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MONTHLY REPORT - AUGUST, 1956

AUTHOR
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SEPARATIONS TECHNOLOGY SECTION MONTHLY REPORT

AUGUST, 1956

Compiled by Members of
the
SEPARATIONS TECHNOLOGY SECTION
ENGINEERING DEPARTMENT

September 11, 1956

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission
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82. thru 86. Technical Information Service, Oak Ridge, Tenn.

VISITORS AND BUSINESS TRIPS

L. A. Ferris, W. K. Eister, R. J. McNamee and C. W. Hancher of Oak Ridge National Laboratory, visited Hanford on 8-20 thru 8-23-56 to discuss solvent extraction and U processing and to attend the UO_3 Conference.

N. Levitz of Argonne National Laboratory, Lemont, Illinois visited Hanford on 8-22 thru 8-24-56 to attend the UO_3 Conference.

W. R. Rossmassler of Union Carbide Nuclear Co., Oak Ridge, Tenn. visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

E. S. Roszkowski of AEC-NBL, visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

R. D. Thorne, AEC-SROO visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

R. E. Leed, AEC-OROO, visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

R. V. Anderson, AEC-Fernald visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

W. N. Munster, AEC, Product Division, Washington, D. C. visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

B. Schwarz, AEC, Feed Materials, Washington, D. C. visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

W. W. Harris and E. J. Barber, Union Carbide Nuclear Co., K-25 Plant, Oak Ridge, Tenn. visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

W. C. Nanser and P. S. Gentile of National Lead of Ohio, Fernald, Ohio visited Hanford on 8-21 thru 8-23-56 to attend the UO_3 Conference.

R. M. Edwards and A. E. Ruehle of Mallinckrodt Chemical Works, St. Louis, Missouri visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

D. A. Vaughn of Battelle Memorial Institute, Columbus, Ohio visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

E. T. Cook of Savannah River Project duPont, Aiken, So. Carolina visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

A. G. Allison, of Battelle Memorial Institute visited Hanford on 8-22 thru 8-23-56 to attend the UO_3 Conference.

L. W. Powers, G.E. West Lynn, Mass. visited Hanford on 8-21-56 to consult on a mass spectrometer.

[redacted]

Visitors and Business Trips (continued)

A. T. Whatley, ANP, Idaho Falls, Idaho visited Hanford on 8/27 thru 8/28/56 to discuss iodine on stack problems.

W. D. Stump and F. Wall, Dow Chemical Company, Rocky Flats Plant, Boulder, Colo. visited Hanford on 8/27 thru 8/28/56 to discuss radiography and autoradiography procedures pertaining to material produced in 234-5; also discuss statistical treatment of analytical data on plutonium.

G. W. Watt, Consultant from University of Texas, Austin, Texas visited Hanford on 8/20 thru 8/24/56 to consult on plant processes sub-section problems.

N. D. Groves of Carpenter Steel Co., Reading, Penn. visited Hanford on 8/29/56 to discuss corrosion techniques.

S. H. Smiley, C. A. Powell, E. Bollinger, of the Union Carbide Nuclear Co., K-25 Plant visited Hanford on 8/29 and 8/30/56 to discuss continuous calciner process.

R. E. Smith of Hanford visited the Los Alamos Scientific Laboratory, Los Alamos on 8/13 and 8/14/56 to discuss plutonium chemistry and metallurgy and the Dow Chemical Company Rocky Flats Plant, Boulder, Colo. on 8/15 to discuss plutonium chemistry and metallurgy.

R. E. Larson and A. Lagani of Knolls Atomic Power Laboratory, Schenectady visited Hanford on 8-22-56 to discuss covering spectrographic analysis of KAPL-120 water samples.

A. J. Zeits of Hanford visited the Aircraft Nuclear Propulsion Dept. Cincinnati, Ohio on 8/27 and 8/28/56 to discuss mutual analytical problems.

K. M. Harmon of Hanford visited the Dow Chemical Company Rocky Flats Plant, Boulder, Colo. on 8/13 thru 8/14/56 to discuss plutonium chemistry and metallurgy and the Los Alamos Scientific Laboratory, Los Alamos on 8/15/56 to discuss plutonium chemistry and metallurgy.

F. A. Scott of Hanford visited New Hampton, New Hampshire on 8/4 thru 8/11/56 to attend the Gordon Research Conference.

A. S. Wilson of Hanford visited New Hampton, New Hampshire on 8/11 thru 8/17/56 to attend the Gordon Research Conference.

J. H. Kleinpeter attended the Maintenance and Protective Coatings School at North Dakota State College, Fargo, North Dakota on 8/1 thru 8/4/56.

ORGANIZATION AND PERSONNEL

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Separations Technology Section	2	2
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Plant Processes Sub-Section: K. V. Seyfrit, Engineer II transferred into the Sub-Section from Manufacturing on 8/1/56. N. A. Taylor, Steno-Typist transferred into the Sub-Section on 8/27/56 from the Stenographic Unit. R. N. Nelsen, Engineer II transferred to GE, Fort Wayne, Indiana on 8/2/56.

Chemical Development Sub-Section: B. E. Lauer, Senior Engineer (Summer Employee) terminated on 8/22/56. Erma M. Chacon, Gen. Clerk "C" transferred from the Sub-Section to Salary Control Records Unit on 8/13/56.

Chemical Research Sub-Section: J. E. Cassidy, Engineer I (Summer Employee) terminated on 8/24/56. D. G. Miller, Engineer I, terminated on 8/24/56. W. P. Van Meter, Engineer I terminated on 8/31/56.

Analytical Laboratory Unit: Martha H. Bucker, Lab. Asst. C transferred into the Unit from Education and Training on 8/13/56. F. E. Holt, Supervisor, Analytical Technology transferred into the Unit on 8/13/56. Jack L. Humason, Engineering Assistant transferred into the Unit on 8/9/56. Carol T. Arneson, Lab. Asst. D was deactivated on 8/30/56.

Technical Shops Unit: S. C. Gettings, Draftsman I terminated from the Unit on 8/10/56. C. E. Zook, Drafting Trainee terminated from the Unit on 8/3/56.

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PLANT PROCESSES SUB-SECTION, O. F. HILL

REDOX PROCESS TECHNOLOGY

Summary

Unstable operation in the extraction battery resulted in a large loss of plutonium to the salt waste during the processing of dissolver heel solutions and equipment flushes of the dissolver and feed preparation cells. This loss, combined with an unusually large plutonium pickup from the cell sumps, was held for rework. The HA, HS, HC, IA, and 2A Columns plus the 2AF feed tanks (E-5, E-6, E-7) and the IAFS concentrator tanks (F-1 and F-2) were flushed with hot(60 to 70 C) 60 per cent nitric acid. These acid flushes, when combined and sampled, showed a plutonium pickup approximately equivalent to one full head-end batch of virgin feed. Consequently, most of the month's operation involved processing virgin feed blended with either salt waste or neutralized acid waste. The processing of this material was generally smooth, although waste losses were five to ten times normal (averaging about 1.5 per cent), and a tendency for unstable operation in the extraction columns owing to the buildup of cruds made the decontamination performance sensitive to operational variables.

The plutonium pickup by the acid flushes is postulated to have occurred as a result of either (1) plutonium(IV) oxalate pickup from last month's storage of plutonium solutions containing hexone or (2) formation of plutonium(IV) polymer.

The average exposure of the metal charged to the dissolvers was 760 (842 to 599) MWD/T, and its average cooling time was 130 (106 to 148) days. Control of iodine-131 emission to the environs was excellent.

On August 23, 1956, the extraction battery was again shut down for conversion from high MWD/T material to low MWD/T material.

Feed Preparation

The majority of the feed batches processed during the month were blends of virgin metal solution and varying amounts of either salt waste, acid wastes, or sump solution resulting from the leak in the IAFS concentrator. The salt waste was blended with the virgin metal solution in a volume ratio of 1.0 to 1.2, while the acid waste was blended in a ratio of one to six or one to three (waste to metal solution). All waste rework batches received 0.03 - 0.02 molar permanganate oxidation treatments. Centrifuge bowl cleanouts were made every third head end run instead of every sixth run during the processing of the acid waste material to assure the best solids separation possible.

Decontamination

Uranium and plutonium decontamination was good considering the large amount of rework processed. Over-all fission product decontamination factors (logarithmic) averaged 6.9 and 7.9 for uranium and plutonium, respectively. All final uranium product batches, except five, met specifications for subsequent processing, and these five batches are being held for silica gel treatment and/or blending with subsequent uranium production. On August 17 and 18, plutonium decontamination was marginal due to flooding in the HA Column on August 15 and an operational upset of the HS Column on August 16. During the rest of the month, plutonium decontamination was above specifications.

Solvent Extraction

The over-all operation of the extraction battery was relatively uneventful during the extended period (August 11 to August 24) of rework processing. During the latter part of the rework period, all of the extraction columns were highly contaminated, and any unsteady operation resulted in increased radioactivity in subsequent process streams. The HA Column became inoperable due to flooding after 3.5 days of processing salt and acid waste rework feed solutions and, after water flushing, was still inoperable. The HS Column was therefore used in place of the HA Column and operated smoothly for the completion of the acid rework (no salt waste rework was processed through the HS Column).

Near the end of the rework period, the final uranium extraction column (2D) was upset due to instrument trouble which allowed highly contaminated interfacial material to overflow with the organic and contaminate five of the final uranium product stream batches to a level about twice the allowable radioactivity specifications for subsequent processing.

Waste Losses

The over-all recoveries for the month were 99.70 per cent and 98.57 per cent for uranium and plutonium, respectively. The poor plutonium recovery was due to two main causes, viz, (1) high solvent extraction losses while processing non-standard feed solutions and (2) the discarding of salt waste solutions which would normally have been reworked to make room in the rework system for nitric acid flush solutions with a much higher plutonium content than the preceding salt waste solution. The high solvent extraction losses (approximately 1.5 per cent of the feed plutonium) occurred during the processing of such non-standard feed batches as dissolver heel removal solutions, dissolver and feed preparation cell flush solutions, and process cell sump solutions.

In the early part of the month, the HA, HS, HC, IA, and 2A Columns, the 2AF feed tanks (E-5, E-6, and E-7), the IAFS concentrator (F-2), and the IAFS feed tank (F-1) were flushed with hot (60 to 70 C) 60 per cent nitric acid. These acid flushes picked up an amount of plutonium approximately equivalent to one full batch of virgin metal solution. Of this amount, approximately 59 per cent came from the HC Column, IAFS concentrator, and IAFS feed tank, 12 per cent from the HS Column, and about four per cent from the IA Column. The source of the remaining 25 per cent was uncertain but may have been the waste cell tanks. The plutonium was contained in two batches, each roughly 2300 gallons of 40 per cent nitric acid. The first batch of acid contained 90 per cent of the total plutonium, with the rest in the second batch. In an attempt to get the

[redacted]

plutonium in a recoverable state, the nitric acid was neutralized with caustic to a final concentration of 1.5 molar, and the solution was made 0.05 molar in sodium dichromate and held at 80 C for 2.5 hours. This was then reworked via the head-end in 300 gallon batches.

The cause of the plutonium accumulation is not definitely known but is very possibly associated with the problem of plutonium precipitation encountered last month when hexone-saturated product solutions were held for a long period of time awaiting the rehabilitation of the final concentration building. The precipitates (as plutonium oxalate or plutonium polymer or both) which were dissolved, flushed from the plutonium cycle vessels, and returned to head-end for recovery, were probably metastable in solution and were slowly reprecipitated in the process of transfer and rework, thus tending to accumulate in the unagitated vessels.

The possibility also exists that the accumulation occurred gradually over a long period of operation due to the acid deficiency of the flowsheet but, based on chronological history and available data, this theory does not fit all known facts as well as the first postulation. An intensive study of the data and Redox operating history is under way, combined with additional laboratory work and plans for plant studies to determine exactly what the problem is and whether or not it is an inherent or a non-recurring one.

Waste Storage

Since the reactivation of the 101-SX air recirculator on June 15, 1956, no tank pressurizations have taken place.

The self-concentration rate of the 101-S and 104-S tanks (first tanks to self-concentrate) had fallen to approximately 0.014 gpm. Therefore, on August 17, the vapor lines were valved off and the tanks placed on total reflux, using the original air condensers.

PUREX PROCESS TECHNOLOGY

Summary

The Purex Plant operated at a capacity factor of 1.44 for the major part of the month. After flushing the plutonium stripper and concentrator to remove the siliceous scale, the plant was started on August 3 and operated for ten hours prior to a shutdown caused by a plugged line from the plutonium concentrator to receiver. The plutonium concentration equipment was again flushed and a considerable amount of organic material removed.

Operation has been continuous since August 9, except for two local electrical power outages of short duration. In addition, a process upset (excess sodium nitrite in the IAF) required recycling the feed to the final uranium cycle for 46 hours to recover the excess plutonium. Although the solvent extraction systems suffered these upsets, the plant was able to maintain specification product during the report period, except for three plutonium batches and eight tons of uranium. About 66 per cent of the uranium produced required treatment by silica gel to reduce the gamma ratio to 2.0 or less. The plutonium concentration equipment has been operating satisfactorily, and no buildup in the equipment has been detected. Although operation of the IO Column T-G2 has been very erratic, caused by frequent flooding, the solvent gamma activity has remained approximately normal. The final concentrated waste volume has been maintained at or less than flowsheet volume, and approximately 82 per cent of the acid to the waste cell has been recovered as 50 weight per cent acid. Underground storage tank 241-A-103 now contains about 331,000 gallons of waste and is self-concentrating at a rate estimated to be three to five gallons per minute. Usually three "bumps" are recorded per day with pressures of five to ten inches of water being generated in the tank.

