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PILOT PLANTS SECTION REPORT FOR APRIL, 1950

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ORNL-702
Chemistry-Separation
Processes for Plutonium
and Uranium

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CHEMICAL TECHNOLOGY DIVISION

PILOT PLANTS SECTION REPORT FOR APRIL, 1950

D. G. Reid

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0.0 ABSTRACT

The monthly report for the Pilot Plants Section of the ORNL Chemical Technology Division for the month of April is presented.

[redacted]

"23" PILOT PLANT DEVELOPMENT

Technical - Jackson, Ferguson, Hylton, Lewis, Nicholson

Operators - Caldwell, Davis, Jones, Grizzell, Lockmiller, Shipwash, Summers, Thomas, Thompson

1.0 23 PROCESS DEVELOPMENT

The final U^{233}-Th separation Run (19T) processing Hanford irradiated thorium was made during April. Eighteen previous runs had demonstrated that the one-cycle process using methyl isobutyl ketone (MIBK) yields a fission product decontamination factor of 2×10^4, with a 23 loss of less than 0.10%. Run 19T was made using diisopropyl ether. The 23 loss for Run 19T was 0.07%, and the decontamination factors for fission products, protactinium, and thorium were 1×10^5, 1×10^6 and 5×10^6, respectively. These separation factors were about five times greater than those obtained with MIBK; however, MIBK remains the favored first cycle 23 solvent because of the low flash point of diisopropyl ether and engineering difficulties encountered with this flowsheet.

A total of 318 grams of 97% isotopically pure U^{233} were recovered during the nineteen runs, and an additional 15 grams of yet undetermined purity were salvaged from samples and analytical wastes.

1.2 Description of Run 19T

During the laboratory development of the 23 process diisopropyl ether was found to give excellent separation of 23 from thorium and fission products. Diisopropyl ether is used for a number of special separations problems, including the final purification cycles for both the 23 and 25 processes, and Run 19T was made in order to obtain a comparison of the two solvents at a high activity level.

23 Process Development (Continued)

The feed makeup for Run 19T was the same as previously reported for the MIBK system. The metal had been irradiated for 100 days at Hanford and cooled for 13 months. Column conditions for both the MIBK and diisopropyl ether flowsheets are given in Table 1.2.

TABLE 1.2-1

23 Process Flowsheets

Solvent	AF Composition	AS Composition	BX Composition	Flow Ratio AS:AF:AX:BX
Diisopropyl Ether	2.5 M $Th(NO_3)_4$ 0.1 N HNO_3	2.5 M $Al(NO_3)_3$ 0.7 M NaF 0.4 N acid deficient	0.04 N HNO_3	1:4:5:1
MIBK	1.6 M $Th(NO_3)_4$ 0.2 N acid deficient	1.0 M $Al(NO_3)_3$ 0.2 N acid deficient	0.04 N HNO_3	1:4:5:1

Operational difficulties were encountered during the early part of Run 19T. The scrub solution solidified when the building temperature dropped to 10° C at night, and essentially all of the solvent was evaporated as it passed through the columns and piping. However, when the building was heated to 20° C and the vacuum on the process vent system was reduced from 4" to 1/4" of water, the run was made without further difficulty. Column temperature was maintained at 21° C during the run.

23 Process Development (Continued)

The decontamination factors obtained for Run 19T are given in Table 1.2-2, and the decontamination factors given by the MIBK flowsheet are shown for comparison.

TABLE 1.2-2

Performance of 23 Process Flowsheets (1)

Decontamination	MIBK Flowsheet	Diisopropyl Ether Flowsheet (Run 19T)
Gross Beta	2×10^4	1×10^5
Gross Gamma	2×10^4	1×10^5
Ruthenium	2×10^3	1×10^4
Zirconium	1×10^5	1×10^5
Cerium	5×10^5	6×10^6
Protactinium	5×10^5	1×10^6
Thorium	$10^4 - 10^5$	5×10^6

(1) The total 23 loss for both flowsheets was 0.10%.

23 Process Development (Continued)

Although the decontamination obtained with diisopropyl ether is a factor of 5 higher than that given by the MIBK flowsheet, diisopropyl ether is less attractive than MIBK for a first cycle 23 solvent because of a longer HETS, lower flash point, engineering difficulties in handling salt solutions near saturation, and the necessity for close temperature control.

