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ORNL 624
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PILOT PLANTS SECTION REPORT FOR JANUARY, 1950

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Chemistry-Separation
Processes for Plutonium
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CHEMICAL TECHNOLOGY DIVISION

PILOT PLANTS SECTION REPORT FOR JANUARY, 1950

D. G. Reid

Date Issued: APR 10 1950

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0.0 ABSTRACT

The monthly report for the Pilot Plants Section of the ORNL Chemical Technology Division covering the development of the U-233, Pu recovery, Radiochemical Waste Disposal, CR Separations, Waste Uranium Recovery, and U-235 processes for the month of January, 1950 is presented. The data and progress represented includes:

1. The first six U^{233}/thorium separations processings in which the "23" product was satisfactorily decontaminated and recovered to yield a total of 75 grams of 98.5% isotopic pure U^{233}.
2. Presentation of data obtained during the recovery of the off standard plutonium stream from the Redox development work, now 75% complete.
3. Continuation and detailed presentation of data obtained during radiochemical waste evaporator evaluations.
4. Statement of conditions and program for separation of the plutonium from the Chalk River irradiated uranium.

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"23" PILOT PLANT DEVELOPMENT

Technical - Jackson, Ferguson, Hylton, Klotzbach, Lewis, Nicholson

Operators - Davis, Gifford, Caldwell, Summers, Jones, Shipwash, Grizzell, Lockmiller

1.0 U^{233} PILOT PLANT DEVELOPMENT

Six U^{233}/Th separations runs processing Hanford irradiated thorium were completed during January. The primary objective of the first four runs was to make a preliminary evaluation of the 23 process flowsheet, particularly with respect to Pa decontamination. In the other two runs the feasibility of using an aqueous feed more concentrated in $Th(NO_3)_4$ was investigated.

Using normal flowsheet conditions, gross fission product decontamination factors averaging 1×10^4 were obtained in one cycle. The protoactinium and thorium decontamination factors were 1×10^6 and 4×10^4 respectively. Increasing the $Th(NO_3)_4$ concentration in the aqueous feed from 1.6 M to 1.8 and 1.9 M decreased fission product decontamination by a factor of 3 with no significant decrease of 23 loss. Total 23 loss for all runs was below 0.2%, and a total of 75 grams of 98.5% isotopic pure 23 was separated.

1.1 Feed Preparation

1.11 Jacket Removal

Aluminum jackets were removed by the standard 10% NaOH-20% $NaNO_3$ procedure. The average 23 loss during this step was 0.06%.

1.12 Dissolving

The production of acid deficient dissolver solutions in the 23 process simplifies feed makeup by eliminating the addition of sodium hydroxide. Metal solutions about 0.2 N acid deficient were produced in Runs 1T-6T by using 65% nitric acid, 0.1 N fluoride ion as catalyst, a dissolving time of 30 hours. The resulting dissolver solution had a specific gravity of 2.10, and was 3.0 M in $Th(NO_3)_4$. Dissolver solutions which were 1.0 N acid deficient were produced when the dissolving time was extended by 3-5 hours.

The thorium metal used for Runs 1T-6T had been irradiated an average of 100 days at Hanford and cooled 27 to 32 months. The Pa activity for Run 3T was obtained by using three, ORNL 6 week irradiated, 7 week cooled thorium slugs.

[redacted]

"23" Pilot Plant Development (Continued)

1.13 Feed Adjustment

The necessary minor acidity adjustments of the feed were made by the addition of concentrated solutions of nitric acid or sodium hydroxide. $Th(NO_3)_4$ concentrations were adjusted by evaporation or dilution on the basis of specific gravity. No operational difficulties were encountered.

1.14 Filtration

After adjustment, the feed solutions were filtered by vacuum through a Micro-metallic, sintered stainless steel filter of 10 micron porosity. Filtration rates varied from 2-5 gal./sq. ft./hr., depending on the condition of the filter. Filtration rates were increased by back-washing the filter with air, water and nitric acid, and by increasing the volume and number of washes of the slugs in the dissolver after jacket removal.

1.2 Column Operation

Runs 1T-4T were made under conditions of the present 23 process flowsheet, Fig. I. For the last two runs (5T-6T) the feed concentration was raised from the normal 1.6 M $Th(NO_3)_4$ to 1.8 M for 5T and 1.9 M for 6T. A summary of decontamination and loss data is given in Table I in the Appendix.

1.21 23 Loss

The average 23 loss was 0.11% in the aqueous raffinate (AR) from the extraction column, and less than 0.01% in the hexone raffinate (BR) from the stripping column. The 0.11% loss in the AR stream was due to an inextractable form of uranium; this phenomenon has previously been observed during the laboratory investigations of 23 systems.

1.22 Decontamination

Table I of the Appendix presents thorium and fission product decontamination factors obtained on Runs 1T-6T.

For runs made under normal flowsheet conditions the gross fission product decontamination factors averaged 1×10^4. Decontamination factors higher by a factor of 2-3 would be expected for metal cooled for 9 months, rather than 32 months, due to the higher per cent of ruthenium in the longer cooled slugs.

"23" Pilot Plant Development (Continued)

1.23 Isotopic Analysis of 23 Product

The results of mass spectrographic analyses on the product from Runs 1T and 5T are given in the following table.

