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ORNL 461
CHEMISTRY-SEPARATION
PROCESSES FOR URANIUM

TECHNICAL DIVISION

PILOT PLANTS SECTION REPORT FOR JULY, 1949

D. G. REID

[redacted]

OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

[redacted]

[redacted]

ORNL-461

Chemistry-Separation processes for Uranium

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TECHNICAL DIVISION

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DATE ISSUED

SEP 29 1949

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Carbide and Carbon Chemicals Corporation
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Post Office Box P
Oak Ridge, Tennessee

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ABSTRACT

A set of ten runs simulating process conditions to be used in recovering the uranium from the Hanford irradiated Al/U^{235} alloy have been completed. Total uranium losses over an entire run, initially unsatisfactorily high, were reduced to essentially the equilibrium value of 0.01% after modification of the extraction column start-up and shut-down operating procedures. The decontamination factors reproduced previous data suitably although not as satisfactory as in previous processings because of lower gross and specific activity, and residual activity from Redox processings. Elimination of ferrous sulfamate in the first cycle extraction column reduced uranium decontamination through the first cycle due to reduced columbium decontamination but did not affect the overall two cycle uranium decontamination if ferrous sulfamate was included in the second cycle.

Equipment decontamination, a necessary prerequisite for plant overhaul prior to Al/25 processing, has started.

The report summarizing the pilot plant Redox development program is in preparation and is expected to be issued in October, 1949.

A shake down and testing of the modifications to the water demineralization building has been made.

The next periodic report to be issued by the pilot plant section will cover the period of August and September, 1949.

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

"25" PILOT PLANT DEVELOPMENT

Technical - Rigstad, Rom, Harrington, Hylton, Landry, Shank and Stewart

Non-Technical - Beeler, Benson, Burnett, Gifford, Grizzell, Groover, Jennings, Land, Ledbetter, Lockmiller, McLellan, Purkey, Sexton, Shields, Shipwash, Spangler, Summers, Thomas, Thompson, Wiggins

I. INTRODUCTION AND SUMMARY

In August, 1948, the ORNL Pilot Plant phase of the 25 process development was interrupted in favor of the Redox investigation. Upon completion of Redox commitment at the end of June, 1949, the 25 process development program was resumed, and a series of ten two-cycle 25 flowsheet runs using Hanford irradiated natural uranium were completed. The general objectives of these runs were to test the 25 process for mechanical operability in equipment which had been modified for the Redox investigation, to check uranium balances at the low uranium concentrations (1 g/l and below) of the 25 system, to test minor process modifications suggested by the Redox investigation, and to make minor flowsheet changes suggested by recent process developments in the ORNL Laboratory and Semi-Works Section.

The two cycle beta decontamination factors obtained for the 25 runs were consistently about 3×10^5. The gamma activity after two cycles was below the limit of measurement. The gross beta activity in the second cycle uranium product stream was less than 30 counts/min/ml, one-fourth of the beta activity of natural uranium. Total column losses for uranium averaged about 0.1%; initial filtration losses were 0.5 - 2.0%, but these losses dropped to 0.15% after uranium remaining from the Redox runs had been thoroughly cleansed from the filter system. No problems of mechanical operability were encountered.

In the next phase of the pilot plant program all equipment will be decontaminated, inspected, repaired, and cleansed of all natural uranium. The 25 process investigation will then be terminated with a series of final verification runs, during which 2200 grams of enriched (95%) U^{235} will be processed.

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II. OBJECTIVES OF RUNS

Certain general objectives of the runs made during the past month were noted in the preceeding section. Specific objectives of the runs were as follows:

First Cycle

1-2YD - To verify the 25 flowsheet in effect prior to Redox testing.

3-4YD - Same as above, except at twice the uranium concentration and at one-half flow rates, and including a revised start-up and shut-down procedure to lower uranium losses during these phases of operation.

5-6YD - To investigate the effect of reducing the aluminum nitrate concentration of the scrub from 1.0 M to 0.75 M.

7,8,9-10YD - To test the flowsheet as shown in Fig. 1, which is identical to the flowsheet of August, 1948, except for the inclusion of mercuric nitrate and the elimination of ferrous sulfamate. (Mercuric ion, required for dissolving, forms a precipitate with sulfamate).

