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TECHNICAL DIVISION

TECHNICAL DIVISION - PILOT PLANTS SECTION REPORT FOR APRIL, 1949

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TECHNICAL DIVISION

TECHNICAL DIVISION - PILOT PLANTS SECTION REPORT FOR APRIL, 1949

D. G. Reid

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TECHNICAL DIVISION - PILOT PLANTS SECTION

ABSTRACT

The results of ten 30% Hanford level Redox runs made under conditions of ORNL basic flowsheets show that plutonium and uranium losses meet process specifications, and that the required uranium gamma decontamination, 3×10^5, can be obtained in only two cycles of operation. The gamma activity of the uranium after two cycles is about twice the gamma activity of natural uranium. An acetone digestion of the feed of two runs in which the ANL and ORNL #1 flowsheets were used in the first and second cycles resulted in two-cycle decontamination factors of 1.5×10^5 and 3.0×10^5. All Redox flowsheets continue to show a high degree of mechanical operability. A decision has been made to use only the ORNL flowsheets in the 100% Hanford level verification runs.

A definite program has been formulated for the resumption of the "25" process investigations.

[redacted]

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REDOX PILOT PLANT DEVELOPMENT

Technical - Jackson, Rigstad, Harrington, Hylton, Kennedy, Sadowski, Shank, and Stewart

Non-Technical - Beeler, Benson, Burnett, Caldwell, Grizzell, Groover, Jones, Land, Ledbetter, McLellan, Sexton, Shields, Spangler, Strader, Summers, Thomas, Thompson, Waters, and Wiggins

I. REDOX PROGRESS SUMMARY

The primary objective of Pilot Plant runs made during the past period was to verify the results of six ORNL flowsheet runs previously made at 30% Hanford activity level. A second important objective was to determine if the ORNL and particularly the ANL flowsheet could be significantly improved by digesting the feed with acetone at 90-100° C. The acetone treatment was given to the feed of one of the four ORNL flowsheet runs, and to two runs made under conditions of the ANL flowsheet in the first cycle and ORNL #1 flowsheet in the second cycle. Split runs were generally made in the second cycle, with a total of eleven second cycle runs being made during the period.

The results of the four ORNL flowsheet runs were consistent with previous ORNL flowsheet data, and an evaluation of the performance of this flowsheet is given in Table I. The performance of the ANL flowsheet is given for comparison.

TABLE I

Evaluation of Redox Flowsheets (1)

First Cycle Flowsheet	Second Cycle Flowsheet	Two Cycle Gamma D.F.
ANL	ANL	7×10^2
ANL	ORNL #1	5×10^4
ORNL	ANL	1×10^4
ORNL	ORNL #1	3×10^5

(1) Plutonium losses for one cycle and uranium losses for two cycles are less than 0.5%.

[redacted]

Redox Progress Summary (Continued)

No significant increase in decontamination was obtained when the feeds for ORNL flowsheet runs were treated with acetone, but the acetone treatment increased the two cycle decontamination given by the ANL-ORNL #1 flowsheet combination to values of 1.5×10^5 and 3.0×10^5 for the two runs completed.

U^{237} gamma activity due to 60 day cooled ORNL slugs was found to account for 50-80% of the gamma activity in the IEU stream during the past period. The disintegration rate of U^{237} in the ORNL slugs at the time of removal from the pile was calculated to be of the order of 1×10^5 d/m/mg U.

On the basis of the results of all ORNL Pilot Plant runs made to date the following conclusions have been drawn on the performance of the various Redox flowsheets.

1. Uranium and plutonium losses for both ANL and ORNL flowsheets meet process requirements.

2. The uranium gamma decontamination specification of 3×10^5 can be consistently obtained in two cycles by the use of ORNL flowsheet in the first cycle and ORNL #1 flowsheet in the second cycle. The ANL-ORNL #1 flowsheet combination fails to meet process specifications by a factor of five to ten.

3. Both ANL and ORNL flowsheets have a high degree of mechanical operability.

4. There is promising preliminary evidence that the process specification for gamma decontamination can be met by a combination of ANL-ORNL #1 flowsheets, if the feeds are digested with acetone.

II. OBJECTIVES OF FIRST CYCLE RUNS

The primary objective of first cycle runs made during the past period was to demonstrate further the ORNL Redox flowsheet. The objective of three of the six runs completed was to determine if an acetone treatment of the feed would give increased decontamination. Details of this acetone treatment are given in Section III-C.

Specific objectives of the runs completed during this period are as follows:

Run 39R - Obtain data on the reproducibility of the ORNL flowsheet.

Run 40R - No such first cycle run made in order to maintain numerical continuity in both first and second cycles.

Run 41R - Determine if the decontamination given by the ORNL flowsheet could be improved by treating the feed with acetone.

Run 42R - Determine if the decontamination given by the ANL flowsheet could be improved by treating the feed with acetone.

Run 43R - No such run made.

Run 44R - Obtain additional data on the reproducibility of the ORNL flowsheet.

Run 45R - No such run made.

Run 46R - Obtain additional data on the reproducibility of the ORNL flowsheet.

Run 47R - Determine if the decontamination given by the ANL flowsheet could be improved by treating the feed with acetone and sodium nitrite.

III. FIRST CYCLE FEED PREPARATION

A. Dissolution for Runs 39R-47R

When using the ORNL flowsheet it is convenient from an operational standpoint to follow a dissolving procedure which yields an acid deficient dissolver solution, and such a dissolving procedure was followed in runs 36R-47R. Some comments on the chemical effects of dissolving to acid deficient conditions are given in Section III-D. The dissolving procedure used on runs 39R-47R is summarized as follows:

1. Add sufficient quantity of metal to obtain a 100-200% dissolver heel after dissolving 80 kg. of metal.

2. Remove aluminum jackets by the standard 10% NaOH - 20% $NaNO_3$ procedure.

3. Add 100 pounds of 55% HNO_3 to the dissolver.

4. Heat the contents of the dissolver to 85-95° C or until the reaction becomes self sustaining at 100-102° C.

5. Add 330 pounds of 55% HNO_3 at a rate of about 3 lb/min. and control reaction with jacket cooling water. The rate of reaction is determined qualitatively by observing the temperature and pressure of dissolver off-gases. During the last half or third of the dissolving, jacket steam may be required to maintain the reaction.

6. Continue the reaction until a specific gravity of 1.85 has been attained.

The above procedure is operationally smooth, and yields a dissolver solution which is 0.1 - 0.3 basic. Additional data on dissolvings are given in Table III.

For all runs made during the past period the slugs charged to the dissolver were 30% by weight Hanford production slugs and 70% by weight ORNL slugs of ~1000 day irradiation. The specific activities of the feed solutions for the first cycle runs are given in Table II.

TABLE II

Specific Activities of Feed Stream, Runs 39-47R

Run	β cts/mg U(1)	γ cts/mg U(1)	Puα cts/mg U(1)	Gms Pu/Metric Ton of U
39	4.3×10^6	1.1×10^4	9.8×10^3	140
41	3.5×10^6	8.7×10^3	1.0×10^4	140
42	3.7×10^6	9.8×10^3	1.1×10^4	150
44	3.8×10^6	1.0×10^3	1.2×10^4	170
46	4.8×10^6	1.2×10^4	1.0×10^4	140
47	4.3×10^6	1.1×10^4	9.4×10^3	130

(1) Betas counted at 10% geometry, alphas counted at 52% geometry, gamma counting efficiency $\sim$ .05%.

B. General Procedure for Oxidation and Acid Adjustment

The general procedure for oxidation and acid adjustment in Runs 36-47R was as follows:

1. Regardless of the acidity of the dissolver solution, make the solution 0.1 M in sodium dichromate, and oxidize the plutonium to the plus six valence state by heating at 85° C for six hours.

2. Adjust the oxidized dissolver solution to 0.2 M acid deficient by the addition of concentrated sodium hydroxide or nitric acid as required.

The oxidation and acid adjustment procedures for Runs 41, 42, and 47R are exceptions to the general procedure described above. The feed preparation for these three runs are described in the following section.

[redacted]

TABLE III

Summary of Data on Dissolving,
Runs 37-47R (1)

Run and Dissolving Number	Slugs Added	Metal Heel, % (2)	Dissolving Time, Hrs.	Residual Acid, N (3)	mols acid / mols U (4)
39R - 1	7W, 49X	180	8	.03b	-
- 2	7W, 49X	140	10	.02b (4)	4.6
41R - 1	7W, 49X	170	8	.14b	-
- 2	7W, 49X	170	13	.22b (4)	5.0
42R - 1	7W, 49X	160	12	.26b	-
- 2	7W, 49X	190	11	.24b (4)	4.8
44R - 1	7W, 49X	170	11	.19b	-
- 2	7W, 49X	150	10	.09b (4)	4.6
46R - 1	7W, 49X	150	10	.08b	-
- 2	7W, 49X	130	14	.23b (4)	4.5
47R - 1	7W, 49X	120	13	.09b	-
- 2	7W, 25X	80	12	.07a (4)	4.5

NOTES:

(1) All dissolvings made with 55% nitric acid, and sp.gr. at end of all dissolvings was 1.85.

(2) Defined as 100 (undissolved metal/dissolved metal) at the end of each dissolving.

(3) a and b denote that the final dissolver solution was acid or acid deficient respectively.

(4) Analysis or calculation made on the composite of both dissolvings.

[redacted]

First Cycle Feed Preparation (Continued)

C. Acetone Treatment of Feed for Runs 41, 42, and 47R

The ORNL Laboratory and Semi-Works Development Section has developed a method for increasing ruthenium decontamination under acid flowsheet conditions by treatment of feed solutions with acetone, and a detailed discussion of the treatment is given in current reports of that section. The increased ruthenium decontamination is effected by some unidentified product of the reaction between acetone and nitric acid.

