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SEPARATIONS TECHNOLOGY SECTION MONTHLY REPORT - APRIL, 1956

AUTHOR

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APRIL - 1956

Compiled by Members of
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SEPARATIONS TECHNOLOGY SECTION
ENGINEERING DEPARTMENT

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May 8, 1956

HANFORD ATOMIC PRODUCTS OPERATION
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VISITORS AND BUSINESS TRIPS

R. L. Dahlstrom and W. B. Watkins of the duPont Company, Savannah River Plant, Aiken, So. Carolina visited Hanford on 4-3 thru 4-5-56 for calcination, solvent extraction and Purex discussions.

P. B. Williams of the Welsbach Corporation, Philadelphia, Pennsylvania visited Hanford on 4-3 thru 4-6-56 for technical consultations regarding redox problems.

H. Schneider and E. W. Murbach of the Phillips Petroleum Company, Idaho Falls, Idaho visited Hanford on 4-18 thru 4-20-56 to discuss instrumentation and separations technology.

Richard Rowe of the General Machinery Company, Spokane, Washington visited Hanford on 4-19-56 for consultations on pump development

J. E. Meinhard of Hanford attended the American Chemical Society Meeting, Dallas, Texas 4-6 thru 4-15-56.

H. H. VanTuyl of Hanford attended the American Chemical Society Meeting, Dallas, Texas 4-6 thru 4-15-56.

R. L. Stevenson of Hanford attended the American Chemical Society Meeting, Dallas, Texas 4-9 thru 4-13-56.

O. F. Hill of Hanford attended the American Chemical Society Meeting, Dallas, Texas 4-9 thru 4-12-56 and visited the Los Alamos Scientific Laboratory, Los Alamos, New Mexico on 4-13-56 to discuss new process developments.

R. E. Isaacson of Hanford visited the Dow Chemical Company, Rocky Flats Plant, Boulder, Colorado on 4-16 thru 4-18-56 to establish neutron counting constants.

H. H. Hopkins of Hanford visited the Argonne National Laboratory, Lemont, Ill. on 4-30-56 to discuss pyrochemical processing.

H. C. Rathvon and W. H. Swift of Hanford visited the Oak Ridge National Laboratories, Oak Ridge, Tennessee on 4-30 thru 5-2-56 to discuss Purex processing.

ORGANIZATION AND PERSONNEL

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Plant Processes Sub-Section: A. G. Graybeal, Engineering Assistant transferred from the Education and Training Unit to the Sub-Section on 4-30-56. R. W. Wirta, Engineer I transferred from the Sub-Section to the Chemical Development Sub-Section on 4/1/56.

Chemical Development Sub-Section: R. W. Wirta, Engineer I, transferred from the Plant Processes Sub-Section on 4-1-56.

Chemical Research Sub-Section: E. C. Kiser, Secretary B transferred to the Sub-Section from the Project Section on 4-9-56. A. C. Jirus, Secretary B, terminated on 4-13-56. C. E. Michelson, Engineer I transferred to the General Engineering Laboratory, Schenectady 4-27-56.

Analytical Laboratory Unit: Carol T. Arneson, Lab. Asst. D transferred from the Stores Sub-Section into the Unit on 4-23-56. Annie D. Couch, Lab, Asst. A transferred from the Manufacturing Dept. into the Unit on 4-9-56. Lowell W. Wilson, Lab. Asst. C transferred from the Community Section to the Unit on 4-9-56. Carol E. Cooper, Lab. Asst. A. terminated on 3-9-56. Laurel L. Verellen, Lab. Asst. B terminated from the Unit on 4-20-56.

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PLANT PROCESSES SUB-SECTION, O. F. HILL

REDOX PROCESS TECHNOLOGY

Summary

Processing of low MWD/T metal was completed at the start of the month. Heels were removed from the dissolvers, all solutions were processed through the plant, and the building was shut down for column and equipment cleanout and maintenance.

Solvent extraction was resumed on April 5 on high MWD/T metal, and continued without interruption (except for a one hour crashdown when the power failed on April 20) for the balance of the month at 120 per cent of the Phase II rate.

The permanganate feed pretreatment was retained throughout the month. Processing was started with single stage waste backcycle, and second stage backcycle was in full effect twenty-four hours later. This was continued through the rest of the month.

Over-all performance, excellent with respect to both product quality and recovery, was highlighted by the best start-up ever experienced at Redox. All batches of both products produced throughout the month were within specifications.

The revised flowsheet (HW-42180), designed to forestall potential critical mass problems in the plutonium cycle feed tanks, was introduced stepwise, starting shortly after the plant recommenced operations. Although not all of the steps were incorporated by report time, most of them were accomplished with complete success. Those still left to be done will be taken care of early in May.

Average over-all decontamination factors (logarithmic) on high MWD/T production for the month were 6.8 and 7.5 for uranium and plutonium, respectively. The presence of ruthenium as the principal fission product contaminant in both products (as well as the intermediate streams) was confirmed by continuing analytical checks throughout the month. With the backcycling of final plutonium concentration wastes and the second and third solvent extraction cycle wastes, solvent extraction waste losses for the month were exceptionally low, averaging about 0.02 per cent for uranium and 0.04 per cent for plutonium across feed preparations and first cycle extraction.

The average exposure of the high MWD/T metal charged to the dissolvers was 815 (991 to 369) MWD/T, and its average cooling time was 148 (214 to 98) days. Concentrated plutonium product ranged from 97.4 to 116.3 grams of plutonium per liter, with an average of 105.4 grams per liter, and the average concentration of nitric acid was 5.07 molar in this final plutonium product.

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Feed Preparation

Due to a jet failure in one of the dissolvers, a revised rinsing procedure was used until the jet could be replaced. No adverse effects were observed during this period. Due to a leak in the jet transfer lines between two of the metal solution storage tanks, this same dissolver was taken out of service near the end of the month since its contents had to pass through the leaking line. The leak amounted to about five per cent of the volume transferred. With one dissolver out of service, barely enough metal solution was available to maintain the desired processing rate for the final few days of the month's operation. The rate was maintained, however, until April 25, when the building was again shut down for what will be henceforth a routine monthly flushout.

Decontamination

Over-all fission product decontamination was approximately the same for uranium (slightly improved, if anything) as that noted last month and, for plutonium, was significantly better than the previous month (logarithmic 7.7 as compared to 7.3). This may largely reflect the greatly improved control of both operating variables and intercycle stream acid concentrations which was established during April, as contrasted with the very erratic control in March. Some variation was seen but was, in general, much less than experienced in March. As a result, the exceptionally high decontamination factors obtained across the final uranium cycle last month were neither observed nor required to meet product specifications, and decontamination factors across individual cycles returned to a more nearly normal pattern. Immediately upon start-up on April 5, and for the balance of the month thereafter, all of the uranium and plutonium produced was within specifications.

Immediately following start-up, analyses showed that the principal fission product contaminant in both products and intermediate streams was the zirconium-niobium couple. Within 48 hours, however, the principal fission product in all samples was ruthenium. This condition persisted for the rest of the month and, as yet, has not been satisfactorily explained. It is obvious that this phenomenon has not presented any serious problems thus far. It raises some question, however, about future results when the permanganate head-end treatment is abandoned.

Solvent Extraction

Mechanisms can be postulated whereby the aqueous feed tanks for the final plutonium cycles can collect hexone as well as aqueous plutonium solution. Under the chemical conditions prevailing in these tanks prior to the first of this month, the distribution coefficient of plutonium between these aqueous and organic phases is high enough to present a potential critical mass problem. In an attempt to minimize this potential, changes in the flowsheet suggested in HW-42180 (March 20, 1956) were begun this past month on a stepwise approach. The basic principle is the use of appreciably more dilute salt solution to butt the plutonium feeds in order to decrease the plutonium distribution coefficient (in the event that hexone should be present). To compensate for this reduced salting strength, the salt concentration in the corresponding extraction column

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scrub stream is raised to a level which gives the same salting strength in the extraction section of that column. The first changes involved the final plutonium cycle (3A Column) scrub stream and feed stream, in that order. The increase of salt concentration from 1.3 to 2.0 molar in the scrub stream was followed by about a three fold increase in the fission product contamination in the final plutonium stream. This was not serious, and the condition was only transient with decontamination returning to normal levels (or above) following the subsequent reduction of the salt concentration in the butt to the feed stream. The partition cycle (IB Column) IBX stream which governs the amount of salt in the feed stream to the next to last plutonium cycle (2A Column), was reduced only part of the way to its final intended salt concentration. The final steps are to be taken early in May. A stepwise approach at this point was considered desirable to insure continued adequate partitioning of the uranium and plutonium in the IB Column, with the lowered IBX salt concentration being simultaneously compensated for by a corresponding increase in the IBS (organic) flow. The 2AS salt concentration was increased to 2.0 molar at the same time as the 3AS. No adverse effects have been observed as a result of these changes. Partly due to the above changes and because the process is tied together by two stages of waste backcycle, more salt is available for the first cycle extraction columns than is required. As a result, the final uranium cycle extraction column scrub flow (3DS) was cut back by about 15 per cent, and the IAA flow rate will be reduced also in the near future.

Waste Losses

With two stage waste backcycle in effect and the final plutonium concentrator condensate being returned to the second stage waste concentrator for recovery, the raffinates from the first cycle extraction columns (IAW and ISW) represent the only points of solvent extraction process loss. These losses were very low for the month of April, averaging about 0.02 and 0.04 per cent for uranium and plutonium, respectively. Other sources of loss are centrifuge cakes from feed preparation, in-cell process piping leaks, and accidents. There were several leaks during the month. Some of the product material was recovered; some was thrown away. The over-all losses for the month, however, were exceptionally low, viz., 0.17 and 0.13 per cent for uranium and plutonium, respectively.

Waste Storage

Although the waste storage production test (HW-41408 - Part II) has not yet been formally approved, extraction wastes were routed to Tank 108-SX on April 5, and thence to Tank 107-SX on April 13. Additional waste was needed in Tank 108 to refill it to the hydrostatic head limit, i.e., to compensate for the boil-off of the past four months. The storage of waste in Tank 107-SX is to be covered in the production test and is expected to represent the most severe heat generating conditions, viz., highest fission product concentration in the smallest volume (high MWD/T metal, two stage waste backcycle). This tank is to be filled to the hydrostatic head limit and permitted to self-concentrate with no provisions for "artificial" release of heat.

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PUREX PROCESS TECHNOLOGY

Summary

The Purex Plant was operated throughout the report period at a capacity factor of 1.44, with the exception of two shutdown periods. One short shutdown was caused by a power failure, and a two day shutdown was required for uranium rework when the partition cycle failed to separate plutonium from uranium. Recovery of uranium and plutonium was excellent, and one waste batch containing approximately 280 units of plutonium lost from the IA Column in February was satisfactorily reworked. Plutonium decontamination across solvent extraction continued to be ten fold below specifications, but concentrated plutonium continued to meet specifications. Along with decontamination achieved across the concentration equipment is an associated plutonium holdup. At month end, this plutonium holdup is being removed by flushing, and modifications are under way to eliminate this buildup problem. Uranium decontamination continued to be inadequate in spite of flowsheet changes aimed at improvement. Since it is evident that decontamination performance of the solvent extraction columns is limited by a severe solids problems in the plant, flushing of equipment is in progress at month end.

Feed Preparation

Irradiated uranium slugs having an exposure of 3.8 to 6.1 MW/T (249 MWD/T) and having a cooling period of 95 to 198 days were dissolved in the two dissolvers. A peak of about nine curies of radioiodine to the stack was observed on April 16, when 16 tons of 95 day cooled uranium were dissolved. Subsequently, the dissolvers were shut down, and the B cell silver reactor was regenerated without any adverse effect on the radioiodine to the stack. The prototype gamma scintillation iodine monitor installation has been completed.

Solvent Extraction - Uranium

Operation of the solvent extraction batteries was maintained at a nominal capacity factor of 1.44 throughout the month. However, the average production rate was somewhat below a capacity factor of 1.44 because:

1. It was necessary to rework the 2DF for two days when the IBX Column failed to partition due to a nitrite recycle (2BW to IBXF).

2. In order to prepare for a plant shutdown at the end of the month, decontaminated uranium was recycled to the precycle for five days. The purpose of the recycle was to reduce the plutonium inventory and activity levels in the plant equipment prior to shutdown.

Because of the failure of approximately 25 per cent of the canyon rotameters (shorted to ground), few major flowsheet modifications were made during the month. The process, being held constant for extended periods, demonstrated a

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uranium decontamination factor (HAF/2EU) of about 1 x 10^6. For plutonium (exclusive of the final plutonium cycle), a decontamination factor (HAF/2AF of about 1 x 10^5 was demonstrated. However, when an upset occurred in the precycle, neither the partition nor final uranium cycle were capable of overcoming the loss of precycle decontamination. An upset in the partition cycle was usually compensated for by the final uranium cycle (when on a low acid flowsheet). Over-all solvent extraction decontamination performance continued to be inadequate by a factor of about five under steady state operation. Data obtained from close scrutiny of the operation indicate that the presence of radioactive solids in the plant is a major cause of poor decontamination performance. A plant flush is in progress at month end.

A reduction of "C" column L/V's from 1.5 to 1.3, 1.2, and 1.2 for the HC, IC, and 2E Columns, respectively, was made in an attempt to increase decontamination. No appreciable increase in waste losses has been noted, but no significant increase in decontamination can be attributed to this change. The "C" columns continued to operate at low pulse frequencies (45 to 55) and a low strip stream temperature (25 to 30 C) to retain benefits in decontamination observed last month by these changes (cf. HW-42219-H).

A high acid 2D Column flowsheet was investigated in conjunction with the low acid IA Column flowsheet and high acid HA Column flowsheet. No improvement in decontamination was noted, and it did not compensate for any upsets occurring in previous cycles. The 2D Column flowsheet was returned to a low acid system similar to the one used at the Savannah River Project. The specifications are as follows:

Stream	HAF = 100 Relative Flow	Composition
2DF	89.4	U = 3.0 lb/gal HNO_3 = 0.03 lb/gal Fe^{++} = 0.03 lb/gal
2DX	345	30 per cent TBP
2DS	33	Demineralized H_2O
2DIS-H_2O	27.1	Demineralized H_2O
2DIS-HNO_3	8.5	60 per cent HNO_3

Solids and/or organic in the 2DF apparently are contributing to the decontamination problem. This was evidenced by turning the 2DF agitator off for three days and diverting the ferrous sulfamate butt to the 2DIS. When the agitator was turned back on and the butt returned to the 2DF tank, the Beckman on 2EU Concentrator E-K4 started to rise. It continued its rise until it read about twice its original value. However, during the test, the iron in the 2EU concentrate increased by a factor of 10 to 100, which was attributed to the ferrous sulfamate diversion to the 2DIS stream. Continued investigation of the problem of solids and/or organic in the 2DF is contemplated. Filters are being installed in several cold streams during the shutdown.