TABLE 1.23-1

ISOTOPIC ANALYSIS OF U^{233} PRODUCT

Run	Per Cent of Total Uranium				
	U-233	U-234	U-235	U-236	U-238
1T	98.35	0.20	0.29	0.04	1.11
5T	98.75	0.30	0.14	0.07	0.76

The 0.2 - 0.3% U^{234} corresponds to the calculated production of this isotope. The 0.29% - 0.14% U^{235} may be due to 25 contamination of the equipment used for the analysis and the 5 ppm of natural uranium in the thorium metal would account for the U^{238} in the product.

1.3 Equipment Performance

The operation of all types of conventional items of equipment, such as column interface controllers and recirculating type samplers, has been satisfactory. The performance of equipment not previously used in pilot plant scale operation is summarized below.

1.31 Bellows Pumps

The average life of bellows used for direct pumping of hot feed has been 300,000 flexes, representing 100 hours of operation. Four bellows failures have occurred, and in each case the failure appeared to be caused by fatigue at or near a seam weld along the length of the bellows. Except for bellows failure, the performance of the pumps has been satisfactory.

1.32 Thermal-electric Flowmeter

The thermal-electric flowmeter used in the feed line to the extraction column continues to be stable and accurate to better than 2% after 600 hours of operation.

"23" Pilot Plant Development (Continued)

1.33 Electrode-Type Flowmeter

A liquid contact, electrode type flow calibrator, is located in a 1" diameter standpipe on the outlet of the feed tank. The measurement of flow by this method continues to be reliable and accurate to better than 2%.

1.34 Process Tubing

Seamless, stainless steel tube and Parker Triple Tube fittings are used for most of the process lines. No leaks have been detected in either the tubes or the fittings.

1.35 Tinned Joints

In most cases, the tube fittings are tinned and screwed directly to couplings welded in the tank covers, and no leaks have been detected in this type joint. Tinned screwed joints, however, have not proven satisfactory where the flow of feed solution is continuous and under pressure, such as in lines on both suction and discharge sides of the feed pump. In this case, it has been necessary to replace tinned screwed joints with welded fittings.

1.4 Program

Fourteen additional runs will be made in the 23 Pilot Plant to determine the effect of lower feed concentration (below 1.5 M thorium nitrate), temperature, hexone impurities and acidity.

PLUTONIUM RECOVERY

Technical - Rigstad, Harrington

Operators - Benson, Burnett, Groover, Jennings, Ledbetter, McLellan, Sexton Shields, Spangler, Strader, Thompson, Wiggins

2.0 PLUTONIUM RECOVERY

Another four batches of the plutonium separated during the Pilot Plant Redox investigations (IBP stream) have been processed representing an overall completion for this problem of about 75%. This uranium/plutonium mixture (off specification IBP stream) was processed through a modified first uranium/plutonium partitioning cycle and a second plutonium cycle.

A number of chemical modifications were necessary to increase plutonium decontamination in the extraction column and obtain adequate plutonium recovery in the uranium/plutonium partitioning (IB) column. The overall operation of the equipment was satisfactory and a concentrated plutonium product varying from 15-37 grams Pu/liter was obtained which had a total beta activity of 2-4 x 10^8 d/m/gm Pu and a gamma activity of 3 x 10^4 mv/gm. Pu ($\sim$6 x 10^7 d/min/gm Pu).

Detailed operating conditions and results are given in Appendix II of this report.

2.1 First Cycle Uranium/Plutonium Extraction and Separation

Feed make-up for the first cycle was satisfactory and without incident as was the extraction in the first column. The losses during extraction were less than 0.01% for both uranium and plutonium. This high recovery, it is felt, is due to the fact that the entire column was run under acidic conditions.

The high losses in the uranium stream from the partitioning column (IBU) necessitated that the $Al(NO_3)_3$ concentration in the extractant be lowered. The high plutonium losses of 8-10% were due, it is felt, to the absence of the back salting effect because of the low uranium content of the hexone phase. Although the extraction section of the 1B column was lengthened, the extractant stream rate increased, and the scrub stream rate decreased, very little reduction in plutonium loss was obtained until the $Al(NO_3)_3$ was lowered from 1.3 M to 0.9 M.

Plutonium Recovery (Continued)

2.2 Second Cycle Plutonium

Operation of the second cycle plutonium extraction and evaporation equipment was satisfactory, but the extraction losses (IIAW) were extremely variable. These high and variable losses (0.002 to 12.5%) are most probably due to deficiency in oxidizing of the feed (IIAF). The material balances from these second cycle runs were poor varying from 89 to 101% due to difficulty in analysis of the highly concentrated plutonium solutions. Development work is in progress on a more satisfactory analytical procedure for highly concentrated plutonium solutions.

2.3 Program

The recovery of the plutonium solutions from the Redox processings is expected to be completed during the coming period, and cleansing and decontaminating of the equipment started. After cleansing of the equipment has been completed the minor modifications necessary to permit processing of the Chalk River irradiated uranium as described in Section 4.0 of this report will be started.

The Pu recovered from the IBP solutions as the IIBP concentrate will be processed through a laboratory purification cycle when facilities are available in about 6-8 weeks.

RADIOCHEMICAL WASTE PROCESSING

Technical - Shank

3.0 RADIOCHEMICAL WASTE PROCESSING

3.1 ORNL Radiochemical Waste Evaporator

The ORNL Radiochemical Waste Evaporator, during the first three weeks of January, processed 118,400 gallons of mixed waste in 12 runs for an average of 9,800 gallons/run to give a 26:1 volume reduction. The evaporator feed contained ~990 curies of beta activity and discharged ~0.72 curies to the settling basin in the condensate for an overall decontamination of 1.4×10^3. Evaporation rate was lowered from 350 gph to 250 gph to obtain an enhanced decontamination while processing the iodine bearing RaLa waste.

