi-Works Column Runs - Second Uranium Cycle

The ANL and ORNL Redox second uranium cycle flowsheets were compared using pilot plant 1CU product for the semi-works second cycle feed with and without ferrous sulfamate. Beta decontamination factors of 60, 142, and 190 were obtained for the ANL, ORNL, and modified ORNL processes, respectively. The addition of 0.05 molar ferrous sulfamate in the metal solution feed increased the decontamination to 161, 173, and 199, respectively, having the largest effect on the ANL flowsheet (see Table XIII). The effect of the ferrous sulfamate was most pronounced by the improvement of the plutonium decontamination.

The run conditions for the Redox second uranium cycle were the same as for the first cycle, except that no sodium dichromate was added.

[redacted]

Table XI

Results of Counter-Current Batch Extraction Runs Comparing the ANL Redox Process Uranium Second Cycle Flowsheet with Three ORNL Flowsheets

Metal Feed solutions for all runs were made from a composite of Pilot Plant 1CU Product from Runs 13 and 14.
Six extraction and four scrub stages.

Run Number	Conditions	Decontamination Factors (Log.) Gross Beta	Gamma	Ru β	Percent U Loss
	ANL (July, 1948)				
C-12	1DS-1.3 M $Al(NO_3)_3$ 1DF-2.0 M $UO(NO_3)_2$, 0.3 N HNO_3	2.0 (0.30)	2.2 (0.34)	2.0 (0.30)	0.3
C-15	1DX-hexone, 0.5 N HNO_3 Flow ratio: DX/DF/DS=4/1/1	2.4 (0.38)	2.1 (0.32)	2.1 (0.32)	0.2
	ORNL Flowsheet #1				
C-38	1DS-2.0 M $Al(NO_3)_3$, 0.2 N acid deficient 1DF-2.0 M $UO_2(NO_3)_2$, 0.2 N acid deficient	340 (2.53)	430 (2.63)	430 (2.63)	0.1
C-43	1DX-hexone, neutral Flow ratio: DX/DF/DS=4/1/1	320 (2.51)	350 (2.54)	450 (2.65)	0.2
	ORNL Flowsheet #2				
C-30	1DX-1.3 M $Al(NO_3)_3$, 0.2 N acid deficient 1DF-1.2 M $Al(NO_3)_3$, 0.9 M $UO(NO_3)_2$, 0.2N acid deficient	1400 (3.15)	2900 (3.46)	2300 (3.35)	0.9
C-32	1DX-hexone, neutral Flow ratio: DX/DF/DS=3/2/1	1500 (3.18)	1200 (3.08)	1500 (3.18)	0.4
	ORNL Flowsheet #3				
C-31	1DS-0.8 M $Al(NO_3)_3$, 0.2 N acid deficient 1DF-1.3 M $Al(NO_3)_3$, 1.0 M $UO_2(NO_3)_2$, 0.2 N acid deficient	1800 (3.26)	660 (2.82)	3000 (3.48)	0.8
C-40	1DX-hexone, neutral Flowratio: DX/DF/DS=4/1/1	1100 (3.04)	-	2000 (3.30)	1.4

[redacted]

[redacted]

Table XII

Comparison of Decontamination Factors Obtained Using the Same Metal Feed Solutions

In Pilot Plant 1D Column and the Laboratory Counter-Current Batch

Extraction Apparatus

Counter-Current	Pilot Plant	Redox Uranium Second Cycle Flowsheet Conditions Used	Decontamination Factors (Log.) Counter-Current Batch β	Ru	Pilot Plant β
C-20	R-15	ANL Redox	3.7 (0.57)	2.5 (0.40)	3.6 (0.57)
C-33	R-18	ANL Redox	27 (1.43)	8 (0.90)	18 (1.26)
C-44		ANL Redox	35 (1.54)	15 (1.18)	
C-41	R-22	ANL Redox	11 (1.04)	6 (0.78)	60 (0.84)
C-42	R-21b	Acid Deficient ORNL # 1	710 (2.85)	1100 (3.04)	700 (2.85)
C-21	R-16	Acid Deficient ORNL # 1	420 (2.62)	550 (2.74)	360 (2.56)
C-36	R-19	Acid Deficient ORNL # 1	210 (2.32)	410 (2.61)	250 (2.40)
C-45	R-23	Acid Deficient ORNL # 1	250 (2.40)	310 (2.49)	240 (2.38)
C-22	R-17	Acid Deficient ORNL # 2	980 (2.99)	1460 (3.16)	1060 (3.03)
C-37	R-20	Acid Deficient ORNL # 2	690 (2.84)	990 (2.99)	540 (2.73)

[redacted]

[redacted]

Table XIII

Semi-Works Redox Second Uranium Cycle Runs

Equipment: 1-1/2" diameter columns packed with 1/4" x 3/8" split rings, 13.5 ft. extraction, 4.0 ft. scrub, 11.0 ft. strip

Run No.	Extraction Feed[a] U M	Al M	H^+ N	Scrub Al M	H^+ N	Ext(b) Flow Ratio	U Loss Ext. %	Decontamination Factors (Log) (c) β	γ	Ru	Pu	Pilot Plant First Cycle Run No.
	ANL (July 1948)											
12	2.0	-	0.3	1.3	0.03	1:1:4	0.004	60 (1.78)	50 (1.70)	26 (1.42)	1 (0.0)	4R
19(d)							0.001	161 (2.21)	55 (1.74)	220 (2.34)	156 (2.19)	7R
	ORNL #1											
	1.9	-	-0.02	2.0	-0.4	1:1:4						
16							0.18	142 (2.15)	126 (2.10)	145 (2.16)	22 (1.34)	6R
17(d)							1.34	173 (2.24)	183 (2.26)	195 (2.29)	62 (1.79)	6R
	ORNL #2											
15	1.2	1.2	-0.2	1.3	-0.2	2:1:3	0.01	190 (2.28)	145 (2.16)	180 (2.25)	3 (0.48)	5R
18(d)							0.24	199 (2.30)	128 (2.11)	328 (2.52)	295 (2.47)	7R

(a) Pilot plant 1CU solution
(b) Metal feed: scrub feed: Extractant feed
1 is equivalent to 38.5 gal/hr x ft^2
(c) γ counting in ionization chamber
(d) 0.05 M ferrous sulfamate in metal feed

[redacted]

3. Plutonium Studies

a. Plutonium Valence State Distribution Coefficients

The comparison of distribution coefficients for the III, IV, and VI valence states of plutonium under acid deficient Redox conditions clearly indicated that plutonium VI was necessary for extraction by hexone (see Table XIV).

Table XIV

Distribution Coefficients of the Plutonium

Valence States

(0.2 Normal Acid Deficient Aluminum Nitrate-Hexone System)

Valence State	$Al(NO_3)_3$ Molarity	D.C. (O/A)
Pu VI	0.9	1.1
"	1.1	3.3
"	1.3	7.6
"	1.5	15.5
Pu IV	1.0	1.04×10^{-2}
"	1.2	1.3×10^{-2}
"	1.4	2.3×10^{-2}
"	1.6	7.4×10^{-2}
PuIII	1.3	4.5×10^{-4}

There are no available data for plutonium V in the hexone - aluminum nitrate system, but its distribution coefficient between hexone and 5 M ammonium nitrate at pH 3 has been reported as negligible. It is probably of the same order as plutonium III since it also shows no tendency to form a nitrate complex which is involved in extraction by hexone.

b. The Absorption Spectra of the Plutonium Valence States Under Acid Deficient Redox Conditions

The determination of the valence states of plutonium in a mixture is most rapidly and easily accomplished by spectrophotometric analysis, once the individual absorption spectra for the solutions of interest are known. Therefore, preliminary to undertaking this type analysis, it is necessary to compile these spectra in 1.3 M $Al(NO_3)_3$, -0.2 N acid deficient solutions.

At this time the compilation of the curves for the four valence states is not complete, and since some discussion of these curves will be necessary, it is advisable to wait until the four spectra are available before reporting the final results.

It has been found that the absorption spectra of the various valence state of plutonium in the acid deficient Redox feed condition is not significantly different from those reported in prior work.

c. The Behavior of Plutonium VI During Extraction with Hexone - Laboratory

Laboratory experiments demonstrated that plutonium VI was reduced in the absence of an oxidizing agent in a 1.3 molar aluminum nitrate, -0.2 normal acid deficient aqueous solution saturated with hexone. However, the plutonium VI nitrate complex in the hexone phase was stable. These results point out the advisability of having an oxidant in the scrub to prevent the reduction of plutonium to the lower valence states which have very low distribution coefficients in the scrub reflux.

In order to determine the rate of disappearance of plutonium VI from the aqueous phase in presence of hexone, the following experiment was made: A feed having the composition

$Al(NO_3)_3$ - 1.3 M
Acidity - 0.2 M acid deficient
Pu VI - 0.00034 M
Hexone - sufficient to saturate the feed

was prepared by saturating the aluminum nitrate solution with hexone previous to the addition of plutonium VI. This feed was analyzed for plutonium spectrophotometrically within fifteen minutes after the addition of the plutonium. The results showed that 10% of the plutonium had disappeared in that time. Finally, the same hexone saturated aqueous phase was equilibrated with an equal

volume of steam distilled hexone for ten minutes and the phases were allowed to settle for three minutes. The change in plutonium VI concentration in the aqueous phase was followed spectrophotometrically (see Table XV).

Table XV

The Change in Plutonium VI Concentration in the Aqueous Raffinate

Total Plutonium Concentration - 0.00009 M

Time elapsed after separation of phases	% Pu VI in Raffinate
0 minutes	38
20 "	33
40 "	28.3
130 "	27.8
160 "	25.8
190 "	25.8
24 hours	24.8

d. The Oxidation of Plutonium V by Sodium Dichromate

While the products of the reaction between hexone and plutonium VI described in the previous section were not identified, the available project literature suggests that plutonium V may be present as a reduction product of plutonium VI, since plutonium V has been demonstrated to be stable in the acidity range which the modified Redox conditions propose.

In connection with the preparation of the absorption curve of plutonium V in 1.3 M $Al(NO_3)_3$, -0.2M acid deficient solution, it was possible to study the oxidation of plutonium V by 0.1 M $Na_2Cr_2O_7$ to plutonium VI (see Table XVI).

Table XVI

The Oxidation of Plutonium V in 1.3 M Aluminum Nitrate 0.2N Acid Deficient Solution by 0.1 M Sodium Dichromate to Plutonium VI

Time after addition of $Na_2Cr_2O_7$ (minutes)	% Pu VI of total Pu
0	10 (A)
23	32.5
29	34.6
34	36
39	40.5
44	40.5
49	40.5
54	43
59	44
65	44.8
75	47
85	48

(A) The feed contained approximately 10% plutonium VI and 90% plutonium V at the start of the experiment

These results agree well with those reported for the oxidation of plutonium V by dichromate in the absence of $Al(NO_3)_3$. The rate appears to level off after about 85 minutes, and it has been reported elsewhere, under similiar acidity conditions and no $Al(NO_3)_3$, that the oxidation was about 80% complete after 18 hours.