1.3 Isotopic Purity of Product

The results of isotopic abundance analyses by the mass spectrographic method on the 23 produced during the program are given in Table 1.3-1. Of the 327 grams of uranium isolated, 318 grams (97.3%) were U^{233}, 7.9 grams (2.4%) were U^{238}, and 0.95 grams (0.3%) were U^{234}. This material will be split into two batches for laboratory processing. Composition of the two batches is shown in the following table:

	% U^{233}	% U^{234}	% U^{238}
Batch 1, 234 grams	98.2	0.3	1.5
Batch 2, 93 grams	95.0	0.3	4.7

It is expected that this material will be processed in the laboratory before June 1, 1950.

1.4 Program

The experimental portion of the 23 Pilot Plant development has been completed, and a summary report is scheduled to be issued during the next period. The 23 Pilot Plant is a soundly designed and constructed unit, and it is contemplated that the facility will be used on a routine basis for further process development work. Beginning about August 1, 1950, this installation will be utilized for pilot plant development of the second plutonium cycle of the Purex Process (See Section 6.0).

[redacted]

TABLE 1.3-1

ISOTOPIC PURITY OF PRODUCT

Analyses by Mass Spectrograph at Y-12

Run No.	Grams of 23	Isotopic Analyses of Product Expressed as Per Cent of Abundance				
		U^{233}	U^{234}	U^{235}	U^{236}	U^{238}
1T	5.66	98.4	0.20	0.3 (b)	0.04 (b)	1.1
2T	8.60	98.3	0.25	0.03 (b)	0.26 (b)	1.1
7T	18.65	98.8	0.32	0.3 (b)	0.07 (b)	0.6
8T	21.49	98.4	0.29	0.7 (b)	0.04 (b)	0.7
9T	18.08	98.3	0.30	0.7 (b)	0.00 (b)	0.8
10T	17.87	94.6	0.34	0.05	0.00	5.0 (d)
11T	17.24	93.6	0.30	0.05	0.02	6.1
12T	18.86	94.6	0.32	0.04	0.00	5.1
13T	17.30	95.7	0.34	0.03	0.02	5.9 (d)
14T	17.00	96.6	0.33	0.02	0.03	3.1
15T	15.97	97.0	0.35	0.02	0.02	2.6
16T	17.32	97.4	0.32	0.02	0.01	2.2
17T	15.04	97.6	0.30	0.02	0.00	2.1
18T	15.27	97.6	0.30	0.02	0.01	2.1
19T	22.32	97.8	0.29	0.01	0.00	1.9
20T (a)	27.82	98.9	0.26	0.01	0.01	0.8
21T (a)	43.98	98.4	0.28	0.01	0.01	1.3
Average	Tot. 318.5 (c)	97.3	0.30	-	-	2.4

(a) The products from Runs 3T, 4T, 5T, 6T were reprocessed in Runs 20T and 21T.
(b) The instrument used for 1T-9T analyses had been previously used for other uranium isotopic analyses, and these unreasonable values are due to contamination present in the instrument.
(c) Another 15 gms. of 23 was salvaged from samples, analytical wastes, etc. which will be kept separate from this material until an isotopic analysis can be made.
(d) The increased U-238 content beginning on Run 10T coincided with a change in buckets of Th metal, and the decrease beginning on Run 13T coincided with the depletion of this bucket.

[redacted]

CHALK RIVER SEPARATION

Technical - Rigstad, Gresky, Landry, Sadowski, Winget

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

2.0 CHALK RIVER SEPARATION

The processing of the first batch of Chalk River fuel material through two cycles of solvent extraction has been completed and the second batch partially completed. An attempt to use the Hybrid Flowsheet in the second cycle plutonium extraction was unsuccessful because of mechanical difficulties.

2.1 First Cycle Feed Preparation

After the first metal dissolving step of Run I it was discovered that the dissolver solution contained about 0.5 M $Al(NO_3)_3$. This caused crystallization of UNH and sampling difficulties at specific gravities normally used in feed preparation. Investigation revealed that the coating removal step had been incomplete due to the use of stock caustic solution having a concentration of a factor of two below specifications. Due to the presence of the $Al(NO_3)_3$, the column feed concentration was lowered to 1.65 M uranium to prevent freezing. Two "cleanout" dissolving procedures were also performed to insure complete uranium metal dissolution. Plutonium loss in the coating removal step was 0.4% due primarily to "particle" losses. These particles were cuased by the slug shearing process.