Second Cycle

1YD - To check optimum flowsheet conditions in effect August, 1948.

2YD - Same as above, except with revised shut-down procedure to lower uranium losses during this period.

3-4YD - Same as 2YD, except that twice the uranium concentration and one-half the mass through-put was used.

5-6YD - Same as 2YD.

7,8,9-10YD - Same as 2YD, and to determine if two-cycle decontamination would be satisfactory on elimination of ferrous sulfamate in the first cycle.

[redacted]

III. FEED PREPARATION

The first step in feed preparation consisted of transferring Hanford irradiated uranium in the form of a UNH solution to the first cycle mix tank. 2 M $Al(NO_3)_3$ was added, and the acidity adjusted. This solution was filtered, and then given a final adjustment for $Al(NO_3)_3$ concentration and acidity.

Feed for the second cycle was prepared by concentrating the first cycle uranium product stream, adding $Al(NO_3)_3$ solution, and adjusting acidity. The addition of all of the $Al(NO_3)_3$ to the second cycle column via the scrub stream was deemed impractical because of the small feed volume as compared to the size of the pilot plant process vessels.

The formation of precipitates during preparation of 0.75 M $Al(NO_3)_3$, 0.2 N acid deficient scrub solutions was traced to the use of NaOH for acid adjustment. For this reason NH_4OH was used for acid adjustment of scrub solutions after Run 6YD.

[redacted]

IV. COLUMN OPERATION

A. First Cycle

The 25 process flowsheet is given in Fig. I. Stream composition, loss, and decontamination data for the first cycle runs are given in Tables I and II. For those runs in which ferrous sulfamate was used, gross beta and gamma decontamination factors averaged about 2×10^4 and 4×10^3, respectively. These results compare favorably with 25 process data obtained prior to the conversion to Redox. On the last four runs, in which mercuric nitrate was used, the beta decontamination was reduced to about 1×10^4 for beta and 8×10^2 for gamma. The poor gamma decontamination in the latter runs was caused by low columbium decontamination factors, which averaged about 200. There has been no previous 25 process experience using mercuric nitrate in the feed stream. The decontamination factors obtained for plutonium averaged about 1000, even after ferrous sulfamate was eliminated from the feed.

Data obtained at equilibrium gave uranium losses of about 0.05%. Composite losses of 1% and 5% were obtained on the first two runs, but these losses dropped to values comparable to the equilibrium losses when a refined shutdown procedure was used. The refined shutdown procedure, given in detail in Table I, consisted essentially of increasing the solvent rate and scrub concentration after expiration of the feed. The apparent filtration losses on the first half of the series of runs averaged about 1%, but these high losses are attributed to uranium remaining in the filter assembly from the Redox runs. The average filtration loss for the last half of the series of runs was 0.15%, or about 0.1 gram per run. Material balances for uranium were reasonable except for the first two runs, where balances of 400 and 200% were obtained. These high balances are a measure of the uranium remaining in the pilot plant system after the Redox program, in spite of the fairly rigerous cleanout procedure used at the end of that program.

B. Second Cycle

In the second cycle, all fission products except ruthenium were decontaminated to approximately background. Values obtained for ruthenium in the product stream were 10-20 counts/ml/min, corresponding to ruthenium decontamination factors averaging roughly 20. These low residual activity values do not permit accurate conclusions to be drawn on the second cycle decontamination given by the 25 flowsheet. However, a beta decontamination of at least 3×10^5 was demonstrated for two cycles. Second cycle uranium losses averaged 0.10%.