For a demonstration of the effect of acetone treatment of the feed, the dissolver solutions for Runs 41, 42, and 47R were treated as follows:

1. Made 0.3 N acid by the addition of nitric acid.

2. Made 0.5% in acetone for Runs 41 and 42R, and made 1.0% in acetone and 0.05 N in sodium nitrite for run 47R.

3. Heated at 80° C for thirty minutes, and then at 90° C for three hours.

4. Made 0.1 M in sodium dichromate and oxidized by heating at 85° C for six hours.

5. Adjusted to 0.2 M acid deficiency in preparation for an ORNL flowsheet run in the case of 41R, or adjusted to 0.3 M acid for ANL flowsheet runs in the case of Runs 42 and 47R.

D. Comments on Future Dissolution and Feed Adjustment Procedures

The IAW plutonium loss for Run 46R was 0.5%, and preliminary data on Runs 48R and 49R (not included in this report) indicate IAW losses of ~1%. The average IAW plutonium loss for ORNL flowsheet Runs 36R-44R is 0.04%. The cause for the higher losses on Runs 48 and 49R has been traced to the feed makeup procedure, and beginning with Run 50R a dissolving, oxidation, and acid adjustment procedure which is more conservative from the viewpoint of preventing plutonium polymer formation and for oxidation of Pu^{+4} to Pu^{+6} will be used. This modified procedure consists of dissolving to an acidity of ~0.2 N acid (rather than 0.2 N acid deficiency), oxidation with 0.1 M dichromate at 85° C for six hours, and then acid adjustment to 0.2 N acid deficiency.

IV. FIRST CYCLE COLUMN OPERATION

The six first cycle runs completed in this period were the last of a series of 30% Hanford activity runs made before proceeding to a series of five demonstration runs at 100% Hanford activity. Column operation continued to be smooth and generally without incident, and to date no significant problems of operability have developed in the ORNL Pilot Plant testing of the Redox process.

A summary of the results of the first cycle runs covered in this report is given in the following tables.

Table V - Summary of Losses and Gross Decontamination

Table VI - Summary of Specific Product Decontamination

Table VII - Distribution of Gamma Activity in IAF, IBP and ICU Streams

A summary of the results of all first cycle runs made to date under conditions of the ORNL flowsheet is given in Table VIII. The ORNL first cycle flowsheet is shown in Figure 1.

The following major conclusions are drawn on the results of first cycle runs.

1. The performance of the ORNL first cycle flowsheet is evaluated in Table IV. The performance of the ANL flowsheet in the ORNL Pilot Plant is given for comparison.

TABLE IV

Evaluation of the ORNL First Cycle Flowsheet

	ORNL Flowsheet	ANL Flowsheet
Total Plutonium Loss - %	0.5	0.01
Total Uranium Loss - %	0.01	0.01
IBP Gross Gamma D.F.	5×10^3	2×10^3
ICU Gross Gamma D.F.	5×10^3	100

First Cycle Column Operation (Continued)

2. The uranium loss for all first cycle flowsheets tested is less than 0.01%, and the plutonium loss for the ANL flowsheet is less than 0.1%. The plutonium loss under ORNL flowsheet conditions has varied from 0.1 to 0.6%, with half of the values being less than 0.2%. Laboratory extractions made on IAW streams from the Pilot Plant runs indicate that losses above 0.1% in the ORNL flowsheet are due to reduced (below plus six valence state), unpolymerized plutonium, and additional laboratory studies are now in progress for the purpose of developing a method for limiting the IAW plutonium loss to 0.1% or below.

3. The uranium decontamination given by the ORNL flowsheet is sufficiently large that a gamma decontamination factor of 3×10^5, the process specification, can be attained in two cycles if the ORNL flowsheet is used also in the second cycle.

4. There is sound Pilot Plant evidence to indicate that the process specification for uranium gamma decontamination can be attained in two cycles by a combination of the ANL first cycle flowsheet and ORNL second cycle flowsheet, if the feeds to both cycles are given a special acetone treatment now being developed by the ORNL Technical Division Laboratory and Semi-Works Section. In the two Pilot Plant runs made with such a flowsheet combination and including acetone treatment, two cycle gamma decontamination factors of 3.0×10^5 and 1.5×10^5 were obtained. These decontamination factors are 5-10 times greater than the factors obtained without the acetone treatment.

The following comments and conclusions on runs covered in the report are made to support and extend the major conclusions stated above:

1. Uranium Losses

For all runs the total uranium loss was below 0.01%. The ICW losses averaged 0.002%, and it is concluded that the use of 0.04 N HNO_3 rather than 0.1 N HNO_3 in the ICX stream is satisfactory.

First Cycle Column Operation (Continued)

2. Plutonium Losses

Beginning with Run 36R, the first cycle feed was oxidized before addition of sodium hydroxide, and on Runs 36-44R the IAW losses were below 0.1%. The plutonium loss on Run 46R was 0.5%, and the preliminary data on Runs 48R and 49R indicate that the losses on these runs were about 1%. Feed samples from Runs 46, 48, and 49 were extracted in the laboratory, and the inextractable plutonium was found to be equal to the inextractable (under acid deficient conditions) plutonium in the Pilot Plant IAW stream. In both Pilot Plant and laboratory raffinates, however, the plutonium extracted when raffinates were made 0.3 N in acid. This data led to the conclusion that (1) the plutonium losses were due to reduced but unpolymerized plutonium, and (2) a more conservative feed makeup procedure would be one in which the dissolving was stopped on the acid side, where oxidation of Pu^{+4} in the presence of dichromate is more rapid than under acid deficient conditions. This modified feed makeup procedure will be used beginning with Run 50R. The 0.5 - 1.0% losses on Runs 46, 48, and 49R have resulted in a laboratory program at ORNL for further study of the behavior of plutonium in feed makeup and in the IA column.

3. Americium and Curium in the IAW Solutions

The intrepretation of much of the experimental data during the past period was complicated by the presence of an inextractable alpha activity which amounted to 0.6% of the total alpha count of the plutonium in the IAF. This 0.6% is an order of magnitude greater than the amount of americium and curium expected from 100 day irradiated, 100 day cooled Hanford slugs, and after identification of this activity as americium and curium it was found that the Hanford slugs being used had actually been charged to the Hanford piles before February, 1948. Some details on the identification of americium and curium are given in Section X-D.

4. Elimination of Precipitation in the IBP Stream

No precipitate has been observed in the IBP stream since the IBX and IBS streams were made 0.05 N in HNO_3. This amount of acid is considered a safe, but not necessarily optimum, condition for prevention of precipitation in the IBP stream.

First Cycle Column Operation (Continued)

5. Fission Product Decontamination, ORNL Flowsheet

The values for gross decontamination and for ruthenium, columbium and zirconium decontamination obtained during the past period are considered highly consistent, and it is concluded that the ORNL flowsheet is highly reproducible. Uranium decontamination values generally varied by less than a factor of two from the values given in Table IV, and plutonium decontamination values generally varied by less than a factor of 1.5 from the values given in Table IV. Acetone treatment of the feed had no significant effect on the decontamination of any of the fission products except ruthenium.

6. ANL Flowsheet with Acetone Treatment of Feed

The two runs made under ANL flowsheet conditions with acetone treatment of the feed gave the following results.

Run 42R

The feed for this run was treated with acetone. The decontamination obtained was identical to that obtained in ANL flowsheet runs not treated with acetone. When the ICU stream for this run was used as feed makeup material for a second cycle run under ORNL #1 conditions (with an acetone-nitrite treatment of the second cycle feed), a two cycle decontamination of 3×10^5 was obtained.

Run 47R

The feed for this run was treated with both acetone and nitrite. The decontamination obtained for the run was a factor of ten greater than that normally obtained for an ANL flowsheet run, due to increased ruthenium decontamination. When the ICU stream for this run was used as feed makeup material for a second cycle run under ORNL #1 conditions (without acetone treatment of the second cycle feed), a two cycle decontamination of 1.5×10^5 was obtained.

On the basis of the above data it is concluded that the acetone treatment applied to the ANL-ORNL flowsheet combination increased the overall decontamination for two cycles by a factor of roughly ten, and that the average two cycle decontamination for the two runs was only a factor of two less than the average of all two cycle runs in which the ORNL flowsheet was used in both cycles. It might prove

First Cycle Column Operation (Contined)

to be significant that the large increases in decontamination (second cycle run 43R and first cycle run 47R) occured on runs where both acetone and nitrite were used in the feed treatment, but it is felt that the amount of experimental data is not adequate to justify a firm conclusion on this point. Large improvements have been noted in the laboratory for both the acetone and acetone-nitrite feed treatments, and the failure to obtain increased decontamination in the first cycle of run 42R is not understood.