Feed Preparation

Irradiated uranium slugs with an exposure of 3.2 to 6.7 MW/T (604 to 859 MWD/T) and cooling times from 111 to 268 days were dissolved in the two dissolvers. Radioiodine to the stack varied between 0.01 and 0.03 curies per day.

After additional acid and a lower end point specific gravity were incorporated into the dissolver procedures to compensate for the change in mol ratio reported last month (from 3.5 to 3.8 mol HNO_3 per mol U), subsequent data indicated no change existed in the mol ratio. A second modification, initiated to improve the capacity of the dissolvers, compensated for the previous flowsheet change. Currently, the metal charged to the dissolvers is 133 per cent of that originally charged, and the metal is dissolved in two cuts. Additional data are being assembled for evaluation of this procedure change.

Solvent Extraction

The Purex Plant started up on August 3 after the completion of the L cell package flushes for the removal of the siliceous scale. However, the plant was shut down after only ten hours of operation because the line between the plutonium concentrator and the plutonium product receiver became plugged.

After a second flushing of the L cell package, plant operation was restarted on August 9 at a nominal production rate of 1.44 capacity factor. Although the first two batches of plutonium exceeded the uranium specification and required processing at the 231 Building, the following batches met product specifications. After three days of operation, the uranium product gamma ratio had decreased from 19 for the initial batch following startup to about two.

A nominal capacity factor of 1.44 was maintained without interruption until August 16. The following table summarizes the performance of the solvent extraction batteries from August 9 to August 16:

Cycle	Log Gamma Decontamination Factor, dF		Per Cent Waste Loss	
	Uranium	Plutonium	Uranium	Plutonium
Precycle	3.3	3.3	----	0.24
Partition	2.4	1.8	----	0.20 (IBU 0.032)
Final	0.9	3.1	0.09	0.06
Over-all	6.6	8.2	----	----

On August 16, the HA and IA Columns were shut down for about two hours because of a local electrical power outage. As a result of the startup, the gamma activity in the uranium product climbed to a gamma ratio of 3.7 before it started to decline. In addition, one batch of plutonium product exceeded the product gamma specification and required processing at Recuplex.

The final uranium cycle was shut down on August 19 because essentially no partitioning of plutonium from uranium was being achieved in the IBX Column. The failure to partition was caused by an excessive sodium nitrite addition rate to the IAF tank. After the sodium nitrite rate had been adjusted, the IBX ferrous iron concentration was temporarily increased from 0.03 M to 0.05 M in order to regain partitioning more quickly. The off-standard 2DF was recycled to HAF for recovery of the plutonium.

On August 20, partitioning was recovered. Shortly thereafter, it became necessary to increase the acidity in the 2AF of the final plutonium cycle from 2.75 M HNO_3 to 3.6 M HNO_3, in order to reduce the plutonium loss via the 2AW, caused by the increased sulfate concentration in the 2AF. When the sulfate concentration in the 2AF returned to normal, the nitric acid concentration in the 2AF was returned to 2.75 M without adverse effects.

On August 21, after the plutonium content of the 2DF was sufficiently low to prevent an excessive loss, the final uranium cycle was restarted. As a result of startup, the gamma activity in the uranium product climbed to a gamma ratio of four before it started to decline. The loss of partitioning caused about 25 tons of uranium to be recycled to the head-end. Also, about 135 units of plutonium in excess of the normal loss were lost via the 2DW.

Another local electrical power outage on August 24 caused the shutdown of the precycle and partition cycle solvent extraction columns for about ten minutes. Although the gamma activity of intercycle streams increased rapidly to about a factor of six over normal activity, the plutonium product remained within gamma specifications. However, the gamma activity of the uranium product climbed to a gamma ratio of 7.8 before it started to decline.

Even though the solvent extraction batteries were frequently upset, the Purex Plant was able to maintain product specifications with only a few exceptions. A total of three batches of plutonium exceeded specifications; the first two batches following the plant startup on August 9 exceeded the uranium specification, and one batch following the electrical power outage on August 16 exceeded the gamma specification. A total of eight tons of uranium product produced during this period will require processing at the TBP Plant. The first four tons produced after the plant startup on August 9 exceeded the gamma specification and could not be reduced by silica gel treatment, and the first four tons produced following the August 21 plant startup exceeded the plutonium specification. Although the solvent extraction batteries decontaminated satisfactorily only 34 per cent of the uranium produced, the remainder was reduced to a gamma ratio of two or less by silica gel treatment.

During the month, a test was conducted to demonstrate the operability of the 2AF tank at increased capacity factors. The purpose of the test was to evaluate the degree of conversion of plutonium(III) to plutonium(IV) with decreased residence time in the tank. Holdup times equivalent to processing rates up to a capacity factor of 3.12 were attained without any detectable increase in the 2AW plutonium losses by lowering the liquid level in the 2AF tank.

Plutonium Concentration

After the plant startup on August 3, the transfer line between the L4 plutonium concentrator and the L6 plutonium receiver plugged which required a plant shutdown for removal of the solids from the concentrator system. Spectrographic analysis of the boiling nitric acid flushes generally indicated strong Na, Cr, Ni, Fe, and P concentrations. A considerable quantity of organic plus a black, oily, semi-solid material was removed by the flushes. Analysis of the organic indicated 50 to 100 g/l of plutonium, while the accompanying aqueous phase analyzed one to five g/l plutonium and five to eight molar nitric acid. After the nitric acid flushes were completed, three 20 per cent caustic flushes were made and the equipment given a final acid flush in preparation for startup.

Prior to startup, the flowsheet was modified as follows:

a. The acid addition was adjusted to give 0.75 $\underline{M}$ HNO_3 in the 2BP to the stripper.

b. Final plutonium concentration was increased to 120 to 130 g/l to reduce the HNO_3/plutonium ratio.

c. The stripping steam was increased 20 per cent during the startup period to assure complete stripping of entrained organic from the L4 concentrator feed.

With the exceptions noted elsewhere in this report, the plutonium product has met all specifications during the report period. However, efforts are being made to reduce the nitric acid concentration of the final plutonium product. This has been as high as 8.3 $\underline{M}$ during periods of recycled uranium but normally analyzes about 7.8 $\underline{M}$. Since the startup on August 9, no evidence of excessive plutonium holdup or solids accumulation in the L cell package unit has been found.

[redacted]

Uranium Process[illegible] Silica Gel

Following regeneration of the silica gel beds, 108 tons of uranium which had gamma ratios of 16 to 2.5 were reduced to a gamma ratio of 1.5. This uranium was processed at a capacity factor of 1.7 (60 gal/(hour)(ft^2) and a temperature of 65 to 85 C. Increasing the feed temperature and reducing the feed storage time prior to processing have improved the performance of the silica gel beds during the month.

Organic Treatment

The over-all performance of both organic treatment systems are summarized below.

Organic Treatment System	Organic Activity, Microcuries/Gallon: Unwashed Max.	Unwashed Min.	Washed Max.	Washed Min.	Average Decontamination Factor	Organic Losses, Per Cent of Gallons Processed
No. 1	1.2^6	1.0^4	5700	400	6	0.41
No. 2	21.0	2.0	30	1	>1	

The wide variations in the activity level of the solvent and the higher than normal solvent losses are the result of four plant shutdowns and the rework of out of specification material. In general, the organic treatment systems contained the upsets, but some activity did break through to the washed solvent because of the unstable operation of the IO Column T-G2. Indications are that the IO Column is becoming increasingly more difficult to control and that the flooding frequency is decreasing.

Since the hot startup of the plant, the solvent has been routinely analyzed for per cent TBP, gamma activity, uranium extraction coefficient (Eå), color, and disengaging time. These analyses were requested to assist in determining a method for evaluating solvent quality. After ten months of operation, a data correlation indicates that gamma activity is the only analysis which is significant for quality control and, therefore, the latter three have been discontinued.

Waste Treatment

The acid recovery and waste treatment sections of the plant have operated without incident while processing both the column flushes and extraction wastes. The final waste (IWW) volume has been maintained at or less than flowsheet volume during the operating period. Approximately 82 per cent of the acid fed into the waste cell has been recovered as 50 weight per cent nitric acid.

Tank 241-A-103 currently contains approximately 331,000 gallons of waste, and the contents have continued to self-concentrate. At the end of the report period, 54,000 gallons of tank space have been made available by this method.

Uneven or bumping boiling has continued without incident with pressures of five to ten inches of water being generated in the tank. Normally, one to three bumps are recorded per day. The estimated average boil-off rate at month's end is three to five gallons per minute.

URANIUM RECOVERY PROCESS TECHNOLOGY

Summary

Process performance was generally good, and feed aged as little as 14 months since irradiation to 250 MWD/T was processed without difficulty. Over-all uranium waste losses averaged 0.7 and 0.9 per cent of the gross and new (Tank Farm) feed uranium, respectively. The REU gamma activity was halved when 0.2 M phosphate ion was added to the second cycle acid scrub and, over the entire report period, averaged 100 per cent that of aged natural uranium.

The bottom of the mild steel liner of Tank 104-U is buckled and possibly ruptured. The condition of the liner and cause of failure are being investigated.

During the report period, one million gallons of scavenged waste with cobalt-60 concentrations less than the maximum allowable in drinking water (MPC) but greater than 0.1 MPC (the HAPO disposal limit) were transferred to crib on a trial basis. Also, one million gallons of scavenged waste with cobalt-60 concentrations greater than MPC were transferred to the ground on a "specific retention" basis.

A Plant scavenging procedure involving two point addition of inert cobalt to the waste was evaluated. Line samples show that cobalt removal from the waste was improved about four fold. Nevertheless, the final sample from the settling tank contained 8.5×10^{-4} microcuries of cobalt per milliliter (vice 4×10^{-5} microcuries per milliliter required for routine cribbing).

Solvent Extraction

Slightly slurry rich feed with an effective age of about 16 months since irradiation to 250 MWD/T was processed with no difficulty. Steady state RAW, RCW, and REW uranium losses were 0.2, 0.1, and 0.05 per cent of the gross feed uranium, respectively. The RCW losses increased ten fold when aged, decomposed organic phase from the RAF feed tank was returned to the in process organic inventory. This organic phase is entrained from the RA Column which is vented to the feed tank. After the transfer, these losses decreased rather consistently and finally returned to "normal" when the organic phase completed about 30 passes through the system.

Gamma decontamination was generally adequate and not significantly affected by the relatively young feed processed. The average over-all logarithmic gamma decontamination factor and REU activity were 5.2 and 100 per cent of that of aged natural uranium, respectively. Three product batches produced during a shutdown and the ensuing startup contained from 200 to 400 per cent of the activity of aged natural uranium. Because of the difficulty of concentrating this material if it were to be reworked, it was shipped to the UO_3 Plant and blended with low activity UNH.

The phosphate concentration of the RDIS was increased from zero to 0.2 M during a steady state period when essentially all the feed was aged about 15 months since pile discharge. As a result, REU activity decreased from 140 to 80 per cent of that of aged natural uranium, and the second cycle logarithmic decontamination factor increased from 2.1 to 2.5. Routine use of phosphoric acid in the RDIS will be recommended.

The amount of "filterable" activity in the RCU and REU has not decreased significantly since installation of cold stream filters during July, 1956. Filtration of samples of RCU and REU continues to give arithmetic decontamination factors of about 4.0 and 1.5, respectively.

Waste Treatment

Approximately one million gallons of scavenged waste with cobalt-60 concentrations less than the maximum permissible in drinking water (MPC; 4×10^{-4} microcuries per milliliter) but greater than the HAPO standard for cribbing (0.1 MPC) were transferred to the BC-3 crib on a trial basis. Eight million gallons of waste were previously cribbed in this site with no gamma emitting isotopes penetrating farther than the 100 foot depth and with no increase in ground water contamination below the crib. Therefore, this disposal is considered safe.

Approximately one million gallons of scavenged waste (the third "in-farm" batch and the 41st plant scavenged batch) containing cobalt-60 concentrations greater than the MPC were transferred to the BC-7 ditch on a specific retention basis.

A scavenging test in which cobalt sulfate was added to the waste was completed. Cobalt was added via the RDIS and the nickel sulfate so that the acid waste and neutralized waste contained 0.003 and 0.009 M cobalt, respectively. Preliminary results obtained during the test show that from three to five fold improvement in cobalt-60 decontamination was obtained. Samples taken from the underground tank after the sludge settled contained 8.5×10^{-4} microcuries of cobalt-60 per milliliter.

Tank 104-U

Photographs of the interior of Tank 104-U taken to determine the condition of the tank show that the mild steel liner is buckled upward. Electrode measurements indicate that the center of the tank is approximately five feet higher than it should be. The photographs do not show that the liner is ruptured; however, about one-half of the tank surface is covered with liquid and could not be observed. Additional photographs will be taken.