During the recycle of decontaminated uranium at month end, approximately 4000 gallons of waste containing approximately 280 units of plutonium were blended into the HAF batches. This high product waste had resulted from a flooded IA Column and had been held for two months in the waste rework tank. It was processed through the HA Column with no apparent effect on the column's stability.

Silica Gel Tail-End - Uranium

Operation of the prototypical silica gel facility was continued, and zirconium-niobium and ruthenium gamma decontamination factors of approximately four were obtained. A third bed of silica gel was added to each of the two parallel units to make each unit have a bed length of 7.5 feet.

Solvent Extraction - Plutonium

During the month, the final plutonium cycle has been operated predominately on the following flowsheet:

> 2AF/2AX/2AS/2BX = 73/14.8/18.2/7.4 (flows relative to HAF = 100) with nitric acid concentrations of 2AF = 6 M, 2AS = 0.5 M, 2BX = 0.1 M.

Gross gamma decontamination factors with this flowsheet ranged from 65 to 700, with 100 being typical. Decontamination appeared to be unaffected by solvent activity, 2A pulse frequency, and 2BX/2AP flow ratio (reduced from 0.5 to 0.4 for a ten day period). Losses to the 2AW stream ranged from 0.01 to 0.6 per cent, with 0.1 per cent being normal.

On April 6 and 7, a low acid flowsheet was briefly tested. This flowsheet was as follows:

> 2AF/2AX/2AS/2BX = 50.1/12.6/6.3/6.3 (flows relative to HAF = 100) with nitric acid concentrations of 2AF = 4.0 M, 2AS = 0.5 M, 2BX = 0.1 M.

No improvement in decontamination performance was noted during the short (33 hour) test period. Plutonium losses to the 2AW were ca. 0.08 per cent. The test was terminated when recycle of nitrite ion in the 2BW was interfering with partitioning in a manner similar to the effect noted during the "cold" plutonium spike run AC-5. The first loss of partitioning in the IBX Column was noted 15 hours after the change to the low acid flowsheet. Subsequent calculations indicated ca. a 50 per cent increase in nitrite recycle could be expected with the low acid flowsheet. Partitioning was recovered by returning to the high acid flowsheet and drastically reducing the 2AF-NaNO$_2$ butt on a temporary basis.

Further flowsheet testing in the final plutonium cycle has been postponed until provision is made to use second cycle organic for the 2AX and return the 2BW to the 20F tank rather than to the IBXF. Temporary or permanent failure of several rotameters, 2B interface capacitance probe, and the 2AW alpha monitor has also been a hindrance to process testing.

Plutonium Concentration

Solvent extraction plutonium product (2BP) has averaged approximately ten fold out of specification for gross gamma decontamination. However, a ten to 100 fold decontamination factor across the plutonium stripper-concentrator package has been observed. Periodic radiation surveys of the accessible portions of the package have shown no excessive buildup of activity (except as noted below), indicating that the activity is lodged primarily in the stripper tower. Plutonium balances across the package have indicated a fairly constant holdup in the system (including the product receiver and sample tanks), about twice the estimated solution holdup.

Starting April 11, a steady increase in plutonium inventory was observed (in retrospect). This inventory reached a level of nearly twice the average holdup on April 19, at which time it was noted that the plutonium stripper tower differential pressure had gradually increased. A 60 per cent nitric acid flush of the tower was made and, upon restarting of the equipment, the line from the Stripper T-L3 to the Concentrator E-L4 plugged. Radiation surveys at the time of the plug indicated that the material flushed from the tower contained large amounts of activity. The plug was broken by back-flushing from E-L4 to T-L3 with 30 per cent nitric acid. Following this flush, the stripper tower differential pressure returned to normal and the plutonium inventory to the previous value. A large portion of the accumulated activity was also removed, necessitating recycle of plutonium product. The plug material is believed to be a mixture of butylphosphates, plutonium(IV) polymer, and general cruds. Equipment modifications are currently under way to eliminate this plutonium buildup problem. Iron contamination of the product has averaged 60,000 parts iron per million parts plutonium.

Ion Exchange Tail-End - Plutonium

A preliminary study flowsheet for a continuous plutonium ion exchange system was drawn up and issued as HW-42471. Plans for building a prototypical facility are under way.

Organic Treatment

Batch washing of the No. 1 Organic System solvent was started on March 29. This was in addition to the continuous IO Column treatment. The results of the combined treatments were very favorable, giving an over-all decontamination factor of ten to twelve. The IO Column averaged a decontamination factor of six, which represented an improvement over previous operation by a factor of three. This improvement resulted from increasing the pulse frequency from 85 to 95 per cent of the flooding frequency. The batch washing contributed to the remaining average decontamination factor but, in addition, contained several high solvent activity surges by achieving peak decontamination factors of 70 or more. The surges were the result of upsets in the extraction columns. Toward the end of the month, the activity level of the treated solvent increased. The increase was due to two factors:

1. The frequency of batch washings was reduced from three to one per day to cut down on the amount of sodium carbonate wash solution going to underground storage.

2. The gradual buildup of radioactive I^{131} in the solvent from 10 to 70 per cent of the total activity.

The activity level of the No. 2 Organic System solvent has remained at a very low level, due to excellent operation of the 20 Column and normal additions of fresh solvent to this system.

The solvent losses during steady state operation have been about 0.3 per cent of throughput. This is about a two fold reduction in steady state losses over last month. One large solvent loss of 4000 gallons occurred when the precycle system was temporarily shut down on April 10.

URANIUM RECOVERY PROCESS TECHNOLOGY

Summary

The plant uranium losses averaged approximately one per cent of the gross uranium processed through the plant, with approximately 0.6 per cent contributed by the solvent extraction system and 0.4 per cent contributed by the plant condensates. Product sent to the 224-U Building had an average fission product activity approximately equal to the gamma activity of aged natural uranium.

During the month, cobalt-60 has been discovered in concentrations above tolerable drinking water concentrations in the ground water beneath the BY cribs. Consequently, disposal of scavenged TBP waste to soil has been restricted, pending the development of modified scavenging techniques which will reduce the cobalt-60 concentration to a tolerable level (see discussion below). The cobalt is present in the feed processed by the TBP Plant. Theorectical calculations indicate that the concentrations present could come from pile irradiation of metallic impurities in the slugs.

Solvent Extraction

The first cycle processed uranium aged a minimum of twelve months since discharge from the piles after irradiation to 200 MWD/T. Although the average feed composition for the month was about flowsheet, individual batches ranged from slurry-rich to supernate-rich, with sodium to uranium mole ratios ranging from 10 to 25. Because of the rather erratic feed composition and the high uranium content (one to fifteen per cent of the feed) of the backcycled RDW, organic phase flow was maintained at about 130 per cent of the flowsheet rate. RAW losses averaged 0.5 per cent of the feed uranium.

Stripping column losses were generally less than 0.1 per cent. The RC Column losses did not increase after three days of operation with the RCX flow reduced from 80 to 75 per cent of the flowsheet rate. When the lower RCX rate was coupled with an abnormally high RCF flow (temporarily increased from 130 to 155 per cent of the flowsheet rate), the resultant low L/V of 0.62 caused a concentrated end "pinch" and losses of 0.3 per cent.

Gamma decontamination performance was generally satisfactory, although four tons of high gamma uranium produced during plant start-ups were reworked through the second cycle. With the exception of these high gamma REU batches, the gross fission product gamma activity of the product averaged 1.1 times the gamma activity of aged natural uranium. Logarithmic gamma decontamination factors for the first cycle processing only Tank Farm feed and the second cycle processing all of the RCU plus an equal amount of Purex rework uranium were 3.3 and 1.6 respectively. Phosphate ion addition to the RDIS to improve decontamination was employed for just a few days during the month since the erratic RAF composition introduced the possibility of increasing RAW uranium losses (RDW backcycled as RAIS).

From November, 1955, to March, 1956, the plant processed metal waste from the 107-U and 101-TX cascades. This uranium was aged about 15 months since irradiation to 200 MWD/T. The average RAF, RCU, and REU gamma activities during this period were 1.4×10^7, 7.6×10^3, and 110 per cent of the activity of aged natural uranium, respectively. The gamma activity of the washed organic phase was 300 and 75 microcuries per gallon in the first and second cycles, respectively. Summary gamma decontamination data are:

	Logarithmic Decontamination Factor			
	Gross Gamma	Zr-Nb	Ru	Ce
First Cycle (RAF/RCU)	3.3	3.0	2.9	3.7
Second Cycle (RCU/REU)	1.8	2.1	1.7	---

The RE Column operated for a week at 1.4 times the instantaneous design rate of Project CG-562. At this rate, using 80 per cent REX flow, the volume velocity was 1000 gallons per hour per square foot (L/V 0.9). REW losses averaged 0.07 per cent of the second cycle feed uranium, about the same as the average for the month.

The cold stream filter test program has been completed. Sufficient data have been collected to permit specification of optimum pore size for replacement of cold stream filter elements. Until the production sized filters are installed, the single element RAS and RDIS test filters will be used by the Manufacturing Department to remove as many solids as possible.

Waste Scavenging

Studies are continuing in the Process Chemistry laboratories to find methods of reducing the aluminum concentrations in three tanks of "in-farm scavenged" TBP waste currently unsuitable for cribbing. The aluminum present in these tanks adversely affects strontium and cesium soil retention properties. The aluminum is present in the tanks since the TBP waste was dumped on top of heels of first cycle and coating waste.

Cobalt-60, half life 5.2 years, has been found in the ground water below the BY crib site. The source of all waste cribbed at this site has been TBP Plant scavenged waste. The cobalt-60 (which is not a fission product) apparently arises from cobalt and/or nickel impurities in the uranium metal and/or aluminum coating by (n,γ) or (n, p) reactions in the piles. Cobalt-60 has been found in irradiated aluminum end caps. Furthermore, cobalt-60 has been found in nearly all samples of TBP Plant feed and waste analyzed for cobalt-60. On the other hand, some recent scavenged supernatants have contained cobalt-60 to less than 0.1 MPC (maximum permissible concentration) and thus have been cribbable on the basis of the cesium and strontium behavior in the soil column. The Process Chemistry Unit is investigating means to assure routine scavenging of cobalt-60 to less than 0.1 MPC, and thus assure routine cribbing on the basis of cesium and strontium behavior.

URANIUM CONVERSION PROCESS TECHNOLOGY

Process

In general, the quality of the UO_3 produced during the month remained excellent. The fission product gamma activity of the product maintained a slight downward trend during the month, averaging about 50 per cent that of aged natural uranium. Particle size bordered on the 40 mesh specification limit, and one out of specification car was shipped on a customer waiver. Total metallic impurities showed a downward trend during the month and averaged about 110 parts per million parts of uranium. The reactivity ("low temperature test") of the powder produced during the month dropped rather sharply from last month's month end high of 1.25 to a low of about 1.0. By the end of this report period, the reactivity had slowly returned to a value of about 1.1. (Sulfamic acid continues to be added in nominal 0.05 weight per cent amounts to each pot charge.)

Tests

During the month, the semi-continuous Luckey pot test was run. The 100 per cent UNH solution was added at a controlled rate to the bed of UO_3 in the pot. At intervals, when a double pot charge of UO_3 had accumulated, feed addition was discontinued and roughly half the UO_3 was unloaded. Eight tons of powder were produced during the test. Five tons were shipped unmilled to Oak Ridge for pilot plant studies to determine the effects of processing blends of pot and semi-continuous UO_3 through the Paducah facilities. A portion of the material will be used at Oak Ridge for fluidized bed reactor studies.

The powder strongly resembled other continuously produced UO_3, ranging roughly from 200 mesh to 40 mesh in size and having a reactivity of about 0.4 (no sulfamic acid was added with the feed).

During the test, 100 per cent UNH feed addition rates of 54 gallons per hour were demonstrated. This represents an instantaneous calcination rate of 6.5 tons of uranium per day, 50 to 75 per cent greater than the current batch capacity. To achieve the above rate, however, the pots must be modified to permit continuous removal of the UO_3 from the pots. When operated semi-continuously, the unloading interruptions reduce the capacity to approximately normal batch rates.

To re-evaluate the effect of the 0.05 weight per cent addition of sulfamic acid on the reactivity of the UO_3 under present production conditions, sulfamic acid was left out of the entire production of one electric pot for a one week period. Sulfate free samples had an average reactivity ratio of 0.93 (800 C test) while samples taken from another "control" pot had an average reactivity of 1.02.

Z PLANT (ISOLATION, PURFICATION, AND FABRICATION) PROCESS TECHNOLOGY

Purex Coupling

Purex PR solution has been processed, through one peroxide strike, to AT solution which has met radiation and purity specifications. Radiation levels (CP reading, window open, through the side of the sample can carrier) for sample cans containing solution from this source may be predicted by the following equation:

$$\text{mr/hr} = 0.175\ (A \times 10^{10})^{0.415}\ (B)^{0.825}$$

where A = G/AT ratio for the PR solution, and
B = grams of plutonium in the sample can.

In order to permit loading the maximum batch size into the sample can, the PR solution should have a G/AT ratio (gamma microcuries per alpha count per minute) of 1.0×10^{-10} or less.

The data thus far obtained also show that for Purex PR solution to be evaporated directly to AT solution which will meet the specifications the G/AT ratio must be not greater than 0.4×10^{-10}.

A decontamination factor of 5.0 to 6.5 was measured for zirconium-niobium in Purex PR solution across the 234-5 Building process. The individual process steps contributed as follows: oxalate precipitation, 2.5 to 3.0; reduction, 1.1 to 1.2; casting, 1.4; and machining, 1.3. Assuming that the fission product activity in Purex PR solution is due to zirconium-niobium and ruthenium, it has been estimated that buttons which will satisfy the product specification for unfabricated metal (HW-29354, Part 2) can be made from solution with a G/AT ratio no greater than $\frac{125 - \%\ \text{Zr-Nb}}{25 \times 10^{10}}$.

Purex PR solution has been processed through Recuplex, giving decontamination factors as high as 30 for zirconium-niobium.

Recuplex

Recuplex technology during the past month has been concerned with the problems described below:

1. Use of Recuplex Slag and Crucible Flowsheet HW 7 (HW-40617) for the dissolution of powders needing recovery, gave dissolution efficiencies as low as 50 per cent. Increasing the dissolution

acid concentration (from 2.1 to 6.7 molar for Task II (hydrofluorination) powders and from 1.25 to 2.9 molar for Task III (reduction) powders) increased the dissolution efficiency to greater than 95 per cent.

2. Slag and crucible dissolution capacity has been limited by the long times required to dry the dissolvers between batches. It is planned to eliminate the drying period by the addition of dip tubes and lines which will allow the dissolver heels to be removed from the dissolvers long enough for the dissolvers to be charged. Dissolution capacity was increased, meanwhile, by a 30 per cent increase in slag and crucible batch size.

3. A rapid buildup of white "crud" occurred on the walls of the glass extraction columns, between the plates, while processing slag and crucible filtrate solution which had been dissolved with the increased batch size. It is not yet known whether the solid is silica or an insoluble fluoride. The "crud" buildup appears to have been halted as a result of (a) an increase in the aluminum:fluoride ratio in the coagulation part of the dissolution process and/or (b) dilution of the slag and crucible solution before its processing through solvent extraction.