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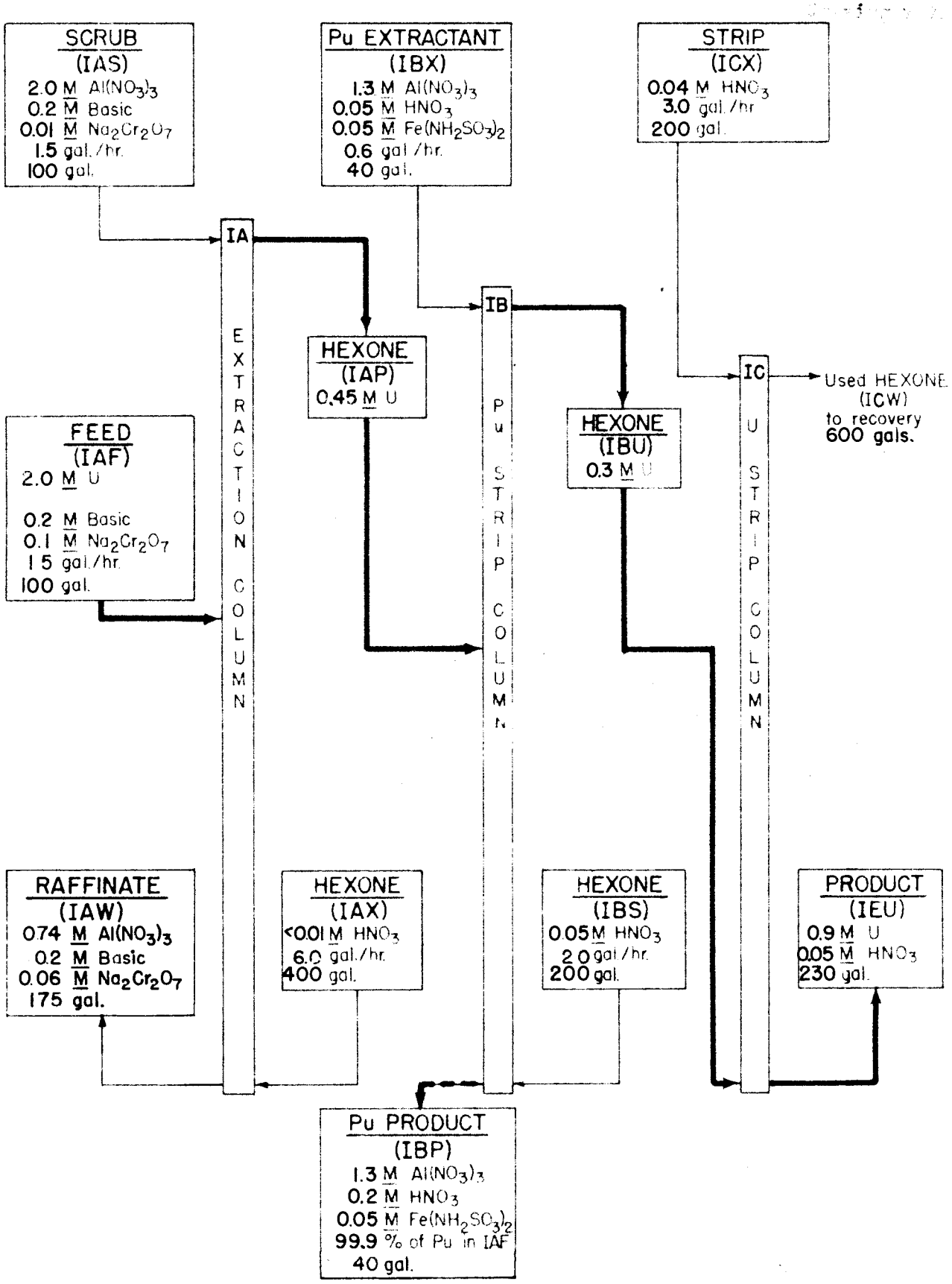

REDOX FIRST CYCLE

ORNL CHEMICAL FLOWSHEET

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TABLE V

Summary of Losses and Gross Decontamination

First Cycle Runs 37-47R

Run	39R	41R	42R	44R	46R	47R
Flowsheet	ORNL	ORNL-G(1)	ANL-G(1)	ORNL	ORNL	ANL-G(1)
URANIUM						
IAF conc, mg/ml	490	490	480	495	505	470
IAP uranium balance, %	97	103	102	104	105	98
IBU uranium balance, %	98	97	96	102	101	99
ICU uranium balance, %	102	99	107	105	106	92
IAW loss, %	.001	.004	.002	.002	.009	.009
IBP loss, %	$1x10^{-5}$	$3x10^{-4}$	$1x10^{-4}$	$1x10^{-4}$	$1x10^{-4}$	.004
ICW loss, %	.002	.006	.001	.001	.001	.001
PLUTONIUM						
Counts/ml/min in IAF	$4.8x10^6$	$4.9x10^6$	$5.2x10^6$	$5.9x10^6$	$5.2x10^6$	$4.4x10^6$
IBP plutonium balance,%	93	88	106	92	98	99
IAW loss, %	0.05	0.08	0.04	0.07	.56	.10
IBU loss, %	.06	.05	.02	.07	.09	.02
ICU loss, %	.09	.08	.02	.10	.04	.02
IBP D.F. from uranium	10^7	$3x10^5$	10^6	10^6	10^6	$3x10^4$
β Radiation(2)						
Counts/ml/min in IAF	$2.1x10^9$	$1.7x10^9$	$1.8x10^9$	$2.1x10^9$	$2.3x10^9$	$2.1x10^9$
Counts/ml/min in ICW	$8.5x10^3$	$7.0x10^3$	$7.0x10^3$	$4.3x10^3$	$3.8x10^3$	$1.9x10^4$
IAP β D.F.	$3.8x10^3$	$5.7x10^3$	100	$4.2x10^3$	$1.0x10^4$	$1.0x10^3$
IBP β D.F.	$1.8x10^4$	$1.7x10^4$	$4.6x10^3$	$1.2x10^4$	$3.0x10^4$	$2.1x10^4$
IBU β D.F.	$4.8x10^3$	$6.6x10^3$	110	$5.5x10^3$	$1.3x10^4$	$1.4x10^3$
ICU β D.F.	$5.2x10^3$	$6.6x10^3$	160	$6.4x10^3$	$1.3x10^4$	$1.7x10^3$
γ Radiation(2)						
Counts/ml/min in IAF	$5.2x10^6$	$4.3x10^6$	$4.7x10^6$	$5.1x10^6$	$5.8x10^6$	$5.0x10^6$
mv/ml in IAF	$1.9x10^6$	$1.7x10^6$	$1.6x10^6$	$2.0x10^6$	$2.2x10^6$	$1.8x10^6$
IAP γ D.F.	$2.0x10^3$	$2.7x10^3$	85	$2.7x10^3$	$5.0x10^3$	600
IBP γ D.F.	$5.0x10^3$	$5.0x10^3$	$2.9x10^3$	$4.6x10^3$	$8.4x10^3$	$6.5x10^3$
IBU γ D.F.	$2.8x10^3$	$4.4x10^3$	90	$3.4x10^3$	$5.3x10^3$	840
ICU γ D.F.	$3.0x10^3$	$4.6x10^3$	115	$4.2x10^3$	$6.1x10^3$	$1.0x10^3$

Notes:

(1) The feeds for runs 41R and 42R were treated with acetone, and the feed for run 47R was treated with acetone and nitrite. See Section III C.

(2) Betas counted at 10% geometry, alphas counted at 52% geometry, gamma counting efficiency $\sim$ .05%.

[redacted]

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TABLE VI

Summary of Specific Fission Product Decontamination

First Cycle Runs 37-47R

		IAF	IBP		ICU	
		% β	% β	D.F.	% β	D.F.
Run 39R						
	Ru	4.8	64	1.4×10^3	85	370
Flowsheet: ORNL	Zr	7.9	30	4.8×10^3	5.5	9.4×10^3
	Cb	1.8	4.7	7.1×10^3	0.8	1.5×10^4
	Ce	46.6	0.2	4.4×10^4	< 0.1	1.2×10^7
Total or Gross	D.F.	61	98	1.8×10^4	91	5.2×10^3
Run 41R						
	Ru	5.3	74	1.2×10^3	77	460
Flowsheet: ORNL-G(1)	Zr	7.1	19	6.2×10^3	14	3.2×10^4
	Cb	1.8	3.9	8.5×10^3	5.8	2.0×10^4
	Ce	52.0	0.2	4.0×10^4	1.4	2.4×10^6
Total or Gross	D.F.	66	97	1.7×10^4	98	6.6×10^3
Run 42R						
	Ru	4.9	90	250	99	8.1
Flowsheet: ANL-G(1)	Zr	7.1	6.9	4.7×10^3	0.5	2.3×10^4
	Cb	1.3	1.0	6.7×10^3	0.1	2.9×10^4
	Ce	51.6	0.1	1.7×10^6	< 0.1	1.3×10^7
Total or Gross	D.F.	65	98	4.6×10^3	100	160
Run 44R						
	Ru	5.4	55	1.1×10^3	71	570
Flowsheet: ORNL	Zr	7.2	26	3.2×10^3	0.8	6.3×10^4
	Cb	1.6	2	9.1×10^3	0.2	4.4×10^4
	Ce	51.2	0.8	7.5×10^5	0.1	1.0×10^7
Total or Gross	D.F.	65	84	1.2×10^4	72	6.4×10^3
Run 46R						
	Ru	5.3	64	2.3×10^3	81	750
Flowsheet: ORNL	Zr	7.7	32	7.1×10^3	5.7	1.7×10^4
	Cb	1.7	4.5	1.0×10^4	0.3	5.7×10^4
	Ce	48.9	3.2	4.4×10^5	< 0.1	2.0×10^7
Total or Gross	D.F.	65	102	3.0×10^4	87	6.1×10^3
Run 47						
	Ru	4.5	92	860	91	71
Flowsheet: ANL-G(1)	Zr	7.9	15	9.1×10^3	0.3	3.7×10^4
	Cb	1.9	3	1.2×10^4	0.1	4.7×10^4
	Ce	50.6	0.1	7.1×10^6	< 0.1	2.5×10^7
Total or Gross	D.F.	65	110	2.1×10^4	92	1.7×10^3

Notes:

(1) The feeds for Runs 41R and 42R were treated with acetone, and the feed for Run 47R was treated with acetone and sodium nitrite. See Section III C.

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TABLE VII

Distribution of Gamma Activity
in
IAF, IBP and ICU Streams
First Cycle Runs 39-47R

		Percent of Gamma Activity and Gross Gamma Decontamination (1)		
		IAF	IBP	ICU
Run 39R				
Flowsheet: ORNL	Ru	6.9	26	73
	Zr	31.1	33	13
	Cb	56.5	41	14
Total or Gross Gamma D.F.		95	5.0×10^3	4.6×10^3
Run 41R				
Flowsheet: ORNL-G(2)	Ru	7.3	35	82
	Zr	25.6	25	4
	Cb	50.0	40	14
Total or Gross Gamma D.F.		82	5.0×10^3	4.6×10^3
Run 42R				
Flowsheet: ANL-G(2)	Ru	5.3	69	100
	Zr	25.5	14	0.1
	Cb	42.6	16	0.2
Total or Gross Gamma D.F.		73	2.9×10^3	115
Run 44R				
Flowsheet: ORNL	Ru	9.6	42	92
	Zr	36.2	55	3
	Cb	51.5	3	5
Total or Gross Gamma D.F.		97	4.6×10^3	4.2×10^3

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Table VII (Con't.)