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URANIUM CONVERSION PROCESS TECHNOLOGY

The quality of the UO_3 produced during August was excellent. The gamma activity, reactivity ratio, and total metallic impurities averaged 50 per cent that of aged natural uranium, 0.98, and 90 parts per million parts of uranium, respectively. Over 99 per cent of the production was capable of passing through 40 mesh screen. Production was somewhat curtailed, however, because of construction activity and pot room equipment failures.

Tests

As part of a program to better understand and to improve the operation of the acid recovery system, the fractionator (T-D-4) bottoms were measured and analyzed. Under normal operating conditions, with half of the UNH feed supplied by the TBP Plant, about nine pounds of uranium and 300 pounds of nitric acid are in 110 gallons of fractionator bottoms per day. It has been recommended that T-D-4 be operated as a phase separator rather than as a fractionator, abandoning the small amount of acid in the evaporator overheads but recovering entrained uranium. Thus, some slight cost saving will be made, and the net dilution of the recovered acid will be decreased.

UO_3 CONTINUOUS CALCINER - PROTOTYPE DEVELOPMENT

The prototype continuous calciner was operated for a series of short runs during the month. Approximately ten tons of uranium oxide were produced containing 300 ppm parts of uranium at a bed temperature of 315 C and an agitator speed of 50 rpm. The reactivity of the UO_3 produced was 0.76 with 925 C and 600 C reduction and hydrofluorination temperatures, respectively. The bulk and packed densities were about 4.4 and 4.8, respectively, for the oxide as produced, and 3.7 and 4.5, respectively, for the milled product.

Sustained operation was hampered by frequent failure of the shaft seal packing, particularly that on the drive end. At month end, improvement in the seal service is being attempted by controlling the trough distortion by means of the furnace temperature distribution. A variety of alternate shaft seal materials have also been designed for testing.

234-5 DEVELOPMENT

Plutonium Polymer

Several tests were run in an effort to establish the limiting conditions for formation of plutonium polymer in Purex 2BP. At acid concentrations above 0.5 M HNO_3, essentially no polymer was formed when 2BP containing five g/l plutonium (50 per cent IV) was boiled under reflux, while below 0.4 M HNO_3 considerable solids were obtained which appeared to be polymer. In 2BP which was butted up to 9.5 g/l plutonium, a negligible amount of polymer, if any, was obtained above 1.3 M HNO_3. Boiling solutions of nearly pure plutonium(IV) (five g/l) at 0.6 M HNO_3, or less, gave a fine white powdery precipitate which, within a few minutes, converted entirely to typical polymer. Solutions of pure plutonium(III) (five g/l) upon boiling oxidized and precipitated polymer within four minutes at 0.4 M HNO_3, but not at 0.6 M HNO_3. At 0.2 M HNO_3, no oxidation or precipitation occurred over one hour.

Precipitated polymer usually had very fine particles which were light green in color, although it appeared yellow when covered by supernate. The precipitate will dissolve in six to eight M HNO_3, sometimes quite readily and other times upon standing for a few hours. However, within a day or two, it dissociates into normal plutonium(IV). Heating the dissolved polymer will also cause dissociation. Polymer in colloidal state has been coagulated by increasing the acidity to ca three M HNO_3.

Purex Tube Bundle Solids

A white solid taken from the product concentrator tube bundle was soluble in boiling 1.0 M and 13 M NaOH and was insoluble in boiling nitric acid and insoluble in six M HNO_3 - 0.1 M HF at room temperature. Spectrochemical analyses indicated the material was predominately silica.

Spectrophotometric Analysis of Redox E-1 and E-3 Tank Material

During the July shutdown of Redox, a slow precipitation of plutonium was observed in some of the tanks. Samples were taken from the E-1 (3AF) and E-3 (3BP receiver) tanks and from the flushes of these tanks after startup. These samples were submitted to the 234-5 Development Laboratory for analysis and plutonium valence distribution determination. The cause of the observed gradual precipitation was not proved, although oxalate precipitation was strongly indicated.

Spectrophotometric analysis made upon immediate receipt of the samples (July 24 and 25) and after intervals of three, six, and eight days showed the solutions to be mainly plutonium(IV) with some trace of plutonium(VI) in the E-3 samples. No indication of plutonium polymer was observed. There was a small amount of precipitate in one sample which was submitted to the analytical laboratory for a carbon analysis. After drying, the sample analyzed 9.1 per cent carbon. Pure plutonium oxalate ($Pu(C_2O_4)_2 \cdot 6\ H_2O$) would analyze 9.2 per cent carbon. The agreement is considered relatively good under the difficult analysis conditions with the small sample available. Hence, the slow precipitation is probably due to plutonium oxalate precipitation.

Examination of Crud from Redox Concentrator Valve

Solids taken from the L-3 to L-4 valve and reported on last month were largely soluble in boiling six M NaOH. A dense black residue was insoluble in the caustic, in boiling concentrated nitric acid, and in aqua regia. Spectrochemical analysis of the as received crud indicates chromium, iron, and silicon to be the predominant constituents. Spectrochemical analyses of the dense black material were inconclusive.

CHEMICAL RESEARCH SUB-SECTION

PUREX

Mini Runs

Two 1A-1C runs were made comparing the decontamination performance of "high-acid" and "low-acid" second cycle flowsheets. Feed used for these runs was prepared from the uranium product (HCP) produced in a low-acid precycle run reported last month.

The flowsheets employed and the decontamination results obtained in these runs are summarized in Table I.

TABLE I

1A-1C DECONTAMINATION

Low Acid Flowsheet:

1AF: 1.7 M U, 0.83 M HNO_3 Flow: 100
1AS: 2.0 M HNO_3 Flow: 67
1AX: 30% TBP in Shell E-2342 Flow: 445

High Acid Flowsheet:

1AF: 1.35 M U, 2.0 M HNO_3 Flow: 100
1AS: 3.0 M HNO_3 Flow: 67
1AX: 30% TBP in Shell E-2342 Flow: 366

DECONTAMINATION FACTORS

Flowsheet	1AF to 1AP			HAF to 1AP	
	Ru	Zr	Nb	Ru	Zr-Nb
Low Acid Precycle + Low Acid 1A	27	49	450	3.5×10^4	7.4×10^5
Low Acid Precycle + High Acid 1A	62	18	>450[a]	8.0×10^4	2.7×10^5

a) Nb activity below gamma spectrometer detection limit.

The product gamma ratios were two for the product of the high acid second cycle run and five for the product of the low acid second cycle runs. Improved ruthenium decontamination was responsible for the better overall decontamination observed with the low acid precycle-high acid second cycle combination. Whereas zirconium and ruthenium contributed about equally to the gamma activity in the product from the high acid second cycle, ruthenium was the predominant gamma activity in the product from the low acid second cycle. Presumably this effect would have been more pronounced had a 1B column been employed since normally ruthenium splits predominantly toward the uranium stream.

It appears from these data that the combination of a low acid precycle flowsheet and a high acid second cycle flowsheet is probably capable of yielding adequately decontaminated uranium product after only two cycles of solvent extraction, at least with "reagent-grade" solvent. Further studies will examine the effect on decontamination of combining a high acid precycle flowsheet with high and low acid second cycle flowsheets.

An unshielded 16-stage Mini unit has been installed as an auxiliary scrub section for the shielded 21-stage Mini unit. With this apparatus, it is planned to study the effect of "tailored" scrub sections on decontamination. For example, one of the two scrub sections can be optimized for ruthenium decontamination, the other for zirconium-niobium decontamination.

The first run made with this revised set up employed the 21-stage unit as a 12-stage extraction, 9-stage scrub dual-purpose unit and the 16-stage unit as a heated auxiliary scrub section. The organic was scrubbed with 1.5 molar nitric acid in the shielded unit, then heated to 60 C and scrubbed with 4 molar nitric acid (at 60 C) in the 16-stage auxiliary scrub unit. The aqueous effluent from this unit was recycled to a feed point three stages deep in the extraction section of the shielded Mini unit. There was no stripping unit employed in this run. The flowsheet employed for this run was as follows:

HAF: 1.7 $\underline{M}$ U, 0.83 $\underline{M}$ HNO_3	Flow: 100
HAS-1: 1.5 $\underline{M}$ HNO_3	Flow: 67
HAX: 30% TBP in Shell E-2342	Flow: 480
HAS-2: 4.0 $\underline{M}$ HNO_3	Flow: 67

Decontamination factors observed, from aqueous feed to organic product, were 6×10^4 for zirconium-niobium, 5.7×10^4 for ruthenium, and 8.0×10^4 for total gamma activity.

This represents an improvement by a factor of about ten for zirconium-niobium decontamination and an improvement by a factor of about sixty for ruthenium decontamination, for this flowsheet as compared with a typical "low-acid" HA column flowsheet.

Zirconium-niobium limited gamma decontamination in this run so further runs will concentrate on means of improving zirconium-niobium decontamination. Attention will be given both to methods which would be applicable to feeds from which both uranium and plutonium are to be recovered and to feeds from which only uranium is to be recovered.

Zirconium Chemistry

Additional successive scrubbing studies have confirmed the tentative conclusion advanced last month, viz., that organophilic zirconium species stem from complexing agents present in minute concentrations in hydrocarbon diluents. Thus, it is found that successive scrubbing of a TBP-CCl_4 extract of zirconium tracer results in no change in the distribution coefficient of zirconium. With a TBP-hydrocarbon extract of the zirconium tracer, however, successive scrubbing results in an apparent fractionation of zirconium into two or more species, at least one of which is highly organophilic. The concentration of the organophilic species, however, appears to be different for different organic diluents (nil for carbon tetrachloride, smaller for Soltrol 170 than for Shell E-2342) and, in fact, different for various batches of the same diluent (Shell E-2342).

It was also reported last month that evidence had been obtained for a "hydrophilic" zirconium species which apparently exists in plant dissolver solutions but not in synthetic solutions. This has been confirmed and traced to an impurity present in uranium metal. It has been found that:

(1) Contacting diluted Purex dissolver solution with 30 percent TBP in Shell E-2342 results in zirconium distribution coefficients three to 10-fold lower than are obtained when organic extracts of Purex dissolver solution are recontacted with cold aqueous solutions of the same gross composition as the original dissolver solution or when solutions prepared from crystalline uranyl nitrate, nitric acid, and TTA-purified zirconium tracer are employed. The effect was found to be more pronounced at low acidity, the distribution coefficients differing by a factor of greater than ten at one molar nitric acid but only by a factor of about three at seven molar nitric acid.

(2) The lower extractability found for the plant dissolver solution can be reproduced by dissolving cold uranium metal in nitric acid and then spiking zirconium tracer into the solution. Further, identical results were obtained whether the dissolution was carried out at ambient temperature and terminated at high acid (6 to 8 molar nitric acid) and low uranium (0.5 molar) or carried out at elevated temperature and terminated at high uranium (2.6 molar) and low acid (1 molar).

(3) Simmering of the dissolved metal solution with urea for 30 minutes prior to spiking with zirconium tracer did not alter the zirconium distribution.

The possibility that silica in the uranium metal is responsible for this effect is being tested at present.

Transfer Rates

An apparatus for the measurement of transfer rates in solvent extraction systems has been completed and its operating characteristics established for a TBP-hydrocarbon solvent system. The apparatus employs individually stirred phases of about 400 ml each separated by an interface about 40 cm^2 in area. Transfer across the interface is followed by withdrawing analytical samples through capillary tubes which extend into each phase.

Representing the transfer process by a simple expression, first order in the transferring species, results obtained in preliminary shakedown runs employing nitric acid and/or uranyl nitrate and TBP in Amsco 125-90W may be summarized as follows:

(1) The rate "constant" for extraction of nitric acid is proportional to the TBP concentration over the range 10 percent to 40 percent TBP in Amsco 125-90W.

(2) The rate "constant" for extraction of uranyl nitrate doubles as the TBP concentration is increased from 10 percent to 20 percent but is constant over the range 20 percent to 40 percent TBP.

(3) The rate "constant" for extraction of nitric acid increases as the initial concentration of nitric acid increases, suggesting that the original assumption of a first-order transfer mechanism requires modification. This is further indicated by the fact that the assumed first-order mechanism appears valid even in a single experiment only during the initial one-third or one-fourth of the transfer process.

Organophosphorus Complexing Agents

The large range of complexing ability observed for the esters of oxyphosphorus acids has suggested the possibility of synthesizing organophosphorus chelating agents. Adding a carboxylic acid group to one of these esters would provide the acid function while retaining the basic oxygen of the phosphoryl group. A compound of this type, dibutoxy phosphoryl acetic acid, has been prepared and its physical properties determined.

The ethyl ester of this compound was prepared by the Michaelis-Arbuzov reaction.

$$(C_4H_9O)_3\,P + BrCH_2COOC_2H_5 \longrightarrow (C_4H_9O)_2\,P(O)CH_2COOC_2H_5$$

The ethyl group was removed by caustic hydrolysis. The structure assignment was supported by titration, molecular refraction and by infrared absorption spectra, the latter showing the presence of P-O-C bonds, P-C bonds and the phosphoryl and carboxylic acid groups. Physical properties measured for this compound are as follows:

n^{25}_{D}	1.444
d_{25}	1.102 g/cm^3
pK_a	3.3

A ten percent solution of this compound in carbon tetrachloride was found to be a very efficient extractant for uranyl nitrate. Further tests will be concerned with differentiating between chelate formation and simple solvation and with determining the relative complexing ability of this compound for zirconium(IV) and plutonium(IV). A fraction of the compound will also be hydrolyzed to the carboxylic phosphonic acid, which presumably should form stable organic-insoluble complexes.