During the coating removal step of Run II, the slug counter indicated that the slug loading had been normal; however, after the metal dissolving step had begun it was discovered that twenty-two slugs had lodged in the chute. It was thus necessary to dislodge the jacketed slugs and charge them to the dissolver containing a solution of approximately 8 N HNO_3 and 200 g/l UNH. This procedure again introduced aluminum nitrate to the first cycle feed.

Chalk River Separation (Continued)

Precautionary measures to be adopted in succeeding runs are as follows:

(1) Stock caustic will be analyzed.

(2) Slug chute will be probed following charging.

2.2 First Cycle Results

Plutonium process loss in the first cycle of Run I was 0.13%, material balance was 94%, and the beta decontamination factor was 7×10^4. Detailed data can be found in Table 2.2.

2.3 Second Cycle Feed Preparation

The IBP was adjusted to 1.3 M $Al(NO_3)_3$, 0.05 N HNO_3 and 0.1 M $Na_2Cr_2O_7$, and heated for four hours at 40° C. Valence state analysis indicated >97.7% Pu^{+6}.

2.4 Second Cycle Results

The first half of Run I was processed using the KAPL modified flowsheet. Due to plugging of column II-A (the first in 2 1/2 years of Pilot Plant operation) with iron precipitate, it was found necessary to revert during the remainder of the run to an acid flowsheet. Due to the operational difficulties during the first half of the run, it was found necessary to recycle about 30% of the original raffinate because of high losses. The entire IIB concentrate must also be reprocessed to separate the plutonium from the $Al(NO_3)_3$ that entered the stripping column because of the plugged extraction column. Loss during the latter half of the run was 0.1%. Complete data on this second cycle will be reported next month.

Chalk River Separation (Continued)

Brief laboratory investigations indicated that the iron precipitate formed most readily at 0.05 - 0.1 N acid deficiency in a 1.3 M $Al(NO_3)_3$ solution and that ammonium fluosilicate prevented the precipitation. The fluosilicate was found to re-dissolve readily the precipitate which plugged column II-A. NH_4F and NaF were found to have no effect on dissolution of the precipitate. Adjusting the second cycle feed to 0.005 M $(NH)_2SiF_6$ was sufficient to prevent iron precipitation when the feed was added to an equal volume of 0.18 N acid deficient scrub solution. Ammonium fluosilicate complexes Pu^{+3}; however, it was observed to have no effect on the cross-over oxidation as determined by adjusting a IBP sample to 0.05 M $(NH_4)_2SiF_6$, and oxidizing with 0.1 M $Na_2Cr_2O_7$ to simulate IIAF preparation. The oxidized solution contained $>$99.0% Pu^{+6} indicating that an acid deficient second cycle is feasible.

The chemical flowsheet to be used in subsequent second cycle plutonium processings is given in Figure 2.4.

2.5 Laboratory Processing Status

No product is yet available for laboratory processing, since Run IRC will be re-processed in the pilot plant to separate plutonium from aluminum nitrate.

[redacted]