		Percent of Gamma Activity and Gross Gamma Decontamination (1)		
		IAF	IBP	ICU
Run 46R				
Flowsheet: ORNL	Ru	6.4	26	79
	Zr	27.3	35	15
	Cb	43.1	39	6
Total or Gross Gamma D.F.		77	8.4×10^3	6.1×10^3
Run 47R				
Flowsheet: ANL-G(2)	Ru	6.0	48	98
	Zr	28.7	21	0.9
	Cb	55.0	31	1.3
Total or Gross Gamma D.F.		89	6.5×10^3	1.0×10^3

NOTES:

(1) Gross gamma decontamination data are experimental; IAF, IBP and ICU gamma distribution data are calculated from specific fission product beta analyses and known beta/gamma ratios for specific fission products.

(2) The feeds for runs 41R and 42R were treated with acetone, and the feed for run 47R was treated with acetone and sodium nitrite. See Section III C.

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[redacted]

TABLE VIII

Summary of ORNL Flowsheet Runs

All Runs Made at 30% Hanford Activity

Run	Decontamination Factor				IAW Losses	
	Plutonium		Uranium		Pu	U
	Beta	Gamma	Beta	Gamma	%	%
32	2.3×10^4	5.0×10^3	3.1×10^4	1.6×10^4	.01	.004
33	1.2×10^4	4.0×10^3	8.5×10^3	2.7×10^3	9(1)	.002
37	4.5×10^4	9.0×10^3	3.5×10^4	7.5×10^3	.10	.20
39	1.8×10^4	5.0×10^3	5.2×10^3	3.0×10^3	.05	.001
41	1.7×10^4	5.0×10^3	6.6×10^3	4.6×10^3	.08	.004
44	1.2×10^4	4.6×10^3	6.4×10^3	4.2×10^3	.07	.002
46	3.0×10^4	8.4×10^3	1.3×10^4	6.1×10^3	.56	.009

(1) This high loss was due to the addition of sodium hydroxide to the dissolver solution before oxidation.

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V. OBJECTIVES OF SECOND CYCLE RUNS 37R - 47R

The primary objective of second cycle runs made during the past month was to demonstrate further that the process specification for gamma decontamination (3×10^5) could be attained in two cycles by the use of acid deficient systems. The effect of acetone treatment of the second cycle feed was studied in five of the ten runs completed. Details of the acetone treatment are given in Section VI-B. Specific objectives of runs made during the past month are as follows:

Runs 37R,38R - Run 37R was made to obtain data on reproducibility of the ORNL #1 flowsheet, and Run 38R was made to determine if an acetone treatment of the feed would increase the decontamination given by the ORNL #1 flowsheet. The ICU stream from first cycle run 37R, an ORNL flowsheet run, was used as a common starting feed material for both runs.

Run 39R - Reproducibility run using the ORNL #1 flowsheet, and using a feed which had been treated with acetone. The ORNL flowsheet was used in the first cycle of this run.

Runs 40R,41R - These runs were made under conditions of the ANL and ORNL #1 flowsheets respectively for the purpose of comparing these flowsheets when the feeds are treated with acetone, and when the ORNL flowsheet is used in the first cycle. The ICU stream from first cycle run 41R, an ORNL flowsheet run, was used as a common starting feed material for both runs.

Runs 42R,43R - These runs were made under conditions of the ANL and ORNL #1 flowsheets respectively for the purpose of comparing these flowsheets when the feeds are treated with acetone, and when the ANL flowsheet is used in the first cycle. The ICU stream from first cycle run 42R, an ANL flowsheet run, was used as a common starting feed material for both runs.

Run 44R - Reproducibility run using the ORNL #1 flowsheet.

Run 45R - This run was made under conditions of the ORNL #2 flowsheet. Work on this flowsheet had previously been discontinued in favor of the ORNL #1 flowsheet, but an additional run was made when preliminary data on second cycle runs 41,43 and 44R indicated that process specifications for gamma decontamination were not being met. It was later determined that the fission product decontamination in runs 41,43, and 44R was satisfactory, and that the interpretation of preliminary data on these runs was complicated by significant quantities of U^{237} from ORNL slugs which had been cooled only 60 days.

Runs 46R,47R - Reproducibility runs using the ORNL #1 flowsheet.

VI. SECOND CYCLE FEED PREPARATION

A. Review of General Procedure for Feed Makeup

No changes in the general procedure for feed makeup have been made during the past month. For split runs in which both ANL and ORNL flowsheets are used the procedure is as follows:

1. The acidity of the ICU stream is adjusted to 0.3 M acid, based on 2 M uranium, by the addition of concentrated (approximately 19 M) sodium hydroxide.

2. This solution is then evaporated to 2 M uranium and a final acid adjustment is made, if necessary, with concentrated nitric acid or sodium hydroxide.

3. One-half of the feed is then dropped to the feed tank for an ANL flowsheet run.

4. The remaining feed is then adjusted to 0.2 M acid deficiency by addition of concentrated sodium hydroxide. If an ORNL #1 flowsheet run is to be made, the feed is dropped at this point to the feed tank. If an ORNL #2 flowsheet run is to be made, the feed is diluted to 1.8 M uranium, and butted to 1.2 M aluminum nitrate by the addition of an equal volume of 2.4 M aluminum nitrate solution which is 0.2 M acid deficient.

When only ORNL flowsheet runs are to be made the ICU stream is adjusted directly to 0.2 M acid deficiency, based on 2 M uranium, by use of concentrated sodium hydroxide, and the solution is then evaporated to 2 M uranium.

The above procedure has presented no operational difficulties. The source of feed for each second cycle run completed during the month and the flowsheets used are given in Table XI.

Second Cycle Feed Preparation (Continued)

B. Acetone Treatment of Second Cycle Feed

For those runs in which the feed is treated with acetone a preliminary makeup procedure is required before the operations described in Section A are carried out. Generally this preliminary procedure consists of making the feed 0.3 N acid, adding acetone (and sodium nitrite in some cases), heating at 90° for thirty minutes, and heating at 100° for three or four hours. Data on the preliminary feed makeup procedure for each run which was given the acetone treatment are given in Table IX.

TABLE IX

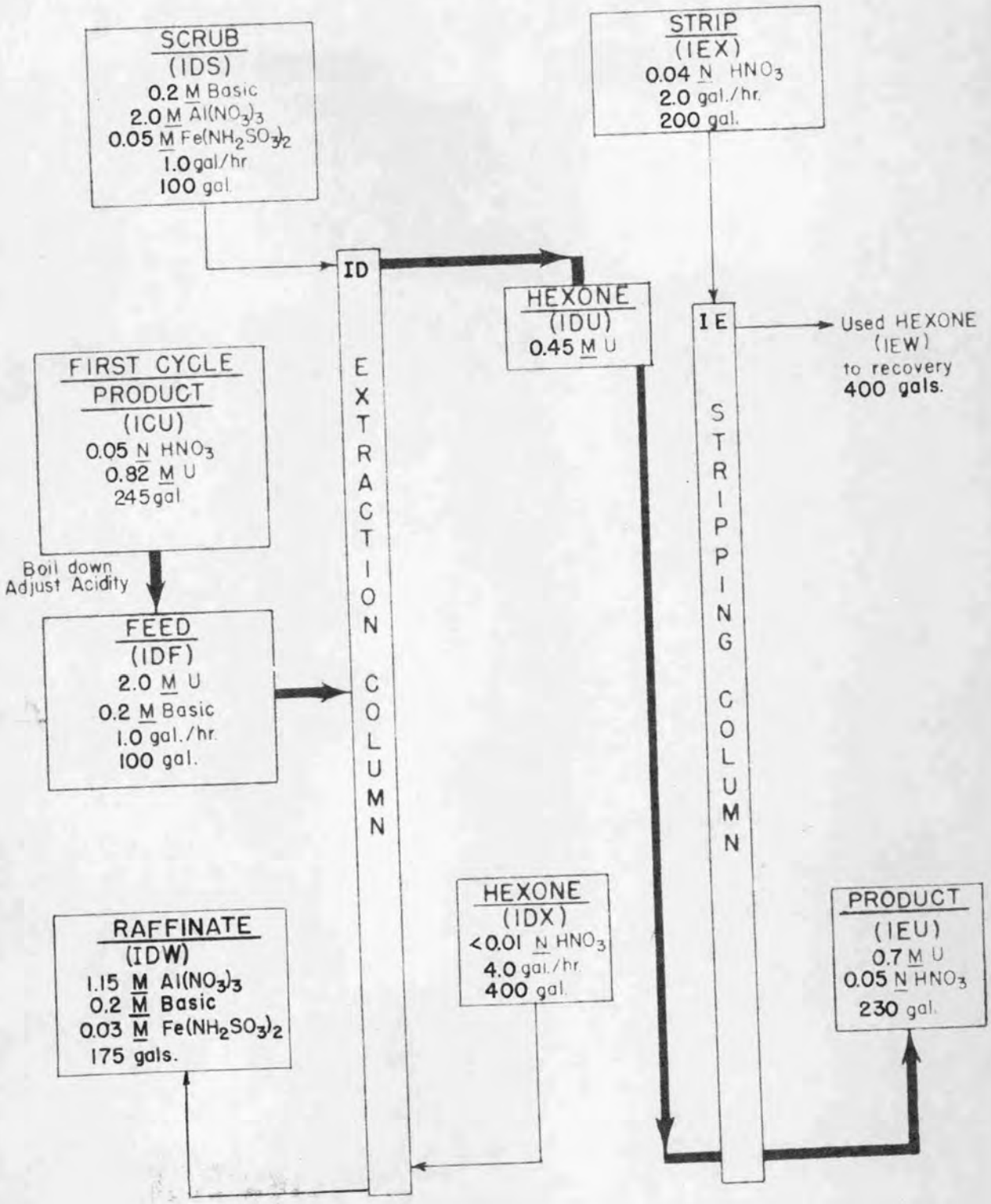
Data on Acetone Treatment of Second Cycle Feeds

Run	Flowsheet	Acetone, %	Sodium Nitrite, N	Acidity Of Feed, N	Time of Heating at 90° C, min	Time of Heating at 100°C, hrs
38	ORNL #1	.25	---	.30	0	4
39	ORNL #1	.50	---	.35	30	3
40	ANL	.50	---	.35	30	3
41	ORNL #1	.50	---	.35	30	3
42	ANL	.50	.04	.35	30	4
43	ORNL #1	.50	.04	.35	30	4

[redacted]

[redacted]

Drawing # 7219



REDOX SECOND CYCLE

ORNL #1 CHEMICAL FLOWSHEET

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VII. SECOND CYCLE COLUMN OPERATION

A. Summary of Data and Conclusions

The following comments are made on the second cycle column operation data which is summarized in Table X.