It would be interesting to investigate whether this reaction would proceed to completion more rapidly under column conditions where the plutonium VI would not build up in the aqueous phase.

4. Ruthenium Studies - Laboratory

Data were obtained which indicated that the ruthenium decontamination by solvent extraction was a direct function of the fraction of oxidizable ruthenium present in the feed solution (see Table XVII and XVIII). Similar results from Chalk River were reported at the Argonne Ruthenium Meeting (December, 1948).

Several procedures for the removal of the oxidizable ruthenium have been found to be satisfactory. After oxidation of ruthenium in a two molar uranyl nitrate - 0.3 molar nitric acid by the addition of 0.01 molar periodic acid, the oxidized ruthenium can be removed by either air sparging at elevated temperatures, or by plating on an organic surface. When oxidizable ruthenium tracer was used, removal of more than 99% of the ruthenium has been consistently obtained by these methods. However, when dissolver and pilot plant solutions were used, only 10 to 30% of ruthenium was removed, which is representative of the fraction of oxidizable ruthenium present. It remains to be determined if the ruthenium decontamination is significantly increased by the removal of the oxidizable ruthenium fraction.

Table XVII

Correlation of Ru Distribution Coefficients with Amount of Oxidizable Ruthenium in Samples Taken During Progress of Slug Dissolution

(X Slug irradiated 1200 days and cooled 80 days)

Sample	%U Diss.	% Oxid. Ru	β D. C. on Ext. (O/A)	Ru D. C. on Ext. (O/A)
A	5.3	24	0.020	0.06
B	23.5	50	0.019	0.057
C	84	29	0.0216	0.041
D	95	23	0.0175	0.031
E	100	19	0.017	0.012

Table XVIII

Comparison of the Fraction of Oxidizable Ruthenium Present in the Pilot Plant IDF with the Ruthenium Decontamination

Flowsheet Conditions	PP Run No.	% Oxidizable Ru in IDF	Ru β Decontamination Factors		
			IBP	ICU	IEU
ANL 1st. and 2nd Cycle	18	52	380	33	12.6
	15	95	150	4	3.8
ANL 1st. Cycle and ORNL 2nd Cycle	21	84	90	10	890
	19	91	200	8	250
	16	95	220	8	360

[redacted]

III. UAP Process Investigation for Hanford Metal Waste Recovery

A. Design of UAP Semi-Works

The major effort of the chemical design group during the past period was expended on the design of semi-works facilities for the investigation of two stages of precipitation for the uranyl ammonium phosphate process for the recovery of Hanford uranium wastes from the bismuth phosphate process. The process has been investigated on a laboratory scale by K-25, and a flowsheet has been proposed for investigation. Only the precipitation steps of the UAP process will be investigated at Oak Ridge National Laboratory on a semi-works scale. These facilities will be installed in the west cell bank of Building 706-HB.

1. Extent of Proposed Investigation

The UAP Semi-Works have been designed to investigate the following:

a. The precipitation of uranyl ammonium phosphate from two year old supernatant solutions from the Hanford metal waste tanks. After investigation runs on Hanford supernatant solution, solutions spiked with enough additional inactive uranium to simulate composite Hanford waste solutions will be investigated, i.e., solutions in which the sludge in the waste tanks has been dissolved.

b. The investigation will cover two cycles of UAP precipitation and the attendant recycle precipitations in accordance with K-25 flowsheets.

The following phases of the UAP process will not be investigated at Oak Ridge National Laboratory:

a. The removal of solutions from the Hanford metal waste tanks and the solution of sludge.

b. The UAP precipitation process for bismuth phosphate wastes that have been stored for less than two years.

c. The hydrofluorination and fluorination steps following the UAP precipitation steps. These studies will be made at Y-12 or K-25.

d. The concentration of the fission product, ammonium nitrate bearing filtrates from the UAP precipitation steps.

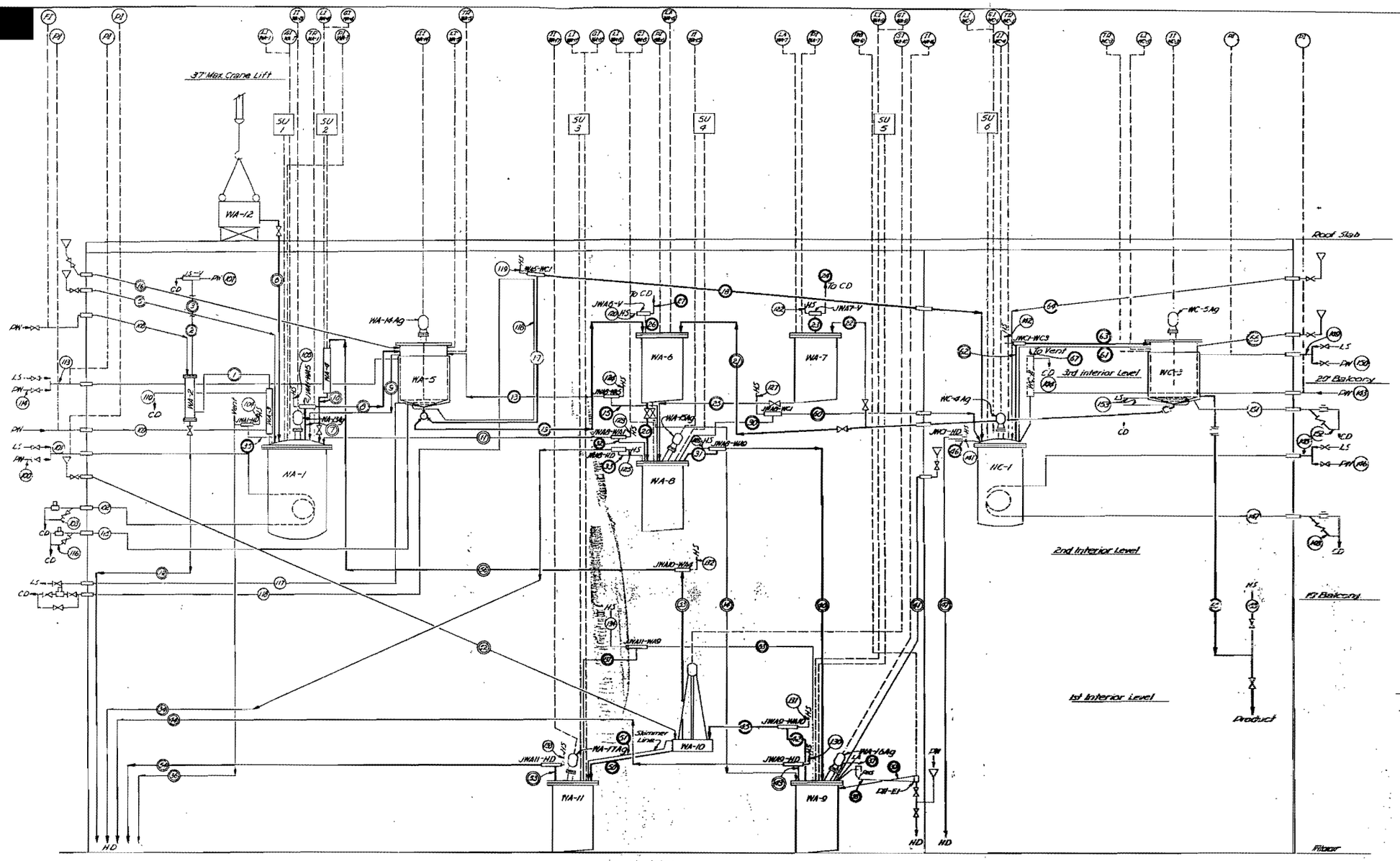
2. Equipment Flowsheet for UAP Semi-Works (See Figure 4)

The Semi-Works equipment has been designed to process a batch of approximately 50 gallons of waste solution. The solution from Hanford will be delivered in shielded vessels to Oak Ridge National Laboratory by K-25. The waste solution is to be fed to a 130 gallon stainless steel feed preparation and precipitation vessel (WA-1), where precipitation of uranyl ammonium phosphate occurs. The salted waste solution is raised to a temperature of 90°C in this vessel and cooled over a period of approximately two hours to a temperature of 25°C. Heating and cooling are accomplished by immersed stainless steel coils. During the cooling period, uranyl ammonium phosphate is crystallized out of the mother liquor. The precipitate is transferred as a slurry to the filter tank (WA-5) and the uranyl ammonium phosphate filtered on a 700 x 60 mesh stainless steel screen. The filtrate is removed from the filter by vacuum to vacuum tank WA-6, from where it drains by gravity to recycle precipitation tank WA-9. Here the residual uranium in the filtrate is precipitated as a mixed uranyl ammonium phosphate - ammonium diuranate salt, and is then fed by a jet to centrifuge WA-10. The supernatant from the centrifuge is collected in catch tank WA-11 where it is analyzed and then discharged to the hot chemical waste drain, if the uranium concentration is sufficiently low. The recycle precipitate is dissolved in nitric acid in the centrifuge bowl and transferred by jet to the recycle sampling tank WA-4, and from there to the precipitator WA-1 where it is combined with the next batch of new material.

The first precipitate collected in WA-5 is washed with 0.01N HNO_3 while on the filter medium. The wash solutions are drawn by vacuum to vacuum tank WA-6 and drained by gravity from there to WA-8 for sampling before discharge through a steam jet to the hot chemical drain.

After washing has been completed, the first precipitate is dissolved in the filter tank in just enough hot nitric acid to obtain solution. The solution is then transferred by gravity to the second cycle precipitator WC-1. Here another uranyl ammonium phosphate crystallization is performed in a manner similar to the first cycle precipitation. The precipitate and mother liquor are transferred by steam jet to the second cycle filter WC-3. The filtrate is drawn by vacuum to filter tank WA-6, from where it drains by gravity to the recycle system in a manner similar to the recycle for the first cycle. The precipitate on the filter is washed with dilute acid solution, with the washes going to vacuum tank WA-7 where they are held for possible use in the first cycle precipitate wash. The second cycle wash can be sampled in WA-8 and discharge by jet to either the hot chemical waste system or used as wash for the first cycle precipitate.