4. Capacity of the extraction columns has been only about 60 per cent as high as was demonstrated earlier, probably as a result of solids in the feed. This resulted in frequent flooding during the early part of the month and the consequent introduction of bulk impurities into the product.

5. Extraction column waste losses continued to be quite variable. Important factors in regulating these losses during this period included (a) the plutonium content of the recycled solvent and (b) the TBP concentration of the solvent. Losses were so high as to require recycling of the waste during a period when the solvent contained only 12 per cent TBP in place of the standard 15 per cent.

234-5 DEVELOPMENT

Valence Studies

Reduction of plutonium(IV) to (III) was studied in preparation for trifluoride precipitation experiments. A plutonium(IV) solution (17 g/l and 2.5 $\underline{M}$ HNO_3, and containing 5000 ppm Al and Fe and 1000 ppm Cr and Ni) was reduced in one hour to 85 per cent plutonium(III) by hydrogen peroxide (0.05 M) or to 28 per cent plutonium(III) by hydroxylamine hydrochloride (0.3 $\underline{M}$). Sulfamic acid (0.3 $\underline{M}$) was used as a holding reductant. No further reduction was noted after 24 hours with hydrogen peroxide, but the hydroxylamine hydrochloride had reduced 65 per cent of the plutonium(IV) to (III).

Complete reduction of plutonium(IV) to (III) was accomplished in a solution containing 70 g/l plutonium, 0.8 M HNO_3, 0.9 M hydroxylamine hydrochloride, 0.3 M sulfamic acid (same impurities as above), after heating to 35 C and allowing to stand for four days.

Continuous Plutonium Trifluoride Precipitation

Two laboratory scale runs have demonstrated the feasibility of continuous plutonium trifluoride precipitation, and a readily filterable slurry was produced at room temperature after three throughputs. Filtrate losses of 0.15 per cent or less were found using sintered fluorothene (15 microns) for the filtering medium. The advantages of such a process are the ease of preparing the compound, low filtrate losses, and omission of the calcining and fluorination steps as are required for plutonium oxalate. The plutonium trifluoride can be dried with cylinder argon and reduced to metal, as demonstrated at SRL. The disadvantages are the lack of a sufficiently pure feed for such a process at the present time, and the difficulty in reducing plutonium(IV) to plutonium (III) in high nitric acid systems.

The first run was made with a feed solution 20 g/l plutonium, 1.3 M HNO_3, 0.1 M sulfamic acid, and a strike solution of 6.0 M HF. The slurry contained 1.0 M HF excess. The filterability and settling time improved after three throughputs. Filtrate loss of 50 mg/l (0.30 per cent) was obtained after start-up and 28 mg/l (0.15 per cent) was obtained after three throughputs. The cake was washed with 1.0 M HF and a filtrate loss of 24 mg/l resuted; however, the cake was still "muddy" until an ethyl alcohol wash produced a powdery cake.

The second run was made with a solution 70 g/l plutonium, 3.3 M HNO_3, 0.3 M sulfamic acid, and a strike solution of 6.0 M HF. The slurry was made 1.0 M HF. Again, the filterability and settling time were greatly improved with the continuous operation. A filtrate loss of 100 mg/l (0.20 per cent) was obtained after the batch start-up, and 50 mg/l (0.10 per cent) was obtained after three throughputs. The cake was washed with ethyl alcohol (one milliliter of ethyl alcohol per gram plutonium), and a powdery cake was produced immediately after filtration. Spectrochemical analysis of the feeds and plutonium powders will be obtained to determine purification factors so that a satisfactory feed may be defined.

Plutonium Trifluoride Precipitation With Fluosilicic Acid

To compare the purity of plutonium trifluoride precipitated by the addition of hydrofluoric acid to that of plutonium trifluoride precipitated homogeneously, attempts were made to precipitate plutonium trifluoride with fluosilicic acid from solutions (a) 20 g/l plutonium, 1.5 M HNO_3, and (b) 17 g/l plutonium, 0.8 M HNO_3. Two moles of fluosilicic acid were added per mole of plutonium, but no visible plutonium trifluoride formed in 24 hours. This slowness in the hydrolysis of fluosilicate to precipitate plutonium trifluoride is contrasted with the readiness of precipitation of plutonium tetrafluoride with fluosilicate (cf. November, 1955, report, HW-40182-H, p. Fc-16). This difference is believed due to the weaker complexing ability of plutonium(III) for fluoride, as compared to plutonium(IV).

Continuous Calcination of Plutonium(IV) Oxalate

A satisfactory operating temperature range for the Task I calciner is 300 to 400 C, cake temperature. This temperature range was determined from tests conducted in the Task 1 prototype at a feed rate of one kg/hr. One run was made at each temperature with a batch size of 670 g plutonium as oxalate. Residence time in the three feet long calciner was 11 minutes per pass. Although both batches were passed through the calciner twice to complete calcination, the 300 C batch was 69 per cent calcined after the first pass, and the 400 C batch was 93 per cent calcined after the first pass.

CHEMICAL DEVELOPMENT SUB-SECTION, R. E. SMITH

HOT SEMIWORKS

Two Hot Semiworks Purex Runs, PX-19 and PX-20, were completed to test the effect of Versene (ethylenediamine tetra acetic acid) and zirconyl nitrate on HA and IA Column decontamination performance. The following tentative conclusions have been reached from an analysis of the data.

a. HA Column instability and inadequate sampling facilities disguised the effect on decontamination performance resulting from the addition of 0.0013 M Versene to the aqueous feeds of the HA and IA Columns.

b. The addition of zirconyl nitrate to the dissolver acid (for isotopic dilution) did not improve decontamination in either the HA or IA Columns.

c. The addition of 0.005 M Versene to the 2AS alone or in combination with 0.001 M Versene in the 2AF neither improved 2A Column decontamination nor increased the 2AW plutonium loss.

A brief description of the more important run information is presented below. Table I contains a tabulation of the performance data for the two runs.

PX-19. A Modified HW No. 3 Purex Flowsheet was used for HA Column operation. The run was divided into two portions, one without and one with Versene in the HAF and HAS. During the first portion of the run an attempt was made to operate the HA Column scrub section under "loaded" conditions to reproduce the decontamination performance obtained in Runs PX-15 and 16. Cyclic flooding in the extraction section was encountered at 16 T./D. (plant equivalent) rates at the higher frequencies (90 - 94 cpm) necessary to maintain a "loaded" scrub section condition. A reduction in frequency to 86 cpm and a decrease in processing rate to 14 T./D. were required to stabilize HA Column operation during the Versene portion of the run. Improved decontamination and decreased waste losses resulted from stable operation.

The IAF (high uranium, 1.8 M; low acid, 1 M HNO_3) was transferred batchwise from the HCP Concentrator into the IAF tank. Versene was added to the IAF and IAS during the last half of the run.

PX-20. Three downdraft dissolver cuts were made with the following amounts of zirconyl nitrate in the dissolver acid: (a) none, (b) 0.001 M, and (c) 0.01 M. These cuts were processed (flowsheet same as PX-19) independently through the HA-HC Columns. In general it appeared that the decontamination became progressively poorer as the zirconium concentration increased. Near the end of the third cut processing, a strong tendency toward flooding in the extraction section of the HA Column was indicated.

The IAF from each of the HA Column feed batches was made 0.001 M in zirconium by the addition of zirconyl nitrate to the HCP Concentrator. The higher IA Column decontamination obtained while processing the third cut was probably due to the increased activity in the IAF.

IBP from all three cuts was combined to form 2AF. The addition of Versene to the 2A Column aqueous feeds (0.005 M in the 2AS and 0.001 M in the 2AF) failed to indicate any improvement in the 2A Column decontamination. High plutonium losses in the 2AW were experienced during the third portion of the run due to flooding in the 2A Column extraction section.

Run PX-21 was started but equipment difficulties necessitated cessation of operations before steady state operation was reached. Equipment decontamination is progressing in preparation for Hot Semiworks maintenance and repairs.

The Waste Self-Concentrator, which duplicates a 39-in. diameter by 36 ft. deep core of a Purex waste tank, has self-concentrated to about 55 per cent of the initial waste volume and now contains 5120 liters of concentrated IWW 22 ft. in depth. Vapor from the tank passes through a 1/2 in. and/or 1-1/2 in. valve before being condensed. During the past 4 months approximately 100 "bumps" have occurred, the majority of them being within the last 6 weeks period. No consistent pattern has been established by the bumps but some characteristic observations are as follows:

a. A maximum pressure of 50 inches of water has been developed when the vapor line was vented through the 1/2-in. valve. The 1/2-in. valve is geometrically equivalent to the 12-in. vapor header in the 75-ft. diameter Redox tanks. (With both valves open the maximum pressure that has been reached is 32 inches.)

b. The maximum quantity of distillate from a single bump has been about 60 liters which is equivalent to about 8500 gal. for a 75-ft. diameter tank. (Maximum flow through both valves has reached about 250 ml./min.)

c. Immediately after a bump the temperature measured 13 ft. (nominally 225 - 230°F.) above the bottom of the tank usually drops an average of 7°F. After 5 to 15 minutes the temperature at a point 7 ft. (nominally 240°F.) above the bottom also decreases by an equivalent amount. The temperatures at the 2.5 and 19.5 ft. levels (nominally 250 and 220°F., respectively) generally remain constant.

d. The initial pressure surge is generally rapid - on the order of 5 seconds. Frequently small increases in pressure occur during the pressure decline which probably indicate localized boiling.

e. On several occasions opening and closing the 1-1/2-in. valve created a new bump while residual pressure (up to 10 in.) remaining from a previous pressure rise was being dissipated through the 1/2-in. valve.

f. The period of duration for bumps have varied from a matter of minutes to hours for the same maximum pressure developed.

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TABLE I

HOT SEMIWORKS RUN DATA[(a)]

	PX-19[(b)]		PX-20[(c)]		
Dissolver HNO_3 Consumption M HNO_3/M U	3.1		3.2		
Zirconium Conc. in Acid, M.	--		0.0	0.001	0.01
0.0013 M Versene in HAF & HAS	No	Yes	No	No	No
HA Production Rate (Plant T/D equivalent)	16	14	14	14	14
HA Frequency (a = 1.07 in.)	80-100	86	86	80-88	86
HAF/HAP dF	2.7-2.9	3.1	2.6	2.6-2.9	2.3
HAW % Pu	17-80 (d)	0.7	0.03-3.0	1.4	2.9-10.0 (d)
HAW % U	1-8	0.04-0.2	0.05-3.0	0.1-3.5	3.5-11.5 (d)
HAF/IAF dF	(e)	(e)	2.6	2.7	2.3
0.0013 M Versene in IAF & IAS	No	Yes	No	No	No
IA Production Rate (Plant T/D equivalent)	14	14	14	14	14
IA Frequency (a = 1.2 in.)	56	56	56	56	56
IAF/IAP dF	(e)	(e)	1.7	1.2	1.6
HAF/IAP dF	4.7	4.9	4.2	3.6	3.8
IAW % Pu	0.01-0.02	0.01-0.2	0.4-7.1	0.3	0.2
IAW % U	0.004	0.003	0.3-5.5	0.2	0.1
IBP % U	--	1×10^{-3}	2.7×10^{-4} to 5.4×10^{-3}		
IBU % Pu	--	0.25	0.3		
IAF/ICU dF	(e)	(e)	1.8 - 2.4		
0.005 M Versene in 2AS	No		No	Yes	Yes
0.001 M Versene in 2AF	No		No	No	Yes
2A Production Rate (Plant T/D equivalent)	10		10	10	10
2A Frequency (a = 0.8 in.)	50		40	40	40
2AF/2AP dF	1.8 - 2.2		2.6	2.6	2.5
2AW % Pu	0.1 - 0.4		0.26	0.17	17.7 (d)
IOF/IOO dF	1.4 - 1.8		1.2 - 1.6		
Gamma Activity in IOO uc/gal.	80 - 200		140 - 300		
Overall dF HAF/ICU	5.2 - 5.3		4.5		
Overall dF HAF/2BP	8.2 - 8.8		7.2 - 7.6		

Notes: See following page

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Notes:

(a) Data shown are taken from periods of stable operation. Downdraft dissolving used throughout. HAF pumped to the column without clarification.

(b) Flowsheet: HW No. 3 Purex Flowsheet with the following modifications:

(1) Single HA Column scrub = 2.3 M HNO_3

(2) HAF:IAF:IAS:IAX = 100:75:56:376

(3) IAF = 1.8 M U: Ca. 1 M HNO_3

(4) Versene added as noted.

(5) No $NaNO_2$ addition to the HAF

(6) IOF:IOS:IOR = 100:33:0

(7) Solvent: 30% TBP, 70% Shell E-2342

(c) Flowsheet: same as (b) except the dissolver acid had the following amounts of zirconyl nitrate added: Cut 1, 0.0 M; Cut 2, 0.001 M; and Cut 3, 0.01 M.

(d) Column flooded intermittently in the extraction section causing high losses.

(e) IAF sampler not working.

PUREX DEVELOPMENT

Process Chemistry

Evaluation of Low Acid 2A Column Flowsheet. Possible gain in fission product decontamination through use of a low acid 2A Column flowsheet was studied by batch contacts using plant feed and solvent and simulating 2A Column conditions. Different aqueous phase nitric acid concentrations were obtained by dilution of the 2AF with water. In each case, the solvent was pre-equilibrated with nitric acid of the same concentration as the 2AF. The following table shows gross gamma distribution ratios for various acid concentrations in the feed.

BATCH CONTACTS SIMULATING 2A COLUMN CONDITIONS
Effect of HNO_3 Concentration in 2AF

HNO_3 Conc. in Feed, M	Versene Conc. in Feed, M	E_a^o, Gross Gamma*
6	0	0.41
6	0.0015	0.39
4	0	0.11
3	0	0.059
2	0	0.020
1	0	0.016
0.5	0	0.016
0.5	0.0015	0.020

*) Greater than 95 per cent Zr-Nb.

The data agree well with published values for Zr-Nb distribution under these conditions (cf. TID-2012) indicating the absence of abnormal Zr-Nb species. Addition of Versene to the 2AF did not significantly change the distribution ratios.

Feed Pretreatments. Decontamination factors of from two to six have been obtained by glass-wool filtration (or adsorption) of plant samples of IAF, 2DF, and IBXF. Miniature pulse column runs using plant 2DF (containing visible black solids) show a two-fold improvement in decontamination (for the solvent extraction only) with filtered as compared to unfiltered feed. Digestion of unfiltered 2DF at the boiling point for 24 hours improved subsequent solvent extraction (miniature pulse column) decontamination four-fold. A similar digestion of unfiltered 2DF made 0.1 M in $K_2Cr_2O_7$ produced essentially the same solvent extraction decontamination improvement. Similar treatments of plant IAF did not improve solvent extraction decontamination. Gamma activity associated with black solids isolated from plant 2DF was 68 per cent Zr-Nb and 32 per cent Ru.