[redacted]

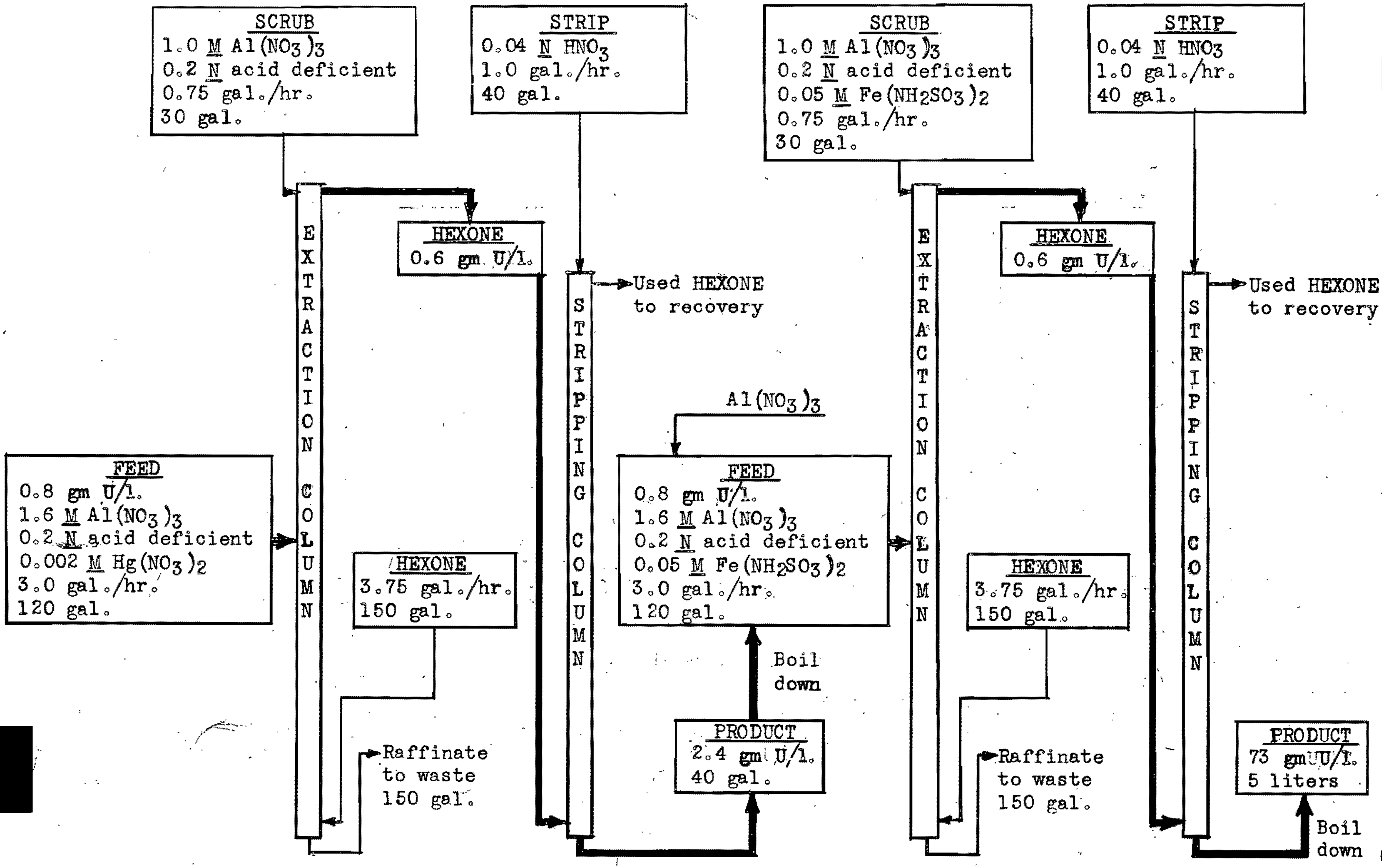

FIGURE I

"25" PROCESS PILOT PLANT FLOWSHEET
8-15-49

[redacted]