[redacted]



LEGEND

INSTRUMENT CODE

- LI ____ Liquid Level Indicator
- SI ____ Specific Gravity Indicator
- TI ____ Temperature Indicator
- TR ____ Temperature Recorder
- TC ____ Temperature Controller
- PI ____ Pressure Indicator
- LA ____ Level Alarm
- PIR ____ PH Recorder
- II ____ Current Indicator
- SI ____ Speed Indicator
- FI ____ Flow Indicator

SYMBOL & SERVICE CODE

- SU ____ Sample Unit
- ____ Funnel
- ____ Jet
- ____ Concrete Plug
- HS ____ High Steam
- LS ____ Low Steam
- HA ____ High Air
- LA ____ Low Air
- FW ____ Filtered Water
- PW ____ Process Water
- HD ____ Hot Drains
- CD ____ Cold Drains
- DW ____ Demineralized Water
- ____ Process Piping
- ____ Service Piping

NOTE:
Tanks are not at elevations shown.

Figure 4

[redacted]

APPRD.	DATE	OAK RIDGE NATIONAL LABORATORY
		706-HB BLDG. UAP PILOT PLANT EQUIPMENT FLOWSHEET
		DRAWN BY C.W. Day — DATE 6-25-48 — SCALE
		CHECKED BY R. Fish — DATE 10-14-49 — DRAWING NO. TD-833 — REV.

REV. NO. | REVISION BLOCK | APPRD. | DATE

The second cycle precipitate is slurried in water and drawn off into a vacuum pot through a line whose inlet is located at the level of the filter plate. The product receiving vessels are located outside of the cell and are used to transport the product to K-25 or Y-12 for subsequent fluorination.

All service lines and instrumentation are shown schematically on the flowsheet. Samplers are provided where shown.

3. Equipment Location and Service Piping (See Figure 5)

The arrangement of other tanks and equipment and all process piping is shown in Figure 5. The UAP Semi-Works will be installed in Cells "A" and "C" of the west cell bank of Building 706-HB.

4. Job Progress

The detailed design of the UAP Semi-Works was completed late in January. Bills of material for this job have been prepared by the Plant Engineering Department and have been transmitted to the J. A. Jones Construction Company. Construction was started on January 17, 1949 and has now progressed to the point of the installation of piping and equipment in the cells. The anticipated completion date for this project is April 11, 1949.

The estimated cost of the UAP Semi-Works, exclusive of design and Oak Ridge National Laboratory field engineering costs, is $101,000.

B. Hanford Metal Recovery - UAP Process - Laboratory

The K-25 uranyl ammonium phosphate precipitation process for the recovery of uranium from Hanford metal waste is being tested in the laboratory before the work is started in the Semi-Works. Three runs have been made on a 500 milliliter laboratory scale, using the K-25 procedure - ammonium nitrate as precipitant for the recovery of uranium as uranyl ammonium phosphate from Hanford waste metal supernatant. Two of these runs were made with cold synthetic solutions, and in the third, full activity Hanford waste metal solution was used. Average uranium losses in the first and second precipitation cycles were 3.5% and 9.1%, respectively. These losses included two washes for each precipitation. Average wash losses were 0.07%. Beta and gamma decontamination factors in the first precipitation cycle were 300 and 175, respectively, while the overall beta and gamma decontamination factors through two precipitation cycles were 2700 and 985, respectively. These values agree well with those reported by K-25 (see Table XIX).

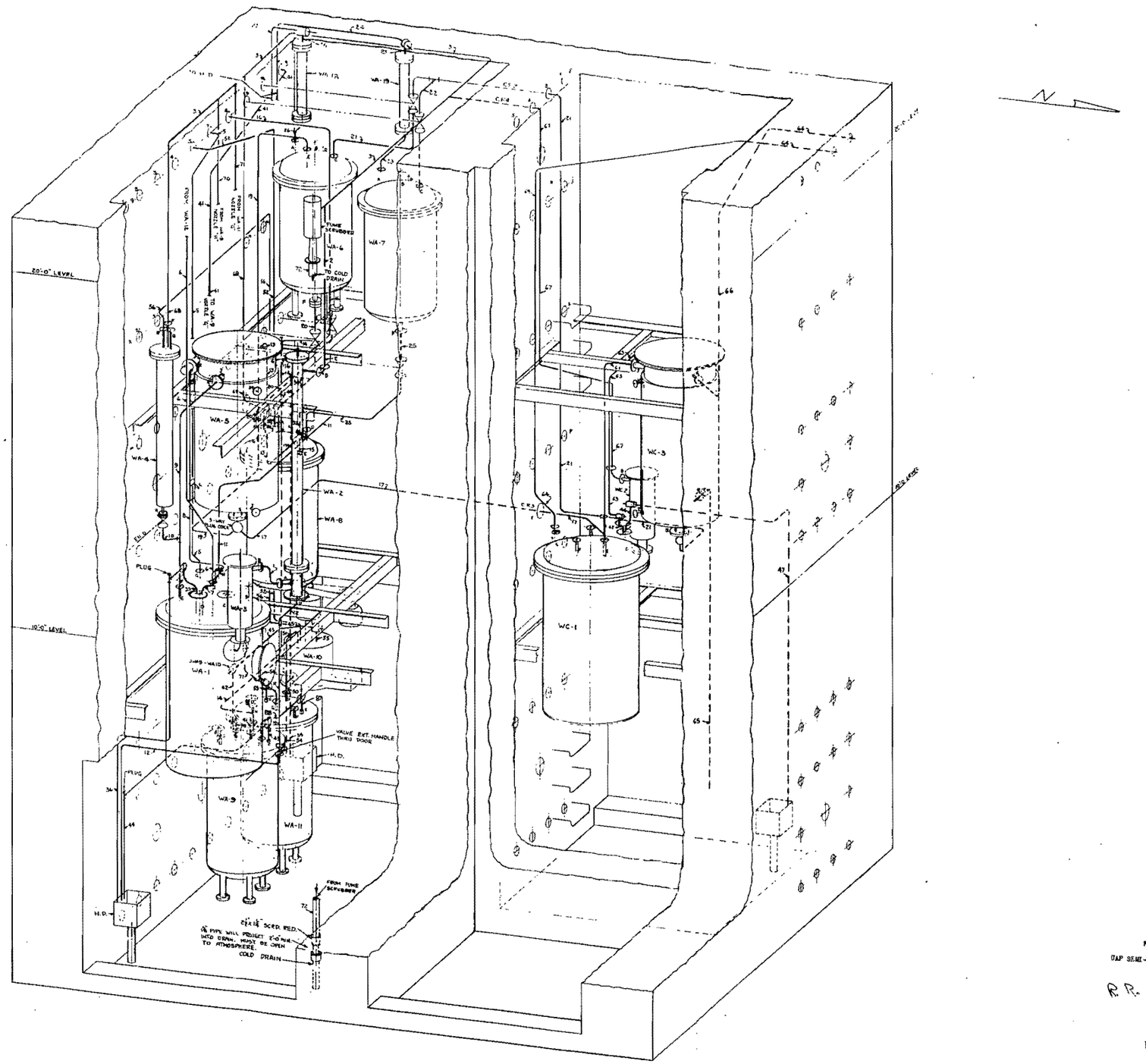


Figure 5

UAP SEMI-WORKS CELL ARRANGEMENT

R. R. Wilson

NOT CLASSIFIED

TOLERANCE UNLESS OTHERWISE SPECIFIED FRACTIONS ± 1/64 DECIMALS ± .005
BREAK ALL SHARP EDGES UNLESS OTHERWISE SPECIFIED.
FINISH MARKS ASA STANDARD.
DO NOT SCALE THIS DRAWING.

APPD.	DATE	OAK RIDGE NATIONAL LABORATORY
		TECHNICAL DIV. — P.O. BOX P — OAK RIDGE, TENN.
		706-HB BLDG. UAP PILOT PLANT PROCESS PIPING
		DRAWN BY BERRY — DATE 1-20-49 — SCALE
		CHECKED BY — DATE — DRAWING NO. 70-1075 — REV.

REV. NO.	REVISION	APPD.	DATE

It has been found that ammonium phosphates may be substituted for ammonium nitrate, resulting in a uranium loss through two precipitation cycles of about 1%, with no sacrifice of fission product decontamination (see Table XX). Preliminary data indicate 40 grams dibasic ammonium phosphate and 76 grams monobasic ammonium phosphate per liter of Hanford supernatant as minimum requirements to reduce uranium loss to 1% (see Table XXI).

Table XIX

Precipitation of Uranyl Ammonium Phosphate with Ammonium Nitrate
(K-25 Procedure)

Conditions: Starting solution 500 ml. full activity Hanford metal waste supernatant (1.85×10^7 beta c/m/ml)
(3.25×10^4 gamma c/m/ml)
(0.115 M U)

First Cycle:

(1) Hanford supernatant neutralized with HNO_3, and precipitate obtained dissolved by heating to 90°C and addition of more HNO_3.

(2) NH_4NO_3 solution added slowly to make 30 grams NH_4NO_3 per liter of starting waste solution.

(3) Mixture cooled to 25°C at rate of 1°C/min.

(4) Agitation continued 2 hours at 25°C.

(5) UAP product washed twice with 375 ml. portions of 0.01N HNO_3 and 3% NH_4NO_3.

Second Cycle:

(6) Dissolve UAP product in 285 ml. 1.5M HNO_3.

(7) Repeat steps 2 through 5.

[redacted]

Table XIX (Con't.)

Operation	Uranium Loss		Decontamination Factors	
	mg/ml	%	Beta	Gamma
First Precipitation Cycle				
Product Precipitation	0.915	3.56	11.6	8.85
1st Wash	0.024	0.07		
2nd Wash	0.009	0.025		
Overall Loss and D.F. 1st Cycle		3.65	300	175
Second Precipitation Cycle				
Product Precipitation	3.79	8.15		
1st Wash	0.09	0.25		
2nd Wash	0.004	0.011	11.4	5.2
Loss 2nd Cycle		8.41		
Overall Loss and D.F. 2nd Cycle		12.06	2700	985

UAP Product Activity: 283 beta cts/m/mg U, 1.35 gamma cts/m/mg U } uncorrected

[redacted]

[redacted]

Table XX

Precipitation of Uranyl Ammonium Phosphate with Dibasic Ammonium Phosphate

Conditions: Same as Table 1 except 40 g. $(NH_4)_2HPO_4$ instead of 30 g. NH_4NO_3 per liter of full activity Hanford supernatant waste solution

Operation	Uranium Loss		Decontamination Factor	
	mg/ml	%	Beta	Gamma
First Precipitation Cycle				
Product Precipitation	0.225	0.98	14.5	17.8
1st. Wash	0.02	0.05		
2nd. Wash	0.016	0.04		
Overall Loss and Decontamination 1st. Cycle		1.07	90	356
Second Precipitation Cycle				
Product Precipitation	0.029	0.08		
1st. Wash	0.002	0.005		
2nd. Wash	0.002	0.005		
Overall Loss and Decontamination 2nd. Cycle		0.09	32.6	3.9
Overall Loss and D.F.- 1st. and 2nd. Cycles		1.16	$2x5x10^3$	$1.3x10^3$

UAP Product activity: 1 γ ct/m/mg U uncorrected

[redacted]

[redacted]

Table XXI

Effect of the Ammonium Phosphates and Phosphoric Acid on 1st Cycle Uranyl Ammonium Phosphate Precipitation Yield

Conditions: Same as steps 1 through 5 of Table I except precipitants as listed in Columns I and IV.