Plant IAF scavenged with Superfiltrol-Separan 2610 (scavenging DF = 2.5) showed essentially the same solvent extraction (mini pulse column) decontamination as an untreated feed. IAF-ICP decontamination factors were increased two- and ten-fold when plant IAF was made 0.0015 M in itaconic acid and Versene, respectively.

In 2D Column miniature pulse column runs (using plant 2DF), 10 and 2.5 g./l. of $ZrO(NO_3)_2$ in the 2DS increased the decontamination by about seven- and two-fold, respectively. At the higher concentration, the sieve plates became organic wet and the capacity of the column was reduced.

Head-End Studies. Solvent extraction decontamination of simulated dissolver solution (2.0 M UNH, 0.1 M HNO_3, 1% Redox dissolver solution) was studied as a function of time after scavenging with five g./l. Superfiltrol - 0.02% Separan 2610. Portions of the scavenged solution were removed at intervals, butted to HAFS composition and contacted batchwise (one extraction, three scrubs, three strips) simulating Purex HW No. 3 Flowsheet HA-HC Column conditions. Unscavenged feed served as control. Decontamination factors obtained are shown in the following table.

		Gross Gamma Decontamination Factors (Arithmetic)				
	Time Aged	Scavenging	Extraction	Scrub & Strip	HA-HC	Overall Feed to HCP
Control	0 hr.	1	64	7.8	5.0×10^2	5.0×10^2
	5 days	1	64	6.6	4.2×10^2	4.2×10^2
	11 days	1	--	--	1.8×10^2	1.8×10^2
Scavenged	0 hr.	4.2	105	4.3	4.5×10^2	1.9×10^3
	3 hr.	4.2	--	--	5.2×10^2	2.2×10^3
	26 hr.	4.2	120	3.2	3.8×10^2	1.6×10^3
	5 days	4.2	220	5.0	1.1×10^3	4.7×10^3
	11 days	4.2	--	--	9.0×10^3	3.8×10^3

The deterioration in solvent extraction decontamination of the non-scavenged feed with aging and the improvement for the scavenged feed are interesting though unexplained.

Other solid absorbents tried as possible head-end scavengers were alumina, activated charcoal, Antra Filt, Alkalex, asbestos, Attaclay, Fuller's earth, Silene, Supercel, Supercel-hyflo, and etched glass wool. None of these produced a gross gamma scavenging D.F. greater than two and in no case was subsequent solvent extraction decontamination significantly improved. Most of these same solids were tried as tail-end scavengers on plant final uranium solution. Maximum DF obtained was with Fuller's earth and this was only 2.6.

Versene in Neutralized IWW. When 8 M $NaNO_3$ containing 0.003 M Versene was refluxed, the concentration of Versene decreased to 0.002 M in 24 hours and to less than 0.0001 M after 96 hours. While not completely definitive, these results indicate fairly rapid destruction of Versene in Purex waste storage tanks. Closer simulation of stored waste was not done because of difficulty in analyzing for Versene in such solutions.

Solvent Quality. Routine quality tests of plant IOO and 200 have continued. Optical density values for 200 indicate a slight degradation. However, other solvent quality tests used show no significant change. The various tests indicate no significant change in IOO quality since shortly after start-up. Degradation appears to have reached a steady state and the solvent is not seriously inferior from a decontamination standpoint to fresh solvent. The I^{131} content of IOO increased markedly as shorter-cooled feeds were processed.

Plutonium Rework. Synthetic HAF, spiked with solution obtained by dissolving some of the solid material which recently plugged the 2BP stripper-to-concentrator line, was extracted batchwise simulating the HA Column. Waste loss after five extractions was less than 0.1 per cent showing the absence of non-extractable plutonium. The material concerned has since been reworked satisfactorily in the plant.

Solids in Concentrated Hot Semiworks 2BP. Solids found in 2BP concentrate were investigated with respect to poor material balances observed across the plutonium stream concentrator. The concentrate sample as obtained contained about two per cent of a solid phase which was insoluble in concentrated HNO_3 or five per cent NaOH but soluble in a HNO_3-$KMnO_4$ mixture. Twenty-two per cent of the total alpha activity and nearly all of the gamma activity were present in the solid phase.

Hot Semiworks Solvent Regeneration. Alkaline permanganate was investigated briefly as a decontamination agent for a badly contaminated HSW solvent (gross gamma activity about 10^5 uc/gal.). Decontamination factors of about 50 were obtained with permanganate washes as compared to two with Na_2CO_3, HNO_3, NaOH, and $Ca(OH)_2$ slurry. However, even the permanganate washes did not restore the solvent to normal HSW quality as shown by batch multiple contacts simulating IA Column conditions.

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Chemical Engineering Development

Pulse Column Studies

Scrub Section Studies. Work continued on the development of a Purex A-Type column scrub section cartridge which would operate with the organic phase continuous (for interface crud entrainment control), and which would have chloride ion decontamination efficiencies equal to or better than the present plant design. (Standard cartridge, stainless steel sieve plates, 1/8-in.-diameter holes, 23% free area, 2-in. spacing).

Seventy-nine A-type column scrub section runs were made in a 3-inch-diameter glass pulse column with 9-ft. cartridges. Purex HW No. 3 Flowsheet modified to include the addition of 0.5 $\underline{M}$ NaCl in the HAF was used throughout. Four runs were made to further define the operating characteristics of the standard cartridge. New cartridges investigated included: two with a polythene packing, six containing both stainless steel and fluorothene sieve plates, and one containing both stainless steel sieve and nozzle plates.

The details of the cartridges and the results of the studies are presented in Tables II, III, and IV. Highlights of the findings are summarized below.

1. The cartridges consisting of fluorothene and stainless steel sieve plates (mixed) when operated with the organic phase continuous gave H.T.U. equal to or less than those obtained with the standard cartridge. The efficiency of mixed cartridges tended to be less sensitive to pulse frequency than was the efficiency of the standard cartridge. When operated with the organic phase continuous (interface at bottom of scrub section), a phase inversion occurred around the stainless steel plates which resulted in alternate continuous phase zones of organic and aqueous. The most promising mixed cartridges tested were:

   Cartridge A. Alternate sets of two stainless steel and two fluorothene sieve plates with 1-inch plate spacing throughout. Stainless steel plates with 0.08-in.-diameter holes, 21% free area and fluorothene plates with 1/8-in.-diameter holes, 23% free area.

   Cartridge B. Same as above except with 3/16-in. diameter holes, 23% free area fluorothene plates. (Teflon spacers were used above fluorothene plates in lieu of stainless steel spacers in this cartridge to minimize the effects of aqueous channeling in the organic continuous zones of the 3-in.-diameter column.)

   Both cartridges were studied with an 0.6-inch pulse amplitude and had nearly identical operating characteristics.

2. Mixed Cartridges A and B with organic phase continuous had flooding frequencies of 95 and 115, and, 105 and 125 cycles per minute at volume velocities of 500 and 250 gal./(hr.)(sq.ft.), sum of both phases, respectively. These may be compared with the standard cartridge (aqueous continuous) flooding frequencies of 95 and 125 cycles per minute at the above volume velocities. (Equivalent to 20 and 10 tons U/day on a plant basis.)

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3. Mixed Cartridges A and B with organic phase continuous had H.T.U. values approximately one-half to two-thirds those of the standard cartridge at frequencies in the range of plant interest. At a volume velocity of 250 and frequencies from 70 to 100 cycles/min. H.T.U. ranged from 1.1 to 1.5 ft. The standard cartridge under comparable volume velocity-frequency conditions but aqueous phase continuous had H.T.U. ranging from 1.8 to 2.9 ft. At volume velocity of 500 and frequencies from 60 to 90 cycles per minute H.T.U. from 1.6 to 2.5 ft. were obtained as compared with standard cartridge values of 2.3 to 3.2 ft.

4. Mixed Cartridge B was investigated with the aqueous phase continuous. H.T.U. were in the range of 3 to 4 ft.

5. One run was made with mixed Cartridge B in which the interface was maintained in the cartridge approximately 2 to 3 feet from the top. Efficiency was poor (H.T.U. = 3.8 ft.).

6. One mixed cartridge consisting of alternate sets of two stainless steel sieve plates and two stainless steel nozzle plates was investigated briefly. With either aqueous or organic phase continuous the cartridge had low flooding frequencies which were sharply sensitive to throughput. With either phase continuous and a 0.6-inch pulse amplitude, flooding frequencies of 90 ± 10 and 50 ± 10 were obtained at volume velocities of 250 and 500, respectively. When operated with the organic phase continuous, i.e., interface at the bottom of the scrub section, the column inverted and operated in a stable condition with the aqueous phase continuous in the plate section. H.T.U. values were promising, ranging from 1.3 to 2.0 feet for both organic and aqueous phase continuous operation.

7. The polythene packings tested were 5/8-in. Raschig rings and 3/4 by 2 in. Tellerettes. Results with either phase continuous were not encouraging; H.T.U. values ranged from equal to or twice those of the standard cartridge. The Tellerettes had a very high flooding frequency, greater than 120 cycles/min. at a volume velocity of 500 gal./(hr.)(sq.ft.).

Stannous Oxide (SnO) Head End Scavenging Studies. "Cold" pilot plant studies were carried out on a stannous oxide (SnO) scavenging process which is being considered for improving Zr-Nb decontamination in the Purex Plant. To investigate the processing aspects the following flowsheet was used: (1) digestion of a simulated dissolver solution 0.05 M in SnO for two hours at 100°C. or for three hours at 55°C., (2) cooling to 25 to 35°C., and (3) centrifugation in a 26-inch, baffled, solid bowl centrifuge.

Technical grade SnO (Metal and Thermite Corporation) was found to be appreciably oxidized to meta stannic acid at HNO_3 concentrations of 1.25 M and above in the feed. Upwards of 75% of the meta stannic acid so formed carried over with the centrifugate at 1100 x G and a hold-up time of 23 minutes. Uranium concentration and digestion temperature appeared to have little effect on the oxidation of the SnO to meta stannic acid. At a digestion temperature of 100°C., however, a strong foaming tendency was evident.

With 0.25 M HNO_3 in the feed, the technical grade SnO was not oxidized, but was difficult to slurry. More than 90% of the SnO was not removed from the well agitated centrifuge feed tank.

Baker's Reagent grade SnO was not oxidized to meta stannic acid when used with 1.5 M HNO_3 in the feed and was easily suspended in the "cold" dissolver solution by agitation. A clean centrifugate was obtained at 1100 x G and a hold-up time of 3.8 minutes. The SnO did not cling to the bowl wall and was removed from the centrifuge without difficulty.

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TABLE II

PUREX 3-IN. HA SCRUB COLUMN FLOODING STUDIES

Flowsheet: Purex HW No. 3. Pu and F.P.'s omitted, NaCl added to HAF. Diluent: Shell E-2342.

Equipment: 3-in. diameter precision bore glass column with a 9-ft. cartridge as described in Table IV.

Run No.	Cartridge(1)	Continuous Phase	Volume Velocity Gal./(Hr.)(Sq.Ft.), Sum of Both Phases	Pulse Ampl., In.	Pulse Flood Freq., Cyc./Min.
3-74-ASH	A	Organic	490	1.0	95 ± 5(2)
3-85c-ASH	E	Organic	500	1.0	75 ± 5(2)
3-86c-ASH	E	Organic	500	1.0	65 ± 5(2)
3-87-ASH	E	Organic	500	0.6	95 ± 5(2)
3-89b-ASH	E	Organic	240	0.6	115 ± 5(2)
3-93-ASH	F	Organic	240	0.6	125 ± 5(2)
3-94-ASH	F	Organic	480	0.6	105 ± 5(2)
3-97-ASH	F	Aqueous	240	0.6	125 ± 5
3-98-ASH	F	Aqueous	480	0.6	105 ± 5
3-105-ASH	F	Organic	480	1.0	85 ± 5(2)
3-107-ASH	G	Aqueous	240	0.6	115 ± 5
3-111-ASH	H	Organic	480	0.6	50 ± 10(3)
3-112-ASH	H	Organic	240	0.6	90 ± 10(4)
3-113-ASH	H	Aqueous	480	0.6	50 ± 10
3-114-ASH	H	Aqueous	240	0.6	90 ± 10
3-118-ASH	I	Organic	480	0.6	75 ± 5
3-119-ASH	I	Organic	240	0.6	95 ± 5
3-122-ASH	I	Aqueous	480	0.6	50 ± 10
3-123-ASH	I	Aqueous	240	0.6	70 ± 10
3-126-ASH	J	Organic	480	0.6	125 ± 5
3-127-ASH	J	Aqueous	480	0.6	105 ± 5

Notes:

(1) Cartridges identification letters refer to Table IV.

(2) The mixed cartridges containing both stainless steel and fluorothene plates operated aqueous continuous around the stainless steel plates and organic continuous around the fluorothene plates giving a column with alternate sections of aqueous and organic continuous.

(3) At all frequencies investigated (40 to 60 cyc./min.), this cartridge resulted in a stable inversion of phases.

(4) At all frequencies investigated (40 to 100 cyc./min.), this cartridge partially inverted. The degree of inversion increased with increasing frequency and ranged from 30% inverted to 100% inverted.

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TABLE III

PUREX 3-IN. HA SCRUB COLUMN EFFICIENCY STUDIES

Flowsheet: Purex HW No. 3, Pu and F.P.'s omitted, NaCl added to HAF. Diluent: Shell E-2342.
Equipment: 3-in. diameter precision bore glass column with a 9-ft. cartridge as described in Table IV.

Run No.	Cartridge(d)	Continuous Phase	Pulse Ampl., In.	Pulse Freq., Cyc./Min.	Volume Velocity, Gal./(Hr.)(Sq.Ft.) Sum of Both Phases	Cl^- D.F.(a)	H.T.U.,(b) Ft.	Hold-Up(c)
3-75a-ASH	A	Organic	1.0	80	490	5.3	3.5	15
3-75b-ASH	A	Organic	1.0	90	480	9.9	2.3	30
3-75c-ASH	A	Organic	1.0	95	490	8.9	2.4	32
3-76a-ASH	A	Organic	1.0	80	710	6.6	3.0	27
3-76b-ASH	A	Organic	1.0	85	730	6.1	3.2	60
3-77a-ASH	B	Organic	1.0	70	480	12.0	2.3(e)	13
3-77b-ASH	B	Organic	1.0	80	490	8.7	2.3(e)	10
3-77c-ASH	B	Organic	1.0	90	490	8.4	2.4(e)	--
3-78a-ASH	B	Organic	1.0	70	440	17.3	2.0	14
3-78b-ASH	B	Organic	1.0	90	480	18.4	1.8	19
3-78c-ASH	B	Organic	1.0	50	500	8.6	2.5	8
3-79a-ASH	B	Organic	1.0	60	720	8.5	2.6	10
3-79b-ASH	B	Organic	1.0	80	710	15.5	1.8	20
3-80a-ASH	C	Organic	1.0	60	500	3.6	5.3	10
3-80b-ASH	C	Organic	1.0	70	490	5.7	3.5	12
3-80c-ASH	C	Organic	1.0	80	470	5.1	3.6	14
3-80d-ASH	C	Organic	1.0	85	470	13.3	2.1	45
3-82a-ASH	D	Organic	1.0	60	490	22.7	1.6	33
3-82b-ASH	D	Organic	1.0	70	480	21.3	1.6	42
3-82c-ASH	D	Organic	1.0	50	490	12.6	2.0	9

Notes: See following page.