TABLE I

ORNL Technical Division - 25 Pilot Plant

First Cycle Operational Data Summary

Run Number	1YD-1	2YD-I	3YD-I	4YD-I	5YD-I	6YD-I	7YD-I	8YD-I	9YD-I	10YD-I
Feed(1)										
U Conc. g/l	1.16	.93	1.41	1.77	1.00	1.02	.93	.84	.81	.82
Acid Def. N	.09	.12	.12	.08	.21	.19	.24	.17	.24	.21
$Fe(NH_2SO_3)_2$ M	.05	.05	.05	.05	.05	0	0	0	0	0
$Hg(NO_3)_2$ M	0	0	0	0	0	0	.002	.002	.002	.002
Flow Rate, gal/hr	3.00	2.99	1.51	1.52	2.99	2.99	2.99	2.99	2.98	3.01
Scrub										
$Al(NO_3)_3$ M	1.0	1.0	1.0	1.0	.75	.75	1.0	1.0	1.0	1.0
$Fe(NH_2SO_3)_2$ M	.05	.05	.05	.05	.05	.05	0	0	0	0
Flow Rate, gal/hr	.75	.75	.39	.38	.75	.75	.76	.76	.76	.77
Solvent										
Flow Rate, gal/hr	3.77	3.73	1.90	1.91	3.74	3.76	3.76	3.71	3.75	3.72
Strip										
Flow Rate, gal/hr	1.00	1.00	0.50	.73	1.01	1.00	1.00	.99	.98	1.01
Shut down Procedure* Revised	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

(1) Specific β activity for all runs was 6.1×10^6 cts/min/mg of U, counted at 10% geometry.

* Initial shut down procedure:

1. MCH pump shutdown when U feed exhausted.
2. Solvent and scrub pumps shut down four hours after MCH off.
3. Strip pump shut down eight hours after MCH off.

* Optimum revised shut down procedure:

1. MCH shut off when feed exhausted.
2. Solvent increased to 5 gal/hr and strip to 2 gal/hr at time MCH pump off.
3. AR composite sample taken.
4. 1.5 M scrub started at 1 gal/hr for 15 hrs.
5. 1.0 M scrub pumped at 2 gal/hr for 2 hrs.
6. AR composite sample taken.
7. Solvent shut off 1 hour after 1.0 M scrub finished.
8. Strip off 1 hour after solvent.

TABLE II

ORNL Technical Division —, 25 Pilot Plant

First Cycle Decontamination and Loss Summary

Run	Gross β x 10^4	Gross β ml x 10^3	Ru β x 10^3	Zr β x 10^3	Cb β x 10^2	Ce β x 10^4	Pu α x 10^3	Extraction Loss, %		Filter Loss, %	Strip Loss, %	Mat. Bal. %
								Equil.	Comp.			
1YD	.6	4.1	.5	76.0	250.0	8.8	.2	0.15	1.11	2.17	.03	443
2YD	2.0	5.8	1.8	1.8	19.0	10.0	3.2	0.1	5.22	---*	.22	192
3YD	1.0	3.1	2.0	3.0	53.0	40.0	.6	0.002	0.03	.52	.006	105
4YD	3.6	7.0	3.0	15.0	32.0	83.0	2.5	0.07	0.15	.18	.003	105
5YD	1.9	2.2	3.0	6.3	9.4	8.7	1.3	0.11	0.88	1.47	.02	98
6YD	.1	.2	1.0	.3	1.3	4.0	.07	0.05	17.5	.34	.007	88
7YD	.8	1.1	2.0	1.9	2.4	3.7	1.3	0.04	0.06	.18	.004	101
8YD	.06	.07	.7	.1	.4	2.3	.01	0.02	0.01	.06	.004	103
9YD	1.0	.8	2.9	3.4	2.8	4.3	1.9	0.05	0.01	.14	.005	109
10YD	.9	.5	2.0	1.7	2.0	3.8	1.1	0.03	0.01	.13	.004	97

* Filter not cleaned

[redacted]

Column Operation (Continued)

C. Quality of Analytical Data

The quality of the radiochemical data obtained for the runs covered in this report was generally poor. This fact is attributed partially to the low level of gross activity, especially in the second cycle, and partially to the presence of small amounts of suspended material which carried activity. The source of the solid material is not definitely known. Filtration ratios for all of the runs were very high, however, and it is possible that insoluble material from the coating removal step could have passed through the filter with the feed.

D. Column Operability

Column operability was good, except for difficulty in controlling the column interface when using 0.75 M $Al(NO_3)_3$ scrub. The difficulty was caused by the high elevation of the jackleg pressure pots, which were designed on the basis of a 1.3 M aluminum nitrate scrub. The introduction of the lower density scrub into the extraction columns reduced the average density in the columns to such an extent that aqueous raffinates barely flowed when the interfaces were at normal height. This difficulty was eliminated in the second cycle by lowering the jack-leg pressure pot 3 1/2 feet.