Ammonium Phosphate, dibasic			Ammonium Phosphate, monobasic		
$(NH_4)_2HPO_4$/L Hanford Supernatant - grams	U in Filtrate mg/ml	U in Filtrate %	$NH_4H_2PO_4$/L Hanford Supernatant - Grams	U in Filtrate mg/ml	U in Filtrate %
10.	1.55	10.9	15.	7.31	47.8
20.	0.30	1.6	30.	1.7	11.0
30.	0.30	1.5	45.	1.28	8.5
40.	0.22	0.98	61.	0.80	5.3
20. + 73 grams H_3PO_4	1.22	7.40	76.	0.176	1.2
20. + 36 grams H_3PO_4	0.72	4.50	38. + 146 grams H_3PO_4	3.20	20.0

[redacted]

IV. Radiochemical Liquid Waste Disposal

A broad program for the concentration and retention of liquid radiochemical wastes is in progress at the Oak Ridge National Laboratory. This includes a survey of presently stored and anticipated liquid wastes and of waste handling and storage facilities. Chemical processes are being developed to remove and decontaminate the bulk non-radioactive components such as aluminum nitrate from solvent extraction and sodium nitrate from the neutralized radiochemical wastes. These processes are combinations of evaporation, ion exchange, precipitation, and crystallization.

As the result of successful operation of a pilot model evaporator, a plant scale evaporator has been designed to handle 50,000 gallons of liquid waste per week with a condensate decontamination of 10^3. This evaporator is scheduled for completion and initial operation in the latter part of April. In addition to the 30,000 to 50,000 gallons per week of anticipated plant liquid waste production, presently stored wastes will be concentrated by the evaporator. It is expected that this evaporator, together with some alterations of current flowsheets, should make presently available storage facilities adequate for from two to four years operation.

A. Liquid Waste Survey

The liquid waste survey report (ORNL-328), as reviewed in the November 30, 1948 Quarterly Report (ORNL-215), will be issued during the coming period.

B. Evaporators for Active Liquid Wastes

The design of an evaporator for radioactive chemical waste solutions has been reactivated as a result of favorable tests on the pilot model evaporator. Construction drawings for the evaporator will be completed by March 1, 1949. Construction by the J. A. Jones Company should be started immediately thereafter, and the evaporator is expected to be completed and in operation in the latter part of April.

1. Results of Pilot Model Evaporator Tests

The results of the pilot evaporator runs have been reported in ORNL-224 "Pilot Model Evaporator for Concentration of Radioactive Chemical Wastes" by S. E. Beall. These results are summarized below.

Satisfactory operation of the pilot model evaporator has indicated the following:

a. An overall heat transfer coefficient of 150 to 250 BTU/(hr)(ft^2)(°F).

b. No scaling under acid conditions, and no detectable scaling under basic conditions.

c. Evaporation rates greater than the 12.8 lbs/hr/sqft heating surface required for satisfactory operation of the plant size evaporator.

d. Decontamination factors greater than 10^3 and perhaps as high as 10^5 (exclusive of iodine).

e. The beneficial effect of vacuum on decontamination was not detectable.

The ionic composition of waste feeding the pilot evaporator during the period from 7/26/48 to 8/26/48 are given in Table XXII. Table XXIII gives the radiochemical composition of evaporator feed solutions.

Table XXII

Ionic Composition of Pilot Evaporator Waste Feeds

Analysis	Concentration - gms/liter	
	Acid Samples	Basic Samples*
U	0.88	0.026
Na	2.1	9.5
Ca	0.037	0.01
Mg	0.005	0.01
Al	0.07	0.4
Fe	0.003	0.001
Cl	0.26	0.35
F	0.005	0.005
CO_3	0.50	2.75
SO_4	0.50	0.9
PO_4	0.003	0.002
NO_3	7.9	17.7

*These samples represent averages of weekly composites.

[redacted]

TABLE XXIII

Radiochemical Analyses of Feed Solutions For Pilot Plant Evaporator

Run No.	pH	Total Solids gms/L	Disintegrations per ml per minute								
			Gross	Gross	Ru	Zr	Ce	Sr	Cs	TRE* (-Ce)	I^{131}
1 (Supernate)	9.20	17.2	1.07×10^6	0.03×10^5	0.38×10^5	0.01×10^5	0.32×10^5	0.87×10^5	4.2×10^5	0.48×10^5	3.07×10^5
1 (Sludge)	----	all	7.0×10^7	-------	0.9×10^5	0.6×10^5	19.0×10^5	3.1×10^5	0.9×10^5	21.0×10^5	neg.
2 (Supernate)	4.20	20.0	4.99×10^6	0.13×10^5	0.61×10^5	0.42×10^5	17.3×10^5	0.37×10^5	0.56×10^5	0.78×10^5	18.6×10^5
3 (Supernate)	4.10	17.6	9.66×10^6	6.0×10^5	1.10×10^5	0.23×10^5	34.0×10^5	15.0×10^5	6.94×10^5	13.7×10^5	1.95×10^5
4 (Supernate)	7.70	10.3	3.50×10^6	4.0×10^5	1.30×10^5	0.13×10^5	2.67×10^5	16.4×10^5	9.20×10^5	2.93×10^5	1.77×10^5
5 (Supernate)	7.20	10.5	3.96×10^6	9.0×10^5	0.11×10^5	0.91×10^5	2.37×10^5	12.6×10^5	1.05×10^5	3.41×10^5	0.58×10^5

* Total rare earths less cerium.

[redacted]

a. Specifications of Pilot Model Evaporator

The following describes the physical characteristics of the pilot model evaporator:

Evaporator Tank:	
Height	4 ft.
Diameter	2 ft.
Volume	100 gal.
Liquid Surface Area	3.1 sq.ft.
Heating Surface/sq.ft. Liquid Surface	5.1
Height of Heating Surface	26 in.
Height of Vapor Space	20 in.
Condenser:	
Heat Transfer Area	50 sq.ft.
Cooling Water Required ($T = 50^{o}F$)	15 gpm
Diameter Vapor Line	$3\frac{1}{2}$ in.
Velocity in Vapor Line	28 ft/sec @ 250 lb/hr.

b. Heat Transfer Coefficients

Table XXIV summarizes the heat transfer coefficients obtained in the evaporator during the period of test.

c. Decontamination

An overall decontamination on the condensate from one evaporation step was readily demonstrated on the pilot model evaporator. It should be noted that the pilot evaporator had insufficient vapor space to permit adequate entrainment settling, had no foam breaker, and had no entrainment separator. The reduction of entrainment in the large

[redacted]

TABLE XXIV

Heat Transfer Coefficients for Pilot Plant Evaporator

Run No.	Duration	Evaporator Heel	Steam Pressure	Evaporator Pressure	Final Concentration Ratio	
Water Run	2 hours	Water	20 psig	atm.		157 BTU/Hr-Ft.^{2}-°F
	2		30 "	"		175 " " " "
	2		40 "	"		192 " " " "
	2		50 "	"		188 " " " "
	2		60 "	"		215 " " " "
	2		110 "	"		235 " " " "
#1	48 hours	pH = 9.2 contained sludge	20 "	"	10:1	150 " " " "
#2	85 hours	pH = 4.2 clear supernate	20 "	"	20:1	156 " " " "
#3	86 hours	pH = 4.1 clear supernate	20 "	"	20:1	170 " " " "
#4	8	pH = 2.0	30 "	"	15:1	160 " " " "
	9	pH = 2.5	45 "	"	20:1	184 " " " "
	8	pH = 2.8	60 "	"	25:1	222 " " " "
	8	pH = 3.8	75 "	"	30:1	278 " " " "
	6	pH = 4.0	90 "	"	35:1	271 " " " "
#5	15	pH = 7.2 clear supernate	10 "	17 in Hg Vac.	5:1	141 " " " "

[redacted]

scale evaporator will be facilitated by a larger vapor space and a cyclone separator following the evaporator. Better decontamination (from contaminants carried as a mist or particles) should be attainable with the large evaporator.

The role of gaseous fission products such as iodine is shown in Table XXV, which gives the radiochemical analysis of the condensates.

These results show that it will be necessary to either complex the iodine in evaporator or to provide decay time for the iodine bearing wastes, either before evaporation or for the condensate after evaporation.

2. Design of Plant Scale Evaporator

As a result of the operation of the pilot model evaporator, several major changes have been made in the 300 gallons per hour plant scale radiochemical waste evaporator. These changes are summarized below:

1) The required area for heat transfer has been recalculated and the design of the steam coils, formerly specified as bowed tubes, has now been changed to a coil type unit.

2) Use of vacuum on the evaporator did not prove valuable on the pilot model. For this reason provisions for vacuum operation have not been made in the new evaporator design.

3) A cyclone separator will be installed on the plant evaporator to reduce entrainment. The cyclone separator has been re-designed for the conditions of atmospheric operation only.

4) Because of the lower vapor velocities possible under atmospheric operating conditions, the number of condensers has been reduced from eight to four.

5) The size of the condensate catch tank has been reduced from 2200 gallons to 300 gallons, making it possible to enclose the entire evaporator in a much smaller structure.

6) Shielding calculations for the evaporator have been made, based upon the activity anticipated from Hot Pilot Plant waste resulting from irradiated enriched 25 runs later this year.

[redacted]

TABLE XXV

Comparison of Activities in Feed Solution and in Product Condensate

FEED								CONDENSATE			
Run No.	pH	I	Sr	Ce	Cs	TRE	Ru	I	Sr	Cs	Ru
1	9.20	30%	8%	3%	40%	5%	4%	---	-not	analyzed	- -
2	4.20	35%	8%	35%	12%	16%	1%	90%	---	---	neg.
3	4.10	2%	16%	35%	7%	14%	1%	90%	---	---	neg.
4 30 psig	7.70	5%	45%	8%	26%	8%	3%	70%	30%	neg.	neg.
45 psig	(Acid heel of run no. 3 not drained)	"	"	"	"	"	"	10%	1%	10%	neg.
60 psig		"	"	"	"	"	"	30%	10%	7%	neg.
75 psig		"	"	"	"	"	"	40%	6%	10%	neg.
90 psig		"	"	"	"	"	"	65%	5%	10%	5%
5 Vacuum)	7.20	1%	31%	6%	27%	9%	1%	10%	20%	65%	6%

[redacted]

7) The structure and evaporator enclosure have been completely re-designed because of the drastic changes in overall concept.

a. Design Information

The re-design of the Waste Chemical Evaporator, using information gained from operation of the pilot model evaporator, is essentially finished and construction drawings will be soon issued.