Table 3.1-1 gives the weekly performance for the evaporator and shows the fluctuation in decontamination due in part as a result of processing feeds of variable composition. Table VII in Appendix III gives the detailed results of nine of the evaporator runs made during the past two months and clearly shows the fluctuation in operation with changing feed characteristics.

TABLE 3.1-1

WEEKLY PERFORMANCE FOR RADIOCHEMICAL WASTE EVAPORATOR

Week Ending	Feed		Condensate		Evaporator(1) Decontamination	Volume(2) Reduction
	Volume (gallons)	β Curies	Volume (gallons)	β Curies		
1-7-50	41,900	233.0	40,200	0.32	730	24.7:1
1-14-50	30,200	262.0	29,100	0.14	1.9×10^3	27.5:1
1-21-50	46,300	491.0	44,600	0.26	1.9×10^3	27.2:1
Total or Average	118,400	986.0	113,900	0.72	1.4×10^3	26.3:1

Notes:

(1) $D.F. = \frac{\beta \text{ curies in Feed}}{\beta \text{ curies in condensate}}$

(2) $\text{Volume Reduction} = \frac{\text{Volume Feed (Gallons)} - \text{Vol. Concentrate (Gallons)}}{\text{Volume Concentrate}}$

Radiochemical Waste Processing (Continued)

3.2 Supplemental Evaporator Studies

T. C. Runion, of the Laboratory Section, has been doing laboratory investigations on the evaporator foaming problem, testing anti-foam agents and possible causes of foaming. The results of these investigations will be reported as completed.

Investigation of modifications to the low-level activity monitor is approximately 10% complete. Laboratory work on a foam level indicator is approximately 25% complete. This work is expected to continue at an accelerated rate during the coming month.

Investigation into the possibility of a quick and simple analysis on evaporator feed to determine operating conditions has been started.

No attempt other than reported by E. L. Nicholson, ORNL-393, has been made to evaluate evaporator efficiencies and overall heat transfer coefficients. Such evaluations, if made, will start late in 1950 as such information is of little practical value at the present. Operation of the evaporator indicates a decreasing heat transfer across the steam coils due possibly to scale formation. It is felt that this scale will be easily removed by nitric acid washes.

SPECIAL CR SEPARATION

Technical - Sadowski

4.0 CR SEPARATION

4.1 Program

The 205 Pilot Plant installation has been requested to separate plutonium from specially highly irradiated uranium. This separation will entail the processing of a series of segregated batches of uranium as listed below.

TABLE 4.1-1

CR SEPARATIONS FEED MATERIAL HISTORY

Batch	Source	Irradiation in MWD/T		Total grams Pu (approx.)
		Maximum	Average	
1	NRX	360	220	30
2	NRX	610	490	70
3	NRX	830	720	100
4	NRX	1010	920	120
5	NRX	1130	1080	140
6	NRX	1205	1180	220
7	HEW	800	750	95

These processings will consist of one cycle of uranium/plutonium separation, a second cycle of plutonium decontamination, and a third plutonium cycle of laboratory purification. The chemical conditions to be used in the first cycle are either the ORNL June, 1949 flowsheet or a more recently developed KAPL flowsheet if sufficient laboratory data can be obtained in time. The second plutonium cycle chemical conditions will be those most recently developed. The conditions of the separations to be done on a laboratory scale have not been definitely established.

A more detailed enumeration of the processing conditions, schedules, and service samples to be obtained, etc. will be given in a memo from D. G. Reid to F. L. Steahly which will be issued on or before February 20, 1950.

4.2 Equipment Modifications

The processing of this highly irradiated material requires certain equipment modifications and additions be made to be able to safely handle these large amounts of plutonium and recover some transuranics and fission products. The equipment modifications will include additional waste storage facilities and a laboratory for processing the plutonium.

The first cycle extraction raffinates, from which the Chemistry Division will separate several isotopes, are to be stored in two, 2,000 gallon stainless steel tanks to be installed in the north tank farm area. Solution transfer lines will be provided to Bldg. 706-C from these tanks as well as storage facilities at 706-C for storage of the separated material.

The plutonium laboratory will be provided by renovation of the 204 Bldg. The renovation will include air conditioning and general cleansing of the building plus the installation of hoods, dry (dust) boxes, alpha counting facilities, and supplemental laboratory facilities.

4.3 Schedule

This Chalk River separation is to be started after the plutonium recovery processings are completed and after the necessary tank farm facilities are available. It is expected that this will begin about March 1, 1950 and continue at a processing rate of about one batch of material every ten days to two weeks and be completed about June 15 to July 1, 1950.

METAL RECOVERY

Technical - Stewart

5.0 ORNL WASTE URANIUM RECOVERY UNIT

The operating conditions necessary for the design of the ORNL Waste uranium recovery unit have been developed to permit calculation of chemical and equipment flowsheets. Preliminary sizing of tanks and building structure has been completed.

[redacted]

"25" RECOVERY PILOT PLANT DEVELOPMENT

Technical - Rom

6.0 25 PROCESS

The final report summarizing all Pilot Plant 25 development is approximately 25% complete and is scheduled for issuance around April 1. A tentative outline of the report is included in Appendix IV.

Development of a method for analyzing the Np^{237} content of the process feed and an investigation of precision and accuracy of the determination of uranium in the feed and product were continued during the past period. In applying the method for Np^{237} analysis to process feeds it was found that insufficient Np^{237} was present for a good test of the method. The work in calculating precision and accuracy of U determinations in the feed and product is to be continued in the coming period with the assistance of the K-25 Statistical Section.