V. ANALYTICAL DATA

Beginning with the enriched 25 runs the colorimetric method of uranium analysis will be replaced by polarigraphic analysis as a routine method. In view of the strict accountability that will be required for the 25 material, volumetric and gravimetric analyses will also be made for product streams in which the activity is not excessive.

[redacted]

[redacted]

VI. PROGRAM

A. Shutdown and Conversion

Upon completion of the series of 25 runs covered in this report, the decontamination of all cells and equipment was started. All equipment will be inspected, repaired and modified as necessary, and cleansed of all natural uranium prior to processing of the enriched 25 material. It is estimated that the entire decontamination and conversion program will take 6-8 weeks, being completed September 15-October 1, 1949.

Decontamination of first cycle equipment in Cells #1 and #1A was started as rapidly as they could be released from service from the "25" test runs. Decontamination of the dissolver was started on July 21, 1949. During decontamination a record will be kept of the various types of treatment given each piece of equipment together with analytical data showing the effectiveness of each treatment. At completion of the decontamination program a report will be issued covering the procedures, results, and conclusions pertinent to the decontamination of pilot plant Redox equipment which has been operated at 100% Hanford activity levels.

During the conversion phase certain equipment modifications will be made to allow for additional flexibility in operation and to insure against a possible loss of "25" material due to equipment failure or operational errors. These equipment modifications include plugging of all floor drains, providing additional sampling and other equipment for operational flexibility, developing procedures for locking all transfer jets, and providing equipment for evaporation of the second cycle uranium product.

B. Recovery Operation Program

Run procedures are being modified to provide against loss of material due to operational errors, and to provide for a periodic physical inventory or process solutions during the course of each run. A tentative list of procedures to reduce the possibility of losses is given below:

1. Valves for all transfer lines for product and raffinate solutions will be locked out, requiring approval before transfer.

2. Product and raffinate solution for each cycle of each run will be collected over the entire run, sampled, and held for analysis, loss evaluation and material balance check prior to any transfer or disposal.

3. A constant periodic check will be made on rates of build up in all catch tanks as compared to volumes of solution charged into the system in order to detect any discrepancy which might occur due to equipment or operational difficulties.

[redacted]

[redacted]

Program (Con't)

Since no work has been done in the pilot plant using mercuric nitrate as a catalyst for the dissolving of aluminum-uranium alloy with nitric acid, it is planned to start test work on this phase of the process as soon as the dissolver is returned to service. The ORNL Semi-Works group has shown that by using 2% $Hg(NO_3)_2$ per weight of slugs, and by controlling temperature and acid addition rate, better than 99% dissolution is obtained. Final dissolutions are 1.6 - 1.7 M $Al(NO_3)_3$, approximately 0.5 N HNO_3 and contain 0.002 M $Hg(NO_3)_2$. 100 dummy alloy slugs are being acquired by the pilot plant to make full scale dissolving runs in the pilot plant dissolver before making the runs with enriched uranium.

VII. REDOX DEVELOPMENT - H. K. Jackson, G. S. Sadowski

A. Supplementary Data - Spectrographic Analysis of IEU Stream

The results of spectrographic analyses on the IEU streams for Runs 47R-53R are given in Table III.

B. Summary Report

A summary report covering the ORNL Redox Pilot Plant program is being prepared for issuance in October, 1949. A condensed table of contents for the report is given below:

Condensed Table of Contents for Summary Report on the ORNL Redox Pilot Plant Development

[redacted]

Redox Development (Con't)

APPENDIX

I. Conversion of Pilot Plant from "25" to Redox Process

II. Detailed Description of Pilot Plant Equipment

III. Decontamination Procedures

IV. Sampling Schedule and Analytical Procedures

V. Safety Procedures

VI. Process Raw Materials

VII. Typical Run Sheets

VIII. Figures

IX. Tables

X. Bibliography

VIII. CHEMICAL WASTE DISPOSAL - E. L. Nicholson

The chemical waste evaporator is being operated above designed capacity to permit attaining adequate active waste storage capacity. No experimental work on this evaporator is planned until adequate storage capacity is available about December, 1949.