1. The majority of the cerium and columbium beta counts, and some of the zirconium counts in the IEU stream are so close to background that the values are of questionable accuracy. These values, however, are believed to be conservative. Ruthenium was in a reasonable counting range for all runs.

2. U^{237} gamma activity was found to account for 50-80% of the gamma activity in the IEU stream. The gross beta and gamma activity, and decontamination values reported are calculated values based on beta analyses for specific fission products. The identification and determination of U^{237} in the IEU stream is discussed in Section X-C.

3. Analyses for plutonium in the IEU stream have been temporarily discontinued pending development of a suitable method for reducing the alpha count ($\sim$40 cts/min) given by blank runs on 1.0 M uranium by both the LaF_3 and TTA methods.

4. As previously recognized, the decontamination obtained for any second cycle run is a function not only of the flowsheet used, but of the history of the feed material for the run. The histories of the feed material for the second cycle runs made during the past period were particularly varied, the corresponding first cycle runs having been made under conditions of both ANL and ORNL flowsheets, and the ORNL flowsheet runs having been made with and without the acetone treatment. The two first cycle ANL flowsheet runs were both made with different acetone treatments of the feed, and the decontamination factors varied by a factor of ten. The varying composition of second cycle feeds which resulted from the various first cycle treatments places a limitation on the conclusions which may be drawn on the second cycle decontamination data. A number of significant conclusions may be drawn, however, especially in those cases where split runs were made in the second cycle. In the interpretation of second cycle results it is felt that the residual activity in the IEU stream is as significant a variable as the gross decontamination.

Second Cycle Column Operation (Continued)

The following conclusions are drawn on the results of the second cycle Runs 37R-47R. In the comments and conclusions below, "G" following a flowsheet designation will denote a feed treatment with acetone.

1. With one exception, the gross decontamination factors for all second cycle runs made during the past period were sufficient to give two-cycle gross gamma decontamination values of 1.5 - 7.5 x 10^5. The one exception (Run 42R) was a two cycle gamma decontamination of 3 x 10^4 obtained by using the ANL-G flowsheet in both first and second cycle.

2. Of the seven runs made during the past month in which the ORNL flowsheet was used in both cycles, five runs met or exceeded process gamma decontamination specification of 3 x 10^5, and two runs failed to meet these specifications by less than a factor of two.

3. The ORNL #1-G flowsheet increases the decontamination given by the ORNL #1 flowsheet by less than a factor of two.

4. Acetone treatment of the feed in second cycle ANL flowsheet runs increases decontamination by a factor of very roughly ten.

5. Assuming the use of the ORNL flowsheet in the second cycle, and considering the early state of development of the first cycle ANL-G flowsheet, it is concluded that the ANL-G, ORNL #1 flowsheet combination offers a very promising method for meeting process decontamination specifications with a reduction in waste volume over the ORNL, ORNL #1 flowsheet combination.

6. For Runs 37-47R, ruthenium accounted for 20-90% of the activity in the 1EU stream. This variation was caused by variations in the two cycle decontamination factors for both ruthenium and zirconium-columbium.

7. Uranium loss for second cycle flowsheet runs was generally less than 0.01%, and in no run was the loss more than 0.06%.

Second Cycle Column Operation (Continued)

B. Plugging in Line Between ID and IE Column

During second cycle run 37R, the 1/4" line carrying the IDU stream from the ID to the IE column became plugged, and a plug in this line has occured on almost every run since that time. The plug in every case has been easily eliminated by breaking the flange at the point where the IDU line enters the IE column, and then flushing the IDU line with low pressure water.

Considerable cloudiness has been noted in the aqueous at the interface in the ID column, and it is believed that the plugging material is formed in the ID column. There has been no evidence, however, of plugging in the ID column itself. The substance which causes the plug in the IDU line is soluble in water, and is composed primarily of iron and nitrate, with some organic material, a trace of chromium, no nickel, and no sulfamate. The plugging is attributed fundamentally to presence of oxidized iron at the relatively high pH in the ID column. Laboratory work is being done to determine more precisely the composition of the "crud", and consideration is being given to a suggestion by ANL to substitute hydroxylamine for ferrous sulfamate as the reducing agent for the second uranium cycle.

[redacted]

TABLE X

Summary of Results,
Second Cycle Runs 37-47R

Run Number Flowsheet	37R ORNL #1	38R ORNL #1-G (1)	39R ORNL #1-G (1)	40R ANL-G (1)	41R ORNL #1-G (1)
Feed Composition					
Uranium, M	2.0	2.0	2.0	2.0	1.9
Free Acid or Base, M	0.16b	0.28b	0.22b	0.21a	0.17b
Scrub Composition					
Al $(NO_3)_3$, M	2.00	1.97	2.17	1.26	2.19
Free Acid or Base, M	0.22b	0.24b	0.20b	0.08b	0.17b
Ferrous Sulfamate, M	0.04	0.04	0.04	0.05	0.05
U Losses and Material Balances, %					
DW	0.002	.0005	0.05	0.05	(3)
EW	0.001	.028	0.011	.004	(3)
DU	97	100	103	106	106
EU	99	105	103	98	96
Beta Radiation (2)					
cts/ml/min DF	1.3×10^5	1.3×10^5	3.6×10^5	2.8×10^5	2.7×10^5
EW	250	330	300	560	340
D.F. . . EU	75	110	370	110	145
Gamma Radiation (2)					
cts/ml/min DF	1.7×10^3	1.7×10^3	2.7×10^3	1.3×10^3	1.2×10^3
mv/ml DF	600	600	970	460	440
D.F. . . EU	155	230	310	50	60

(1) The feeds for runs 38R thru 43R were treated with acetone. See Section VI B for discussion.
(2) Betas counted at 10% geometry with 20 mg. of solids on counting plate; gamma counting efficiency ~ 0.05%.
(3) Incomplete data due to plug between ID and IE column. See Section VII B for discussion.

[redacted]

[redacted]

Table X (Con't.)

Run Number	37R	38R	39R	40R	41R
Flowsheet	ORNL #1	ORNL #1-G	ORNL #1-G	ANL-G	ORNL #1-G
Specific Fission Products					
Beta cts/ml/min in IEU					
Ru	600	390	340	810	340
Zr	120	140	60	160	140
Cb	13	10	30	100	100
Ce	8	6	18	13	160
Decontamination Factor for IEU					
Ru	30	55	270	100	210
Zr	280	270	570	40	40
Cb	290	400	300	30	30
Ce	10	15	15	5	4
% Gamma Activity in IEU, calculated (1)					
Ru	58	52	36	31	16
Zr	24	38	14	13	15
Cb	18	10	50	56	69

(1) Calculated from measured beta activity and known beta/gamma ratios.

[redacted]

[redacted]

Table X (Con't.)

Run Number	42R	43R	44R	45R	46R	47R
Flowsheet	ANL-G	ORNL #1 -G	ORNL #1	ORNL #2	ORNL #1	ORNL #1
Feed Composition						
Uranium, M	2.01	1.95	2.05	0.91	1.98	2.04
Free Acid or Base, M	0.40a	0.16b	0.16b	0.16b	0.14b	0.25b
Al $(NO_3)_3$, M	None	None	None	1.18	None	None
Scrub Composition						
Al $(NO_3)_3$	1.38	2.07	2.22	1.28	2.22	2.19
Free Acid or Base, M	0.10b	0.18b	0.24b	0.24b	0.26b	0.10b
Ferrous Sulfamate, M	0.06	0.05	0.05	0.02	0.03	0.04
U Losses and Material Balances, %						
DW	0.006	(1)	0.002	0.003	0.002	0.004
EW	0.005	(1)	0.001	0.001	0.003	0.002
DU	96.7	(1)	100	103	105	102
EU	99.7	(1)	100	97	95	100
Beta Radiation						
cts/ml/min DF	1.1×10^7	1.0×10^7	8.8×10^5	3.8×10^5	2.1×10^5	1.1×10^6
D.F. EW	1600	900	700	1400	1000	800
D.F. EU	390	3600	180	200	60	180
Gamma Radiation						
cts/ml/min DF	3.2×10^4	3.1×10^4	2.6×10^3	1.2×10^3	940	4.6×10^3
mv/ml DF	1.44×10^4	1.40×10^4	1.20×10^3	540	350	1.70×10^3
D.F. EU	240	2700	140	170	60	135

(1) Incomplete data due to plug between ID and IE column. See Section VII B for discussion.

[redacted]

[redacted]

Table X (Con't.)

Run Number	42R	43R	44R	45R	46R	47R
Flowsheet	ANL-G	ORNL#1-G	ORNL#1	ORNL#2	ORNL#1	ORNL#1
Specific Fission Products						
Beta cts/ml/min in IEU						
Ru	1.2×10^4	1.2×10^3	2.0×10^3	1.6×10^3	1.5×10^3	2.6×10^3
Zr	180	120	50	25	50	90
Cb	300	10	20	8	5	50
Ce	15	10	20	8	10	25
Decontamination Factor for IEU						
Ru	370	3900	140	160	40	180
Zr	36	60	40	70	120	20
Cb	7	250	25	55	120	10
Ce	10	20	5	10	80	5
% Gamma Activity in IEU, Calculated						
Ru	71	77	83	90	89	73
Zr	2	15	4	3	6	6
Cb	27	8	13	7	5	21

[redacted]

VIII. URANIUM DECONTAMINATION FOR TWO CYCLES

A summary of fission product decontamination for Runs 27R-47R is given in Table XII. Runs 27-30R and 39-47R were made with SS Solvent, and the zirconium-columbium data on these runs should be quite representative. A mixture of SS Solvent and regular Shell Hexone was used in Runs 31-37R, and the MIBC content of this hexone mixture was close to, and occasionally exceeded, the specification of .03%. It is felt that the data in Table XII give a reasonably true picture of the performance of the various flowsheet combinations which have been under consideration.