MISCELLANEOUS

7.0 MISCELLANEOUS ADMINISTRATIVE

There has been only minor progress on the 205 permanentization during the past period consisting of minor revisions of drawings and completion of removal of the old structure by ORNL employees.

E. C. Stewart, Chemical Engineer, was loaned to the Design Section starting January 1, 1950, to participate in design of the ORNL Waste Uranium Recovery Unit.

R. E. Purkey, Research Operator, on loan to the Operations Division to assist in the training of personnel for the demineralized water operation was returned to the Pilot Plants Section January 23, 1950.

[redacted]

APPENDIX I

23 PILOT PLANT DEVELOPMENT

From a study of the data of Table I, the following salient points and conclusions are drawn:

1. Increasing the $Th(NO_3)_4$ concentration to 1.8 - 1.9 M in the aqueous feed (AF) decreased the gross fission product decontamination to 3×10^3. This was due primarily to decreased Ru and and Pa decontamination.

2. The Ce decontamination factor was about 1×10^5 for all six runs, being unaffected by the increase in $Th(NO_3)_4$ concentration of the feed.

3. Zr decontamination was also not affected by feed salt concentration, remaining about 2×10^4 throughout the runs.

4. The Ru decontamination factor was about 1×10^3 for the normal flowsheet runs, but dropped to 100 with the increased AF salt concentration.

5. Pa decontamination was also decreased from 1×10^6 at normal flowsheet conditions to 4×10^4 at the higher feed $Th(NO_3)_4$ concentration.

6. In Run 3T, 87% of the beta activity of the feed was Pa beta, and the higher gross decontamination on this run was the result of the 1×10^6 Pa decontamination factor obtained.

7. Thorium decontamination was adequate, 1×10^4 or greater, on all runs except 6T. The low (3×10^3) thorium decontamination factor obtained on Run 6T is attributed to the high feed concentration on that run.

[redacted]

TABLE I

ORNL 23 PILOT PLANT-SUMMARY RESULTS OF RUNS 1T-6T(1)

Run	Feed $Th(NO_3)_4$ Conc., M	Uranium Loss, %		Decontamination Factor						
		AR (2)	BR	Gross β	Gross γ	Ru	Ce	Zr	Pa	Th
1	1.60	0.14	0.002	7×10^3	7×10^3	900	1.0×10^5	(4)	(4)	1×10^4
2	1.60	0.18	0.004	8×10^3	1.0×10^4	1.4×10^3	8×10^4	(4)	(4)	1×10^4
3	1.52	0.12	0.009	9×10^4(3)	1.5×10^5(3)	5×10^3	3×10^5	1.7×10^4	1×10^6	3×10^4
4	1.60	0.08	0.002	2×10^4	3×10^4	2×10^3	2×10^5	2×10^5	2×10^4	7×10^4
5	1.80	0.10	0.001	3×10^3	3×10^3	110	1.4×10^5	1.7×10^4	4×10^4	1×10^5
6	1.90	0.06	0.001	3×10^3	2×10^3	(5)	(5)	(5)	(5)	3×10^3

(1) See Fig. I for flowsheet conditions.

(2) The uranium loss in the AR stream appears erratic on a percentage basis; the variations are due primarily to differences in the feed 23 concentrations. The concentration of 23 in the AR was consistently about 0.1 γ/ml and was "unextractable" uranium.

(3) The high gross decontamination is attributed to the high Pa decontamination and high Pa activity from short cooled Th slugs (See Section 1.12).

(4) AF activity too low to measure decontamination factor.

(5) Fission product analyses on Run 6T not available.

[redacted]

[redacted]