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TABLE III (Cont'd)

Run No.	Cartridge$^{(d)}$	Continuous Phase	Pulse		Volume Velocity, Gal./(Hr.)(Sq.Ft.) Sum of Both Phases	Cl^- D.F.$^{(a)}$	H.T.U.,$^{(b)}$ Ft.	Hold-Up$^{(c)}$
			Ampl., In.	Freq., Cyc./Min.				
3-83a-ASH	D	Organic	1.0	60	710	9.8	2.4	48
3-84a-ASH	D	Organic	0.6	90	490	8.0	2.6	12
3-84b-ASH	D	Organic	0.6	110	480	13.5	1.9	40
3-84c-ASH	D	Organic	0.6	70	480	9.3	2.5	24
3-86a-ASH	E	Organic	1.0	40	480	8.9	2.6	10
3-86b-ASH	E	Organic	1.0	60	490	33.0	1.4	20
3-88a-ASH	E	Organic	0.6	90	470	23.9	1.6	30
3-88b-ASH	E	Organic	0.6	70	480	9.7	2.4	9
3-88c-ASH	E	Organic	0.6	50	480	6.8	2.9	10
3-90a-ASH	E	Organic	0.6	100	250	43.2	1.1	22
3-90b-ASH	E	Organic	0.6	80	250	20.0	1.4	10
3-91a-ASH	E	Organic	0.6	60	490	11.0	2.0	11
3-91b-ASH	E	Organic	0.6	80	480	11.0	2.1	18
3-92a-ASH	E	Organic	1.0	50	470	15.5	1.8	16
3-92b-ASH	E	Organic	1.0	40	480	9.3	2.5	10
3-95a-ASH	F	Organic	0.6	50	490	7.5	2.9	8
3-95b-ASH	F	Organic	0.6	70	470	11.5	2.1	16
3-95c-ASH	F	Organic	0.6	90	480	18.8	1.6	30
3-96-ASH	F	Organic	0.6	90	240	22.1	1.5	11
3-104a-ASH	F	Organic	0.6	70	250	20.0	1.5	10
3-104b-ASH	F	Organic	0.6	100	250	50.0	1.2	--
3-99-ASH	F	Aqueous	0.6	80	490	6.4	3.3	10
3-100-ASH	F	Aqueous	0.6	90	240	6.5	3.0	7
3-101-ASH	F	(f)	0.6	80	480	5.4	3.8	--
3-102-ASH	F	Aqueous	0.6	90	470	5.6	3.6	14
3-103a-ASH	F	Aqueous	0.6	100	240	6.0	3.2	9

Notes: See following page.

TABLE III (Cont'd)

Run No.	Cartridge[d]	Continuous Phase	Pulse Ampl., In.	Pulse Freq., Cyc./Min.	Volume Velocity, Gal./(Hr.)(Sq.Ft.) Sum of Both Phases	Cl^- D.F.[a]	H.T.U.,[b] Ft.	Hold-Up[c]
3-103b-ASH	F	Aqueous	0.6	70	240	4.1	4.4	8
3-108-ASH	G	Aqueous	0.6	60	240	5.7	3.2	6
3-109-ASH	G	Aqueous	0.6	80	250	7.3	2.6	8
3-110-ASH	G	Aqueous	0.6	100	240	14.8	1.8	23
3-115-ASH	H	Aqueous	0.6	50	480	14.1	2.0	15
3-116-ASH	H	Organic	0.6	40	470	21.9	1.3	15
3-117-ASH	H	Organic	0.6	80	240	17.1	1.7	28
3-120-ASH	I	Organic	0.6	90	240	8.6	2.5	8
3-121-ASH	I	Organic	0.6	70	490	5.3	3.6	22
3-124-ASH	I	Aqueous	0.6	50	500	7.5	2.9	38
3-125-ASH	I	Aqueous	0.6	70	240	8.5	2.7	43
3-127-ASH	J	Organic	0.6	120	500	5.7	4.0	11

Notes:

(a) Defined as $\dfrac{Cl^- \text{ concentration in influent organic}}{Cl^- \text{ concentration in effluent organic}}$.

(b) Height of a transfer unit, overall organic-film basis.

(c) Percent holdup of the dispersed phase. Measured by shutting off all streams and measuring change in the interface position.

(d) See Table IV for description of cartridges.

(e) Stainless steel plates were found to be partially preferentially wet with organic.

(f) Interface was maintained in the cartridge 2 to 3 ft. from the top of the column.

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TABLE IV

DESCRIPTION OF CARTRIDGES USED IN 3-IN. HA SCRUB COLUMN STUDIES

Cartridge	Description
A	Alternate sieve plates of stainless steel and fluorothene; 2-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 3/16-in.-diameter holes, 23% free area.
B	Alternate sieve plates of stainless steel and fluorothene; 1-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 3/16-in. diameter holes, 23% free area.
C	Alternate sieve plates of stainless steel and fluorothene; 1-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 1/16-in.-diameter holes, 8% free area.
D	Alternate sets of 2 stainless steel sieve plates and one fluorothene sieve plate; 1-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 3/32-in.-diameter holes, 23% free area.
E	Alternate sets of 2 stainless steel sieve plates and 2 fluorothene sieve plates; 1-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 1/8-in.-diameter holes, 23% free area.
F	Alternate sets of 2 stainless steel sieve plates and 2 fluorothene sieve plates; 1-in. spacing throughout. Stainless steel plates - 0.08-in.-diameter holes, 21% free area. Fluorothene plates - 3/16-in.-diameter holes, 23% free area. Stainless steel spacers above each stainless steel plate and Teflon spacers above each fluorothene plate.
G	Stainless steel sieve plates, 1/8-in.-diameter holes, 23% free area, 2-in. plate spacing (standard cartridge).
H	Alternate sets of 2 stainless steel sieve plates and 2 stainless steel nozzle plates; 1-in. spacing throughout. Sieve plates - 0.08-in.-diameter holes, 21% free area. Nozzle plates 1/8-in.-diameter holes, 10% free area.
I	Packed column with 5/8-in. polythene Raschig rings.
J	Packed column with 3/4 x 2 in. Tellerettes.

URANIUM RECOVERY DEVELOPMENT

Process Chemistry

Continuous Calcination of UNH. Uranium oxide powder produced during 321 Bldg. Run B-25 was hydrated continuously in the three-inch laboratory unit. The powder contained 530 ppm S (U basis) and, prior to hydration, had a reactivity ratio of 0.67 (800°C. reduction - 410°C. hydrofluorination). During hydration powder and shell temperatures were 85 and 140°C., respectively, and the hold-up time averaged two hours. Water was introduced beneath the bed at a rate equivalent to four times the stoichiometric amount required for formation of the monohydrate. Water content of the product powder was 5.5 to 6.0 per cent indicating essentially complete monohydrate formation. Reactivity ratio (800-410) was 0.98. Operation of the unit was very smooth under these conditions and flow characteristics of the product were good. Lowered agitator speed (from 137 to 65 rpm.) corrected a tendency toward build-up of the bed.

Portions of the hydrated UO_3 were dehydrated batchwise at 250 and 300°C. in the three-inch calciner and at 350°C. in a muffle furnace. Water content was reduced to one per cent in 2.5 hours at 250°C. and in 0.5 hours at 300°C. Approximately 70 per cent of the water was removed when powder temperature reached 220°C. Reactivity ratios (800-410) of powders dehydrated at 250 and 350°C. averaged 1.18 and 1.27 for those dehydrated at 300°C. Reactivity ratios for the dehydrated powders were independent of hold-up times during dehydration ranging from 0.5 to 5.0 hours. It is interesting to note that the reactivity ratio increase during hydration and dehydration of this powder (0.6 unit) was about the same as reported last month for similar treatment of a powder having an initial ratio of 0.29.

Preliminary (beaker-scale) experiments showed that UO_3 of high reactivity ratio can be produced by decomposition of UNH with formic acid. A single run has been made in the three-inch calciner in which formic acid was added continuously through a feed point separated from but adjacent to the UNH feed point. One-half the stoichiometric amount of formic acid necessary for complete denitration of the UNH was added. Reactivity ratios are not yet available.

WASTE TREATMENT

Process Chemistry

Distribution ratios for Cs^{137} and Sr^{90} determined by batch contacts between soil and scavenged wastes with and without aluminum present confirm Soil Sciences Unit findings that small amounts of aluminum seriously interfere with adsorption of Cs^{137} and Sr^{90} by the soil. Modifications to the scavenging procedure (primarily concerning pH) to reduce the residual aluminum after scavenging are under study but data are not yet available due to difficulties in aluminum analyses at the low levels concerned.

[redacted]

The discovery, by Biophysics Section personnel, of Co^{60} in Uranium Recovery Process wastes before and after scavenging and that cobalt is apparently not removed from scavenged wastes by soil has prompted a study of means to remove Co^{60} from the wastes to less than ground water tolerance. Preliminary data show that use of cobalt in lieu of nickel in the scavenging process will effect appreciably Co^{60} decontamination.

MISCELLANEOUS DEVELOPMENT

Process Planning

U-237 Formation and Decay. Inadequate "cooling" of the uranium product from separations plants causes personnel exposure problems during calcination operation because of U-237, a short-lived beta-gamma-emitting isotope of uranium. The effects of cooling time and reactor power level on the content of U-237 have been calculated and documented in HW-42505, "Lag Storage Requirements for U-237 Decay," by A. M. Platt and E. A. Coppinger. Typical values indicate that 110 days total cooling from pile discharge should be provided for uranium irradiated to 10 MW/T in order to reduce the U-237 gamma ratio to 2.5 (measured with a GSC using 1.7 $g./cm.^2$ Pb).

Chemical Engineering Development

Cesium Recovery. "Cold" pilot plant studies of the processing aspects of the Chemical Research Sub-Section flowsheet for the recovery of cesium from Purex IWW were started. Initial investigations have been concerned with the removal of ferric hydroxide from the neutralized IWW by centrifugation in a 26-inch baffled, solid-bowl centrifuge operating at 1100 x G. The composition of the neutralized IWW was 5.5 M $NaNO_3$, 0.07 M $Fe(OH)_3$, and 0.07 M Na_2SO_4.

At a pH of 11, centrifugation removed 98.4% of the $Fe(OH)_3$ at a 28-minute hold-up time. Only 60% was removed at a pH of 1.5 with a 21-minute hold-up time.

The centrifuged $Fe(OH)_3$ packed into lumps which were difficult to break up by slurrying, but were readily dissolved by 30% HNO_3.

Hydroclone Studies. A nominal 1 gal./min. hydroclone, fabricated from ORNL drawings, was installed in a test stand so that dissolver solution solids removal and solvent deentrainment studies could be made. When operating with water at one gal./min., the pressure drop across the clone was 47 lb./sq.in. Pressure drop was essentially independent of the ratio of under flow/overflow.

Separations Equipment Development

In-Line Chemical Instrumentation

pH Measurement. The application of pH measurement to determine nitric acid concentration in streams such as Redox 2DF and 1AFS is under investigation. Experimental data obtained from prototype equipment indicate that changes in stream pH are detected rapidly (ca. 10 minutes). Also the data recorded from any one solution are very consistent, less than ± 0.03 pH unit variation in twenty-four hours. In the range - 0.1 to - 0.3 molar nitric acid, a pH change of 0.05 pH units corresponded to a 0.025 M change of acid molarity for a given uranium concentration.

Sample Dilution. A dilution system has been tested in the dilution range 50:1 to 100:1 using nitric acid as the sample and pH as the measure of consistency. The diluted samples are measured as they pass through a pH flow cell and the values are recorded on a Brown strip chart recorder having a full scale range of 2 to 4 pH units. The data obtained show that the unit is consistent within ± 0.02 pH units. Random portions of the diluted samples were also titrated with standard base, results of comparable consistency were obtained.

A reliable dilution system will have many applications in the in-line instrument program since it will make it possible to extend the applicable range of such instruments as pH, polarograph and alpha monitors.

Plutonium Valence. Preliminary experiments conducted using synthetic Purex 1BP solution indicate that a direct potentiometric measurement using a noble metal electrode may be indicative of the plutonium valence state. Over the range 100 to 25 per cent ferrous iron the potential increases about 250 millivolts and plutonium remains in the plus three valence state. When the ferrous iron drops below 25 per cent, the potential rises rapidly and the plutonium begins to appear in the plus four valence state. The Process Chemistry Unit is repeating the experiments using Purex Plant solutions. Should equally encouraging results be obtained, a flow cell similar to the pH flow cell will be equipped with a noble metal electrode and a prototype installation will be made in the plant.

Purex Plant Instruments. The pH flow cell installed on the R-2 (20W) sampler has operated satisfactorily and has indicated carbonate depletion in at least two instances. All Purex pH installations are being equipped with flow cells in place of the probe cells originally applied.

In two instances valves have given trouble in the gamma monitor installations. Entrained organic swelled the Hypalon disc in one valve installed on the HC concentrator condensate line and solids have plugged the 1/16-inch port of the drain valve on the L-3 (2BP) monitor. Entrained aqueous gets trapped in the degasser for the 1BXF pump tank sample and causes abnormally high readings when it goes through the sample cell.

To date, a satisfactory sample of 2EU has not been obtained. A new jumper equipped to supply an air lift assist at the intake of the sampler instead of at the top of the tank will be installed as soon as possible.

Mechanical Equipment

Deepwell Turbine Pump. The wear rings were removed from the P-19-7 pump used to test bearings in 60 per cent nitric acid. Operation of the unit disclosed that axial impeller adjustment can effect the pumping characteristics more than elimination of the wear rings. For example, the discharge head ranges from 65 to 95 feet of water at 25 gallons per minute capacity with wear rings installed. With the wear rings removed the discharge head was 62 feet of water at 25 gallons per minute capacity. Corresponding results were obtained at other flow rates.

Piston-Bellows Pulse Unit. The Teflon bellows installed on the Hot Semiworks HC Column pulse generator failed after 2.75 x 10^6 cycles. The leakage past the piston was estimated before shutdown to be 70 ml./min., however, leakage rates measured using water during decontamination flushing did not exceed 30 ml./min.

The prototype unit operated in 321 Building pulsing a demonstration unit extraction column was taken out of service after 10 x 10^6 cycles. Average diametral clearance at removal was 3 mils, compared to 1.5 mils when installed. The cylinder bore and piston surface were polished but no unusual wear pattern was apparent.

Acid Fractionator. A titanium bayonet heat exchanger has accumulated over 500 hours operation in boiling nitric acid. The exchanger was used to boil 60 per cent nitric acid spiked with 10 ppm chloride ion for 270 hours and to boil 30 per cent nitric acid spiked with 10 ppm chloride ion for 248 hr. No detectable weight loss has occurred to date.