The following conclusions are drawn on the data presented in Table XII

1. Hanford specifications for uranium gamma decontamination can be met in two cycles if ORNL flowsheets are used. An evaluation of the ORNL flowsheet is given in the following table.

TABLE XI

Overall Gamma Decontamination for Two Cycles Given by the ORNL Flowsheets (1)

	Gross β	Gross γ	Ru	Zr	Cb
D.F.	5×10^5	3×10^5	3×10^4	1×10^6	1×10^6

(1) ORNL flowsheet in first cycle, ORNL #1 flowsheet in second cycle.

2. The overall decontamination given by the ORNL flowsheet has been highly consistent. The flowsheet has generally slightly exceeded the process specification, and in no instance has this flowsheet failed to meet process specifications by more than a factor of two.

Uranium Decontamination for Two Cycles (Continued)

3. There is promising evidence that the process decontamination specification can be met by a combination of ANL-ORNL flowsheets, if the feeds are given a special acetone treatment. In the two runs made to date, two cycle decontamination factors of 3×10^5 and 1.5×10^5 have been obtained. This ANL-ORNL flowsheet combination is attractive for two reasons, (1) reduction in aluminum nitrate waste, and (2) as a standby process if serious difficulty should ever arise in the recovery of plutonium from an acid deficient system. In order to meet process specifications with the present Redox flowsheets, it is necessary to obtain a zirconium-columbium decontamination factor of about 1×10^6 in order to compensate for the relatively low decontamination factor obtained for ruthenium. It is felt that the success of the ANL-ORNL flowsheet combination, with acetone treatment, depends to a great extent on the ability to obtain consistently the required high zirconium-columbium decontamination in an acid system, in which minor hexone impurities have a large detrimental effect on zirconium-columbium decontamination. Pilot Plant data indicate that the acetone treatment of the feed does not affect the decontamination of zirconium or columbium.

4. From the data in Table XII it is concluded that the flowsheet combination for the ORNL Pilot Plant demonstration of the uranium recovery cycles of the Redox process at 100% Hanford activity should be the ORNL flowsheet in the first cycle and ORNL #1 flowsheet in the second cycle.

[redacted]

TABLE XII

REDOX PROCESS

Overall Decontamination for Two Cycles

Redox Runs 27-47R Inclusive

Run	Flowsheets (1)		Decontamination Factor					% Ru Gamma
	1st Cycle	2nd Cycle	Beta	Gamma	Ru	Zr	Cb	in IEU
27	ANL	ANL	2.0×10^{3}	7.3×10^{2}	70	1.1×10^{6}	1.5×10^{5}	100%
28	ANL	ORNL #1	3.8×10^{4}	1.7×10^{4}	1.3×10^{3}	1.4×10^{6}	3.2×10^{5}	97%
29	-	ORNL #2	9.0×10^{4}	4.4×10^{4}	3.6×10^{3}	1.9×10^{6}	3.5×10^{5}	93%
30	ANL	ORNL #1	1.8×10^{5}	8.0×10^{4}	7.0×10^{3}	8.6×10^{6}	1.7×10^{6}	92%
31	-	ANL	4.6×10^{4}	1.1×10^{4}	2.2×10^{3}	1.8×10^{5}	1.2×10^{4}	46%
32	ORNL	ORNL #1	7.2×10^{5}	3.0×10^{5}	6.2×10^{4}	3.4×10^{5}	1.5×10^{5}	24%
33	ORNL	ORNL #2	8.8×10^{5}	5.5×10^{5}	9.3×10^{4}	4.8×10^{5}	9.7×10^{5}	53%
34	ORNL Mod	ANL	5.0×10^{5}	7.4×10^{4}	6.5×10^{4}	2.1×10^{5}	2.7×10^{4}	28%
35	ORNL Mod	ORNL #1	1.5×10^{6}	7.0×10^{5}	1.2×10^{5}	3.0×10^{5}	1.9×10^{6}	32%
36	ORNL Mod	ORNL #2	1.3×10^{6}	6.0×10^{5}	1.2×10^{5}	4.3×10^{5}	1.1×10^{6}	32%
37	ORNL	ORNL #1	1.0×10^{6}	5.0×10^{5}	5.7×10^{4}	4.8×10^{5}	1.3×10^{6}	52%
38	-	ORNL #1-G	1.5×10^{6}	7.5×10^{5}	9.5×10^{4}	4.5×10^{5}	1.8×10^{6}	43%
39	ORNL	ORNL #1-G	2.1×10^{6}	6.0×10^{5}	1.5×10^{5}	1.3×10^{6}	6.1×10^{5}	36%
40	-	ANL-G	6.6×10^{5}	1.5×10^{5}	4.5×10^{4}	3.0×10^{5}	1.2×10^{5}	31%
41	ORNL-G	ORNL #1-G	9.0×10^{5}	1.9×10^{5}	1.0×10^{5}	3.2×10^{5}	1.2×10^{5}	16%

[redacted]

[redacted]

Table XII (Con't.)

Run	Flowsheets (1)		Decontamination Factor					% Ru Gamma
	1st Cycle	2nd Cycle	Beta	Gamma	Ru	Zr	Cb	in IEU
42	ANL-G	ANL-G	6.5×10^4	2.8×10^4	3.3×10^3	2.9×10^5	3.9×10^4	70%
43	-	ORNL #1-G	6.1×10^5	3.1×10^5	3.5×10^4	4.9×10^5	1.4×10^6	76%
44	ORNL	ORNL #1	4.2×10^5	2.3×10^5	2.4×10^4	1.2×10^6	5.6×10^5	83%
45	-	ORNL #2	4.7×10^5	3.0×10^5	2.6×10^4	2.2×10^6	1.4×10^6	90%
46	ORNL	ORNL #1	6.4×10^5	3.7×10^5	2.7×10^4	1.3×10^6	2.3×10^6	89%
47	ANL-G	ORNL #1	3.3×10^5	1.5×10^5	1.5×10^4	7.6×10^5	3.3×10^5	73%

(1) "-G" following a flowsheet designation denotes a feed treatment with acetone. See Sections IIIC and VI B.

Brackets indicate second cycle runs having a common feed makeup material prepared by combining the ICU streams of the first cycle runs shown between spaces.

[redacted]

IX. HEXONE PURIFICATION AND RECOVERY

After run 37R the Pilot Plant inventory of hexone, which consisted of a mixture of SS solvent and regular Shell hexone, was drained from the system and replaced with pure SS solvent, and only SS solvent has been added to the system since that time. The following pretreatment was given to the SS solvent added to the system after run 37, and to all subsequent makeup SS solvent.

1. SS solvent was washed for one hour with a tenth volume of solution which is 1.0 M in sodium dichromate and 0.2 N in nitric acid,

2. washed thirty minutes with a fifth volume of water,

3. given two additional fifth volume water washes, and

4. steam distilled from a tenth volume of 3% sodium hydroxide.

The following recovery treatment was given to recycle hexone for all runs since 37R, except run 47R.

1. Recycle hexone was washed for ten minutes with a tenth volume of water, and

2. steam distilled from a tenth volume of 3% sodium hydroxide.

The above recovery procedure was used over a period of seven weeks, and no growth of reducing normality of the hexone in the Pilot Plant system could be detected. The decontamination values for zirconium and columbium for the runs during this period indicated that the purity of the solvent was satisfactory.

In first cycle run 47R (ANL flowsheet), recycle hexone was recovered by washing thirty minutes with a half volume of 2% sodium hydroxide, followed by two twenty minute washes with one-third volumes of water. The decontamination for zirconium and columbium in this acid flowsheet run was 4×10^4, indicating that the elimination of the steam distillation step had no adverse effect on decontamination.

X. ANALYTICAL DEVELOPMENTS

A. Factors for Conversion Between Beta, Gamma, and Ion Chamber Determinations

Factors for converting between beta, gamma, and ion chamber determinations are used in the Pilot Plant for interpreting data and for determining the consistency of data. These factors are particularly useful in second cycle work, and on occasions (see Section X-C, for example) the use of these factors has lead to developments of major significance.

During the past month the various factors used were redetermined. The experimental procedure consisted of separation of the various fission products from a dissolver solution, separate separations being made for beta and gamma determination in order to obtain good counting rates for both. After gamma counting was done the solids on the counting plate were placed in a glass tube and the corresponding ion chamber values were determined. A summary of the experimental results is presented in Table XIII. The ratios are estimated to be accurate within 10%.

TABLE XIII

Factors for Conversion Between Beta, Gamma and Ion Chamber Determinations

	β/γ Ratio	β/mv Ratio	γ/mv Ratio
Ruthenium	270	700	2.6
Zirconium	110	310	2.8
Columbium	14	45	3.2
Dissolver Solution	380	1000	2.6

NOTE: Betas counted at 10% geometry with 20 mg of absorber on counting plate. Efficiency of gamma counting was ~0.05%. Dissolver solution prepared from slugs which had cooled 60-100 days.