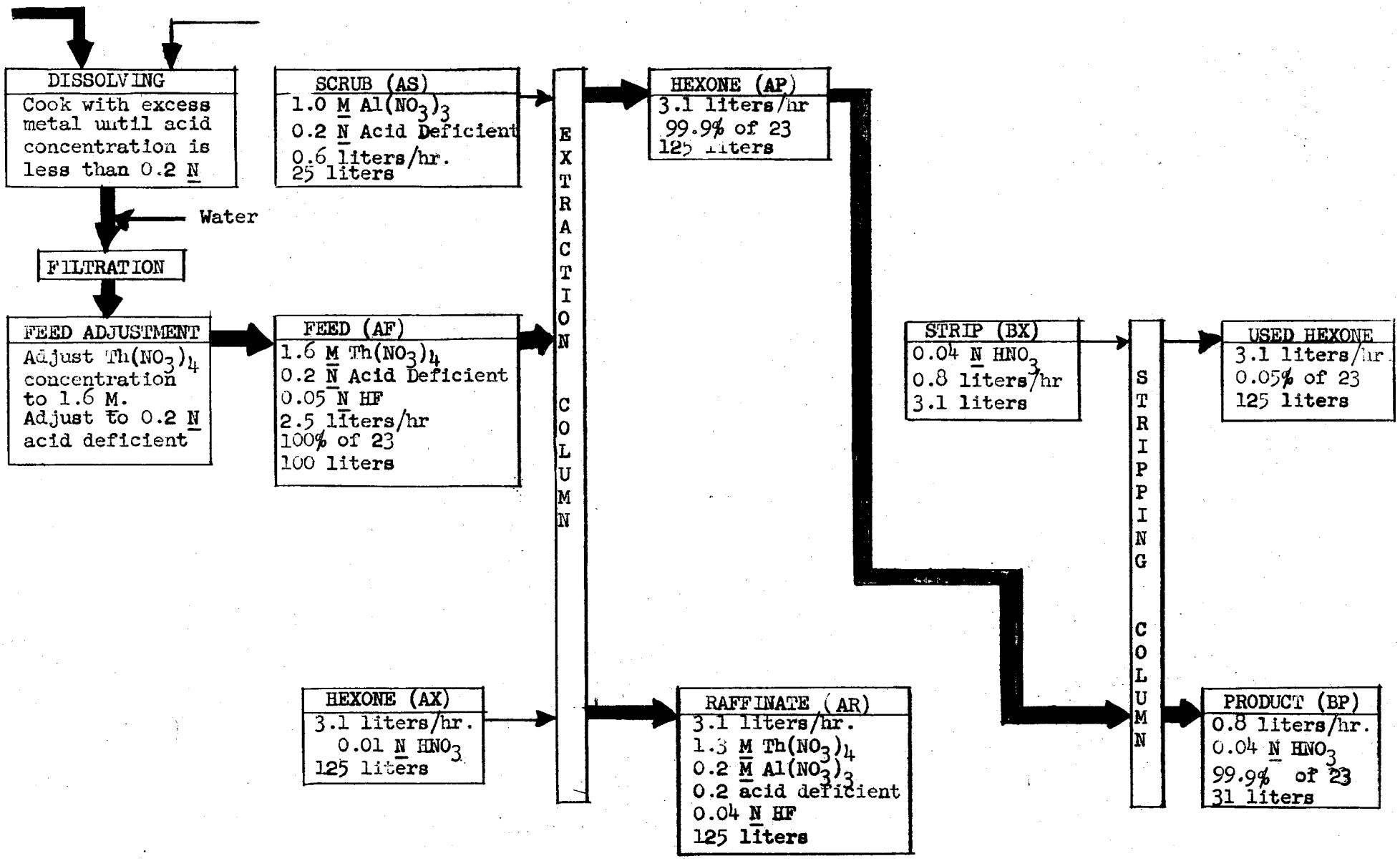

FIGURE I

23 PILOT PLANT CHEMICAL FLOWSHEET

11-15-49

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APPENDIX II

PLUTONIUM RECOVERY FROM REDOX SOLUTIONS

Original objectives of the ORNL Pilot Plant in the Redox development program was to determine the ultimate number of uranium extraction cycles necessary to give adequate uranium decontamination for the Redox production plant at HEW. For this reason, it was necessary to operate the first cycle to provide feed material for subsequent uranium cycle process investigations. To conserve plutonium it was necessary that the plutonium separated out during the operation of the first cycle be stored in a manner to permit ultimate and if necessary quick recovery so that the material could be returned to production channels. Extension of ORNL participation in the Redox flowsheet, resulted in the storage of a considerable quantity of plutonium. Although the recovery at this time was questionable it was decided to reclaim this material in preparation for the Chalk River separations program explained in Section 4.0 of this report.

Tabulated data as to composition of the stored Redox IBP solutions, specifications desired for the final product solution, and tentative processing flowsheet conditions were given in the October-November Report, ORNL-506. Material from storage tank F2 was completely processed in Runs 1 & 2, and material from tank E2 is being processed in Runs 3-8, inclusive.

A. First Cycle Feed Preparation

Batches of the separated plutonium stream (IBP) which have been stored were returned to the First Cycle Feed Makeup Tank for feed adjustment. The aluminum concentration, reduced through transfer jet dilution, was brought up to feed specifications by addition of concentrated aluminum nitrate solution after which sufficient nitric acid and sodium dichromate was added to obtain the desired feed specifications. This adjusted solution was filtered at a satisfactory rate.

The Pu solutions separated under acid flowsheet conditions had a very high ruthenium and cerium activity. To avoid plutonium precipitation, which previously was thought to occur if aqueous plutonium solutions stood for long periods of time the initially separated IBP stored solution made 0.3 N in HNO_3 and 0.1 M dichromate about August 1, 1949. Laboratory counter-current batch experiments of the material before oxidation showed adequate decontamination could be obtained under decidedly acidic conditions such as were used in Runs 1 & 2. A repitition of this experiment just prior to pilot plant processing showed that the decontamination of these solutions was very poor under acidic conditions due most probably to prolonged oxidation which resulted in a change in the chemical composition of the fission products (Ru & Ce). As a result of this counter-current batch experiment the chemical conditions for processing the stored material were modified by reducing the HNO_3 concentration of the scrub (IAS), from 0.3 N to 0.05 N and increasing the hexone extractant (IAX) HNO_3 normality from neutral to 0.05 N.

The chemical composition of the individual runs are given in Table II.

B. First Cycle Column

The operation of three first cycle columns was without incident. No operational difficulties were encountered. The extraction column data presented in Table III show:

1. The decontamination of all processings irrespective of first cycle history was approximately equal.

2. The combining of the first cycle plutonium product from Run 4 with the first cycle feed for Run 6 resulted in an apparent lower overall decontamination for Run 6.

3. The plutonium losses during extraction were satisfactory with either type acid conditions.

The plutonium losses to the uranium stream (IBU) in partitioning during the first run were high. To alleviate this condition, the flow rate for the extractant (IBX), the flow rate of the scrub (IBS), the length of the scrub section, and the concentration of the aluminum nitrate of the IBX were varied. From the operational data obtained on the running and re-running of this batch and subsequent runs the following information was obtained on the partitioning column operation:

1. Doubling the IBX flow rate had no major effect on decreasing the loss of plutonium to the IBU stream.

2. Reducing the IBS flow by a factor of two did not substantially reduce plutonium losses to the IBU stream.

3. Lengthening the scrub section from an initial 12 to an ultimate 16 feet did not reduce these plutonium losses.

4. Reducing the concentration of aluminum nitrate in the IBX from 1.3 to 0.9 M reduced the plutonium losses to a satisfactory level.