Corrosion coupons of 304L, 347, and 312 stainless steel and coupons of titanium were suspended in the liquid and vapor above each plate in the fractionator and in the vapor above the reboiler. Evaluation of the corrosion rates on these samples will be made by the Corrosion and Welding Unit, Pile Technology Section.

Liquid samples taken above each plate during steady state operation were analyzed for nitric acid and chloride ion concentration. Maximum chloride ion concentration was observed near the bottom of the fractionating column where the nitric acid concentration was 20 per cent.

Gasket Development. A sample of Vyflex-L-10 installed between two flanges with the bolts tightened to 25 foot pounds torque cold flowed allowing the bolts to become finger tight. The sample was maintained at 120°C. during the time the flow took place.

CHEMICAL RESEARCH SUB-SECTION, W. H. REAS

PUREX

Versene for Solvent Clean-Up

The results of 1A Mini runs summarized in Table I show that incorporation of Versene in the sodium carbonate solvent wash solution does not improve the decontamination performance of Purex Plant IOO. Significantly better decontamination performance was noted when fresh solvent was substituted for Purex IOO. There is a possibility that the equipment used in this run may have been contaminated with Versene-containing solutions employed in earlier Mini runs, however.

It is planned to repeat the run comparing decontamination performance of Purex IOO and fresh solvent with new equipment.

TABLE I

EFFECT OF VERSENE WASHING ON DECONTAMINATION PERFORMANCE OF PUREX IOO IN 1A MINI RUNS

Solvent	Solvent Treatment	M Versene in 1AF	Zr-Nb Decontamination Factors 1AF/Fd. Plt.	1AF/1AP	1AF/1CU
Plant IOO	A	0	10	26	60
Plant IOO	B	0	6	20	130
Plant IOO	A	0.0013	48	50	190
R-1-A(1)		0	>1000(2)	>1000	>1000
R-1-A		0.0013	>1000	>1000	240(3)

Solvent Treatment

A--Two batch washes with 5 percent Na_2CO_3 - 0.01 M Versene followed by one batch wash with 3 M HNO_3, 0.07 M Versenol. All washes 1/2 hour at 50 C.

B--One batch wash with 5 percent Na_2CO_3 for 1/2 hour at 50 C.

Flowsheet

Plant 1AF: 1.6 M U, 0.73 M HNO_3; Flow:100
1AS: 1.5 M HNO_3; Flow: 67
1AX: 30 percent TBP; Flow:430

(1) Plant make-up solvent
(2) Minimum value based on gamma spectrometer detection limit of 5 percent of total gamma.
(3) Steady state presumably not yet reached.

Effect of Versene on Partition Equilibria for Zirconium

A number of batch distribution measurements were made in an attempt to determine the mechanism by which Versene and Versenol suppress extraction of zirconium out of high acid Purex systems. Zirconium tracer prepared by TTA extraction of Purex dissolver solution was employed in these experiments. The detailed data are presented in Table II. Highlights of the findings to date are as follows:

1. Concentrations of Versene as low as 7×10^{-5} molar sufficed to reduce the distribution coefficient for zirconium by a factor of twenty-eight. Increasing the Versene concentration above this level by a factor of eighty resulted in only a two-fold decrease in the zirconium distribution coefficient. A similar effect was noted with Versenol; concentrations of 8.0×10^{-3} and 7.7×10^{-2} molar Versenol being about equally effective in reducing the extractability of zirconium.

2. Versene is not effective in suppressing the extraction of zirconium at acidities in excess of four molar nitric acid.

3. Versene at a concentration of 3×10^{-4} molar does not significantly alter the extraction coefficient for plutonium.

4. Increasing the temperature from room temperature to 50 C does not produce a significant change in the distribution coefficient for either zirconium-niobium or plutonium in the presence of 3×10^{-4} molar Versene. Thus, the beneficial effect observed on increasing the temperature in earlier Mini runs employing Versene (cf. HW-42219 H, P. Fc-42) must be ascribed to improved scrubbing kinetics.

Further work will be necessary to elucidate the mechanism by which Versene represses the extraction of zirconium. About the only conclusion that can be drawn at present is that the data are not consistent with any simple chelation mechanism.

Diffusion of Zirconium in TBP Solvent Systems

Diffusivities for radiozirconium in TBP solvent systems are summarized in Table III. The zirconium tracer employed for these experiments was prepared from Purex dissolver solution by TTA extraction. As will be noted from the data of Table III, the variation in the diffusivity of zirconium in TBP-hydrocarbon solvents with nitric acid concentration, with uranium concentration, and with hydrocarbon diluent can to a large extent be accounted for by the concurrent variation in viscosity of the system. This is not the case when carbon tetrachloride is employed as the diluent, however. It appears that a totally different diffusion mechanism must be responsible for the much more rapid diffusion observed for zirconium in this system.

TABLE II

EFFECT OF VERSENE ON EXTRACTION OF ZIRCONIUM INTO 30 PERCENT TBP

A: EFFECT OF CONCENTRATION OF VERSENE OR VERSENOL
(2 M HNO_3 in Aqueous Before Equilibration)

M Versene	E_a^o (Zr)	M Versenol	E_a^o (Zr)
0	0.013	0	0.011
3.5×10^{-5}	0.011	8.0×10^{-4}	0.0047
7×10^{-5}	0.00046	8.0×10^{-3}	0.0010
7×10^{-4}	0.00020	3.2×10^{-2}	0.0020
5.6×10^{-3}	0.00025	7.7×10^{-2}	0.0017

B. EFFECT OF AQUEOUS PHASE ACIDITY

M HNO_3 in Aqueous	E_a^o (Zr)	
	No Versene	7×10^{-5} M Versene
0.88	0.0046	0.0008
1.67	0.039	0.0005
2.67	0.166	0.0046
4.1	0.630	0.320
7.5	3.9	3.1
9.3	8.6	5.9

C: EFFECT OF TEMPERATURE
(2 M HNO_3 in Aqueous After Equilibration)

Temp.	M Versene	E_a^o (Pu)	E_a^o (gross gamma)(1)
Room	0	4.3	0.012
50 C	0	4.4	0.014
Room	3×10^{-4}	4.0	0.0022
50 C	3×10^{-4}	3.9	0.0026

(1) Ninety-five percent of gamma activity was zirconium-niobium.

[redacted]

TABLE III

DIFFUSIVITIES FOR ZIRCONIUM IN TBP SOLVENT SYSTEMS

A. VARIATION WITH HNO_3 CONCENTRATION IN 30 PERCENT TBP-SOLTROL
(No uranium present)

g/l HNO_3	$D \times 10^7$ (cm^2/sec)	$D\eta \times 10^6$ (Dynes)
3.0	ca. 10	0.022
6.3	12	0.027
18.3	12	0.028
43.4	12,16	0.028,0.038

B. VARIATION WITH U CONCENTRATION IN 30 PERCENT TBP-SOLTROL (12 g/l in all cases)

g/l U	g/l HNO_3	$D \times 10^7$ (cm^2/sec)	$D\eta \times 10^6$ (Dynes)
11.4	--	11	0.027
23.1	12	12	0.031
33.6	--	7.5	0.022
47.9	12	9.7	0.029
56.2	--	6.5	0.021

C. VARIATION WITH DILUENT (30 Percent TBP)
(43 g/l HNO_3, No U)

Diluent	$D \times 10^7$ (cm^2/sec)	$D\eta \times 10^6$ (Dynes)
Amsco 125 - 90W	20	0.033
Shell E-2342	18	0.035
Soltrol 170	ca. 10	0.022
CCl_4	4900	6.2 (!)

DECLASSIFIED

Measurement of the activation energy for the diffusion of zirconium in both hydrocarbon diluent and carbon tetrachloride diluent systems is contemplated as well as measurement of zirconium diffusivities in hydrocarbon diluent systems containing higher concentrations of uranium.

Profile Pulse Column Studies

A one-inch diameter "profile" pulse column has been constructed for use in studying the kinetics of transfer of fission products in the Purex system. A description of this unit as it has been used to date is shown in Table IV.

TABLE IV

DESCRIPTION OF PROFILE PULSE COLUMN

Extraction Section:	Packed height 4 ft, 48 sieve plates
Scrub Section:	Packed height 4.5 ft, 50 sieve plates
Cartridge:	Stainless sieve plates, 0.05 in holes, 30 percent free area, 1 inch spacing
Sampler Locations:	21, 28, 35, 40, 45, 48, 53, 58, 65, 76, 85, and 98 plates above bottom of cartridge

Nine runs were made with this unit during the report month. Feed for these runs was prepared by spiking synthetic feed with zirconium tracer prepared by TTA extraction of Purex dissolver solution. The flowsheet employed in these runs was essentially the HW #3 1A column flowsheet, but with an increased solvent flow, such that the uranium saturation of the organic product was only about 65 percent.

The decontamination data obtained in these runs are summarized in Table V. It will be noted that all conditions employed to date have resulted in consistently poor zirconium decontamination (arithmetic factors of 11 to 14). This column proved operable as a dual-purpose extraction scrub column only over a rather narrow range of pulse frequency, but it should be noted that the region covered in these studies ranged from partial mixer-settler operation in the scrub section to the cyclic flooding threshold.

A plot of the logarithm of the zirconium concentration in the organic phase versus the number of sieve plates traversed by the organic is approximately linear through the first 40 to 45 plates of the extraction section. The peak organic zirconium concentration occurs at the point where the uranium concentration in the organic is about 20 grams per liter, about 3 to 8 sieve plates below the feed introduction point. The zirconium profile is approximately linear also over the top thirty to forty sieve plates of the scrub section.

The rate at which zirconium is extracted in the dilute uranium region proved to be relatively insensitive to pulse frequency. The slope of the organic zirconium profile in this region increased by a factor of only 1.3 as the frequency was increased from 40 to 160 cycles per minute. The peak organic zirconium activity increased by a factor of about two as the frequency was increased from 60 to 160 cycles per minute.

TABLE V

PROFILE COLUMN DECONTAMINATION DATA

	Run Conditions$^{(a)}$				Zr Decontamination Factors		
	Vol. Velocity (gal/hr, ft^2)						
Run No.	Ext'n	Scrub	Frequency (cycles/min)	U Loss %	AF to Max. Organic Zr Concen.	AF to Fd. Pt.	AF to AP
			Dual Purpose Column				
640	420	350	40	0.078	2.8	3.6	11
660	420	350	60	0.031	2.5	3.3	12
760	210	170	60	0.023	2.4	4.0	14
780	210	170	80	0.010	1.7	2.2	14
			Extraction Section Only				
960	420	--	60	0.018	2.2	2.5	
9160	420	--	160	0.0014	1.1	1.6	
8140	210	--	140	0.0083	1.2	1.9	
8160	210	--	160	0.0038	1.0	1.6	
	420$^{(b)}$	--	85	--	1.3	1.8	

(a) Pulse amplitude 0.5 in. in all runs.
(b) Entire column operated as extraction section.

The rate of uranium extraction appears to be somewhat more sensitive to pulse frequency. A plot of the logarithm of the organic uranium concentration versus number of sieve plates traversed by the organic is approximately linear throughout the entire extraction section, and the slope of this profile increased by a factor of about 2.5 as the frequency was increased from 40 to 160 cycles per minute.

The rate of zirconium scrubbing increased slightly as the pulse frequency was increased in this unidiameter column. The slope of the linear portion of the organic zirconium scrub profile increased by a factor of about two as the frequency was increased from 40 cycles per minute (at a scrub volume velocity of 340 gal/hr, ft^2) to 80 cycles per minute (at a volume velocity of 170 gal/hr, ft^2). The former condition resulted in "mixer settler" operation through about half the scrub section while the latter condition gave intermittent cyclic flooding in the scrub section.

The zirconium scrub profile showed no inclination to level off in any of the runs made to date, indicating that the zirconium in the organic product is still "scrubable". This point has not yet been checked experimentally, however.

The 48 plate extraction section used in these runs apparently represented about two theoretical extraction stages for uranium at the least efficient condition and about three stages at the most efficient condition employed.

Plans for the immediate future involve application of this column to testing of the decontamination behavior of the mixed fluorothene-stainless scrub cartridge which has been shown by the Chemical Development Sub-Section to be superior for decontamination from chloride ion. Purex plant 2DF will be used as feed for these studies.

Fate of Activity in Purex IOO

In an effort to ascertain the extent to which "bound" activity in Purex solvent is harmful to decontamination, experiments were performed to determine the path of such bound activity when the solvent is recycled. The solvents used in these studies were Purex Plant IOO as received, after a batch carbonate wash, and after a batch wash with a carbonate-Versene solution. Both washes resulted in reduction of the solvent activity level by about 25 percent. These solvents were employed in batch cycles consisting of the following steps:

1. A batch extraction in which 2.5 ml of synthetic (cold) feed was contacted with 5 ml of solvent.
2. A batch scrub in which the organic product from 1. was contacted with 2 ml of synthetic (cold) scrub solution.
3. A batch strip in which the organic product from 2. was contacted with 20 ml of water.

The data obtained are summarized in Table VI. Unfortunately, the results must be interpreted in the light of an apparent analytical uncertainty by a factor of two, so their meaning is somewhat obscure. Certainly any benefits derived from the solvent washing procedures employed were at most minor.

Heterogeneity in the solvent feed samples may account for the poor material balances observed in these experiments, and this possibility will be taken into account in any further work along these lines.

Extraction Rate Studies

An apparatus is currently under construction which will permit measurement of rates of transfer of pertinent species between agitated liquid phases and across interfaces of controlled area. It is hoped that such data, together

TABLE VI

DISTRIBUTION OF GAMMA ACTIVITY ON RE-USE OF PUREX PLANT IOO

Solvent	Solution	Percent of Initial Solvent Gamma Activity in Indicated Solution
Purex IOO (As received)	Initial Solvent	100
	Aqueous from Extraction Step	38
	Aqueous from Scrub Step	13
	Aqueous from Strip Step	19
	Final Solvent	60
		130 (Mat'l Bal.)
Purex IOO (Carbonate-Washed)	Initial Solvent	
	Aqueous from Extraction Step	45
	Aqueous from Scrub Step	12
	Aqueous from Strip Step	67
	Final Solvent	71
		195 (Mat'l Bal.)
Purex IOO (Washed with carbonate and Versene)	Initial	
	Aqueous from Extraction Step	47
	Aqueous from Scrub Step	21
	Aqueous from Strip Step	40
	Final Solvent	64
		172 (Mat'l Bal.)

with data presently available and to be obtained from profile pulse column studies and diffusivities in static systems, will provide a basis for prediction of HTU's for species of interest in contacting equipment of varied design.

In preparation for this study, previously published data for the rates of extraction of uranium and nitric acid into TBP solvent systems have been recently reviewed. These data have been supplemented by recent measurements of rates of transfer in systems employing carbon tetrachloride and dibutyl cellosolve as TBP diluents and by measurements of rates of stripping from TBP - hydrocarbon solvents.