Solvent Treatment

Work reported previously has shown that used solvent may be effectively decontaminated by contact with alkaline permanganate or by contact with preformed hydrous oxides of manganese.

Studies completed during the report month indicate that effective decontamination of solvent can also be accomplished by contact with manganese oxides prepared by calcination of manganese(II) carbonate at 350 C or 500 C. These materials have very high specific surface areas (134 m^2/g for the 350 C product, 54.2 m^2/g for the 500 C product) and exhibit a different x-ray diffraction pattern than does the readily available pyrolusite (manganese dioxide).

Results obtained in studies in which solvents of various origin were contacted with these materials (mainly the product of the 350 C pyrolysis) may be summarized as follows:

(1) The efficiency of removal of fission products by this scavenging process varies with the treatment to which the solvent is subjected prior to the scavenging step. Treatment of a sample of Purex G-7 solvent (obtained May 25) with 12 g/l of this solid at 25 C resulted in gamma decontamination factors of 1.6, 2.7, and 13 when the solvent was subjected to pretreatments consisting of, respectively, three washes with equal-volume portions of one molar nitric acid, two washes with equal-volume portions of three percent sodium carbonate, and two washes with equal-volume portions of 10 percent sodium hydroxide.

(2) The efficiency of removal of fission products increases with increase in temperature. For example, scavenging of a Purex G-7 sample (obtained May 25) with 12 g/l solid resulted in a gamma decontamination factor of 13 at 25 C versus 35 at 70 C.

(3) Presence of a bulk aqueous phase (water or 3 percent sodium carbonate) prevents effective scavenging by these materials.

(4) Partial removal of solvent degradation products is accomplished by scavenging with manganese oxides. This is shown by the fact that the color of degraded solvents is decreased, "C" contact E_a^o (U) values are reduced, and decontamination performance is somewhat improved by this treatment.

(5) As little as [illegible]0 grams per liter of the solid manganese oxides suffices to yield adequate decontamination from fission products.

(6) This scavenging process is effective in removing dibutyl phosphate also.

WASTE TREATMENT AND FISSION PRODUCT RECOVERY

Cesium Recovery from Purex Waste

Work on the zinc cesium ferrocyanide process for the recovery of cesium from Purex IWW was continued during the month. Major emphasis was directed at determining the effect of aluminum on cesium recovery, measuring the amount of cesium "volatilized" in the calcination - chlorination reaction, and establishing the radiation stability of zinc cesium ferrocyanide itself.

Large concentrations of aluminum will be introduced into the Purex process if co-dissolution of cans and slugs is adopted. For present Hanford slugs, this would result in an aluminum nitrate concentration of about 1.8 M in the IWW, and hydrolysis of this aluminum (even in the absence of nitric acid) yields a pH of about zero, much too low for satisfactory scavenging of cesium with zinc ferrocyanide. Attempts were accordingly made to neutralize the solutions to a pH of 3 to 4, where the scavenging is effective. Neutralization to pH 3 with sodium hydroxide resulted in hydrous aluminum oxide precipitates which redissolved only slowly upon prolonged boiling. Urea hydrolysis formed very stable gels at pH 4. These gels were not affected by heating, either with or without addition of water, but were readily dissolved by addition of acid. The work is continuing.

The formation of a small amount of a white deposit on the colder portions of the apparatus has been observed during the calcination - chlorination conversion of zinc cesium ferrocyanide. From a chemical viewpoint volatilization of cesium under these conditions is unlikely; nevertheless, this material was soluble in water and gave a positive test with chloroplatinic acid, which suggested that it might be a cesium compound, perhaps CsCN. Although this was equivalent to the loss of only a few percent, at most, of the charge, it could constitute a severe contamination problem. Some quantitative experiments were accordingly carried out with zinc cesium ferrocyanide traced with cesium-137 to determine the severity of the problem. The off gasses were passed through scrubbers, and the furnace tube and connectors were washed free of any deposit following the chlorination. These solutions were combined and assayed. The cesium losses were found to be very low. Calcination - chlorination of a zinc cesium ferrocyanide which had been dried at 110 C for 24 hours "evaporated" only 0.008 percent of the cesium. A nearly identical loss of 0.01 percent was obtained with a precipitate which had been dried for four hours. An air dried material gave a loss of 0.039 percent. The bulk of the white deposit and the positive test with chloroplatinic acid is probably an ammonium compound formed by reaction of ferrocyanide and water.

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A preliminary measurement was made of the radiation stability of zinc cesium ferrocyanide by exposing a seven gram sample for 216 hours in the cobalt-60 source and determining the rate of gas evolution. The yield was equivalent to 1.7 x 10^{-5} moles of gas per watt hour or to 0.045 molecules of gas per 100 ev. This would correspond to about 0.15 moles of gas per year from a 500 curie Cs-137 source and to a time of about one year for complete decomposition, assuming the rate remained constant and that no steady state was attained. It is possible, however, that these figures are grossly in error due to the low dosage rate (4.7 x 10^5 r/hr), to the possible formation of gas by decomposition of sealing agent, to trapping of gas in the crystal lattice, or to adsorption on the equipment. Experiments in an all glass system with the higher flux of a Van der Graff generator will, it is hoped, resolve these points.

Strontium and Cerium Recovery from Purex Waste

As pointed out last month, the study flowsheet given in HW-43835 recovers cesium satisfactorily but was found to give unexpectedly poor yields of strontium and cerium. Recently completed analyses indicate that less than ten percent of the strontium was contained in the final strontium rich fraction and that less than one percent of the initial cerium was found in the cerium product. Intensive work is therefore being carried out on alternate schemes for separating and recovering strontium and the rare earths from the uranium rich solution which is obtained by dissolving the uranium cake from the second (high pH) precipitation in the proposed flowsheet.

A number of schemes have been investigated for separating the uranium from the strontium and cerium. These include: fluoride precipitation of strontium and cerium; uranyl peroxide precipitation of uranium; extraction of the uranium with tributyl phosphate; hydroxide precipitations with carbonate complexing (and solubilization) of uranium; and hydroxide precipitation with glycerol complexing of uranium. The first three worked very well, but the latter two failed. Thus precipitation of the rare earth and alkaline earth fluorides with 1 M hydrofluoric acid gave a small volume cake and strontium recovery of better than 95 percent. Uranyl peroxide precipitation of pH 1 was quantatitive and resulted in negligible carrying of the desired fission products, which can then be recovered from the supernate. A single batch extraction of cake solution with a volume of 30 percent TBP equivalent to one-tenth of the initial IWW removed sufficient uranium to permit oxalate precipitation of the rare earths. Carbonate complexing, on the other hand, failed to hold uranium in solution, and glycerol complexing was too effective, i.e., much of the strontium and cerium was also retained in solution.

Additional work was done to develop satisfactory methods for recovering and purifying strontium and cerium from the above solutions. Oxalate precipitation was found to give a good separation of the rare earths from strontium when carried out in acidic solution. Thus addition of 0.5 M oxalate to a peroxide supernate 0.1 M in nitric acid precipitated 95 percent of the cerium

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and only seven percent of the strontium. With 0.1 M oxalate, only four percent of the strontium appeared in the precipitate. A nitric acid concentration of 0.1 M was near optimum. Cerium recovery was only 70 percent at 0.5 M HNO_3 and little or no precipitate was obtained at 1 M HNO_3. From these results it appears that oxalate precipitation will be a satisfactory step for rare earth recovery following uranium removal by either peroxide precipitation or TBP extraction.

Two methods were found for recovering strontium from the oxalate supernate. Barium carbonate precipitation, after destruction of excess oxalate with bromate, carried 99.2 percent of the strontium. High pH precipitation of ferric hydroxide carried 99.5 percent. The latter did not require destruction of the oxalate.

Separation of cerium from the other rare earths was best accomplished by a homogeneous iodate precipitation. This involved persulfate oxidation of an iodate containing solution and gave a cerium purity of better than 95 percent.

Flowsheets are being prepared, based on these findings, for purposes of economic and engineering evaluation.

FISSION PRODUCT CHEMISTRY

Solvent Extraction Behavior of Ruthenium

Multiple extraction - scrub studies have been performed both on Purex plant feed solution and on plant dissolver solution in an effort to determine the number and relative abundance of ruthenium species present. (c.f. HW-44219-H, p. 55 and HW-44580-H, p. 39). Qualitatively, the results indicate that most of the ruthenium is present as an organophobic species with a low distribution coefficient (E_a^o) but that a small fraction consists of one or more organophillic species, at least when 30 percent TBP-Soltrol 170 is employed as extractant. Analyses were also performed for zirconium, and it exhibited a very similar behavior. Quantitative interpretation of the data was rendered difficult by the very large analytical uncertainty in the numbers, particularly in the case of the successive scrubs since the final activity was very low.

Zirconium Isotopic Dilution Experiments

The effect of inert zirconium on the distribution of radio zirconium into TBP from 3 M and 6 M nitric acid solutions was reported previously. Additional experiments indicate a very similar behavior in the case of hexone extraction from 0.5 M HNO_3, 1.5 M ANN solutions. Increasing the total zirconium from tracer concentration to 0.1 M caused the fission product zirconium extraction coefficient to decrease from a value of 0.22 to 0.05, or by very nearly the same factor that was observed in the 3 M HNO_3, 30 percent TBP - Soltrol case.

In other experiments, the distribution coefficients of "cold" zirconium and tracer zirconium between 3 M HNO_3 and 30 percent TBP - Soltrol were shown to be equal (at the same total zirconium concentrations). This appears to confirm the theory that a labile equilibrium exists between the zirconium monomer and zirconium polymer.

URANIUM PROCESSING

Flurex Processing

Further experiments have been performed to determine the current efficiency for reduction of uranyl ion as a function of the cathode current density. The electrical resistance of Nepton CR 61 membrane has been studied as a function of current density and concentration of electrolyte, and some tests have been carried out on other recently acquired membranes to determine their utility in the Flurex process.

Data from four runs in which 0.05 molar stannous ion was added to the catholyte are recorded in Table II.

TABLE II

RUN SUMMARIES - FLUREX PROCESS

Feed solution: 0.6 M $UO_2(NO_3)$

Catholyte: 1 M F^-, 0.05 M Na^+, 0.05 M Sn^{++}, 0.2 M UO_2^{++}
Anion Transfer Membrane: Permutit 3148
Cation Transfer Membrane: Nepton CR 61; except Run 18, Permutit 3142

Run No.	Cathode Current Density amp/in^2	Membrane Current Density amp/in^2	Cell Voltage V	Current Passed F	Reduction Occurring$^{(a)}$ eq.	Current Eff.	Energy Yield$^{(b)}$ lbs/kwh
15	2	0.22	40-45	0.154	0.149	0.97	0.22
16	3	0.33	50-55	0.360	0.338	0.94	0.18
17	3	0.33	43-50	0.342	0.327	0.96	0.20
18	4	0.44	44-55	0.446	0.413	0.93	0.18

a) Based on uranium(IV) and tin metal found in cathode.

b) Calculated from lbs/KWH $= 9.8 \frac{C.E}{V} = 9.8 \frac{C.E.}{IR}$

The energy yield of Run 15 is believed to be low as earlier runs at 2 amp/in^2 current density gave values of 0.24 and 0.28 lbs/KWH. The low yield in Run 15 results from an unusually high IR drop across the CR-61 membrane, for which there is no obvious explanation. In fact, all evidence points to a constant resistance for the CR-61 membrane. Data from five Flurex runs in which the membrane current density was varied from 0.2 to 0.6 amp/in^2 showed an average membrane resistance of 90 ± 10 ohms per square inch based on rather crude IR drop measurements across the membrane using platinum probes in the solutions adjacent to the membranes and a vacuum tube voltmeter.

A more formal study of membrane resistances as a function of concentration and current density was carried out in a cell in which a single CR-61 membrane (one square inch in area) was used to separate a catholyte of 0.1 molar nitric acid from the anolyte containing the ion under study. Measurements were again made with a vacuum tube voltmeter, this time with the platinum probes actually touching the membranes on both sides. The membrane resistance in the presence of uranyl ion was relatively constant (68-72 ohms) in the range of 0.1 to 0.4 amp/in^2 current density but was considerably lower than the value from Flurex runs. The technique of measurement is believed responsible for the discrepancy. The data are summarized in Table III. The much higher resistance of the membrane to passage of uranyl ions as compared to hydrogen or sodium ions is evident from these data.

TABLE III

VARIATION OF APPARENT RESISTANCE OF CR-61 MEMBRANE WITH CURRENT DENSITY

Anolyte	Membrane resistance (ohms)					
1 M UNH	52	60	68	70	74	72
1 M NaCl			23	16	13	11
0.5 M HCl		29	15	9	6	5
Current density amp/in^2	0.024	0.05	0.10	0.20	0.30	0.40

The effect of temperature on the resistance of the membranes is unknown, but the variation is believed small over the range of these experiments.

Permselectivity studies on Permutit 3148 anion transfer membranes showed it to be superior to Amberplex A-1 with respect to nitrate transfer into nitric acid solutions. The transference numbers for nitrate as a function of anolyte nitric acid concentration are reported in Table IV.