5. The increase of a factor of 100 in uranium in Runs 3, 4 and 5, it is felt, was a major factor for reducing the plutonium losses in these runs by a factor of 10.

Operation of the stripping column was without incident. The uranium separated from this column was sent to the Tank Farm.

C. Second Cycle Feed Preparation

The feed for the second cycle plutonium was prepared by the addition of nitric acid and dichromate to the IBP stream from the first cycle. In some of the runs aluminum nitrate salt solution was added to increase the aluminum nitrate concentration.

The chemical compositions of the individual runs are given in Table IV.

[redacted]

TABLE II

ORNL PILOT PLANT - PLUTONIUM RECOVERY

CHEMICAL COMPOSITION OF FIRST CYCLE FEED STREAM

Run No.	1 RBP	2 RBP	3 RBP	4 RBP	5 RBP	6 RBP
IAF:						F2 Cleanout + Re-Run 4 RBP
$Al(NO_3)_3$, M	1.0	1.0	1.2	1.2	1.2	1.2
HNO_3, N	0.17	0.28	0.47	0.29	0.31	0.43
$Na_2Cr_2O_7$, M	0.07	0.05	0.07	0.07	0.07	0.085
IAS:						
$Al(NO_3)_3$, M	1.3	1.3	1.3	1.3	1.3	1.3
HNO_3, N	0.3	0.3	0.0	0.05	0.05	0.05
IAX:						
HNO_3, N	0	0	0.05	0.05	0.05	0.05
IBX:						
$Al(NO_3)_3$, M	1.3,0.9	0.9	0.9	0.9	0.9	0.9
Fe^{++}Sulf., M	0.05	0.05	0.05	0.05	0.05	0.05
IBS:						
HNO_3, N	0.05	0.05	0.05	0.05	0.05	0.05
ICX:						
HNO_3, N	0.04	0.04	0.04	0.04	0.04	0.04

[redacted]

D. Second Cycle Plutonium Extraction and Concentration

The operation of the second cycle plutonium column was without incident. The data for the second cycle processings are given in Table V. These data show:

1. The decontaminations are lower on the plutonium originally separated under acid deficient (ORNL) conditions. This is due to the higher specific activity of the acidic separated plutonium.

2. The high losses in the II AW stream of Run 2 are attributed to low dichromate concentration in the II AF.

3. The low losses on the first run may be due to the slightly higher acid conditions.

The operation of the continuous evaporator was satisfactory although the losses are slightly higher than desired. The product from each run was concentrated to a volume of 2 liters resulting in product solutions that varied from 15 to 37 grams per liter. The largest source of trouble in this operation is the difficulty in obtaining accurate and reliable analysis of this highly concentrated plutonium solution. The analytical laboratory is developing a remote control procedure to alleviate this problem.

The concentrated plutonium product will be transferred to the laboratory when facilities are available for further purification, decontamination, and concentration. It is not yet known what procedure will be used but it is felt that this purification will be done by solvent extraction.

E. Overall Decontamination

The overall two cycle decontamination data are given in Table VI. These data show that the overall decontamination was higher for those solutions originally separated under acid conditions than under acid deficient conditions because of the higher initial activity, but yield a product which is essentially the same. The condition of the product solutions is such that an additional laboratory purification is definitely necessary to eliminate the inert impurities such as aluminum nitrate, corrosion products, and hexone decomposition products.

[redacted]

TABLE III

ORNL PILOT PLANT-PLUTONIUM RECOVERY

FIRST CYCLE PLUTONIUM DECONTAMINATION AND LOSS DATA

Run No.	Gross β	Gross γ	U-II AF Mg/gm Pu	Filtration Loss-%	IAW Loss %	IBU Loss %	ICW Loss %	Material Balance %
1 RBPI	15.6	21.5	0.528	0.12	.006	8.7(1)	0.80	98.1
2 RBPI	43.7	87.1	0.154	0.01	.0034	1.95	0.035	97.6
3 RBPI	17.3	48.9	3.535	0.008	0.017	0.185	0.066	94.7
4 RBPI	78.2	153	--	0.072	0.010	0.160	0.0086	--
5 RBPI	56.2	114	19.02	0.016	0.0085	0.23	0.0089	97.4
6 RBPI	5.3	18.3	--	0.045	0.004	--(2)	0.0016	98.9

(1) Recycled thru first cycle. No loss to process.

(2) Combined with 7RBP-I.

[redacted]

[redacted]

TABLE IV

ORNL PILOT PLANT - PLUTONIUM RECOVERY

CHEMICAL COMPOSITION OF SECOND CYCLE FEED STREAM

Run No.	1 RBP	2 RBP	3 RBP	4 RBP	5 RBP	6 RBP
II AF:						
$Al(NO_3)_3$, M	1.3	0.9	0.9		1.3	
HNO_3, N	0.17	0.10	0.23		0.04	
$Na_2Cr_2O_7$, M	0.09	0.04*	0.11	No such run made	0.10	No such run made
II AS:						
$Al(NO_3)_3$, M	1.3	1.3	1.3		1.3	
HNO_3, N	0.05	0.05	0.05		0.05	
IIAX:						
HNO_3, N	0.05	0.05	0.05		0.05	
II BX:						
HNO_3, N	0.04	0.04	0.04		0.04	

* Reported originally as 0.14, re-checked at 0.04 M, results questionable.