Analytical Developments (Continued)

B. Beta and Gamma Activity of Natural Uranium

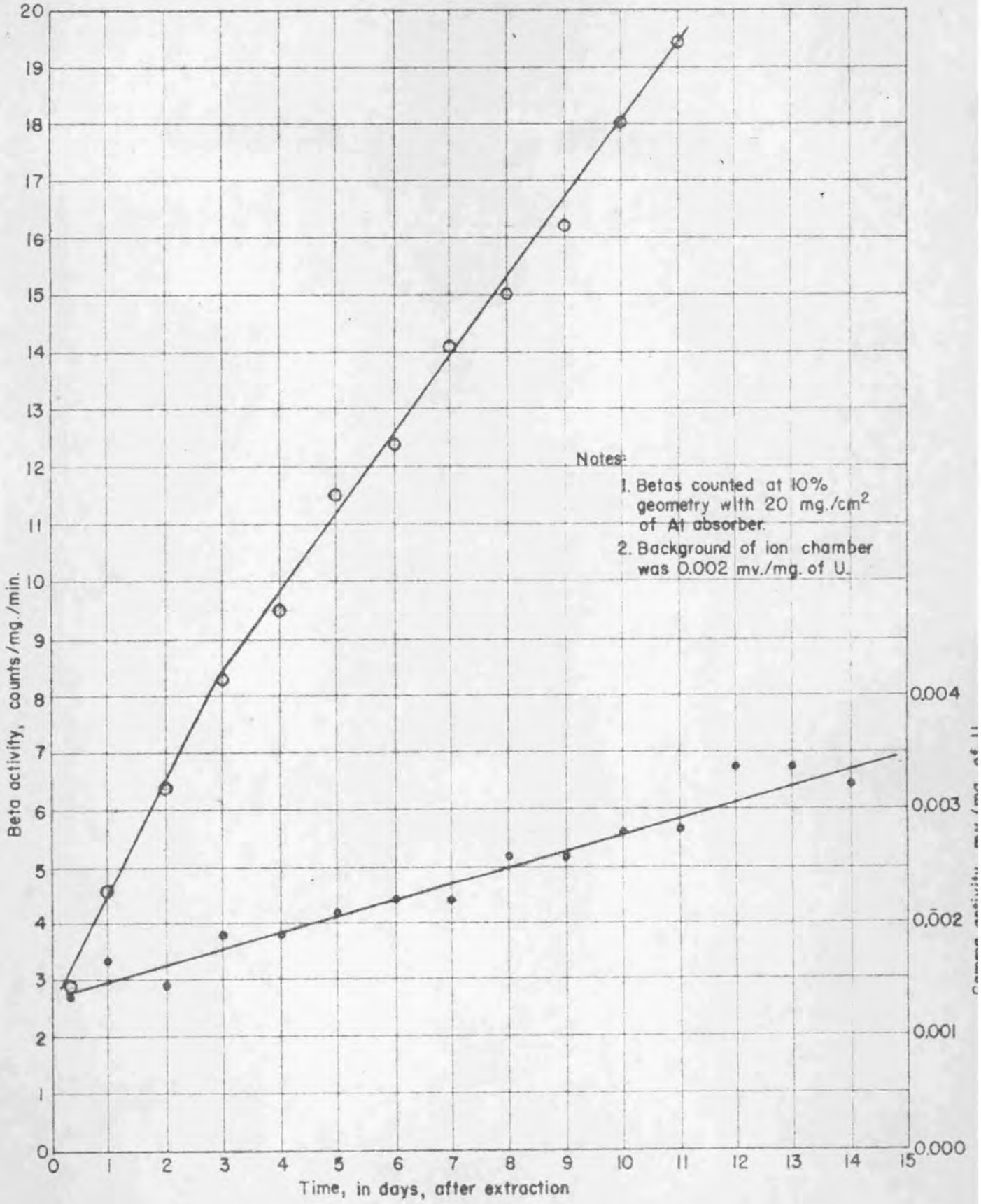
With the IAF stream at 30% Hanford activity level and a two cycle gamma decontamination of 3×10^5, the specific beta and gamma activity in the IEU stream is about 20% and 200% respectively of the activity of natural uranium at equilibrium with its decay products. These decay products are separated from uranium during solvent extraction processes, but frequently they grow back in to a significant degree before the process streams are analyzed. For this reason it is necessary to know the rate of approach to equilibrium of the decay products of uranium, and specifically for UX, which accounts for essentially all of the beta and gamma activity. It is also necessary to know whether the activity due to such minor gamma sources as U^{235} is significant.

The growth of gamma activity in freshly extracted uranium was investigated during the past month, and in connection with this investigation the growth of beta activity was redetermined. The separation of uranium from UX was done in a laboratory horizontal extractor having five extraction stages and four scrub stages. The feed to the extractor was 2 M uranium having a gamma activity of 2.2 mv/ml and a beta activity of 2.8×10^4 beta cts/ml/min. Betas were counted at 10% geometry, using a 20 mg/cm^2 aluminum absorber to filter out UX betas. The scrub was 2.0 M $Al(NO_3)_3$, and the extractant was hexone. Flow ratios for feed, scrub and extractant were 1, 1, and 4 respectively. The gamma activity in a 200 ml sample of the extractant was measured each day in a high pressure (50 atmospheres) ion chamber. The beta activity of the extractant was measured each day by counting as described above.

The data obtained is plotted in Fig. 3. The initial slope of the beta growth curve is 2.0 beta cts/min/mg U/day, and the slope of the curve is in good agreement with previous data on the beta growth after extraction. The beta intercept at zero time (time of extraction is 2.6 beta cts/min/mg of U. On two previous determinations an intercept of 1.8 beta cts/min/mg of U was obtained. The intercept for the gamma growth curve is 0.0013 mv/mg of U. The slope of the gamma curve is 1.5×10^{-4} mv/mg of U/day. This is in very good agreement with a theoretical value of 1.4×10^{-4} calculated from the beta curve by assuming that all of the growth of gamma activity is due to UX.

[redacted] [redacted]

Drawing # 7220



GROWTH OF BETA & GAMMA ACTIVITY
IN FRESHLY EXTRACTED URANIUM

[redacted]

Analytical Developments (Continued)

C. Determination of U^{237} in the IEU Stream

The first cycle feed material used for runs during the past month contained 70% by weight ORNL irradiated uranium which had been cooled for periods varying from 50 to 70 days by the time the feed was processed through to the IEU stream. The source of the remaining 30% of the uranium feed was Hanford production material which had been cooled for about 100 days. It was found that in these runs the U^{237} gamma activity accounted for 50% to 80% of the residual activity in the IEU stream, and a correction for this activity was necessary in order to evaluate the fission product decontamination given by the flowsheets under consideration. In general, the IEU gamma activity due to fission products was calculated from analyses for ruthenium, zirconium, and columbium betas, and by known beta/gamma ratios, with the U^{237} activity being determined by difference. In one run, however, U^{237} was identified and quantitatively determined. The experimental procedure and the results of the investigation are summarized below.

The separation of U^{237} was made from a IEU flowing stream sample from Run 46R. Analysis of this sample, together with other pertinent calculated data, is given in Table XIV.

TABLE XIV

Composition of IEU Stream in Run 46R

	β cts/ml/min(2)	mv/ml(3)	mv/mg(4)
Gross Activity	4.5×10^3	5.0	.024
Fission Product Activity(1)			
Ru	1.5×10^3	2.30	.0110
Zr	49	0.16	.0007
Cb	6	0.13	.0006
Total	1.6×10^3	2.6	.012

(1) Analyses for iodine, lanthanum and cerium were negative.

(2) Betas counted at 10% geometry with 20 mg of absorber on counting plate.

(3) Data on fission products were calculated from known β/mv ratios.

(4) Uranium was 210 mg/ml.

Analytical Developments (Continued)

Essentially all of the zirconium and columbium, and 85% of the ruthenium was removed from a portion of the original sample by A. T. Gresky of the ORNL Laboratory and Semi-Works Development Section. The zirconium and columbium was removed by three cycles of batch extraction and stripping, and the ruthenium was removed by plating out on tygon after oxidation with periodic acid. Half life and beta energy determinations were then made on the "U^{237} extract".

For half life determination 200 ml of the "U^{237} extract" was sealed in a 4.4 cm glass tube, and the ion chamber measurements were made each day for 14 days. A 200 ml sample of the original IEU solution was also measured each day in the ion chamber. The values obtained each day were corrected for UX gamma background (see Section X-B) and for ion chamber geometry (92% using 200 ml samples vs 98% using 100 ml samples). The corrected ion chamber values were reduced to specific activities, and the results are plotted in Figure 4. The 0.01 mv/mg difference between the curves for the original IEU stream and the "27 extract" is a measure of the fission product activity removed from the original IEU sample, and this value of 0.010 mv/mg is in good agreement with the value of 0.012 mv/mg calculated on the basis of the fission product analyses given in Table XIV. From Fig. 4 the half life for the activity in the "27 extract" is 7.7 days. This is in good agreement with the actual value of 6.7 days.