The design basis is the atmospheric evaporation of 300 gallons per hour of radioactive waste, using 125# steam for heating with a maximum of 1/8" of scale on heat transfer surface. The predicted decontamination factor, based on pilot model results, is greater than 10^3. The evaporator is to be operated batchwise with a 20:1 concentration factor.

Additional design data is given by the following table:

Overall Heat Transfer Coefficient	U = 110 BTU/hr/sqft/°F/ft
Total Heat Transfer Area	= 185 sq.ft.
Vapor Velocity in Evaporator Tank	0.49 ft/sec
Vapor Velocity in Vapor Line to Cyclone	32.5 ft/sec
Vapor Velocity at Cyclone Entrance	50 ft/sec
Vapor Velocity Through Condenser Tubes (top)	45.9 ft/sec
Maximum Particle Diameter Leaving Evaporator	= 60.1 microns
Maximum Particle Diameter Leaving Cyclone	10 microns
Condenser Heat Transfer Area	200 sq.ft.
Number of Condensers	4

The bowed, restrained end heating tubes were abandoned when calculations revealed that the thermal shocking operation to crack off scale would stress the tubes beyond the yield point. The heat transfer surface now consists of six removable coils fabricated of 3/4" pipe. If scaling does not occur, the evaporator may be operated at greater than design capacity providing that adequate decontamination can be maintained.

The cyclone separator design incorporated features developed by the Buell Company, which should make it more effective for the small particle sizes.

The shielding design (Memo from H. E. Goeller to F. L. Culler, dated 1-26-49, "Shielding for Waste Tank Farm Evaporator" C.F. - 49-2-25) was based on evaporating the hottest anticipated wastes which will come from the Hot Pilot Plant processing of enriched 25. Three feet of concrete will be sufficient to shield the evaporator, and two feet of concrete will be sufficient to shield the remaining equipment. The building is designed so that an additional two feet of concrete blocks may be stacked as supplementary shielding in case extremely active wastes are processed.

b. Flowsheet (See Figure 6)

Contaminated chemical waste is steam jetted to the feed tank from storage tanks W-1, W-2, W-5, and W-12 and the Building 706-HB chemical waste tank. The evaporator feed then flows by gravity through a bellows sealed control valve into the evaporator. The evaporator steam coil pressure is held constant, and the liquid level in the evaporator is controlled by the feed rate. Vapor from the evaporator passes through a cyclone separator for removal of entrained material and is condensed by four parallel condensers. The condensate stream is continuously monitored to detect a dangerous activity level and flows into a condensate catch tank which is emptied at intervals by an automatic syphon to the settling basin.

Concentrate from the evaporator is drained to tank W-6 for semi-permanent storage. Off-gas for the system is furnished by a scrubber which utilizes the exit condenser water.

Appropriate instrumentation, sampling, and solution transfer facilities are provided to gain maximum flexibility.

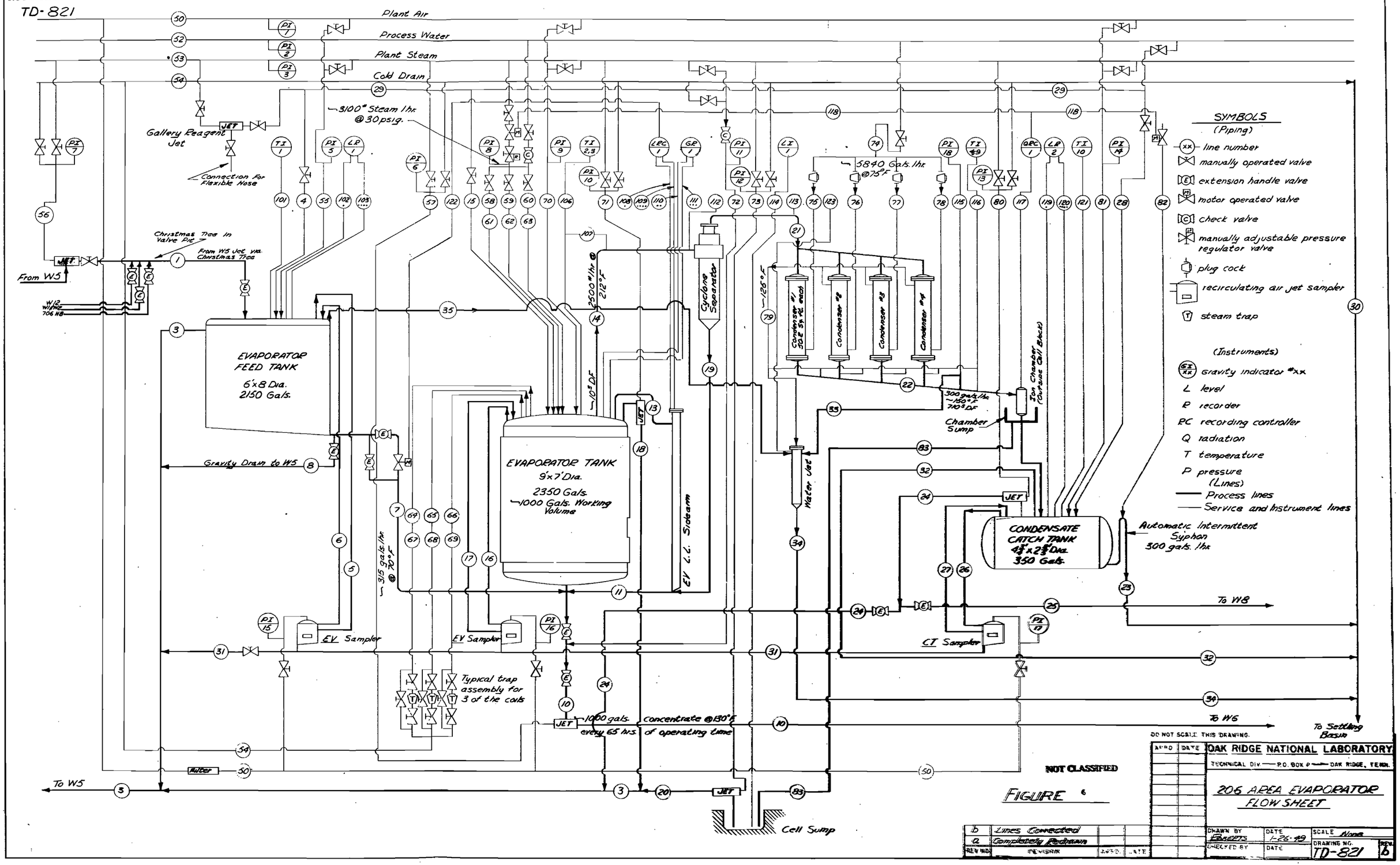
c. Equipment (See Figure 7)

Available equipment has been used wherever possible. It is hoped that an additional saving may be realized by using decontaminated flanges and piping from the burial ground.

The evaporator feed tank is a 2000 gallon, 6' high by 8' diameter, flat bottom tank of type 347 stainless steel. Modifications to this tank include installation of two additional nozzles and appropriate dip piping. The feed tank is mounted on a platform for gravity drainage to the evaporator.

NOT CLASSIFIED

TD-821



NOT CLASSIFIED

FIGURE 6

REV NO.	REMARKS	APPD.	DATE
b	Lines Connected		
a	Completely Redrawn		

APPD.	DATE

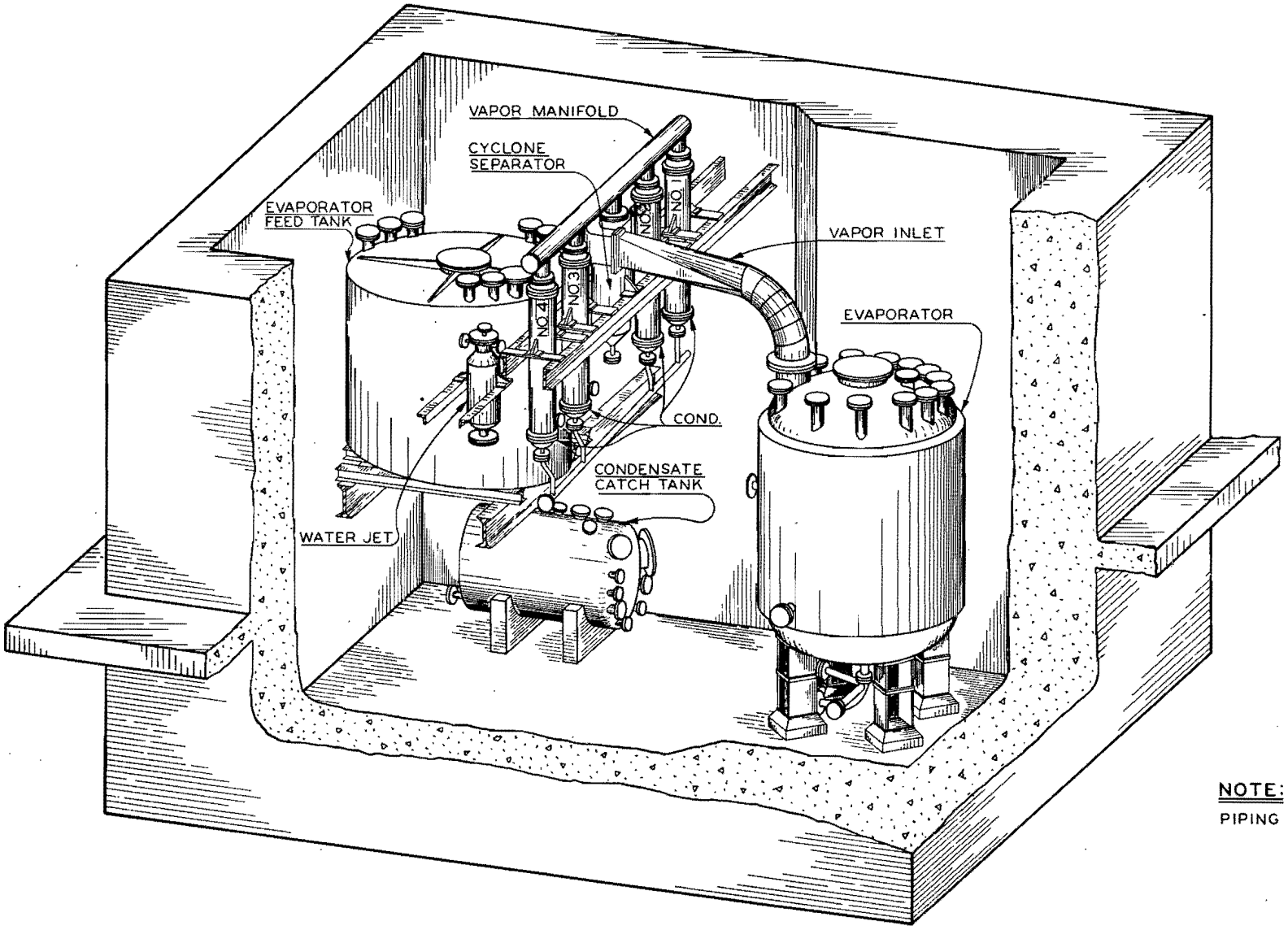
DO NOT SCALE THIS DRAWING.