[redacted]

[redacted]

TABLE V

ORNL PILOT PLANT-PLUTONIUM RECOVERY

SECOND CYCLE PLUTONIUM DECONTAMINATION AND LOSS DATA

Run No.	Gross β	Gross γ	II AW Loss %	II BW Loss %	Prod. Evap. Loss-%	Material Balance-%
1 RBP-II	11.7	30	0.0023	0.001	0.136	89.3
2 RBP-II	6.4	42.0	12.5	0.0009	0.023	98.04
3 RBP-II	238	44.6	0.44	0.002	0.136	92.5
4 RBP-II	--	--	--	--	--	--
5 RBP-II	118	33.5	1.43	0.0009	0.14	100.84

[redacted]

[redacted]

TABLE VI

ORNL PILOT PLANT-PLUTONIUM RECOVERY

TWO CYCLE DECONTAMINATION AND LOSS DATA

Run No.	Decontamination		Column Losses %	Overall Losses %	Product Activity	
	Gross β	Gross γ			β dis/min/gm Pu	γ Mv/gm. Pu
1 RBP	182	645	9.51 (1)	9.77 (1)	4.04×10^8	6.15×10^4
2 RBP	248	3680	14.49 (2)	14.52 (2)	2.16×10^8	3.3×10^3
3 RBP	410	2180	0.71	0.85	4.21×10^8	3.43×10^4
4 RBP			No second cycle run made			
5 RBP	660	3820	1.68	1.98	3.29×10^8	2.09×10^4

(1) Essentially entire amount due to high IBU (partitioning) loss which is not a true loss since most (8.7%) was returned to process.

(2) Caused by the lack of oxidant in feed to second cycle extraction column.

[redacted]

[redacted]

APPENDIX III

RADIOCHEMICAL WASTE PROCESSING DEVELOPMENT

Classification of evaporator feed as metal waste supernate, RaLa, etc. and consequent operation and evaluation of the evaporator is difficult with the existing facilities due to the necessity of using an intermediate tank (W-5) for evaporator feed storage. Various types of wastes are transferred to W-5 prior to their entry into the evaporator resulting in a gradually changing, non-specific feed composition. Table VII shows the changing effect in operation by a changing evaporator feed. The results listed are insufficient to draw conclusions, but pertinent facts and indications are pointed out below.

1. Metal waste supernate permits overdesign capacity evaporation rates but gives lower decontamination and concentration ratio.

2. RaLa waste requires lower evaporation rates but gives higher decontamination and concentration ratio.

3. Volume reduction varies by a factor of 13 on the reported runs.

4. High decontamination in metal waste supernate (Run 180) may be due to the high free base concentration.

5. pH does not appear to give a consistent free base indication due possibly to the variation in ionic concentration of the feed.

6. pH determination on normal waste is possibly more indicative of free base than on process waste due to a lower ionic strength and interference. In Runs 191, 192, 193, a pH of 11.0 may indicate a high free base resulting possibly in the higher ruthenium and cesium decontamination. This effect may also be noted in Run 180.

7. No correlation between free base analyses can be made due to change in analytical procedure. A comparison is being made to determine what relationship does exist.

8. Counting accuracy decreases on low activity samples affecting decontamination determinations.

9. Foam-overs are usually more frequent during metal waste supernate runs.

10. Four foam-overs occurred on Run 238 while Runs 239, 240 had no foam-over. Lower decontamination on Run 238 may possibly be due to these foam-overs which were a result of a tailing effect from metal waste supernate.

[redacted]

11. Complete ionic and spectrographic analyses are not available on the nine runs listed in Table VII. Preliminary results indicate moderate to high concentrations of sodium and aluminum in the feed. As yet, no correlation between ionic concentration and degree of foaming can be made. Substances other than salts, such as organic matter, may be the prime cause of foaming.

12. Gross decontamination factors are dependent on gross beta counting accuracy. A decrease in accuracy on samples containing a large per cent of radio-iodine may be seen from RaLa Runs 238, 239, and 240 where iodine β cts/m/ml were, in some cases, greater than the gross β cts/m/ml. This is attributed to the volatilization of iodine during the drying step. Radio-iodine analyses may be corrected from the known loss of iodine carrier used in its determination. This, however, is impossible on gross determinations.

[redacted]

TABLE VII

DETAILED RESULTS OF NINE EVAPORATOR RUNS

MADE DURING DECEMBER AND JANUARY

Run	Feed(1) Characteristics	Constituents(2)	Feed	Condensate	Decontamination Factor(4)	Average(6) Rate(gph)	Volume(7) Reduct.	Length of(8) Run (hrs.)
179	Metal Waste Supernate	Gross β	2.70×10^5	1.9×10^3	150	420	6.3	6.5
		Gross γ	830	--(3)	---			
	pH - 11.0	I β	7.1×10^4	560	130			
	N^B - 0.8	Ru β	1.0×10^5	690	150			
		Cs β	9.2×10^4	460	210			
		Vol. (gal.)	2860	2740(5)	---			
180	Metal Waste Supernate	Gross β	2.60×10^5	230	1.4×10^3	410	2.4	5.0
		Gross γ	840	---	---			
	pH - 11.0	I β	6.3×10^4	100	800			
	N^B - 2.1	Ru β	9.3×10^4	60	2.0×10^3			
		Cs β	9.0×10^4	40	2.9×10^3			
		Vol. (gal.)	2590	2040	---			
181	Metal Waste Supernate	Gross β	2.3×10^5	1.6×10^3	150	410	6.0	6.0
		Gross γ	75		---			
	pH - 11.0	I β	5.8×10^4	420	140			
	N^B - 0.8	Ru β	8.3×10^4	450	190			
		Cs β	7.4×10^4	490	160			
		Vol. (gal.)	2580	2470	---			
191	Metal Waste Supernate	Gross β	7.3×10^4	110	640	390	12.7	14
		Gross γ	250	---	---			
	pH - 11.0	I β	5.6×10^3	20	270			
		Ru β	3.2×10^4	10	3.1×10^3			
		Cs β	3.6×10^4	90	390			
		Vol. (gal.)	5260	5460	---			