The report covering design and initial operation of the evaporator, ORNL-393, has been issued.

TABLE III

Spectrographic Analyses on IEU Streams

For Redox Runs 47-53R

Values are in PPM

Sample Number	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	Ga	Ge	Hg	In
47R	50	<20	<2	1.0	7	<.02	<1	30	<.2	<1	2	4	~180	<2	<.4	<4	<.4
48R	30	<20	<2	1.8	4	<.02	<1	20	<.2	<1	1	3	~200	<2	<.4	<4	<.4
49R	30	<20	<2	.9	4	<.02	<1	30	<.2	<1	2	2	~180	<2	<.4	<4	<.4
51R	30	<20	<2	.9	4	<.02	<1	50	<.2	<1	1	3	~150	<2	<.4	<4	<.4
52R	20	<20	3	.9	7	<.02	<1	40	<.2	<1	<1	4	~80	<2	<.4	<4	<.4
53R	30	<20	<2	.9	3	<.02	<1	50	<.2	<1	<1	6	~300	<2	<.4	<4	<.4

Sample Number	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Pd	Sb	Si	Sn	Sr	Ti	Tl	V	Zn
47R	1	<10	2	<4	~2500	<1	<100	4	<1	<2	20	<2	<10	20	<4	<.5	<10
48R	1.5	<10	3	<4	~2500	2	<100	4	<1	<2	30	<2	<10	20	<4	<.5	<10
49R	1	<10	3	<4	~2500	2	<100	3	<1	<2	20	<2	<10	15	<4	<.5	<10
51R	1	~200	3	<4	~2500	2	<100	2	<1	<2	80	<2	<10	30	<4	<.5	<10
52R	1	20	2	<4	~2500	2	<100	7	<1	<2	60	<2	<10	15	<4	<.5	<10
53R	.8	40	3	<4	~2500	2	<100	3	<1	<2	50	<2	<10	15	<4	<.5	<10

[redacted]

IX. PATROL - Fairchild, Caldwell, Davis, Jones, Strader

The operation of the 807 Bldg. and miscellaneous patrol work has been without incident the past period. Some additional patrol work has been assumed for the Physics Division.

A shake-down test of the 807 Bldg. to test capacity and miscellaneous modifications made to the demineralized water system in the past six months has been completed. These tests show the capacity of the building to be 65 gpm as compared to the rated capacity of 40 gpm, and show that additional mechanical adjustment and modifications of the instruments are necessary. During this testing approximately 12 gpm of water were sent to the 105 Bldg., 5 gpm to the 205 Bldg., and 50 gpm to the pile mock-up. The pile mock-up water contained 5 ppm of sodium dichromate and sufficient sodium hydroxide to adjust the pH to 6.0-6.5.

Operating Summary 7/1 - 7/31/49

Filtered H_2O to Bldg.		1178,200 gallons
Demineralized water to:		
Bldg. 105		560,000 gallons
Bldg. 205		89,500 gallons
Bldg. 101 and 807		13,220 gallons
Bldg. Mock-Up		272,500 gallons
	TOTAL	935,220 gallons
Operating Efficiency		79%

	Dearested	Demineralized
Average pH	5.6	4.7
Average Resistance	416,000	140,000 ohms

[redacted]

[redacted]

X. GENERAL ADMINISTRATIVE

A 500 ml sample of the ICU stream from Run 51 was sent to ANL, 1 liter each of IEU concentrate and ICU were sent to HEW from Redox Run 52R. 100 ml of IEW from 52R were sent to KAPL.

Dr. F. W. Hurd of the K-25 plant has agreed to return 75 pounds of IEU concentrate previously sent him from Redox Run 49. This will increase the amount of uranium as metal available for reprocessing at Mallinkrodt to 465 pounds.

The report giving solvent plant design and operating recommendations is in the final rough draft stage and expect to be issued within the next period.

The expanded and recommended version of the 205 permanentization plans giving a far more satisfactory building arrangement and floor area has been submitted to and accepted by laboratory management, AEC, and Austin Company. The necessary design information has been submitted to Austin Company and design on the new arrangement has been started. A realistic schedule for the start of construction is estimated to be November 1, 1949.

This report [illegible] future.

[redacted]