OAK RIDGE NATIONAL LABORATORY

TECHNICAL DIV. — P.O. BOX P — OAK RIDGE, TENN.

206 AREA EVAPORATOR FLOW SHEET

DRAWN BY Barrett	DATE 1-26-49	SCALE None
CHECKED BY	DATE	DRAWING NO. TD-821 REV. b



NOTE:
PIPING NOT SHOWN.

RADIOCHEMICAL WASTE EVAPORATOR

FIG. 7

Drawing # 7043

NOT CLASSIFIED

The diaphragm operated feed control valve is available on the plant site. All extension handle valves are to be standard gate valves with Teflon packing.

The evaporator tank is a 2300 gallon, 1000 gallon working volume, 9' high by 7' diameter dished top and bottom, type 309 SCb stainless steel tank. Modifications for this tank include installation of three additional nozzles, steam coil guides, and appropriate dip piping. The heating surface will consist of six removable helical coils fabricated of type 309 SCb pipe.

The 10" diameter vapor line, the 13" diameter by 5' - 10" high cyclone separator, and the condenser manifold are to be fabricated of type 347 stainless steel.

The four condensers have type 347 stainless steel tubes with a black iron shell and have forty-four 6' by 3/4" O.D. by 18 gauge tubes in each. Both the cyclone and the condensers are mounted vertically.

The condensate catch tank is a 350 gallon, 43" diameter x 57", dished end type 347 stainless steel tank mounted horizontally on concrete piers under the feed tank. Five additional nozzles and appropriate dip piping are to be added to the tank.

The 12" diameter by 4' high wall-mounted water jet-scrubber is to be fabricated of type 347 stainless steel.

The sampling facilities for the process consists of a three-compartment, shielded, sliding door blister. Standard CL#5 air jets are to be used in recirculating samplers.

d. Instrumentation

Liquid level for the evaporator feed tank and the condensate catch tank is to be recorded on a two pen Taylor Recorder.

The evaporator liquid level is to be recorded and controlled by a two pen Taylor Fulscope Recorder-Controller. The other pen on the Fulscope will record evaporator specific gravity.

Manometers are to be provided to measure the cell sump liquid level and the off-gas vacuum.

The condensate stream monitor will consist of a modified Geiger-Mueller tube detecting and amplifying unit, a Brown "Electronik" recorder, and a device to shut off the evaporator stream supply and stop the condensate tank syphon in case of a sudden rise in activity level.

The instruments will be mounted on a small panelboard in the operating gallery.

Pressure gauges for the system will be mounted on the service piping.

e. Building (See Figure 7)

The external dimensions of the evaporator cell are 28' long by 14' wide by 18' deep. The cell extends 8' above the gallery floor which is about three feet above ground level. Three feet of concrete will shield the evaporator section, and two feet will shield the remainder of the cell. The roof will consist of one foot thick concrete slabs which are available in the Oak Ridge National Laboratory burial ground. Space is provided for stacking concrete blocks if additional shielding is needed. External pits are provided for the manifolded feed system and for the condensate monitoring device. Piping into the cell is to be case in the wall.

The enclosed operating gallery is 8' wide and extends the full length of the east side of the building.

C. Alterations to the Waste Disposal System

At the request of the Operations Division, alterations and additions to the liquid waste disposal systems and to the waste tank system are being studied. These alterations will be designed to accomplish the following:

1) Separate the waste metal disposal and storage system completely from the hot chemical waste system.

2) Remove non-active sources of liquid waste from the hot chemical waste system.

3) Provide individual metal solution (i.e. solutions containing uranium, thorium, or plutonium) collection tanks for those buidings that are not already so equipped.

4) Provide individual radioactive chemical waste tanks for each building that produces this type of waste.

5) Integrate the new hot chemical waste system with the chemical waste evaporator.

This project is now in the study stage; a preliminary design and cost estimate will be completed during the next period.

D. Aluminum Nitrate Decontamination - Laboratory

1. Crystallization Process

A laboratory investigation of the recovery and decontamination of aluminum nitrate from Redox or "25" wastes by recrystallization from 85 percent nitric acid has been completed. This method (first reported by Knolls Atomic Laboratory) is to be investigated further on a larger scale at that laboratory. The results show that the aluminum recovered from a 2.4 molar aluminum nitrate solution (3×10^6 beta cts/min/ml, "X" activity) may be decontaminated by factors of 10^4, approximately 700, and 10^4 for beta, gamma, and plutonium, respectively, in a two cycle process with equally good decontamination for all major fission products with the possible exception of columbium (see Table XXVI). Decontamination of columbium is lower by a factor of 6 to 10 than for the other fission products. A radiochemical analysis of a product aluminum solution showed 40% and 47% of the gross beta counts to be columbium and ruthenium, respectively (see Table XXVII). Theoretically, an aluminum yield of about 98% is possible (calculated from the solubility of aluminum nitrate in nitric acid). The aluminum yields for a two cycle process were found to be a maximum of 95 percent. This included a step to recover the aluminum from the filtrate and wash solutions, after concentrating them by evaporation, by recrystallization from 85 percent nitric acid. The accuracy of the aluminum yields are in some doubt as a result of poor material balances.

A run was made under the conditions listed above in which the feed contained potassium dichromate in order to simulate Redox raffinate. The results for one cycle were 90% aluminum yield and beta and gamma decontamination factors of 924 and 205, respectively. About 64 percent of the chromium was found in the filtrate, however, so that the volume reduction of the filtrate by evaporation will be limited.

[redacted]

Table XXVI

Recovery and Decontamination of $Al(NO_3)_3$ by Crystallization from 85% HNO_3

Notes:

*Accuracy of cts. in question.
(a) Yields reported = 100% - 1% Al loss in washes+filtrate.
(b) ( ) = actual yields.

Conditions: Recrystallization: 85% HNO_3, 25°C (1st and 2nd Cycle) (by addition of 98% HNO_3)

Washing: 3 washes, each approximately equal to volume of crystals

Recovery from wash + filtrate: Solution boiled down to approx. Al concentration of original solution. $Al(NO_3)_3$ recovered as above.

Molarity of Al In Starting Solution Al:	2.0					2.4				
	Yield %	Loss %		Decontamination Factors		Yield %	Loss %		Decontamination Factors	
		Filt.	Wash	Beta	Gamma		Filt.	Wash	Beta	Gamma
1st Cycle	92.8(a) (86.2)(b)	4.71	2.43	582	160	95.3 (87.8)	3.03	1.68	173	135
1st Cycle Recovery	50.0 (20.9)	43.1	6.8			36.0 (14.5)	51.5	12.5		
Overall 1st Cycle	96.4			342	69	97.0			158	99.4
2nd Cycle	92.9 (83.1)	5.04	2.1	82.8	5.76	91.3 (87.9)	6.74	1.9	88	10.3
2nd Cycle Recovery	86.7 (59.4)	8.7	4.6			57.1 (17.4)	36.6	6.3		
Overall 2nd Cycle	99.0			67.9	1.4	94.7			76	6.9
Total (1st & 2nd Cycle)	95.5			2.3×10^4	95.9*	ca.92			1.2×10^4	ca.700

Table XXVII

Individual Fission Product Decontamination After Recrystallization of $Al(NO_3)_3$ from 80% HNO_3

Conditions: Recrystallization: 2 cycles, 80% HNO_3, at 25°C
2.0M Al in original feed.

Washing: 3 washes, 80% HNO_3 each approximately equal to volume of crystals.

Spike: dissolver solution

Al yield for 2 cycles 75%
Gross Beta D.F. = 8.4×10^4
Gross Gamma D.F. = 760

Fission Products	Beta cts/min/ml	Decontamination Factor
Gross	100	-
Ru	47	3.7×10^3
Cb	40	420
Pu	1	2.0×10^4

Note: 47% of final beta activity is Ru.

40% of final beta activity is Cb.

2. Ion Exchange Process

The flowsheet for decontamination and recovery of aluminum nitrate from "25" or Redox wastes by ion exchange, presented in the quarterly report ending November 30, 1948 (ORNL-215), has been revised to include more recent developments (see Figure 8). In the old process, the plutonium decontamination factor was not higher than 2 although the beta, gamma decontamination factors were 10^3. Further development has shown that a plutonium decontamination factor of 5000 can be obtained by the use of an additional "break through" ion exchange column, prior to the aluminum adsorption column (see Table XXVII).

In this process, the filtrate from the scavenging step is acidified with nitric acid and reduced with hydroxylamine and passed through the "break through" ion exchange column. The Pu^{+3} is held very strongly while the aluminum, after saturating the resin, breaks through. The effluent is then passed into the next column for beta, gamma decontamination. It has been calculated that 20 times the amount of aluminum held on the resin can be passed through the "break through" column before the plutonium will break through, corresponding to an aluminum yield of 95.4%. Experiments have shown that in order to obtain quantitative reduction of plutonium, the reduction must be carried out under acid conditions.

[redacted]

Figure 8

ALUMINUM DECONTAMINATION FLOWSHEET - ION EXCHANGE

Secret Drawing No. 6659

FEED:
Simulated "25" or "Redox" Raffinate
Ca.1.0M $Al(NO_3)_3$
Gross $\beta=3.6\times10^6$ cts./min./ml.
" $\gamma=5.0\times10^3$ cts./min./ml.
" $\alpha=8.1\times10^3$ cts./min./ml.
Composition of β-activity:
Ru=4.6% Cs=3.6%
Zr=5.7% Sr=9.6%
Cb=0.7% T.R.E.=75.0%
Volume=0.7 Liter pH ca. 2.0
Add 0.7 Liter H_2O

Step I
SCAVENGING PRECIPITATION:
0.01% Fe^{+3} as $Fe_2O_3 \cdot nH_2O$
0.01% Mn^{+4} as $MnO_2 \cdot nH_2O$
Filter or Centrifuge:
Gross β D.F.=1-1.5
" γ D.F.=7-13

TREATMENT OF FILTRATE:
Alternate I: β and γ Decontamination Only
Add 5.6 Liters H_2O
Alternate II: β, γ and Pu Decontamination
Make 0.1M Hydroxylamine
0.1M HNO_3
Let stand 24 hours.
Add 5.6 Liters H_2O.