TABLE 2.2

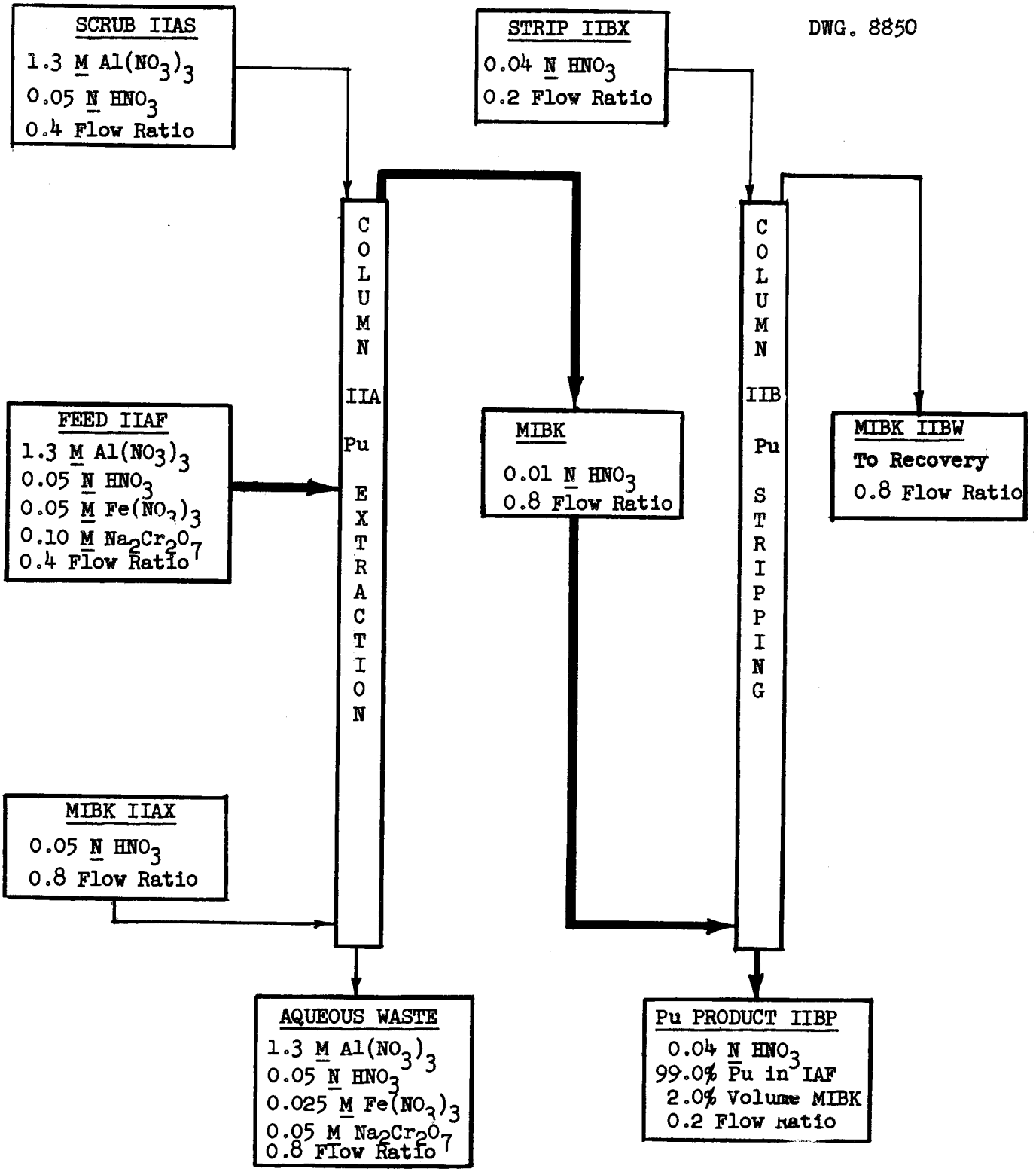
Process Data on Run IRC Plutonium First Cycle

Run No.	Pu in Feed Tot. Gms	Pu Loss %			Decontamination Factors						Mat. Bal.
		AW	CU	Tot.	Beta	Gamma	Ru	Zr	Ce	Cb	%
IRC-IA	23.2	.057	.043	0.10	9.3×10^4	2.4×10^4	-	-	-	-	-
IRC-IB	9.53	.069	.034	0.10	9.5×10^4	1.56×10^4	-	-	-	-	-
IRC-IC	2.47	.46	.077	.53	-	-	-	-	-	-	-
Overall	35.2	.08	.050	.13	6.9×10^4	2.3×10^4	5.9×10^3	2.8×10^4	4.3×10^6	1.2×10^5	93.8

[redacted]

[redacted]

FIGURE 2.4
DWG. 8850



REVISED REDOX FLOWSHEET

ORNL CHALK RIVER PROCESSINGS

SECOND PLUTONIUM CYCLE

April, 1950

[redacted]

Chalk River Separation (Continued)

2.6 Equipment Development

Studies of the two stage plutonium product (IIBP) evaporator have indicated that the hexone flashing step caused $< 0.01\%$ loss due to entrainment; however, it was apparent that the second stage introduced a loss in the order of 0.5%. This latter effect will be studied more closely in the succeeding runs.