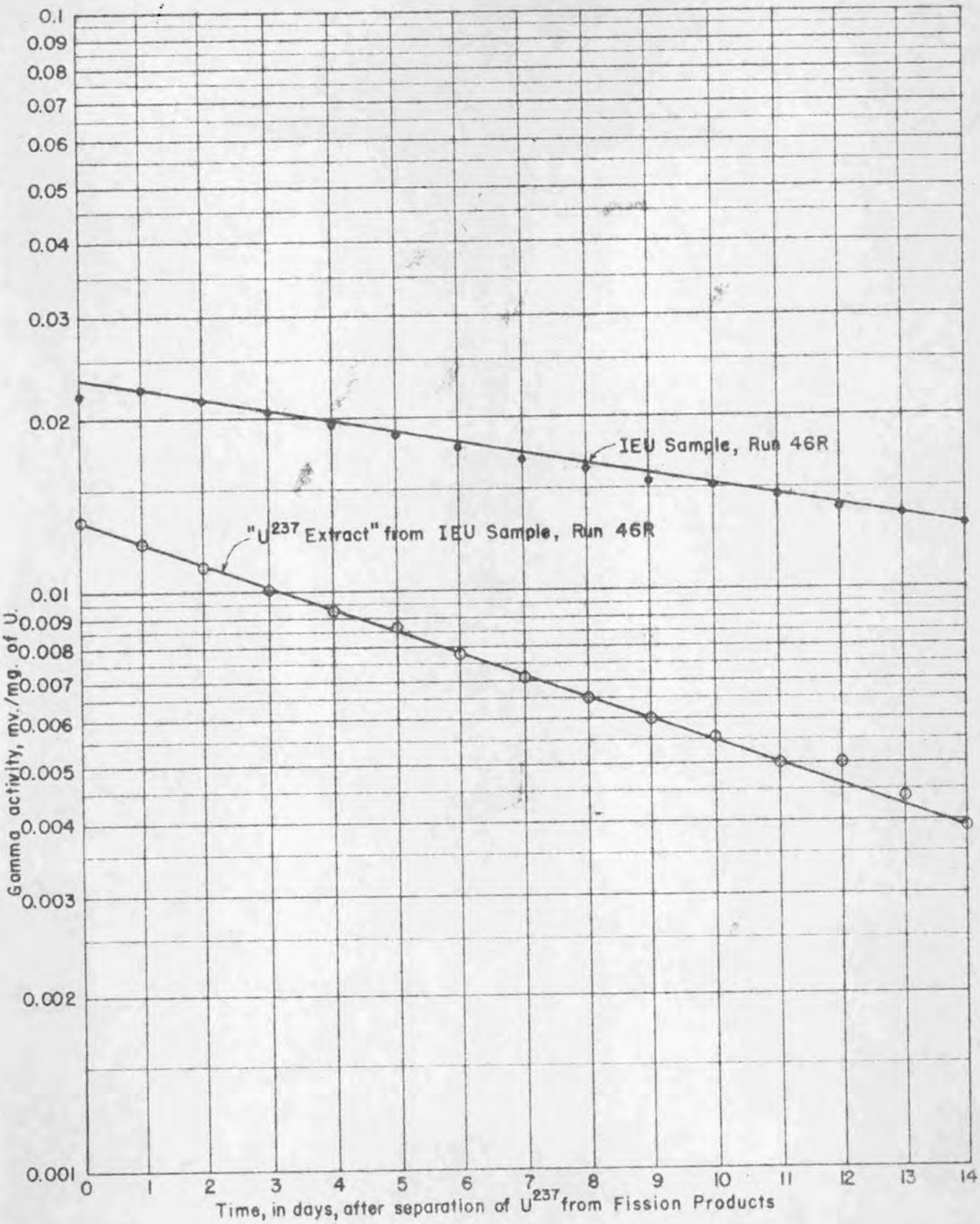
The half-thickness of the soft beta attributed to U^{237} has been determined to be in the order of 4-8 mg Al/cm^2, which is in agreement with the reported value of 6 mg Al/cm^2 for U^{237}. The samples studied by absorption contained a small fraction of Ru^{103} and Ru^{106}, so the exact determination was difficult due to a similar soft beta from the Ru^{103}. The identification of the U^{237} beta was done by studying the change in the ratio 0.26 Mev β /3.5 Mev β after purification and again after three U^{237} half lives. All samples were observed with constant sample weight (20 mg U), constant geometry (10%), and constant window thickness. Under these conditions it is estimated that at the beginning of the study sixteen absolute beta counts/min/ml were due to U^{237}.

From the data in Fig. 4 and from the approximate cooling time of the ORNL slugs it is estimated that the U^{237} disintegration rate at the time the slugs were removed from the ORNL pile was about 1×10^5 d/m/mg of U. A value of 4×10^4 d/m/mg U in ORNL slugs has been reported by Bruce and Baldwin in MonT-199.

[redacted]

FIGURE 4

Drawing # 722



IDENTIFICATION OF U^{237}

BY HALF LIFE DETERMINATION

[redacted]

Analytical Developments (Continued)

D. Identification of Americium and Curium in the IAW Stream

In the course of the investigation of the ANL flowsheet at ORNL activity level it was observed that the plutonium loss in the IAW stream as determined by the lanthanum flouride and TTA methods amounted to 0.1% and ~.01% respectively. The apparent loss given by the lanthanum flouride method was attributed to americium, but early attempts to identify americium by pulse analysis were unsuccessful because of the high beta activity on the counting plate.

In runs 44-50R the alpha activity which was inextractable under both acid and acid deficient conditions increased to ~ 0.6% of the plutonium in the feed, and this increase was attributed to americium and curium from Hanford slugs which were charged to the Hanford piles before February, 1948. In order to demonstrate that this alpha activity was not polymerized plutonium, the following experiments were done by the Analytical Section of the Chemistry Division. All experiments were done on a IAW solution prepared in the laboratory by extracting with neutral hexone a 50R-IAF solution prepared by mixing one ml of feed from run 50R, four ml of a 2 M UNH solution which was 0.2 N acid deficient, and 5 ml of IAS solution.

Experiment 1: LaF_3 Analysis

Alpha activity as determined by the conventional LaF_3 gave an apparent loss of 0.5%.

Experiment 2: TTA Analysis

Analysis of the IAW solution by TTA analysis gave ~ .01% loss. In order to break up possible polymer the IAW was boiled nearly to dryness three times with concentrated nitric acid before extraction.

Experiment 3: Modified LaF_3 Analysis

An aliquote of the IAW was oxidized for fifteen minutes at 90° C with 0.1 M dichromate, precipitated under oxidizing conditions with LaF_3, and the precipitate washed with nitric and boric acid. The precipitate was redissolved, the above procedure repeated, and the precipitate counted. The apparent loss was again 0.5%.

Experiment 4: TTA Extraction at Elevated pH

An aliquot of the IAW was adjusted to a pH of 3.45 with sodium hydroxide and extracted with an equal volume of 0.5 M TTA in xylene. Under these conditions it would be expected that about 60% of the americium would extract, but the extractability of curium is not known. The extract was stripped with 8 M nitric acid, and was found to contain 30% of the alpha activity in the original aliquote of IAW. By pulse analysis the composition of the strip was determined to be 65% curium, 35% americium, and less than 2% plutonium.

From the results of the four experiments described above it is concluded that 0.5% of the alpha activity in the feed to run 50R was due to americium and curium.

XI. MISCELLANEOUS REDOX

A new 1BP catch tank and 1BP storage tank have been installed in Cell 6 to increase plutonium storage capacity in the Pilot Plant. The new catch tank (F-1) is of 50 gallon capacity while the storage tank (F-2) is a 2000 gallon stainless steel tank. A cocoon has been spun around both tanks to determine if this method is suitable for alpha control.

The Redox equipment flowsheet scheduled for issuance this month has been postponed one month.

XII. REDOX PROGRAM

The ORNL Pilot Plant development of the Redox process will terminate with a series of six process verification runs to be made at 100% Hanford activity level. These runs will be completed by June 1. The flowsheets used for these runs will be the ORNL flowsheet in the first cycle and ORNL #1 flowsheet in the second cycle. Operational procedures, including sampling schedule, will remain the same as for the 30% level runs.

At the conclusion of the 100% level runs there will have been accumulated about 1400 gallons of IBP solution. This solution will be stored until after completion of the "25" process demonstration runs, at which time the plutonium will be further decontaminated in the extraction columns before returning it to Hanford.

MISCELLANEOUS

XIII. CHEMICAL WASTE EVAPORATOR - E. L. Nicholson

Construction of the Chemical Waste Evaporator is in the final stages and is scheduled to be completed in the next two weeks.

The condensate monitor was redesigned so the Geiger tube is suspended above the flowing condensate stream. This change was made when it was discovered that fission products were plating out of solution on the immersed Geiger tube.

Tank calibration and leak checking will be done in the final stages of construction. Runs planned before handling full activity waste are a water run, a dilute nitric acid cleanup run, and one or two chemical runs spiked with W5 waste to test decontamination, foaming, and operability.

XIV. 25 SEPARATIONS PROCESS - A. M. Rom

A. Progress Report Status

The 25 Separation Progress Report covering all Pilot Plant investigations from the issuance of ORNL-109 until Redox conversion is ninety per cent complete.

B. Summary of Memorandum on 25 Alloy Calculations

A study of the irradiated enriched slugs was made to predict activity levels and maximum obtainable decontamination factors. The enriched slugs were put in the Hanford piles during the last week of July, 1948. Three separate batches were discharged from the Hanford piles as follows:

(1) 95 slugs on November 16, 1948

(2) 21 slugs on January 21, 1949

(3) 101 slugs on February 21, 1949

The calculations made brought out the following points:

1. If the slugs which were discharged on November 16, 1948, are processed on October 1, 1949, they will then contain 45 curies/slug. The Pilot Plant would be handling 950 curies/day processing these slugs, and a gamma decontamination of 3×10^6 could be demonstrated.

2. If the slugs which were discharged on February 21, 1949, are processed on June 1, 1949, they will contain approximately 525 curies/slug. The Pilot Plant would be handling 11,000 curies/day in processing these slugs, and a gamma decontamination factor of 3×10^7 could be demonstrated.

These and other cases between the two extreme cases chosen as examples are contained in a memo at present being prepared. It is interesting to note that 123 grams out of 2280 grams of U^{235} were depleted in the Hanford piles, and 0.038 grams of plutonium were formed from the 160 grams of U^{238} at present.

The ORNL Laboratory and Semi-Works Section is investigating the problem of dissolving U-Al slugs with the view of recommending a procedure for the Pilot Plant to use in dissolving the 217 enriched uranium-aluminum alloy slugs.

25 Separations Process (Continued)

Prior to processing the enriched material the Pilot Plant will make several runs with natural irradiated uranium. This will be done to note any effect on the process caused by equipment changes for Redox and also to recheck the flowsheet to be used in the 25 Process.

XV. PATROL

Operation of patrol has been without incident the past month.

All necessary piping modifications within the confines of Bldg. 807 have been completed. A complete testing of all piping modifications, instruments and miscellaneous equipment recently installed will be made within the coming month to determine the actual capacity of the equipment.

Both demineralizer units are being completely recharged. This recharging consists of replacement of the gravel and resin.

OPERATING SUMMARY

Total Filtered Water to Bldg.	759,300 gallons
Demineralized water to:	
Bldg. 205	12,070 gallons
Bldg. 105	536,580 gallons
Bldg. 101 and 807	52,827 gallons
Bldg. Mock-Up	105,023 gallons
TOTAL -	706,500 gallons
Operating efficiency	93%
Average pH	5.7
Average Resistance	667,000 ohms.

XVI. GENERAL ADMINISTRATIVE

Permanentization and conversion of the 205 Bldg. to a Pilot Plant installation has progressed to the stage prior to the preparation of actual working drawings.

40 liters of IBP solution from each of runs 44, 46, and 49 have been shipped to ANL during the past period for further plutonium processing.