FILTER CAKE:
Dissolve in a minimum of HNO_3 - H_2O_2
97 % Of total Ru
Ca.99.5% " " Zr
Ca. 90 % " " Cb
Volume = Ca. 1 ml.

Step IA
PRE-COLUMN DOWEX-"50"Resin
Pu/α D.F.=5000
Al Yield for a large volume of feed=97.7%

Make 0.016M Oxalic Acid

Step II
WASH SOLUTION:
0.016M Oxalic Acid
Volume=2.0 Liters

Step III
ELUTING AGENT:
0.4M Oxalic Acid
Volume=7.6 Liters

Step IV
REACTIVATION BACKWASH:
6N HNO_3
Volume=5.0 Liters
RINSE:
Deionized H_2O
Volume=2.0 Liters

Step V
OXIDIZING AGENT:
70% Nitric Acid

DOWEX-"50" RESIN BED
Resin Mesh =100-200
Diam. Glass Column =1.5 in.
Ht. " " =4.0 ft.
Vol. Wet Resin =1.0 liter
1 Free Column Volume =0.5 Liter
Temperature =25°C.
Resin initially in H^+ Form
95% Resin saturated with Al.

EVAPORATOR:
Oxalic Acid Recovery by Sublimation
Decomposition of Aluminum Oxalate Residue.

Recovered Oxalic Acid

EVAPORATOR

RESIDUE:
For "Hot" Liquid Storage:
1- 3 % Of total Al
60-99 % " " β
Ca. 15 % " " γ
Ca. 10-40 % " " Pu
99.9% " " Cs
3.0% " " Ru
0.4% " " Zr
Ca. 10.0% " " Cb
99.99% " " T.R.E
Volume=7-21 ml.

CONDENSATE:
Decontamination Factors=Ca. 10^4
Volume= Ca.23 Liters

PRODUCT: *
Aluminum Yield=97-99%
Decontamination Factors:
Gross β and $\gamma=10^3$
" Pu=Ca.1.5
Cs=3×10^3
Ru=600-1000
Zr=3×10^3
Cb=500-1000
Sr and T.R.E.=10^4

This Drawing Classified As Secret
For R. E. Blanco-J.R.Higgins
2/7/49

* Disposition Of Aluminum Product:
(1) Reused as $Al(NO_3)_3$ salting agent in "25" or "Redox" processes.
(2) Store as solid $Al_2O_3 \cdot nH_2O$ (20-40 ml.)
(3) Permanent disposal if adequate decontamination can be obtained.

Note: Numerical values in tables are for β-γ process only. Use of oxalic acid elutriant at pH 2.5 results in a γD.F. of 10^4 and Al yield of 96%.

[redacted]

[redacted]

Table XXVIII

Plutonium Decontamination by the "Break-Through" Method

Conditions: Temperature = 25°C
Flow Rate = 0.5 ml/min/cm^2

Resin: Dowex - "50"
Mesh = 60-80
Volume = 30 cc (wet)
Capacity for Al^{+3} = 613 mg or 227 ml 0.1M Al

$$\text{Al Yield} = \frac{\text{Gms. Al in Effluent}}{\text{Gms. Al in Feed}}$$

Note: (Pu break-through had not occurred when these runs were discontainued.)

Feed: Run 1 - "25" raffinate previously scavenged with $Fe_2O_3.nH_2O$ and $MnO_2.nH_2O$, diluted 10 times to 0.1M Al.

Runs 2 and 3 - Unscavenged "25" raffinate diluted to 0.1M Al, then reduced with hydroxylamine over a 24 hour period.

Run 4 - "25" feed made 0.05 M $K_2Cr_2O_7$ to simulate "Redox" raffinate; reduction made before dilution to 0.1M Al.

Run 5 - Pu tracer reduced in 10 ml volume, before dilution to 1 liter with 0.1M Al.

Run 6 - Same as 4, except Pu tracer used, and no $K_2Cr_2O_7$.

Run 7 - Same as 6, with no acid.

Run No.	Reduction Conditions: Acidity	Reduction Conditions: Concentration of Hydroxylamine	Pu Alpha cts/min/ml in Diluted Feed	Al Yield %	Overall Average Pu D.F.
1	pH = Ca. 2.5	0	*946	91.5	3.5
2	"	0.01 M	*1146	86	53
3	"	0.10 M	1146	76	48
4	1.0 M HNO_3	1.00 M	634	92	158
5	"	1.00 M	9.7×10^4	75.5	1000
6	0.1 M HNO_3	0.10 M	9.9×10^4	88.5	5824
7	pH = 2.5	0.10 M	9.7×10^4	ca.88.5	ca.4292

* Run 1 - Pu^{+3} = 4,425 cts/min/ml; Pu^{+6} = 2636 cts/min/ml
Run 2 - Pu^{+3} = 1,038 cts/min/ml; Pu^{+6} = 126 cts/min/ml

E. Sodium Nitrate Decontamination by Crystallization - Laboratory

Scouting runs have been made to determine the feasibility of obtaining further volume reduction of the Oak Ridge National Laboratory radiochemical wastes after evaporation by removal of the sodium salt by crystallization. By four successive crystallizations of sodium nitrate from a 70% nitric acid solution, a decontamination of 2.5×10^4 was obtained, with a 3% loss of salt in the mother liquor. The volume of the final mother liquor is kept small by using a minimum of 70% nitric acid during the crystallization and for washing. Further volume reduction and increased salt yield is obtained by fuming the nitric acid from the mother liquor. The decontaminated nitric acid can be recycled and the fission products stored in a very small volume. Semi-works equipment is being installed for remote control crystallization of about ten liter batches of concentrated W-6 solution. To prevent clogging of the filter and carry over of contamination, it is necessary to make a sodium hydroxide precipitation of the W-6 concentrate to remove insoluble material.

F. Evaporation Studies - Laboratory and Semi-Works

The major process features in evaporation of plant waste have been studied in a laboratory evaporator (300 ml) and a semi-works (2400 ml) evaporator, with the following principal conclusions:

1) Condensate to pot solution decontamination factors in excess of 10,000 were obtained consistently, without special entrainment separators, using basic (pH 9) feed solution.

2) No scaling of steam coil was observed.

3) All samples of plant waste foamed severely at pH 8-10.

4) Foaming is reduced but the decontamination is also lowered by decreasing the pH from 10 to 2 or 3, with nitric acid.

5) Foam was effectively broken by maintaining liquid level at midpoint of vertical steam tube coil. Foam bubbles were then broken in passing over the upper portion of the coil.

[redacted]

V. 25 Separations Design and Development

A. Design Progress

The design of the 1200 Area for the recovery and decontamination of enriched uranium from the Development Reactor has been inactive during the past three months.

B. Pilot Plant Development

No further experimental manpower has been expended by the Pilot plant group on this problem in the past period because of the plant's having been converted to Redox work. A summary report covering all experimental work since issuance of ORNL-109 and up to the Redox conversion, is being compiled and is scheduled for issuance during the coming period.

The 25 aluminum alloy being irradiated at Hanford for process verification has had the irradiation time extended, to permit a higher fission product-to-uranium ratio, and to obtain a decay time that will more closely approximate actual 1200 area conditions.

VI. 23 Separations Semi-Works Design

The design of the 1300 Product Semi-Works, to be installed in Building 706-HB, is now essentially complete. Almost all purchase orders have been filled, with the exception of one level alarm instrument and most of the bellows seal valves. Final purchase of necessary pipe for this job will be made after a complete bill of materials has been prepared.

Fabrication of all except three tanks has been completed. Panelboard fabrication has been started, and structural alterations in the Building 706-HB cells, are complete. It is now planned to have the J. A. Jones Construction Company complete the installation of this project.

VII. Unit Process Development

A. Dynamic Ion Exchange Column Study

Development work is proceeding on a dynamic ion exchange column. In such a column the resin is allowed to drop counter-current to the liquid feed, in a manner similar to column solvent extraction. Preliminary runs, using resin sized by water flotation to 20 to 50 micron diameter distribution, resulted in Al losses of 0.7% to 6% for a column one meter in height. Apparatus is being prepared to measure and control the rate of resin slurry feed more accurately. It has been found advantageous to have the diameter

[redacted]

of the water wash section at the bottom of the column only one-half the diameter of the adsorption section, so that the velocity of the wash water will be fast enough to prevent the higher density aluminum solution from sinking through the wash.

A series of batch equilibrations has shown that the aluminum distribution coefficient between liquid and resin will vary by a factor of 1000 between the top and the bottom of the column (see Table XXIX).

The distribution coefficients of the fission products in this system indicate a good possibility of separating ruthenium and cesium from aluminum by the use of one dynamic column. (see Table XXX) The aluminum would then be separated from the other fission products by oxalate elution in a succeeding dynamic column.

TABLE XXIX

Batch Tests for Determination of Expected Equilibrium Distribution Coefficients

At the Top and Bottom of a Dynamic Resin Column

Conditions: Temperature - 25° C

Absorbate: Reagent $Al(NO_3)_3$

Distribution Coefficient = $\frac{\text{mg. Al/ml. supernatant}}{\text{mg. Al/ml. wet resin}}$

Resin: Dowex - "50"
Mesh - 250-300
In H^+ form at beginning of batches 1A and 2.
In Al^{+3} form at beginning of batch 1B; resin from 1A used in 1B.

Batch Number	Volume Wet Resin (ml.)	Volume and Concentration of Al Absorbate	Shaking Time (Hours)	Mg./ml. Al in Supernatant	mg.Al/ml. wet Resin	Distribution Coefficient
1 A	13	67 ml. 1.0 M Al^{+3}	1	23.40	13.35	1.82
1 B	13	100 mg. 0.1 M Al^{+3}	2	3.78	6.81	0.56 (at bottom of column)
2	8.5	66 ml. 0.1 mg/ml Al^{+3} 0.3 N HNO_3	1	.0005	.841	0.0006 (at top of column)

TABLE XXX

Distribution Coefficients of Fission Products

Between "25" Raffinate and the Al form of Dowex 50

Conditions: 7 ml. of Dowex 50 resin which had been saturated with Al was shaken for one hour with 25 ml. of 0.1 M Al "25" raffinate

$$\text{Distribution Coefficient} = \frac{\beta \text{ cts/ml. solution}}{\beta \text{ cts/ml. wet resin}}$$

Fission Product	Distribution Coefficient
Ru	0.32
Zr	4.5×10^{-3}
Cb	0.25
Cs	0.1
Sr	4.6×10^{-2}
TRE	1.6×10^{-3}
Pu	5.1×10^{-2}

VIII. Equipment Development

A. Pilot Plant Samples

The usual air jet actuated recirculating samplers being used in the pilot plant have required modification. Sampling of dense, near-saturated solutions has been found to cause the air jet to cease to operate because of crystallization in the jet throat when the recirculating solutions are passed through the jet. Some of the pilot plant jets sampling active and near-saturated solutions have been modified by installing a liquid-air cyclone separator between the sample tube and the jet suction to eliminate drawing the process solutions through the jet. This modification has greatly reduced jet pluggings, but additional modifications are required to refine this alteration and to provide for more adequate shielding.