The available data, the bulk of which has been previously reported in Chemical Research Quarterly Reports for 1953, can be conveniently correlated on the assumption of the first order rate law

$$\frac{d\ Co}{dt} = k_1\ (C_{AI} - C_o) - k_2\ C_o$$

where C_o is the concentration of the transferring species in the organic phase, C_{AI} is the initial aqueous concentration of the transferring species and k_1 and k_2 are the rate "constants" for, respectively, the forward reaction (extraction) and the reverse reaction (stripping). On the further assumption that the same rate "constants" are valid at equilibrium the constants for the forward and reverse reactions can be related by the expression

$$\frac{k_1}{k_2} = \frac{C_o\ (eq)}{(C_{AI} - C_o\ (eq))} = E_a^o$$

which is applicable for the equal-volume contactings employed for these measurements.

Recognizing that the rate "constants" k_1 and k_2 include the interfacial area, which is known to vary with time in the pulsed-plate contactor employed for these studies, the fact that the experimental data can be fitted to this expression must be regarded as fortuitous. Apparently, the variation of interfacial area with time is compensated by other time-dependent factors. Although such a treatment of the data is hardly rigorous, it proves convenient in that transfer rates in different systems can be compared on the basis of the single parameters k_1 and k_2.

Treatment of the data in this fashion leads to the following conclusions.

1. For extraction of uranyl nitrate or nitric acid, k_1 is proportional to the initial TBP concentration in the organic phase.

2. The value of k_1 for extraction of uranyl nitrate is about 50 percent higher in systems salted with nitric acid, sodium nitrate, or aluminum nitrate than in systems containing only uranyl nitrate.

3. The value of k_1 for extraction of uranyl nitrate is about three times that for extraction of nitric acid. However, in simultaneous extraction of both uranyl nitrate and nitric acid the value of k_1 for nitric acid is greater than that for uranyl nitrate.

4. Increasing the temperature from 25 C to 50 C approximately doubles the value of k_1 for uranyl nitrate, indicating an activation energy of 4 kilocalories per mole for this process.

5. Substituting organic-continuous mixing for aqueous-continuous mixing increases k_1 for uranyl nitrate by about 50 percent.

6. A concentration of 50 to 100 parts per million of a hydrophilic surfactant depresses k_1 for uranyl nitrate by a factor of about six.

7. Decreasing the viscosity of the organic phase increases k_1 but by a lesser amount than would be predicted on the basis of the change in bulk phase diffusivities.

8. Use of carbon tetrachloride as the TBP diluent instead of AMSCO-125-90W increased the value of k_1 for uranium by only 5 to 10 percent. The value of k_1 is the same with dibutyl cellosolve diluent as with AMSCO 125-90W.

9. The value of k_2 for stripping of uranyl nitrate from an organic phase initially 0.4 molar in uranyl nitrate is about four times the value of k_1 for extraction of uranyl nitrate out of an aqueous phase initially 0.4 molar in uranyl nitrate.

Uranium Tail-End Decontamination Studies

Studies comparing the decontamination performance of a commercial zirconium phosphate cation exchanger and silica gel were extended to high temperature operation. Employing a synthetic 2EU concentrate solution prepared by spiking plant 1AF activity into a cold solution of the composition of 2EU concentrate, it was found that operation at temperatures of 85 to 95 C improved decontamination with the zirconium phosphate exchanger. The gross gamma decontamination was 6.7 through 130 column volumes at 85 to 95 C versus 1.8 through 100 column volumes at 25 C. Runs at 70 C indicated better decontamination on silica gel than on the zirconium phosphate exchanger, however. Through 60 column volumes gross gamma decontamination factors were 5.2 for silica gel versus only 2.7 for the zirconium phosphate exchanger. The flow rate through the silica gel column was some 30 percent lower than through the zirconium phosphate exchanger.

Additional studies were also made employing the tannin-niobium complex. Scavenging experiments employing the pre-formed tannin-niobium complex yielded gross gamma decontamination factors of 6 to 9 for amounts of niobium equivalent to 1.2 to 6 pounds niobium per ton of uranium. A scavenging experiment employing the co-formed reagent yielded a gross gamma decontamination factor of 5.5 with only 0.03 pounds niobium per ton of uranium. Co-forming the reagent in the presence of oxalic acid as a complexant for niobium resulted in a niobium decontamination factor of 16 with 0.3 pounds niobium per ton of uranium. Preferential removal of niobium is evident from the fact that the gross gamma decontamination factor was only 7.4.

No successful method has yet been contrived for preparing this reagent in a form suitable for use in a fixed bed. Attempts to incorporate tannin in silica gel failed; dehydration of the tannin-silicic acid complex resulted in a simple dispersion of tannin in silica gel from which the tannin was easily removed by washing with water.

Surprisingly, however, tannin proved to be strongly adsorbed on the aforementioned zirconium cation exchanger and the decontamination performance of this exchanger was thereby improved. Employing the tannin-containing zirconium phosphate exchanger in conjunction with a synthetic acid-deficient feed at 25 C, a gross gamma decontamination factor of 3.1 was obtained through fifty column volumes versus a factor of only 1.1 with the untreated exchanger.

This line of investigation will be pursued further when more appropriate feeds are available.

Solvent Recovery Studies

Preliminary studies have been made of the decontamination of solvent by contact with alkaline permanganate, a treatment suggested by R. F. Maness and successfully applied in the Hot Semi-Works. It has been found that such treatment is effective in removing both the gamma activity and at least certain of the solvent degradation products. It has further been found that permanganate is not essential, the mechanism for removal of both the fission products and the solvent degradation products being apparently adsorption on hydrous oxides of manganese. Contacting Purex plant IO0 with preformed hydrous oxides of manganese prepared by two methods resulted in effective decontamination from both fission products and solvent degradation products.

Removal of solvent degradation products is effective only at low temperature, no decontamination from these materials being observed at 60 C or higher temperatures. However, no colored products result from contact of 0.1 molar potassium permanganate in 3 percent sodium carbonate with "CP" solvent for one-half hour at 70 C.

Adsorption on alumina has also been studied as a means for decontaminating solvent. In the initial experiment, employing Purex IO0 at 25 C, 10 column volumes were obtained before break-through of solvent degradation products and 27 column volumes before break-through of gamma activity. The average gamma decontamination factor was 4.7.

[redacted]

On the assumption that water present in the solvent was displacing solvent degradation products off the alumina column, a 4.0 cm x 1.0 cm silica gel column was employed upstream of the 7.5 cm x 1.0 cm alumina column in subsequent experiments. Using this arrangement at 25 C with Purex 100, about 16 alumina column volumes were obtained before break-through of solvent degradation products and about 35 column volumes before break-through of gamma activity. There was no evidence of adsorption of the colored solvent degradation products on the silica gel. An average gamma decontamination factor of 6.9 was obtained with this dual column. It is of interest to note that the average gamma decontamination factor was 8.6 prior to break-through of solvent degradation products and 4 after this break-through. Washing the column with methanol removed the bulk of the colored solvent degradation products but very little of the gamma activity.

Increasing the column temperature to 66 C gave no improvement in removal of solvent degradation products but did increase the capacity of the column for gamma activity. At this temperature with Purex 100, break-through of solvent degradation products occurred at 16 column volumes, as before, but 47 column volumes were obtained before break-through of gamma activity. The average gamma decontamination factor was 9.5 prior to break-through of solvent degradation products and 5.5 thereafter.

Washing the column with methanol removed only about 3 percent of the adsorbed gamma activity but removed all but traces of the colored organic materials. Washing with 5 percent oxalic acid solution removed only about 11 percent of the gamma activity. Acetic acid removed no detectable amount of activity. Washing with 20 percent hydrochloric acid removed virtually all the gamma activity (presumably through partial dissolution of the alumina column).

It is evident that the major problem in the use of such a column would be regeneration, and further studies will be concentrated on this point.

Stannous Oxide Head-End Studies

The decontamination on solvent extraction following head-end scavenging with stannous oxide has been explored in batch extraction scrub experiments employing in one case Purex plant dissolver solution diluted to 15 percent activity level with cold feed and in the other case with full-level Purex plant dissolver solution. The only data yet available are those from the experiments employing 15 percent level feeds and are summarized in Table VII.

A net improvement in zirconium-niobium decontamination by a factor of about 100 is apparent, this improvement stemming largely from removal of niobium which limited decontamination in the control run. Although zirconium was scavenged efficiently, with decontamination factors of 120 to 250, the net improvement in zirconium decontamination through solvent extraction was only a factor of about ten. The fragmentary data thus far available on the full-level experiments indicate

TABLE VII

DECONTAMINATION ON SOLVENT EXTRACTION FOLLOWING HEAD-END SCAVENGING WITH STANNOUS OXIDE

	Head-End Treatment[a]		Decontamination Factors Through Designated Step							
			Head-End		Extraction		1st Scrub		2nd Scrub	
Expt.	M U	M HNO_3	Zr-Nb	Ru	Zr-Nb	Ru	Zr-Nb	Ru	Zr-Nb	Ru
42-B	Untreated Control		--	--	180	90	940	550	1500	700
42-A	2.09	1.05	>80	1.1	>9000	41	1.7×10^4	170	$>1 \times 10^5$	330
42-C	2.21	0.62	>75	1.2	$>1 \times 10^4$	56	2.6×10^4	260	$>1 \times 10^5$	500
42-D	2.12	0.15	130	1.1	$>1 \times 10^4$	53	$>7 \times 10^4$	240	2.7×10^5	600

Individual Fission Product Decontamination Factors

	Zr	Nb	Zr	Nb	Zr	Nb
42-B	--	--	83	330	4300	890
42-A	230	280	5200	--	3.3×10^4	--
42-C	250	1500	2.3×10^4	--	4.7×10^4	--
42-D	120	1000	1.8×10^4	--	3.8×10^4	--

similar behavior for zirconium in these experiments. No information is as yet available on niobium behavior in the full-level experiment.

Additional tracer-level experiments have been performed to further define the effect of variables on removal or zirconium-niobium by scavenging with stannous oxide. These experiments, which employed Hot Semi-Works dissolver solution diluted to 0.1 percent full level, showed imperceptible (i.e., less than 5 percent) carrying of ruthenium-rhodium, cesium-barium, or cerium-praseodymium. It was also found that room temperature digestion gave much less efficient carrying of zirconium-niobium (decontamination factors of 5 at 25 C versus factors in excess of 100 at approximately 100 C). Uranium concentrations up to 1.65 molar and nitric acid concentrations up to one molar did not appear to be detrimental for carrying of zirconium-niobium. Higher concentrations gave somewhat poorer decontamination. Removal of niobium was observed to be more efficient than removal of zirconium.

Analytical data are not yet complete on experiments designed to evaluate the effect of time of digestion and quantity of stannous oxide, but the indication is that stannous oxide concentrations significantly lower than the values of 0.05 to 0.1 molar employed to date may be adequate. A zirconium-niobium decontamination factor in excess of 100 was obtained with only 0.01 molar stannous oxide.

Tracer-level experiments were also performed to compare the behavior of a technical grade stannous oxide marketed by the Metals and Thermit Company (New York) with the "CP" grade material (Marketed by the J. T. Baker Chemical Co.) which has been used in all the laboratory studies. The technical grade material proved readily soluble in dilute nitric or hydrochloric acid and in uranyl nitrate - nitric acid solutions, behavior in marked contrast with that exhibited by the "CP" material. Dissolution of this material in a synthetic, tracer-level feed, followed by digestion at elevated temperature resulted in precipitation of a voluminous, difficultly centrifuged solid (presumably meta-stannic acid) and poor removal of zirconium-niobium.

Comparison of the x-ray diffraction patterns and surface areas of these two materials gave no clue as to the reason for the different behavior observed with these two materials. The x-ray diffraction patterns were essentially identical, except for lines suggesting a trace of stannic oxide in the "CP" stannous oxide. The technical grade material, which exhibited a rapid rate of dissolution in mineral acids, has a much lower specific surface area than the "CP" material (0.3 square meters per gram versus 8.5 square meters per gram). It is suspected that the different behavior exhibited by these two materials stems from different heat treatments employed in manufacture, and this possibility is currently being examined.

Additional studies have also been made of the carrying of plutonium on stannous oxide. It was found that plutonium(VI) is not carried to any substantial extent. Digestion of 0.05 molar stannous oxide in 1.47 molar uranyl nitrate, 1 molar nitric acid containing plutonium(VI) prepared by preoxidation with dichromate resulted in carrying of only 0.07 percent of the plutonium, as compared with values of 1.6 to 3.5 percent found in earlier experiments employing plutonium(IV).

Experiments employing ferrous sulfamate indicate that possibly plutonium carrying could be reduced by maintaining the plutonium as plutonium(III) during the scavenging. Digestion of a plutonium-containing solution 1.5 molar in uranyl nitrate, one molar in nitric acid, and initially 0.1 molar in ferrous sulfamate for one hour in contact with 0.05 molar stannous oxide resulted in carrying of only about 0.38 percent of the plutonium. The concentration of ferrous ion and the plutonium valence state in this solution after the one-hour digestion are not known, but the extent of plutonium carrying observed was lower by a factor of 5 to 10 than has normally been observed with plutonium(IV).

Further work along these lines will concentrate on evaluating the effect of stannous oxide concentration on the carrying of plutonium(IV) and on methods for maintaining plutonium(III) under the high temperature conditions conducive to good zirconium-niobium scavenging.

Suppression of Chloride Evolution in Acid Recovery

The study of the effect of mercuric ion in suppressing the volatilization of chloride in the acid recovery operation has been completed. The results obtained are summarized in Table VIII. The quantity K_{Cl} in this table is the partition coefficient for chloride between vapor and liquid (g/l chloride in distillate divided by g/l chloride in still bottoms). The quantity R is the factor by which K_{Cl} is decreased by mercury.

These data indicate that chloride volatilization is effectively prevented by as little as a one to one mole ratio of mercury(II) to chloride, and that the efficiency with which chloride ion is complexed by mercury(II) decreases only slightly as the concentration level is reduced. It is of interest to note that the efficiency of complexing is increased by increasing the acidity.

Preliminary data indicate that mercury(II) is also effective in reducing the corrosion rate of type 304L stainless steel in the presence of chloride. Corrosion rates in the presence of mercury(II) and chloride were essentially identical with those in the presence of nitric acid alone.

NEW PROCESSES

HNO_3 - H_2O - HF Liquid-Vapor Equilibria

Liquid-vapor equilibrium data for this system at atmospheric pressure have been previously reported. The equilibria at a pressure of 100 mm Hg are currently being measured. Under these conditions the volatility of trace fluoride from boiling nitric acid appears to be almost identical with that previously observed at atmospheric pressure. This is in marked contrast with the behavior observed for both chloride and nitric acid. In both of these cases the partition constants were lower at lower pressure. The volatility of fluoride is, therefore, greater than that of nitric acid at both atmospheric pressure and at 100 mm Hg, but by a greater margin at 100 mm Hg.