TABLE IV

TRANSFERENCE NUMBERS OF NITRATE ION AS A FUNCTION OF CONCENTRATION OF NITRIC ACID IN THE ANOLYTE

Anolyte Concentration	Nitrate Transference Number	
	Amberplex A1	Permutit 3148
0.1 M	0.74	0.88
0.5 M	0.37	0.67
1. M	--	0.33

Preparation of Uranium Hexafluoride

Continued study of the reaction of sodium uranic fluoride ($NaUF_5$) with fluorine has been concerned with the effect of temperature on the rate of fluorination and the feasibility of complete consumption of the fluorine.

Five gram samples of 0.25-inch diameter pellets of $NaUF_5$ were supported in a 5/8-inch I.D. vertical reactor, and a 50 volume percent argon-fluorine mixture was passed through the bed at a rate of 100 ml/min for 30 minutes. (Under these flow conditions, the fluorine was about 400 percent in excess). The effect of temperature on the completeness of conversion was studied over a bed temperature range from 300 to 550 C. The data are recorded in Table V and show the desirability of an operating temperature of about 450 C. A similar experiment at 550 C resulted in fusion of the contents within five minutes after admission of the gas mixture. Changing the gas mixture to 25 percent fluorine delayed the time of fusion to 12 minutes. Using fused and ground (4-16 mesh) $NaUF_5$ under the initial conditions also resulted in fusion within five minutes at 550 C.

TABLE V

CONVERSION OF $NaUF_5$ TO UF_6 - EFFECT OF TEMPERATURE ON YIELD

Temperature	-	C	300	350	400	450	500
Residual U	-	%	47	18	0.29	0.03	0.03

Two experiments were also performed in a 1.37-inch I.D. reactor. In the first (at 400 C) insufficient time resulted in incomplete conversion; however, residue at the bottom of the column contained less than 0.5 percent uranium. In the second experiment (at 450 C) with 100 percent excess fluorine, the bed residue contained only 0.7 percent of the initial uranium and this mostly in a few unreacted lumps at the top of the column. A sample from the bottom contained about 0.1 percent uranium. Some fusion occurred during this experiment. A thermochemical study will be made to establish maximum fluorination rates permissible under a variety of conditions.

The feasibility of completely scavenging fluorine from a gas stream was demonstrated in an experiment in which 28 grams of $NaUF_5$ pellets (a bed 3.5" deep in the 5/8" I.D. reactor) were exposed to a 50 ml/min flow of 50 percent argon-fluorine at 450 C for 25 minutes. The fluorine was about 37 percent of the stoichiometric amount for conversion to UF_6. The effluent gas was passed through a dry ice trap for removal of the UF_6 and then into standard sodium hydroxide solution. No change in the normality of the caustic was considered evidence for complete consumption of the fluorine. This experiment suggests a mode of operation in which diluted fluorine would be passed consecutively and counter currently through two columns containing $NaUF_5$. Diluted fluorine would be introduced at the bottom of the second column from which NaF would be removed. The upstreaming gas would react with the contents and leave the top of the column as a mixture of diluent, fluorine and uranium hexafluoride. The latter would be removed and the depleted fluorine would be cycled to the bottom of the first column. In this column, the fluorine would be completely removed and intermediates capable of complete conversion to UF_6 would be formed. The effluent gas stream would contain only the diluent gas and uranium hexafluoride. Such a processing scheme would have the advantage of good heat distribution and no fluorine recycle.

UO_3 Studies

Experiments were continued to determine the feasibility of converting uranium trioxide to uranic fluoride by reaction with ammonium fluoride. Uranium trioxide (0.02 moles) and ammonium fluoride (0.08 moles) were heated in a magnesia lined bomb to 460 C over a period of 30 minutes and held at that temperature for the same time interval. A maximum pressure of 270 psig was observed which fell to 10 psig on cooling. Ammonia was produced as well as a thin layer of green powder, but the residue was mainly UO_3 or possibly UO_2F_2. Attack of the magnesia crucible and the stainless steel bomb indicated a loss of hydrofluoric acid to these sources. A second experiment using a 15 percent excess of ammonium fluoride, intimate mixing of the reactants and omission of the magnesia liner resulted in a solid residue of olive green powder with a bright blue-green surface layer. The product has not been identified.

ISOTOPE SEPARATION

Thermal Diffusion

Additional analyses of profile samples from the refrigerated uranyl nitrate-TBP experiment reported in HW-41702-H have been received. The results are summarized in Table VI.

TABLE VI

URANIUM-235 CONCENTRATION PROFILE - THERMAL DIFFUSION

Column Annulus: 0.20 mm
Coolant Temperature: -21 C
Steam Temperature: 116 C
Steam Consumption: 1.9×10^5 cal/min
Product Removal Rate: 1 ml/day.

Displaced Liquid ml	Uranium-235 percent
0 - 0.8	0.7167
0.8 - 1.3	0.7173
4.5 - 6.5	0.7131
12.0 - 14.0	0.7120
20.2 - 22.2	0.7096
26.2 - 28.5	0.7127

The anomalous rise at 28 ml is undoubtedly due to an eccentricity of the inner tubes which caused a distortion in the heat flow and resulted in an external hot spot. The effective length of the column was about four feet, and in this length a separation factor of 1.011 was achieved.

Little difference was found in behavior of "dilute" (220 g/l U) and "concentrated" (330 g/l) uranyl nitrate - TBP solution in the 0.20 mm thermal diffusion column - after about a week the enrichment (0.718 percent U-235) was nearly the same for both cases.

Chemical Exchange

A batch contacting experiment conducted under such conditions as to give a two theoretical stage separation showed no isotope effect. In this experiment an aqueous phase containing 0.014 M MCl_4 and 1 M HCl was equilibrated with 0.094 M TTA in benzene. No further work under these conditions is comtemplated.

NEW PROCESSES

Plutonium Anion Exchange Process

Continued work has been done to test the feasibility of recovering plutonium from the Purex IWW stream. Seven liters (about 580 column volumes) of synthetic IWW solution containing 50 mg/l plutonium and flowsheet concentrations of uranium, iron, sulfate, phosphate, sodium, and nitric acid were passed through a 40 cm long, 0.6 cm I.D. column of Dowex-1, X-8 (50-100 mesh). The effluent was sampled at intervals to establish the break-through characteristics of the system. Although analyses are incomplete, it appears that an average loading of about 25 milligrams of plutonium per milliliter of wet resin was obtained (about 300 mgs or 500 column volumes) before appreciable breakthrough occurred. At conclusion of the run the effluent concentration was about 20 percent of the feed concentration and 92 to 95 percent of the feed plutonium was on the column. Breakthrough did not occur until the visibly green plutonium band was about 4 to 5 cms from the bottom of the resin bed.

Slugs and emulsions of 30 percent TBP - Soltrol were found to have almost no effect on the sorption of plutonium from seven molar nitric acid. In fact, Dowex-1 which had been wet with seven molar nitric acid would slowly sorb plutonium from 30 percent TBP - Soltrol.

Since Purex IWW can vary somewhat in nitric acid concentration, experiments were performed to determine the breakthrough characteristics of feed solutions either 6 or 7.2 M in HNO_3. Analytical results are incomplete.

Elution studies have so far disclosed no wholly suitable eluting agent. Dilute nitric acid is the only elutant which does not cause some gassing, but its elution kinetics are slow.

Fused Salt Electromigration Process

The dissolution of a five gram piece of uranium - zirconium alloy, placed in a $BaCl_2$ - NaCl-KCl eutectic mixture, was effected by anodic chlorination at 620 C. After passage of 300 ma for four hours, a sharply bounded layer of UCl_4 had displaced the eutectic originally in the anode chamber and separation tube. The zirconium appears to have sublimed, as the chloride, from the anolyte to a cooler portion of the anode tube. Zirconium content of the UCl_4 was <0.5 wt percent as compared to 4.7 wt percent in the original alloy.

ANALYTICAL DEVELOPMENT

Coulometric Titrations

The studies of coulometric titration techniques applicable to plutonium assay were continued using ceric and dichromate standards in the study of titration conditions. In the use of ceric to oxidize plutonium the excess oxidant must be removed without affecting the plutonium valence state or the subsequent titration. The use of chloride and sodium azide as reductants, and of fluoride as a complexing agent were studied. In 2 M perchloric acid, a 100-fold excess of chloride appears to reduce the ceric ion completely at 90 C in ten minutes. Azide reduces some dichromate in addition to ceric so it is expected to reduce Pu(VI) as well, while the fluoride-ceric complex did not completely eliminate the interference of ceric with a dichromate-ferrous endpoint. Accordingly, ceric would also interfere with a plutonium-ferrous endpoint (ferrous generated electrolytically).

Uranium Isotopic Analysis

The laboratories have been asked to perform confirming analyses of uranium-aluminum alloy enrichment slugs for uranium and U-235. The slugs are "standard" pieces used to calibrate reactivity test piles (Hanford 305 Pile and DuPont NTG at Savannah). The first group of slugs are from the Savannah River plant, and a subsequent group of HAPO "C" slugs is anticipated. Lacking a mass spectrometer suitable for the isotopic analyses, an attempt is being made to adapt the U-235 gamma count method previously reported by D.G. Miller (HW-39969). Questions to be resolved are (1) the influence of daughter equilibrium, (2) the best physical form for the counting samples, and (3) calibration standards preparation. The work thus far indicates that direct gamma counting of dissolver samples of the slugs is feasible.

Miscellaneous

Calibrations were completed on the five gas scintillation fission counters previously discussed. For calibration, two plutonium samples of known Pu-240 content were used and the results were in good agreement. A subject report describing the instrument is being prepared.

A "Tracerlab" five peak analyzer for gamma spectrometry was received and checked out for use in analytical service activities. The instrument meets all specifications.

A universal mount for multiplier phototube-scintillation crystal combinations which will permit simple interchange of crystals and multipliers in any size up to five inches was designed. Four inches of lead shielding is provided.

IN-LINE ANALYSIS

Uranium Photometry

Development was continued on the "Dual beam" photometer sensing unit mentioned previously. The incentive for this work is the substitution of a simple internal standardization for remote standardization by means of solutions. For aqueous uranium solutions, a 1-millimeter cell has been chosen and a neutral density filter of an optical density of about two was found necessary in the red light beam (the "standardize" position with a Corning 3484 filter) to give comparable light intensities in the blue and red filter positions. The sensitivity of the prototype for uranium is excellent and the design principle is sound. Some long-term stability problems remain.

Dielectric Constant

A high frequency dielectric constant meter (Sargent Oscillometer) is being tested for stability and used to study the analysis of plant streams for uranium and TBP. The dielectric constant method is used in the HAPO laboratories for the determination of TBP in kerosene-type diluents. The Sargent Oscillometer proves to be not sufficiently reproducible and stable for an in-line analysis application although it is a good laboratory instrument. The dielectric constant method is, however, a very sensitive one for monitoring TBP in the 1TO-and 2TO-type samples, and a suitable instrument can probably be developed if the need for TBP monitoring arises.

The application of the dielectric constant technique for monitoring uranium in organic phases is also being explored. This is not feasible in the case of TBP solvents (Purex) because of the aforementioned sensitivity to TBP concentration variations. However, in the case of Redox hexone streams, the sensitivity to uranium seems adequate. The method will be studied further since uranium photometry is not applicable to hexone solutions because of the organic color.

Uranium Polarography

Continued work was carried out on the use of square wave polarography as a possible in-line analysis method. The gating circuit for use in the square wave polarography instrument was completed and tested. The square wave polarograph was proven to be practical and was shown to allow analysis of metal ions at concentrations as low as 1.0 x 10^{-5} moles per liter, with the possibility of going lower with minor

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improvements. Using this instrument, determinations of uranium in nitric acid solutions at concentrations as low as 0.003 grams per liter without interference from iron or dissolved oxygen were demonstrated. Small amounts of TBP interfered with this determination, but the TBP was effectively removed from the water phase by mixing the solution with a small amount of kerosene by gas sparging. This eliminated the TBP interference. The square wave polarograph is a possible in-line instrument for monitoring plant streams for uranium, but the present circuit will have to be carefully redesigned to obtain linearity and greater stability.

Because of the wave generated when TBP was present, some polarograms were run with nitric acid solutions of TBP alone. It was shown that the square wave polarograph may be used to measure low concentrations of TBP in aqueous solutions.

LABORATORY SERVICES

Laboratory Services activities may be summarized as follows: 90,000 gallons of crib-level waste was transported to 200 West Area for disposal. Average plutonium analysis was 5.5×10^{-5} uc/ml. Average beta analysis was 3.7×10^{-2} uc/ml.

Approximately 3,000,000 gallons of retention-level waste was discharged to the 300 Area pond. Average alpha analysis was less than 4.5×10^{-7} uc/ml. Average beta analysis was less than 8.0×10^{-7} uc/ml.

Decontamination personnel made three trips to the 300 North Burial Ground with hot waste from the 327 Building. Readings on the waste were as high as 15 r at 10 feet.

All other decontamination, building services, and laundry functions were completed in a routine manner.

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CHEMICAL DEVELOPMENT SUB-SECTION

HOT SEMIWORKS

Decontamination. During the month, A Cell flushing reduced the Beckman readings by a factor of 9 (1800 mr to 200 mr). The badly pitted concrete and paint has been a major problem and source of radiation. Samples of contaminated paint were submitted to Process Chemistry and the recommended 6 molar nitric acid and 10 per cent sodium dichromate flush has shown some success in removing floor contamination.