[redacted]

[redacted]

TABLE VII (Continued)

Run	Feed[1] Characteristics	Constituents[2]	Feed	Condensate	Decontamination Factor[4]	Average[6] Rate (gph)	Volume[7] Reduct.	Length of[8] Run (hrs.)
192	Normal Waste	Gross β	1.3×10^5	140	930	380	8.5	9.3
		Gross γ	430	- (3)	---			
	pH - 11.0	I β	4.3×10^3	10	430			
		Ru β	6.0×10^4	45	1.3×10^3			
		Cs β	6.8×10^4	80	850			
		Vol. (gal.)	3530	3540[5]	---			
193	Normal Waste	Gross β	1.5×10^5	75	2.1×10^3	420	6.2	6.8
		Gross γ	490	---	---			
	pH - 11.0	I β	3.6×10^3	10	380			
		Ru β	6.8×10^4	10	7.1×10^3			
		Cs β	8.0×10^4	40	2.1×10^3			
		Vol. (gal.)	2990	2860	---			
238	RaLa Waste	Gross β	4.7×10^5	720	560	240	28.4	5.5
	pH - 11.0	Gross γ	1.6×10^3	---	---			
	N^B - .06	I β	4.2×10^5	490	740			
		Ru β	2.9×10^3	25	100			
		Cs β	1.0×10^4	100	90			
		Vol. (gal.)	11,400	13,300	---			
239	RaLa Waste	Gross β	6.6×10^5	550	1.1×10^3	340	32.0	45
	pH - 10.0	Gross γ	1.8×10^3	---	---			
	N^B - .02	I β	6.2×10^5	550	1.0×10^3			
		Ru β	2.9×10^3	10	260			
		Cs β	1.0×10^4	20	450			
		Vol. (gal.)	13,900	15,400	---			
240	RaLa Waste	Gross β	5.5×10^5	480	1.0×10^3	260	15.5	26 hrs.
	pH - 10.0	Gross γ	1.5×10^3	---	---			
	N^B - .06	I β	5.5×10^5	490	1.0×10^3			
		Ru β	3.0×10^3	10	370			
		Cs β	1.0×10^4	30	300			
		Vol. (gal.)	6000	6740	---			

[redacted]

NOTES

(1) Metal waste supernate effects on feed are felt after a transfer of metal waste supernate is made to W-5

RaLa waste effects on feed are felt after a RaLa start-up. Automatic transfer of dissolver scrubber water to W-5 is maintained.

Normal waste is waste from other than distinct processing operation.

N^B - Normality Free Base

Runs 179, 180, 181 - analyses by adding an excess HCL and back-titrating to a potentiometric endpoint with NaOH.

Runs 191, 192, 193 - Not analyzed.

Runs 238, 239, 240 - analyses by titrating to a potentiometric endpoint with HCL.

(2) Counting at 10.18% geometry cts/min/ml.

(3) No gamma count taken on condensate.

(4) Decontamination factor determined as follows:

$$\frac{\text{Gross } \beta \text{ cts/m/ml Feed}}{\text{Gross } \beta \text{ cts/m/ml Condensate}} \times \frac{\text{Volume Feed}}{\text{Volume condensate}}$$

(5) Volume condensate = Volume Feed - Volume Concentrate + 42 (Length of Run)
(42 gph water spray used for foam breaker.

(6) $$\text{Average Rate} = \frac{\text{Volume Condensate}}{\text{Length of Run}}$$

(7) $$\text{Volume Reduction} = \frac{\text{Volume Feed} - \text{Volume Concentrate}}{\text{Volume Concentrate}}$$

(8) Length of run - from time at boiling to time steam off.

(9) Volumes recorded in gallons and length of run recorded in hours in all calculations.

APPENDIX IV

25 PILOT PLANT DEVELOPMENT

A tentative outline and table of contents for the report summarizing all Pilot Plant development at ORNL is given below.

1.0 Abstract

2.0 Introduction

- 2.1 Purpose of Process
- 2.2 History of Process
- 2.3 Scope of Report

3.0 Summary

- 3.1 Description of Process
- 3.2 Decontamination
- 3.3 Uranium Loss
- 3.4 Equipment
- 3.5 Cost

4.0 Experimental Results

- 4.1 First Cycle
- 4.2 Second Cycle
- 4.3 Decontamination
- 4.4 Uranium Loss

5.0 Cost

- 5.1 Initial Cost
- 5.2 Operating Cost

6.0 Appendix

6.1 Table of Operating Conditions

6.2 Table of Gross Decontamination Factors

6.3 Table of U Losses

6.4 Chemical Flowsheet

6.5 Equipment Flowsheet

6.6 Run Sheets

6.7 Evaporator Drawings

6.8 Column Equilibrium Curves

6.9 Uranium Accountability Procedures

6.10. Security Procedures