IX. RaLa Process Design Studies

At the request of the Operations Division the Technical Division has undertaken a study of the RaLa (radioactive lanthanum) production process and operating facilities located in Building 706-D. The purposes of this investigation are:

1. To improve the efficiency of the process by improving design of specific equipment pieces.
2. To investigate equipment capacity and make recommendations for increasing RaLa batch sizes to 10,000 curies.
3. To improve general cell conditions from the standpoints of reduction in air-borne radiation hazard and ease of operation.

X. Personnel

The chart, Table XXXI, lists the personnel whose work is represented by the material in this report.

Table XXXI

Technical Division Personnel
as of March 1, 1949

M. D. Peterson, Director

- W. M. Hawkins, Assistant Director - Administration
- F. L. Steahly, Associate Director - Chemical Development
  - F. L. Steahly, Chief, Section I - Chemical Process Development
  - D. G. Reid, Chief, Section VI - Pilot Plants
- J. A. Lane, Associate Director - Design and Pile Coordination
  - W. R. Gall, Chief, Section III - Design
  - A. D. Mackintosh - Architect
- C. E. Winters, Associate Director - Engineering Research & Development
  - C. B. Graham, Chief, Section II - Engineering Development
  - F. Kerze, Chief, Section IV - Engineering Materials
  - R. N. Lyon, Chief, Section V - Engineering Materials

Personnel	Monthly		Weekly		Hourly		Total
Administration		7		5		0	12
Chem. Proc. Dev.	23		30		1		
Pilot Plants	11		2		25		
Chemical Development		34		32		26	92
Design & Pile Coordination		22		8		0	30
Eng. Dev.	11		8		0		
Eng. Mat'l.	17		10		0		
Eng. Research	5		3		0		
Engineering Res. & Dev.		33		21		0	54
Totals: (3-1-49)		96		66		26	188

M. D. Peterson, Director
- W. M. Hawkins, Assistant Director - Administration
  - Technical Division Library
  - F. A. Kocur, Assistant to Director - Projects & Safety
  - C. F. West, Jr., Administrative Assistant - Procurement and Maintenance

Louise Bond*, Secretary
Jeanne Doran, Secretary
Evelyn W. Dicks, Clerk
Eunice Greenway*, Secretary

Virgil Reynolds, Clerk
Eunice Greenway*, Secretary

- F. L. Steahly*, Associate Director - Chem. Process Development
  - F. L. Steahly*, Chief, Section I - Chem. Process Development
    - C. W. Schersten, Assistant to Chief, Administration
    - W. K. Eister, Assistant Chief - Semi-Works
    - F. R. Bruce, Laboratory Supervisor
      - W. B. Lanham, Group Leader - Redox
        - A. T. Gresky
        - L. E. Morse
      - Special Assignment Group
        - R. E. Blanco - Pro. Waste Treatment
        - Arlene Kibbey
        - C. V. Ellison - Metal Recovery
        - J. W. Gost - Air Decontamination
        - R. E. Leuze - Dry Fluoride
        - D. C. Overholt - Metal Recovery
        - T. C. Runion - Ruthenium & Section Reports
    - J. O. Davis, Semi-Works Supervisor
      - A. C. Jealous, Assistant Semi-Works Supervisor
      - E. O. Nurmi - 25 and Redox Reports
      - I. R. Higgins, Group Leader - Process Waste Treatment
        - W. H. Lewis

June Hale, Secretary
Agnes Hair, Secretary

Jean Schaich, Secretary

Technicians

G. C. Blalock, L. A. Byrd, H. B. Graham, A. B. Green, W. B. Howerton, E. R. Johns, C. F. Keck, R. C. Lovelace

Technicians

J. W. Clark, J. L. Bamberg, J. M. DeLozier, V. L. Fowler, ~~Vannessa Rowe~~, R. B. Quincy, H. F. Soard

Technicians

J. B. Goodman, W. H. Luster, D. B. Masters, W. E. Shockley

* Dual Capacity

J. B. Ruch, Group Leader - Metal Recovery
C. D. Hylton
W. A. Horne

Technicians

G. B. Dinsmore
G. R. Guinn
T. D. Napier
R. O. Payne
F. L. Rogers
J. C. Rose

C. D. Watson, Group Leader - Semi-Works Design
G. A. West

Technicians

J. E. Farmer
Guy Jones, Jr.

(Hourly) A. Johnson, Janitress

C. E. Winters, Associate Director - Engineering Research & Development

Louise Bond*, Secretary

C. B. Graham, Chief, Section II - Engineering Development

Thelma Sutton, Secretary
Gladys Darnell*, Secretary

S. E. Beall, Group Leader - Control Elements
T. H. Mauney - Magnets
J. W. Hill

A. L. Davis, Tech.
J. J. Hairston, Tech.

James Reed, Group Leader - Flow Corrosion
W. K. Stromquist, Group Leader - Fluid Flow
R. VanWinkle, Group Leader - Scale Formation & Water Treatment

G. H. Johnstone, Tech.
C. M. Burchell, Tech.
W. B. Krick, Tech.

C. P. Coughlen, Group Leader - Dust Collection Measurements
H. C. Savage
Irving Spiewak
R. H. Wilson

R. Smith, Tech.

J. A. Lane, Associate Director - Design and Reactor Coordination

Wanda Jones*, Secretary

R. B. Briggs - Special Assignment
J. C. Carter - Special Assignment
A. D. Mackintosh - Architect

W. R. Gall, Chief, Section III - Design

Wanda Jones*, Secretary
Mildred Waller, Typist
Lucille Kuykendall, Clerk

R. M. Jones*, Associate Section Chief
F. L. Culler, Group Leader - Chemical Process Design

F. N. Browder - Liquid Waste
H. E. Goeller - RaLa, UAP
R. J. Klotzbach - 1300 Area
F. C. McCullough - Particle Problem
[illegible] P. Milford - UAP
[illegible] G. Stockdale - Air Contamination
[illegible] E. Unger - UAP, RaLa
[illegible] A. Vaughan - UAP, RaLa

R. M. Jones*, Group Leader - Mechanical Design
(Development Reactor and Mock-up)

J. P. Gill
D. J. Mallon
J. R. McWherter
W. L. Scott
C. L. Segasser
W. E. Sholl, Jr.
T. H. Thomas
F. C. Zapp

Draftsmen

(Chief) H. L. Watts
C. W. Day
R. C. Ellerbe
A. S. Ludlow
J. E. Roberts

C. E. Winters, Associate Director - Engineering Research & Development

F. Kerze, Chief, Section IV - Engineering Materials

Ruby Bullard, Secretary
Gladys Darnell*, Secretary

E. C. Miller, Assistant Section Chief
C. D. Smith, Group Leader, Rolling Mill
G. M. Adamson (Reduction and Melting)
H. J. Wallace

F. M. Blacksher, Tech.
C. F. Cutcher, Tech.
T. W. Fulton, Tech.

F. W. Drosten, Group Leader - Fabrication

G. E. Cooley, Tech.
J. N. Hix, Tech.

Individual Assignments
G. M. Carlton - Metallography
J. E. Cunningham - Beryllium and Thorium
J. T. Howe - Inspection, Design, and Maintenance

J. L. English, Group Leader - Laboratory Corrosion
A. R. Olsen
S. H. Wheeler

R. N. Tench, Tech.

T. Rockwell, Group Leader - Shielding
C. E. Clifford
J. D. Flynn
R. B. Gallaher
V. L. McKinney

V. L. DiRito, Tech.
W. Q. Hullings, Tech.
D. J. Kirby, Tech.

R. B. Krum, Shielding Program, on loan from Navy Dept.
J. D. Averback, Shielding Program, on loan from NEPA.
H. P. Sleeper, Shielding Program, on loan from KAPL.

* Dual Capacity

R. N. Lyon, Chief, Section V - Engineering Research

- R. N. Lyon - Heat Transfer
- O. Sisman, Group Leader - Radiation & Stability of Materials
  - C. D. Bopp
- A. S. Kitzes - Coolant Problem
- W. S. Farmer - Solvent Extraction

M. Richardson, Tech.
W. K. Kirkland, Tech.
R. L. Towns, Tech.

F. L. Steahly*, Associate Director - Chemical Process Development

- D. G. Reid, Chief, Section VI - Pilot Plants
  - A. M. Rom, Supervisor - 25 Process Data
  - H. K. Jackson, Supervisor - Redox Process Data
    - D. E. Ferguson
  - N. J. Rigstad, Chief Supervisor - Pilot Plants
    - G. S. Sadowski, Senior Supervisor (Days)
    - E. C. Stewart, Senior Supervisor (A)
    - E. M. Shank, Senior Supervisor (B)
    - F. E. Harrington, Senior Supervisor (C)
    - K. K. Kennedy, Senior Supervisor (D)

Phyllis Ann Davis, Secretary
R. B. Waters, Draftsman

Operators

L. L. Fairchild, Chief (Patrol & 807)

T. R. McLellan, Chief
R. F. Benson
R. M. Burnett
J. F. Lockmiller
D. E. Spangler
C. H. Jones

W. E. Ledbetter, Chief
N. L. Beeler
W. Jennings
D. H. Summers
H. R. Thomas
R. E. Purkey

E. E. Shields, Chief, Acting
H. S. Caldwell
J. F. Land
B. J. Strader
J. T. Wiggins
R. C. Shipwash

H. L. Sexton, Chief
G. O. Davis
C. A. Gifford
J. H. Groover
H. C. Thompson
F. M. Grizzell

George W. Pomeroy, Hanford Trainee

E. L. Nicholson, (on loan to Design Section for Evaporator)

* Dual Capacity

Transferred Out, Terminated, or Extended Leave of Absence:

W. H. Carr, Chemical Engineer, Section VI
Dave Nicoll, Mechanical Engineer, Section III
Juanita Kennedy, Secretary, Section VI
Stuart McIain, Associate Director, Administration
C. A. Clark, Technician, Section I
Eleanor Pippin, Secretary, Administration