Purex Waste Self-Concentration Performance. The waste self-concentrator tank has been maintained at approximately 15 ft. liquid level since June 20, 1956. The condensate has been collected in 125-150 liter batches, sampled, and drained back to the concentrator. At the start of the total reflux test, the waste had been concentrated to approximately 35 per cent of the volume originally charged to the tank. Due to failure of the vapor header heaters, condensate flow has occurred only when the tank contents "bumped". During periods of normal boiling, all vapor has condensed in the vapor header and refluxed back to the concentrator. Vapor from the tank passes through a 1/2-in. and/or 1-in. (1-1/2-in. valve with 1-in. reduced plug and seat) valve before being condensed.

The constant liquid level study was divided into two distinct periods of operation. During the first period (June 20 to July 30) the waste self-concentrator was operated with the 1-in. vapor valve open and the 1/2-in. valve closed. No consistent pattern was established by the "bumps" but some characteristic observations are as follows:

a. The maximum pressure ranged from 2 to 17 inches of water with an average pressure of 10 inches.

b. The pressure duration varied from 10 to 30 minutes with an average duration of 20 minutes.

c. Maximum condensate rate (based on volume change in condensate catch tank) varied from 30-115 lb./hr. with an average rate of 90 lb./hr.

d. The condensate collected per "bump" varied from 15 to 60 pounds with an average value of 45 pounds.

e. A total of 21 "bumps" occurred during the 40-day test period.

f. Immediately prior to any "bump", the liquid temperatures were about 235°F. in the 10-15 ft. level increasing with liquid depth to 254°F. at the 2.5 ft. level and 270°F. at the 0.6 ft. level. During a bump, little change was observed in the liquid temperatures in the 10-15 ft. level or at the 0.6 ft. level. However, the liquid temperatures in the 2.5 - 8.5 ft. level dropped to 230-235°F. with the 8.5 ft. level temperature decreasing first followed by the successively lower levels. After a bump the lower level temperatures increased first with the 8.5 ft. level temperature being the last to increase.

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g. Several hundred liters of condensate were collected during this period.

During the second period of operation (July 31 to August 28) at constant liquid level, the waste self-concentrator was operated with the 1/2-in. vapor valve open and the 1-in. valve closed. The "bumps", which generally occurred at 35-40 hr. intervals, had the following characteristics:

a. The maximum pressure ranged from 2 to 13 in. of water with an average pressure of 9 in. water.

b. The pressure duration varied from 185 to 255 minutes with an average duration of 200 minutes. The pressure generally remained at 75 to 100% of the maximum for 50 to 90 minutes.

c. Maximum condensate rate (based on rotameter readings) ranged from 5 to 20 pounds per hour with an average maximum condensate rate of 14 lb./hr.

d. The condensate collected per "bump" varied from 30 to 50 pounds with an average value of 45 pounds.

e. The previously described temperature pattern existed also during the 1/2-in. valve studies. During a "bump", however, only a 5-10°F. temperature decrease (as compared to a 20-25°F. change for the 1-in. valve) occurred at the 2.5 and 3.5 ft. levels. The liquid temperature in the 4.75-ft. to 8.5 ft. level dropped to 230-235°F.

f. Four hundred liters of condensate were collected during this period.

PUREX DEVELOPMENT

Process Chemistry

Organic from Purex L-Cell. A sample of "red oil" obtained during flushing of the Purex L-cell equipment was studied in the laboratory. The oil was thought to be associated with a line plug which formed between the concentrator and the receiver tank. It had a specific gravity of 1.35 and contained about 150, 40, and 800 g./l. of Pu, U, and dibutyl phosphate respectively. The remainder was presumably tributyl phosphate and diluent degradation products. The oil was neither dispersed nor dissolved by concentrated or dilute HNO_3, $FeSO_4$ solution, or acidic dichromate solution. Acetone, methanol, and tributyl phosphate dissolved it completely; diluent (Shell E-2342) dispersed it but did not dissolve it. Sodium hydroxide, at concentrations between one and 25 per cent produced a fine dispersion with the oil; at concentrations above 25 per cent, a gray-green precipitate was formed. Twenty per cent Na_2CO_3 dissolved the oil completely although some precipitation occurred when the solution stood overnight. Lower concentrations of Na_2CO_3 dispersed the oil but did not dissolve it. All of the above tests were made at 25°C.

Batch contacts simulating Purex HA and HC Columns were made in which Purex 1AF containing 1000 ppm "red oil" served as feed and laboratory solvent as extractant. As expected, considering the composition of the oil, Pu loss to the HCW increased from 0.03 per cent in a control run to 1.5 when the feed contained the "red oil". Similarly, gross gamma decontamination through extraction and scrub contacts was reduced from 590 in the control run to 31 in the spiked feed run. After the solvent from the spiked run was carbonate washed, it had a "C" contact value of 0.07 showing definite reduction in quality. Strip column DF was not affected by the presence of the "red oil".

Purex Decontamination Studies. Simple batch contacts (one extraction and six or eight scrubs) were made to study the effect of feed filtration and the presence of Versene in feed and scrub on decontamination. In one series of runs synthetic HAF spiked with two per cent Redox dissolver solution served as feed. In a second series, full level Redox dissolver solution, adjusted to HAF composition, was used as feed. Pertinent experimental conditions, and gamma decontamination factors obtained follow.

PUREX HA DECONTAMINATION

		Accumulated Gamma DF				
		Extraction	Scrub Contacts			
Run	Experimental Conditions		1	3	6	8
A	Control. 2% Spike	74	780	1.6×10^4	4.2×10^4	--
B	As A. HAF passed through Filtrol as filter(1)	206	1170	1.6×10^4	4.2×10^4	--
C	As A. HAF and HAS made 0.001 M in tetrasodium Versene	594	5100	2.8×10^4	4.8×10^4	--
D	Control. Full level HAF. (Redox source)	5	19	4800	7.8×10^4	6.1×10^5 (2)
E	As D. HAF passed(1) through 5 micron sintered S.S. filter	8	73	5200	3.4×10^4	2.0×10^5 (2)
F	As D. HAF and HAS made 0.001 M in tetrasodium Versene	352	2400	2.1×10^4	5.9×10^4	--

Notes: (1) Filtration DF's were 2.7 for the two per cent feed and 1.4 for the full level feed.

(2) Water used as scrub solution. All other scrubs 3M HNO_3.

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While filtration and the presence of Versene resulted in higher accumulative decontamination factors for the extraction and first scrub contacts, their effect was almost completely eliminated by exhaustive scrubbing. Gamma activity in the final organic solutions was, in all cases, greater than 80 per cent Zr-Nb. The low extraction stage decontamination factors observed for full level feed without Versene have not been explained. During runs with unfiltered feeds, considerable radioactive material (presumably solids) adhered to the equipment after the solutions were removed; this did not occur with the filtered feeds.

Purex Waste Rework

Recent plant difficulties with rework of off-standard wastes for recovery of Pu prompted a reinvestigation of the rate of hydrolysis of DBP and TBP in these wastes as a function of refluxing time. Batch contacts simulating the HC Column showed that as little as 15 ppm of DBP in the solvent caused significant retention of Pu in the organic after exhaustive stripping.

To study TBP and DBP hydrolysis rates, simulated 1WW ($8 \underline{M}$ HNO_3) solutions were spiked with TBP and held at elevated temperature (100 and 105°C.). DBP in the aqueous phase was determined quantitatively (Brite method) as a function of time. Enough TBP (19.45 g./l. of 1WW) was added to form a second phase since it is suspected that a two-phase system may exist in the waste receiving tanks.

In the solution held at 105°C. the concentration of DBP in the aqueous phase rose rapidly (within five hours) to about three grams per liter and remained at that value for about 20 hours. From then on the concentration decreased in agreement with a first order rate equation in which K is 0.17 hr.$^{-1}$ (T/2 = 4.2 hr.).

The aqueous DBP concentration pattern for the sample held at 100°C. was similar to that for the sample held at 105°C. but with a longer time at constant concentration (ca. 60 hr.) and a K for the first order portion of 0.131 hr.$^{-1}$ (T/2 = 5.3 hr.). Further confirmation of the marked effect of solution temperature on rate of DBP hydrolysis was shown by a series of experiments in which $8 \underline{M}$ HNO_3 solutions containing two g./l. DBP were simmered at various temperatures and DBP content was followed as a function of time. Half-life values increased almost linearly from about 1.8 hr. at 110°C. to 9.4 hr. at 90°C.

These data show the expected rapid conversion of TBP to DBP and the slower hydrolysis of the DBP. Obviously the total time required to reduce the DBP concentration to an acceptable level will depend on the initial amount of TBP present and the temperature maintained. In the experiment at 105°C. in which the initial TBP content was about two volume per cent, a total of nearly 120 hr. would be required to reduce DBP concentration to 15 ppm.

Chemical Engineering Development

Solvent Extraction Studies

10 Column. Since the start-up of the Purex Plant, the operation of the 10 Column has not been fully satisfactory. The organic decontamination across the column has been inadequate and the column frequently floods. To dissipate a flood it has been necessary to shut off the scrub flow for as long as 2-1/2 hours. Studies have been initiated to develop an improved cartridge for the 10 Column or to define better operating conditions for the present cartridge (stainless steel nozzle plates, 10 per cent free area, 1/8-inch holes, 4-inch plate spacing, 0.035-in.-deep nozzles pointed downward).

Thirty-five "cold" 10 Column flooding runs were made during the month in a 3-in.-diameter glass column with a 21-ft.-high cartridge. Purex HW No. 3 Flowsheet was used with the influent streams both at the ambient temperature or heated to 50°C. The cartridges tested were:

1. Stainless steel nozzle plates
2. Fluorothene plates
3. Stainless steel Raschig rings
4. Fluorothene Raschig rings
5. Stainless steel louver plates

Cartridge details and flooding conditions are described in Table I. Highlights of the findings are summarized below:

1. The nozzle plate and the fluorothene plate cartridges operating at the ambient temperature gave essentially the same flooding curves as shown in the Purex Technical Manual (HW-31000).

2. Unlike the A-type scrub column, the cleanliness or wettability of the stainless steel nozzle plates has little or no effect on the flooding frequency.

3. With the influent streams heated to 50°C., the flooding volume velocities of the various cartridges were up to 30 per cent higher than those measured with the unheated influent streams.

4. Once a flood developed in an unheated nozzle plate run, it was necessary to shut down the column to dissipate the flood. Removal of all the aqueous holdup in the column was necessary to prevent immediate reflooding of the column upon restarting.

5. A reduction in frequency or volume velocity was sufficient to dissipate a flood in the heated nozzle plate runs and in the heated or unheated runs made with the other cartridges.

6. The same flooding capacity factor (3.75 ± 0.25) was measured in heated runs with the fluorothene plates, fluorothene Raschig rings and louver plates at a frequency of 60 cycles per minute.

7. At an organic rate corresponding to a capacity factor of 1.44, the flooding scrub rates for the cartridges tested were generally higher at 50°C. than at 25°C.

8. The column packed with stainless steel Raschig rings was inoperable with the organic phase continuous at rates equivalent to a 1.44 capacity factor. However, the column was operable with the aqueous phase continuous.

In the studies made to date, it appears that with a heated column both fluorothene and louver plates exhibit: (1) as high a flooding volume velocity, (2) more uniform dispersion, and (3) better operability characteristics than stainless steel nozzle plates.

Scrub Section Plate Cleaning. The capacity and efficiency of the A-type column scrub section are affected by the degree of organic wettability of the stainless steel plates which is controlled to some extent by the dirtiness of the plates. An experimental program was undertaken to devise an adequate but simple method of cleaning plates.

The experimental procedure consisted of washing the plates and then determining the direction of the meniscus when the plates were inserted in a beaker containing both an aqueous and an organic phase. Plates were used directly from storage and were also artificially dirtied by dipping in organic and drying and by smearing with a lubricating oil.

Hilco cleaner, Na_3PO_4, NaOH, Na_2CO_3, and HNO_3 solutions were used as cleaners. Of these, Na_2CO_3 proved to be the most effective. When used with plates taken from storage or coated with dried organic, the Na_2CO_3 cleaned the plates sufficiently to give a meniscus consistently pointing into the organic phase. When used on plates smeared with lubricating oil, the cleaning was not effective consistently.

When cleaned with any of the other solutions, the plates tended to be wet by the last phase with which they had contact; i.e., the menisci pointed into the aqueous phase when the plates were moved from the organic layer into the aqueous and pointed into the organic phase when moved from the aqueous layer into the organic. Hilco cleaner and Na_3PO_4, however, were found to be more effective in removing gross quantities of oil and dirt from the plate surfaces than was Na_2CO_3.

Pulsed Spray Column. To determine the applicability of a pulsed spray column to the Purex Plant solvent cleanup system, studies were undertaken in a 12-ft.-high, 1-in.-diameter column. Twenty runs were made using 30% TBP in Shell E-2342 diluent as the solvent, 2.5% sodium carbonate as the aqueous phase, and an L/V (aqueous-to-organic flow ratio) of approximately 0.33. Flooding characteristics were determined for organic continuous operation with the following:

1. Empty column.
2. Four stainless steel sieve plates with 1/16-in.-diameter holes and 23% free area located 1, 4, 7, and 10 feet from the bottom of the column.
3. Four stainless steel nozzle plates having 1/8-in.-diameter holes and 23% free area, located as above.