2.7 Program

It is expected that at the end of the coming period three or four of the six batches of Chalk River material will be available for laboratory processing. Delays in procurement of laboratory ventilation equipment may make it impossible to fulfill the problem commitments on schedule.

RADIOCHEMICAL WASTE PROCESSING

Technical - Shank

3.0 RADIOCHEMICAL WASTE PROCESSING DEVELOPMENT

3.1 Evaporator Operating Summary

During April the ORNL Radiochemical Waste Evaporator processed 145,000 gallons of mixed wastes containing 2000 curies of activity. Overall beta curie decontamination factor (D.F.) for the month was 850 giving a condensate discharge activity averaging 5×10^{-9} curies/cc. This lowering of D.F. from last months 2×10^{3} is attributed to the processing of the supernate from the solids which had crystallized from previous evaporator concentrate. This material, having a much higher total solids than normal, gave higher entrainment and consequently lower D.F.

3.2 Development Progress

Installation of the evaporator foam level indicator has been delayed due to the inability to produce sufficient representative foam in the laboratory investigation. An unsuccessful attempt was made to use actual evaporator feed to measure and observe certain foam characteristics. A redesigned heating coil has been installed and the investigation will be repeated.

Radiochemical Waste Processing Development (Continued)

A conductivity cell has been installed in the evaporator condensate monitor tank and connected to a Micromax Conductivity Recorder for investigating the following:

A. True indication of a foam-over.

B. Pre-indication of a foam-over.

C. Indication of high entrainment.

D. Monitoring of activity.

The investigation consists of the comparison of beta activity with the chart reading. No numerical data has been taken but observation of the instrument indicates the possible usefullness as both a foam-over and high entrainment indicator.

3.3 Program

A more extensive evaluation of evaporator operation to include volume reduction and beta curie D.F. calculations is to be started next month.

Further laboratory investigations in de-entrainment and ion exchange is scheduled to begin by June 15. This work has been delayed due to insufficient laboratory space.

ORNL WASTE URANIUM RECOVERY UNIT

Technical - Stewart

4.0 ORNL METAL RECOVERY PLANT

June 16, 1950 has been established as the date for the completion of engineering details on the ORNL Metal Recovery Building. Design details of the process equipment have begun and purchase inquiries have been made to vendors of such equipment. Tentative instrumentation requirements have been discussed and transmitted to the Instrument Department.

25 RECOVERY

Technical - Rom

5.0 25 RECOVERY PROCESS

During the past period the following reports and memos have been issued completing the present phase of the Pilot Plant program:

1. "Terminal Report of ORNL Pilot Plant Development of the MTR Recovery Process", ORNL-676, by A. M. Rom.
2. "ORNL 25 Recovery Process Development: Fission Burnup of Enriched Uranium Used in Process Verification" by R. B. Briggs and A. M. Rom.
3. "ORNL 25 Recovery Process Development: Material Balance for Enriched Uranium Used in Process Verification" by A. M. Rom.

Pilot Plant personnel have been or will be transferred to the Design Section to assist in design of the Chemical Processing Area at the Reactor Testing Station at Idaho Falls, Idaho.

PUREX PROCESS

Technical - Jackson

6.0 PUREX PROCESS

Laboratory development of the Purex Process is sufficiently advanced to indicate that Pilot Plant development should begin about August, 1950. The scope of the Pilot Plant development program will include the first uranium-plutonium separation cycle, the second uranium cycle, the second plutonium cycle, and waste stream processing. It is planned that the process will be ultimately demonstrated at full Hanford activity level.

7.0 MISCELLANEOUS

Permanentization of the 205 Bldg. is 15% complete. All concrete foundations have been poured and main structural steel erected. During the coming period, the brick masonry and metal roofing and siding installation is scheduled to start.

During the past period the following Pilot Plant service samples have been shipped to the requesting project sites as indicated below:

Sample	Sample Size	Run No.	Shipped To
IAW	100 ml	2RC-I	KAPL
IBP	500 ml	52R-I	HEW
IAW	25 ml	52R-I	HEW
IAF	25 ml	52R-I	HEW