The flooding data are summarized in the following table:

PULSED COLUMN FLOODING STUDIES - PUREX IO SYSTEM

Equipment: 12-ft. length of 1-in.-diameter glass column
Continuous phase: Organic
L/V: 0.33 to 0.45

Cartridge[a]	Purex Plant Capacity Factor	Pulse Amplitude, In.	Flooding Frequency, Cycles/Min.
A	1.2	0.5	463 ± 12
A	2.4	0.5	425 ± 25
A	1.2	1.5	312 ± 12
A	2.4	1.5	312 ± 12
B	1.2	0.5	412 ± 12
B	2.4	0.5	288 ± 12
B	1.2	1.5	188 ± 12
B	2.4	1.5	90 ± 10
C	1.2	0.5	263 ± 12
C	2.4	0.5	238 ± 12
C	1.2	1.5	113 ± 12

Note: (a) A = empty column.
B = four 23% free area sieve plates 1, 4, 7, and 10 ft. from bottom.
C = four 23% free area nozzle plates 1, 4, 7, and 10 ft. from bottom.

It appears that in the ranges studied an empty column flooding frequency is influenced by pulse amplitude but not by volume velocity. With the columns containing plates, both amplitude and volume velocity influence flooding frequency.

Continuous Ion Exchange. An efficiency run in the 5-in.-diameter Higgins-type continuous ion exchange unit was made utilizing 1.2 g./l. Fe^{+++} in 0.5 M HNO_3 as feed and 5 M HNO_3 as strip solution. Extraction column waste loss was less than 0.1%, and a five-fold concentration with essentially complete recovery was achieved. Preliminary calculations indicate an H.T.U. of nine inches in the extraction column and nine inches in the stripping column.

Take-off collectors consisting of cylinders of porous stainless steel (35 microns mean pore diameter) normal to the resin flow were demonstrated to be satisfactory from the standpoint of resin movement and low pressure drop for liquid removal.

Two varieties of influent stream distributors were tested and shown to be satisfactory.

Coalescer Studies. A coalescer scaled down from the design proposed for installation in the Purex Plant HAP and IAP streams for solids and aqueous deentrainment was constructed. The unit consists of a horizontal length of 4-in.-diameter glass pipe with provision for 18 in. of packing at the inlet to effect coalescence followed by an 18-in. section containing horizontal stainless steel baffle plates to effect settling of the coalesced aqueous phase.

The unit was installed in the 100 stream, leaving a 3-in.-diameter glass 10 Column for preliminary scouting studies. Efficiencies of the packings were determined by both visual observation and laboratory analyses of the entrained aqueous in the influent and effluent streams. The lower limit of detection of entrained aqueous was 0.05%.

Details of the packings tested and the experimental results are given in Table II. It appears that coalescence can be effected in the unit if packing of small fiber size and/or large surface area is used. To date, the baffle plates have not been shown to serve any useful purpose.

TABLE I

PUREX 3-IN. 10 COLUMN FLOODING STUDIES

Flowsheet: Purex HW No. 3. U, Pu, and F.P.'s omitted. Diluent: Shell E-2342.
Equipment: 3-in.-diameter precision bore glass column with a 21-ft. cartridge as described in the notes.
Continuous Phase: Organic

Run No.	Cartridge	Volume Velocity, Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	L/V Aqueous/Organic, Vol. Flow Ratio	Pulse Ampl., In.	Pulse Freq., Cyc./Min.	Temp., °C.
3-84-OH	(a)	635	0.334	0.65	75 ± 5	25(f)
3-85-OH	(a)	770 ± 30	0.615 ± 0.056	0.65	70	25(g)
3-86-OH	(a)	635	0.327	0.65	75 ± 2	25(f)
3-87-OH	(a)	615	0.318	0.65	70 ± 10	25(f)(g)
3-88-OH	(a)	630	0.353	0.65	85 ± 5	50(h)
3-89-OH	(a)	675 ± 35	0.45 ± 0.07	0.65	80	50
3-90-OH	(a)	875	0.325	0.65	65 ± 5	25(f)
3-91-OH	(a)	870	0.330	0.65	82 ± 2	50(h)
3-92-OH	(b)	630	0.349	0.5	92 ± 2	25
3-93-OH	(b)	885	0.328	0.5	72 ± 2	25
3-94-OH	(b)	1185 ± 60	0.340	0.5	60	25
3-95-OH	(b)	690 ± 25	0.456 ± 0.049	0.5	80	25
3-96-OH	(b)	630	0.324	0.5	102 ± 2	50
3-97-OH	(b)	875	0.338	0.5	92 ± 2	50(i)
3-98-OH	(b)	885 ± 25	0.860 ± 0.065	0.5	90	50
3-99-OH	(b)	1650 ± 150	0.33	0.5	60	50
3-100-OH	(c)	635	0.33	0.5	0, 40, 60	25, 50(j)
3-101-OH	(c)	635	0.35	0.5	85 ± 5	25(k)
3-102a-OH	(c)	900 ± 100	0.28	0.5	60	25(k)
3-102b-OH	(c)	1060 ± 60	0.31	0.5	40	25(k)(l)
3-103-OH	(d)	640	0.344	0.5	95 ± 5	25(h)
3-104-OH	(d)	690 ± 20	0.455 ± 0.040	0.5	90	25
3-105-OH	(d)	1340 ± 60	0.33	0.5	60	25
3-106-OH	(d)	640	0.332	0.5	112 ± 2	50
3-107-OH	(d)	850	0.79	0.5	95 ± 10	50
3-108-OH	(d)	1690 ± 40	0.295	0.5	60	50
3-109-OH	(e)	635	0.330	0.5	85 ± 2	25(m)
3-110-OH	(e)	875	0.325	0.5	72 ± 2	25(n)
3-111a-OH	(e)	1090 ± 70	0.318	0.5	60	25
3-111b-OH	(e)	1460 ± 50	0.324	0.5	50	25
3-112-OH	(e)	755 ± 20	0.598 ± 0.040	0.5	75	25
3-113-OH	(e)	635	0.331	0.5	85 ± 5	50(o)
3-114-OH	(e)	885	0.332	0.5	82 ± 2	50
3-115-OH	(e)	1640 ± 20	0.326	0.5	60	50
3-116-OH	(e)	870 ± 20	0.868 ± 0.038	0.5	75	50

Notes: See following page.

TABLE I (Cont'd)

Notes:

(a) Stainless steel nozzle plates, 1/8-inch holes, 10% free area, 0.04-inch deep nozzles pointed downward, 4-in. plate spacing.

(b) Fluorothene plates, 3/16-inch holes, 23% free area, 4-inch plate spacing.

(c) Packed column with 1-inch stainless steel Raschig rings.

(d) Packed column with 1-inch fluorothene Raschig rings.

(e) Stainless steel louver plates, 25% free area, 4-inch plate spacing.

(f) Reducing frequency did not break flood.

(g) Plates "dirtied" by allowing to stand in an empty column for two days.

(h) Flood broke when the frequency was reduced to 80 cyc./min.

(i) Flood broke when the frequency was reduced to 85 cyc./min.

(j) Column inoperable under all conditions listed.

(k) Column operated with the aqueous phase continuous.

(l) Shutting off the pulse generator did not break the flood.

(m) Flood did not break when the frequency was reduced to 80 cyc./min., but did break when the frequency was reduced to 75 cyc./min.

(n) Flood broke when the frequency was reduced to 70 cyc./min.

(o) Flood did not break when the frequency was reduced to 85 cyc./min., but did break when the frequency was reduced to 80 cyc./min.

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TABLE II

PUREX LIQUID-LIQUID DEENTRAINMENT STUDIES

Equipment: See Note (a)

Coalescer Packing	Packed Density, Lb./Cu.Ft.	Throughput, Gal./(Hr.)(Sq.Ft.)	Pressure Drop In. H_2O	Visual Observation(b)
York Mesh, 0.005-in.-diam. stainless steel wire	13.7	280 to 700	< 0.5	No coalescence
York Mesh, 0.01-in.-diam. stainless steel wire	9.0	280 to 790	< 0.5	No coalescence
Steel Wool, Grade 0 ~0.002-in.-diam. wire	11.5	280 to 580	1.0	Complete coalescence
Steel Wool, Grade 3 ~0.01-in.-diam. wire	9.5	280 to 700	< 0.5	Little coalescence
Glass Wool, dense packed	7.7	390	40	Good coalescence
Glass Wool, loose packed	4.6	810	47	Good coalescence
York Mesh, combination stainless steel and fiber glass	8.5	280 to 580	< 0.5	No coalescence
Raschig Rings, 1/4-in. stainless steel	(c)	280 to 810	< 0.5	Very little coalescence
100-mesh stainless steel screen on 1-in. spacing. Alternate spaces packed with glass wool.	--	280 to 700	4	Moderate coalescence

Notes:

(a) 4-in.-diameter standard bore glass pipe horizontal coalescer 46-in.-long. The internals of the coalescer consisted of: (1) 3-in.-long entrance section; (2) 18-in. of coalescer packing as indicated in the table; (3) 3-in. void section; (4) three 18-in.-long horizontal stainless steel baffle plates, spaced 1-in. apart, extending the full width of the coalescer; and (5) 4-in. void exit section. The effluent organic overflow was placed at a height to cause the coalescer to operate approximately 3/4 full. The aqueous effluent was continuously removed through an adjustable jack leg which maintained the aqueous-organic interface at or near the bottom of the coalescer. The coalescer was placed in the organic effluent line of a 3-in.-diameter 10 Column.

(b) Estimate of the effectiveness of the coalescer packing by observation of the relative cloudiness of the influent and effluent streams arising from entrained aqueous.

(c) Void volume of 74 per cent.

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URANIUM RECOVERY DEVELOPMENT

Process Chemistry

Reduction of UO_3 with Ammonia. The following table summarizes thermobalance studies of the effect of ammonia reduction of UO_3 to UO_2 on hydrofluorination of the UO_2.

HYDROFLUORINATION OF UO_2 PREPARED BY AMMONIA AND HYDROGEN REDUCTION OF UO_3

Powder	Reductant	Temp. of Reduction °C.	Temp. of Hydrofluorination, °C.	Time for 98% Conversion to UF_4, Min.
HAPO Pot	H_2	925	600	42
HAPO Pot	H_2	925	500	39
HAPO Pot	H_2	925	400	40
HAPO Pot	NH_3	925	600	26
HAPO Pot	NH_3	925	500	23
HAPO Pot	NH_3	925	400	11
321 Bldg. Cont.	H_2	925	600	90
321 Bldg. Cont.	H_2	925	500	72
321 Bldg. Cont.	H_2	925	400	40
321 Bldg. Cont.	NH_3	925	600	102
321 Bldg. Cont.	NH_3	925	500	68
321 Bldg. Cont.	NH_3	925	400	34
HAPO Pot	H_2	590	600	38
HAPO Pot	H_2	590	500	36
HAPO Pot	H_2	590	400	60
321 Bldg. Cont.	H_2	590	600	114
321 Bldg. Cont.	H_2	590	500	114
321 Bldg. Cont.	H_2	590	400	130
321 Bldg. Cont.	NH_3	590	600	45
321 Bldg. Cont.	NH_3	590	500	20
321 Bldg. Cont.	NH_3	590	400	52

Brown oxides (UO_2) produced by ammonia reduction at 925°C. of HAPO pot UO_3 hydrofluorinated more rapidly than UO_2 obtained by hydrogen reduction at 925°C. Brown oxides prepared by reduction at 925°C. of 321 Bldg. continuously produced UO_3 had about the same hydrofluorination rate whether reduced with ammonia or hydrogen.

When continuously produced UO_3 was reduced at low temperature (590°C.), the UO_2 prepared by ammonia reduction hydrofluorinated much more rapidly than that prepared by hydrogen reduction.

[redacted]

WASTE TREATMENT

Process Chemistry

Plant Test of Modified Scavenging Procedure. Favorable laboratory results led to a plant test of a modified scavenging procedure in which inert cobalt was added at two separate points, one prior to ferrocyanide addition (actually in RDIS) and one with nickel immediately before neutralization. Co^{60} content of grab samples (WR002) of the scavenged waste during the test averaged about 2×10^{-4} uc/ml., a factor of three lower than for samples taken immediately before the test and higher than 0.1 M PC by a factor of five. Co^{60} analyses on supernatant liquid from the settling tank are not yet available.

Adsorption of Cobalt on an Anion Exchange Resin. Reported strong adsorption of the hexacyanocobalt (III) ion on anion exchange resins suggested such resins as means to obtain additional Co^{60} decontamination in waste solutions. Permutit S-1 (a strong-base anion exchanger) readily adsorbed $Co(CN)_6^{-3}$ from a low-salt solution. However, little or no adsorption occurred when the complex was present in a synthetic stored waste (high salt). Also, when actual stored waste was made 0.005 M in KCN and digested 30 min. (in an attempt to convert any cobalt present to the cyano complex), cobalt was not effectively removed by the resin during batch contacts at pH's from one to nine. When a stored waste which had already been scavenged with nickel ferrocyanide and strontium nitrate was contacted with the resin about 50 per cent of the cobalt present was removed if the waste was first brought to pH's from one to six. Cobalt removal was considerably less at pH 8.

Further attempts to remove Co^{60} from stored wastes by scavenging with nickel or cobalt cobalticyanides and with cobaltamine ferrocyanides have been unsuccessful.

Scavenging of Co^{60} from stored wastes by inert cobalt sulfide, as discussed in the July report, remains the most promising procedure yet found for treating these wastes. An economic evaluation of the procedure is being made by Plant Processes personnel. Further laboratory work has been aimed at determining optimum conditions and reproducibility of results.

MISCELLANEOUS DEVELOPMENT

Separations Equipment Development

In-Line Instrument Development

Continuous Ion Exchange Column Controls. Preliminary tests with a H.A.P.O. type gamma absorptometer indicate inadequate sensitivity for determining the plutonium concentration on the resin bed. However, based on information available, the Ohmart dual ion chamber type instrument appears to have sufficient sensitivity for this determination. An Ohmart unit is being purchased for test and evaluation. Development and testing of a conductivity probe for (elutriate) acid-water interface control is continuing. Similar probes for measuring the resin-water interface have performed satisfactorily in laboratory tests.

Remote Sample Flow Indicator. The Brooks flo-gard (remote indicating flowmeter; flow-no-flow) was tested with 300 feet of RG62/V cable, and found to operate satisfactorily. It has been recommended for plant use where remote indication of sample flow is deemed necessary.

Technical Specifications. The technical specifications for in-line pH monitors (HW-44917) were issued this month.

Plant Assistance. The plutonium gamma absorptometer at Purex was returned to service during the last plant shutdown. Unfortunately it is not possible to be certain of the cause of the failure reported last month. It was assumed that the maintenance work on the valve downstream of the absorptometer had caused the source to shift the collimated gamma beam so that it missed the chamber window. A shift of 7-1/2° would have caused this. It was not possible to feel a shift of this magnitude under conditions that prevailed during maintenance. Moreover, measurement of the signal cable resistance to ground indicated a low value (approximately 40 megohms) at the time of failure. Measurement after service was resumed indicated a satisfactory (1000 megohms) resistance to ground.

A new thulium-170 source was installed in the Recuplex plutonium gamma absorptometer. Calibration data to date do not agree consistently with the laboratory results. Additional work on recalibration is expected.

The Purex prototype iodine-131 gamma scintillation monitor failed to operate satisfactorily when the differential analyzer failed. A new differential analyzer was installed, the unit was in operation at month's end.

Mechanical Equipment

Plug-Piston Pulse Generator. Water loss from a 3-inch-diameter column has continued to be less than 5 ml./hr. during pulsing by a 4-inch-diameter graphite plug-piston. Total cycles on the pulser components (120 cycles/min., 1/2 to one inch stroke) are:

(1) Piston and cylinder - 19 million
(2) 17-4 PH stainless steel piston rod - 9.5 million
(3) Polypenco K-51 Throttle bushing - 9.5 million
(4) Teflon chevron packing - 16.5 million

Inspection No. 3, at 15.5 million cycles on the piston, showed no piston rod corrosion and no appreciable piston wear, since the previous inspection (13 million cycles).

Piston leakage rates of 1000 ml./hr. developed during a test with the air purge line connected between the piston and the throttle bushing. The air purge is normally connected between the chevron packing and throttle bushing.

A 4-inch-diameter graphite plug-piston pulser has accumulated 7 million cycles pulsing water in the Hot Semiworks 10 Column, without measurable leakage during normal operation. Leakage rates up to 100 ml./hr. developed when the air supply was shut off, but returned to normal when air flow was reestablished. The 5 million cycle inspection revealed eccentric wear of the piston on the lower end (2 mils vs. 5 mils wear on diametral axis) and heavy scoring of the piston rod by the spring-loaded Teflon chevron packing.

Slug Handling. Installation of a reciprocating-tube slug feeder and hopper in 321 Building was completed, and operating trials (without slugs) started. The hopper will be charged with slugs now available in 321 Building during the coming month.

Prototype Calciner Shaft Seals (224-U Building). Service life of conventional shaft packing (Durametallic D-10, Johns-Manville No. 392) in the drive end gland housing has varied from 10 to 70 hours during current operation of the prototype calciner. Outboard (discharge) end packing has been relatively troublefree. Both housings deflect with reference to the shaft due to shell warpage. The biggest apparent difference lies in the solid coupling which attaches the drive end stub shaft to the agitator, and may transmit agitator shock loading to the stub shaft as deflection. Four approaches to this problem are being considered currently:

(1) Cone-shaped gland followers to more effectively squeeze the packing into the shaft.

(2) Brass wool packing.

(3) Labyrinth-type packing rings machined from bronze to replace all or part of the conventional packing.

(4) Wholly mechanical seals with spring-loaded, hard-faced wear rings as seals.

Approach (3) is scheduled for first installation, with (1), (2), and (4) to follow as the need is demonstrated, and materials become available.

Miscellaneous

Slug Jacket Removal by Pyrometallurgy. The facilities of the Fuel Element Development Unit in 306 Building were used in a preliminary approach to removal of aluminum slug jackets by pyrometallurgical methods. Three jacketed slugs were placed in a high frequency induction coil (50 KW, 10 KC) and heated until melting of the jacket occurred. Considerable "dross" was formed, as well as Al-U compounds on the slug surface. Results indicate that higher power and frequency would be desirable for further work.

A fourth jacketed slug immersed in an Al-Si molten bath (approximate temperature - 635°C.) for 65 seconds was stripped clean of its jacket, leaving a coating of Al-Si on the slug. Problems of operating such a bath in remote zone are under consideration.

Titanium Testing. Commercially pure titanium has been boiled in uranyl nitrate - nitric acid mixtures for over 600 hours. No significant change in weight has occurred and the metal surface has remained bright except for thin spotty white-to-gray discoloration. No pyrophoricity has been noted at any time.

The titanium on test is a steam heated bayonet-type heating element used to boil the various solutions. This element has been subjected to the following conditions:

(1) 385 hours of boiling in an essentially neutral solution of UNH ranging from 400 to 900 g./l. uranium.

(2) 155 hours of boiling in a UNH - HNO_3 solution containing 200 g./l. uranium and 420 g./l. (~35%) HNO_3.

(3) 75 hours of boiling in a UNH - HNO_3 solution containing 360 g./l. uranium and 655 g./l. (~50%) HNO_3.

Chemical Compatibility Tests. Johns-Manville "Volseal" caulking compound was tested for resistance to various solutions at room temperature. All tests were terminated after nine days. The material proved unsatisfactory for application where Separations Plant solvents may be encountered. The test results are tabulated below:

Solution	Results and Remarks
60% Nitric Acid	Lost adhesion. No other effect noted.
50% Caustic Soda	Adhered well. No visible effect.
30% TBP-Soltrol	One day - swelled. Two days - dissolving. Nine days - softened badly. Completely dissolved below liquid level.
CAX	One day - failed completely. Dissolved.
Hexone	One day - swelled 5%. Two days - swelled 10% Nine days - became very soft, swelled, lost adhesion.
Distilled Water	Lost Adhesion.

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Polypenco K-51 was tested in boiling solutions of nitric acid and pure water for 24-hour periods. In distilled water, 10% nitric acid and 20% nitric acid this material did not change in weight significantly nor did it soften as indicated by Shore Sclerescope hardness. There was less than 0.1% change in weight by the samples. In 40% nitric acid there was no significant change for 4 hours. After 24 hours the sample had decreased in weight by 7% and softened noticeably. In 60% nitric acid the material lost 5% in weight and softened noticeably after 4 hours. Twenty-four hours of exposure to this solution caused a 40% reduction in weight and the loss of strength. The material broke readily in the fingers. The degradation of this material was accompanied by a whitening. The whitened material was quite friable.

The same test was run using a solution of 420 g./l. UNH, 10 g./l. nitric acid. The sample showed no change in weight or hardness.

ANALYTICAL LABORATORIES UNIT

General Chemical

Total uranium analysis was completed for the nine Savannah River slugs (95% aluminum - 5% uranium) mentioned last month. Average precision was ± 0.9%, 95% CL. The method showed a 0.1% error. Slug wafers continued to dissolve from the center toward the circumference. Optimum dissolution was achieved simply with concentrated hydrochloric acid. Past HAPO effort had indicated smoothest dissolution with hydrochloric acid containing bromine oxidant. Omission of oxidizing agent also simplified the final ceric sulfate titration which requires quadrivalent uranium. Error of the method was estimated by preparing and analyzing a simulated slug solution with the source of uranium being spectrographically pure U_3O_8.

A spectral energy recording attachment (SERA) was installed on the Beckman DU flame photometer. Important wave length regions of unknowns may be scanned and recorded. Scans can be accomplished in 1 to 100 minutes depending upon requirements. After suitable calibrations a variety of metal ions occurring simultaneously and some anions may be detected and estimated from position and height of characteristic wave length peaks. For example 0.05% copper was readily detected and measured in dissolved steel.

The laboratory is prepared to furnish analytical support to UO_3 prototype calciner studies.

Radiochemical

As an aid in defining pile exposure of selected Metallurgy Research Sub-Section specimens, uranium burn-up is being determined. Burn-up includes direct U-235 fission as well as U-238 consumption by way of Pu-239 and other fission. To insure adequate sampling, large pieces are being dissolved. Necessary shielding has been obtained through cooperative use of a Process Chemistry facility for a limited number of dissolutions. Metallurgy expects continued need for that service; therefore, plans are being made for establishing a suitable dissolving facility in the 325 Building.

Vacuum extraction determination of gases in metals continued. Expected intensity warranted transfer of that work to non-exempt status. Satisfactory non-exempt progress indicates that current close supervision can soon be relaxed.

Two of the five fission counter chambers have been calibrated and are being used to determine Pu-240 in accumulated samples. Standardization is proceeding for the remaining chambers.

Spectrometry

Mass: All spectrometers were in operation two days after a scheduled 325 Building power outage. The uranium mass spectrometer sustained temporary loss of the sensitivity required for support of isotope enrichment studies. However, sensitivity was adequate for analyzing five (5) Manufacturing UO_3 samples.

Transfer of the GE spectrometer to Chemical Research has been delayed due to continued trouble with the IR spectrometer.

Emission: A final working curve is being prepared for determining 12 elements in water. Sensitivities will be 1 to 10 ppb. Some method change is required for reporting cobalt in KAPL-120 filter water.

Water Quality: The KE-KER Unit has released major use of the KER Chemical Laboratory for ALU modification. The laboratory will be used to supply analytical support for organic coolant studies.

Laboratories work volume statistics are as follows:

	JULY		AUGUST	
	No. of Samples	No. of Determinations	No. of Samples	No. of Determinations
Research & Development				
Pile Technology				
Physics Research	7	235	-	-
Metallurgy Research	5	91	45	149
Pile Materials	559	1549	436	1754
Pile Engineering	4	20	15	75
Fuel Technology	44	201	38	516
Separations Technology				
Plant Processes	5	71	17	303
Chemical Research	711	1101	1036	1738
Chemical Development	629	1189	366	1011
Process Technology	524	960	640	1434
Other Customers	106	457	138	817
Total	2594	5874	2731	7797

[redacted]

TECHNICAL SHOPS UNIT -

Mechanical Shops

The influx of new work dropped to a low level the latter half of the month permitting some inroads to be made in the large backlog existing at the start of the month.

Overtime work required to complete urgent projects amounted to 133 hours which is much lower then the average for the past year.

A total of 74 craftsmen was furnished by the Manufacturing Department which was within one of the desired complement. No unusual work or incidents occurred during the month and all demands for service were met in a satisfactory manner.

Buildings and Grounds

IR-200 Graphite Machining Facility

This work was completed and accepted during this period.

CA-685 Alterations of 325 and 326 Buildings

This project was approved by the AEC.

General

As part of the reorganization study, space allocations were determined. The resulting moves were coordinated and the landlord function was established for all of the Hanford Laboratory facilities.

Drafting and Design

Requests for service again exceeded the available supply of man power and considerable shifting of personnel was required to complete the more urgent projects. Personnel remained on loan from the Design Section and Graphics Unit and additional assistance was provided by these groups through the acceptance of jobs originally assigned to the Technical Shops. One termination occurred and no acceptable applications were received in reply to the personnel requisitions on file with the Employment Group.

Glass Shop

Total productive man hours for the month was 980 with 125 jobs being completed, 22 of which were fabricated from quartz. The work load continued moderate to light permitting excellent service to be rendered. Unusual jobs included a 3 stage vacuum bell jar equipped with an internal winch and hook which are operable from the outside of the jar.

Photo Laboratory

All requests for service were met promptly and the work completed by the desired date.

CONTACT ENGINEERING UNIT

Operations proceeded routinely throughout the month.

INVENTIONS

All Separations Technology Section personnel engaged in work that might reasonably be expected to result in inventions or discoveries advise that, to the best of **their** knowledge and belief, no inventions or discoveries were made in the course of their work during August, 1956 except as listed below. Such persons further advise that, for the period therein covered by this report, notebook records, if any, kept in the course of their work have been examined for possible inventions or discoveries.

Inventor(s)	Title
Ko, Roy	The Preparation of Dilute Solutions for Spectrographic Analysis

R. B. Richards

Manager, Separations Technology
ENGINEERING DEPARTMENT

RB Richards:khs