URANIUM PROCESSING

Uranium Reduction

A further test of the reduction of uranium dioxide with lithium metal resulted in a mixture of unreacted lithium and powdered uranium metal; the reaction mixture appeared free of lithium oxide and uranium oxides. As a result of this experiment, it was decided to pursue the following two courses: (1) continuation of lithium reduction experiments in an apparatus designed to give quantitative rate and yield information and, (2) an investigation of the volatility of lithium oxide. Preliminary experiments have verified the volatility of lithium oxide and indicate it to be roughly four times as great at 885 C as at 800 C.

Flurex Process

Experiments were conducted to determine the effect of stannous ion in the catholyte on the current density-current efficiency relationship. With 0.05 molar stannous fluoride in the catholyte, a current density at the cathode of

TABLE VIII

SUPPRESSION OF CHLORIDE VOLATILIZATION BY MERCURY(II)

A. EFFECT OF MERCURY(II) CONCENTRATION AT CONSTANT CHLORIDE CONCENTRATION

Initial Chloride Conc. = 0.034 M (2 g/l NaCl)
Initial HNO_3 Conc. in Pot = 8 M

M Hg(II)	K_{Cl}	R
0	7.3	1
0.0042	4.67	1.6
0.0084	2.65	2.8
0.0174	2.4×10^{-2}	304
0.034	6.3×10^{-3}	1160
0.1	4.4×10^{-3}	1660

B. EFFECT OF CONCENTRATION LEVEL ON DEPRESSION OF CHLORIDE VOLATILITY

Nitric Acid = 8 M
M Hg(II) = M Cl = M

M	K_{Cl}	R
0.17	3.1×10^{-3}	2350
0.034	6.3×10^{-3}	1160
0.017	6.25×10^{-3}	1170
0.0084	6.25×10^{-3}	1170
0.0034	6.7×10^{-3}	1090

C. EFFECT OF NITRIC ACID ON MERCURY(II) COMPLEXING OF CHLORIDE

M Hg(II) = M Cl^- = 0.034 M

M HNO_3 (Pot)	K_{Cl}	K_{Cl}*	R
4.3	4.1×10^{-3}	0.24	59
8.5	6.3×10^{-3}	10	1.6×10^3
11.4	0.0102	120	1.8×10^4
14.9	0.109	$\sim 5 \times 10^3$	4.6×10^4

* In absence of mercury.

1.6 amp/in^2 was obtained without significant hydrogen evolution. In the absence of tin, on the other hand, copious hydrogen evolution is noted at this current density. At current densities of about 3 amp in^2 considerable damage to the C-1 membrane occurred, undoubtedly due to gas formation brought about by power dissipation within the membrane. A probable maximum allowable current density is 1.5 to 1.75 amp/in^2 at room temperature. Tests on different lots of Amberplex C-1 membranes showed them to be identical with respect to conductivity when in the same form.

A 100 hour continuous run is in progress using Purex 2DF as a feed source. The objective of this experiment is to test decontamination, fission product behavior, and operating conditions under prolonged operation.

Chemical Preparation of Uranium(IV) Fluorides

Continued work on the ferrous reduction process has been done to determine the fate of metallic ion and fission product impurities in the process. A uranyl nitrate solution containing copper, chromium, cobalt, nickel, manganese, tin, aluminum, and magnesium (each to the extent of one percent of the uranium) was processed according to the procedure of Run III-3 (HW-42219H, page Fc-51). Copper (10 ppm), tin (150 ppm) and aluminum (120 ppm), only, were found in the initially precipitated salt; after reprecipitation these values were 0.2, 2 and 5 ppm, respectively. The same procedure was used to process uranyl nitrate solution derived from Purex 2DF (the uranium stream after the co-decontamination and partition cycles). The data disclosed a gross gamma decontamination factor of 11 and a gamma ratio of 2.4* for the final product. Since the gamma activity of the starting material was greater than 90 percent zirconium-niobium, this experiment does not represent the behavior of a broad fission product spectrum. An experiment using about one percent dissolver solution was also run, but results are incomplete as yet.

On the basis of data so far obtained, this process is capable of producing sodium uranic fluoride essentially free of the common ionic impurities. It is, also, capable of at least moderate decontamination with respect to fission products.

UO_3 Studies

Collection of further data on the constitution of uranium oxides has been continued with emphasis on electron microscopy, x-ray diffraction and surface area measurements. Useful correlation of these data must wait for rates of reduction and hydrofluorination. These rate studies are imminent as the apparatus is near completion.

A study has been initiated to determine the feasibility of preheating the UNH feed to the continuous calciner and flashing it into the bed. The possible advantages to such a procedure are two fold: (1) the product would be essentially

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* Gamma ratio is the ratio of the gamma activity of the processed uranium to that of aged natural uranium.

flash calcined, possibly amorphous and more reactive, and (2) the rate of production can possibly be increased since introducing heat via the liquid uranyl nitrate is more efficient than through the solid bed.

Preliminary experiments indicate uranyl nitrate trihydrate(?) has a decomposition pressure of 200 psig at 270 C and 600 psig at 290 C. These tests will be continued to determine whether an equilibrium pressure is reached during decomposition.

ISOTOPE SEPARATION

A uranyl nitrate-TBP run in the 0.20 mm column is in its eighth week. The first five weeks were conducted in the normal manner (by displacing sample with the starting material) in order to establish steady-state conditions. Following this period, samples were displaced with tributyl phosphate in order to bring about dilution in the column so that the possible existence of an enhancing effect on the separation (suggested by past runs) can be proved or disproved. To date analytical results for samples taken at 0, 1-1.2 and 7.1 - 7.8 days have been received. Respectively, these samples contain 0.7113, 0.7134 and 0.7176 percent uranium - 235 indicating an improvement in separation over that obtained in the 0.25 mm column.

An attempt was made to prepare uranyl dibutyl phosphate in the absence of nitrate by reacting stoichiometric quantities of UO_3 and dibutyl phosphate. After three days some oxide remained unreacted. The supernate was removed and tested for thermal stability at 127 C. The solution darkened after an hour but no precipitate occurred. This complex is being investigated because of the relatively high (35 percent) uranium content.

Chemical Exchange

A continuation of the studies of the rate of exchange of uranium in the system uranium(IV) - uranium TTA complex shows the half-time to be in the two to four minute range. It was also found that nitrogen blanketing effectively prevented oxidation of the uranium(IV) during a series of contactings.

Aqueous Electromigration

Although complete data on Run 14 reported in HW-42219H are not available, a 0.4 g sample from the cathode end of the column collected during the final five days of operation contained 0.7133 percent uranium-235. A similar sample taken from the anode end two weeks before termination of the run contained 0.7106 percent uranium-235. Complete results are necessary for better evaluation of this experiment.

Fused Salt Electromigration

Mass spectrographic analysis of a sample of UCl_4 from a fused salt electromigration run showed a separation factor of 1.006 for about 10 percent of the charge. The conditions were far from optimum; current density was only 0.7 amp/cm^2 and the operating interval was divided into 10 and 7 hour portions by a 10 hour period of inoperation.

Because of continued difficulty with pyrex and "Vycor" high silica glass, these materials have been abandoned in favor of graphite and zircon porcelain as materials of construction.

Ion Exchange

The ion exchange run reported in HW-39260H using the sharp band technique resulted in a significant separation of plutonium-239 and plutonium-240. Plutonium from the leading edge of the band was enriched in Pu-240 to the extent of about two percent over that from the trailing edge; however, the material analyzed was no more than one percent of the total in the band. This is believed to be the first known separation of plutonium isotopes by the ion exchange technique.

NEW SEPARATIONS

Electromigration

Uranium metal containing added metallic impurities and low level fission product activity has been prepared as starting material for the evaluation of a separation process based on fused salt electromigration (see HW-41782H, p. Fc-49).

Anion Exchange Process

A study has been instituted to assess the usefulness of anion exchange resins in HAPO separations processes. The initial application will be to the plutonium stream, with a concurrent but secondary study aimed at the partition of uranium and plutonium. Batch equilibrium experiments have been designed to determine the anion exchange behavior of uranium and plutonium in sulfate and acetate systems; systems in which these elements exist as anionic species according to transference data.

The following data were derived from experiments in which five grams of resin were equilibrated at room temperature with 25 milliliters of various solutions each containing 0.1 molar uranium. The distribution coefficient (K_D) for uranium between Dowex-1 in the acetate form and aqueous solutions containing 0.1 to 2 molar acetic acid and 0.1 molar nitric acid was relatively constant at 400. The distribution coefficient of uranyl sulfate (0.1 $\underline{M}$) on Dowex-1 in the sulfate form was about 150; however, when the uranyl sulfate solution was made two molar in sodium sulfate, sulfuric acid, nitric acid and sodium perchlorate, respective K_D values of 40, 2.1, 1.5 and 0 were obtained.

RUTHENIUM CHEMISTRY

Homogeneous Carrier Precipitation with Mercuric Sulfide

Scavenging of ruthenium by homogeneously precipitated mercuric sulfide followed by Purex-type extraction-scrub study of the residual ruthenium was reinvestigated in an attempt to explain the poor decontamination behavior observed in a prior precipitation-solvent extraction experiment (HW-41702H, p 54). Mercuric sulfide was precipitated with thioacetamide from two milliliters of full activity level Purex feed and the subsequent solvent extraction ruthenium decontamination determined along with that from an unscavenged control with the following results.

TABLE IX

PRECIPITATION-EXTRACTION BEHAVIOR OF RUTHENIUM

Precipitation Conditions: 1.6 M UNH, 0.2 M HNO_3, 0.04 M sulfamic acid, 0.008 M $Hg(NO_3)_2$, 0.04 M thioacetamide (reagent grade); heated to 105 C for 15 minutes, cooled, centrifuged. Dissolver solution made from HSW-HAF by the addition of UO_3 and water.

Extraction Conditions: Mix organic and aqueous for 5 minutes, centrifuge to separate phases.

Feed: 1.14 M UNH, 2.1 M HNO_3, 0.03 M $NaNO_2$

Extractant: 30 percent TBP-Soltrol, equilibrated with 2 M HNO_3

Scrub: 4.5 M HNO_3

Volume Ratio: F : X : S : : 1:3:1

Operation	Ru Decontamination Factor Relative to U			
	HgS - Treated		Control	
	S*	C*	S	C
Precipitation	36	36	-	-
Extraction	107	3.9×10^3	480	480
1st Scrub	7.4	2.9×10^4	6	2.9×10^3
2nd Scrub	2.1	6.1×10^4	3.6	1.0×10^4
3rd Scrub	1.9	1.1×10^5	2.7	2.8×10^4

* S - step-wise DF; C - cumulative DF

Although somewhat higher than that of the previous precipitation-extraction experiment, the precipitation decontamination factor was substantially lower than those obtained in earlier tracer experiments (ranging from 660 to 2300, cf HW-42219H, p 56). Poor physical separation may have been responsible for the low precipitation decontamination as the precipitate tended to float and stick to the test tube walls. The slight improvement in cumulative decontamination observed with the mercuric sulfide-treated solution as compared to the control appears insufficient to warrant further attention, especially in view of the much more favorable results formerly obtained with copper sulfide precipitation - extraction.

[redacted]

WASTE TREATMENT

Cesium Removal from Purex Waste

Removal of cesium from synthetic neutralized Purex IWW supernate (IWW-NS) by zinc cesium ferrocyanide precipitation has been determined as a function of cesium concentration. The IWW-NS solutions at pH 5 were made equimolar in zinc and ferrocyanide, allowed to stand for one hour, and then centrifuged for 15 minutes.

TABLE X

RECOVERY OF CESIUM BY ZINC CESIUM FERROCYANIDE

IWW-NS Solution: 6 M $NaNO_3$, 0.05 M Na_2SO_4, pH 5

Cesium Concentration, M	Zinc and Ferrocyanide Concentration, M	Cesium Recovery % Obsd.	Specific Activity Curies/g, Calcd.
4×10^{-4}	2.5×10^{-4}	98	16
2×10^{-4}	2.5×10^{-4}	99	12
1×10^{-4}	2.5×10^{-4}	98	7.7
5×10^{-5}	2.5×10^{-4}	93	3.9
4×10^{-4}	3.0×10^{-4}	99	15
2×10^{-4}	1.5×10^{-4}	90	14

As indicated in Table X, cesium recovery is satisfactory in each case, and the specific activity appears suitable for many applications, even though it is somewhat low at low cesium concentrations. The cesium concentration in IWW-NS is, of course, proportional to the goal exposure of the metal from which it is derived, being 1.5×10^{-4} M for 200 MWD/T exposure, for example. Thus, these data indicate that cesium may be recovered adequately, even when processing low exposure metal.

Strontium Removal from Purex Waste

Capacity measurements have been made on those ion exchange resins which gave encouraging preliminary results reported last month. The most promising of these was the zirconium phosphate exchanger, RC-25, produced by Minnesota Mining and Manufacturing Company. Its "ultimate" capacity was determined using both the H - Na and H - Ba cycles, first displacing the hydrogen ion with excess metal ion and then reversing the process. Capacities were found to be 0.97 and 1.58 meq/g for the H - Na and H - Ba cycles, respectively. The discrepancy may be due to failure to attain equilibrium and was not resolved since either value corresponds to approximately 1000 column volume capacity for removing strontium plus barium from Purex IWW-NS.

"Process" capacity was then determined by passing strontium-traced IWW-NS through a column in the H - form. The strontium removal was uniformly poor (ca. 45%) from the outset to the passage of over sixty column volumes of IWW-NS. Much better results were obtained with the column in the Na - form, with an initial strontium recovery of 99.9 percent decreasing to 95 percent after passage of thirty column volumes.

The IWW-NS used in the foregoing tests was prepared by neutralization of synthetic IWW, filtration of hydrous ferric oxide and adjustment to pH 8. To avoid the possibility of solids filtered from the solution affecting the results, a IWW-NS was synthesized with the calculated composition: 5.7 $\underline{M}$ $NaNO_3$, 0.15 $\underline{M}$ Na_2SO_4, 2.8×10^{-4} $\underline{M}$ $Sr\ (NO_3)_2$ and 1.8×10^{-4} $\underline{M}$ $Ba\ (NO_3)_2$. The barium and strontium, corresponding to expected fission product concentrations, appeared to be largely precipitated, presumably as the sulfate. The clear solution was spiked with tracer strontium, and the pH adjusted to 8.4. On passage of this solution through a column in the Na - form, strontium recovery was 99.7, 97, 91, 63 and 45 percent after 10, 16, 21, 100, 170 column volumes, respectively.

The observed precipitation of barium sulfate in the preparation of IWW-NS caused some concern as to whether or not this same precipitation would occur in the plant IWW before neutralization. To check this a synthetic HAW was prepared and evaporated to about 80 percent the volume of IWW, i.e., a concentration factor of approximately 12 instead of the plant value of 8. No precipitate was observed, nor was it in two subsequent preparations of IWW, one of which included all fission products expected to be present at a concentration greater than 5 mg/l except rubidium, molybdenium, technetium, rhodium, palladium, and promethium. Thus, strontium should not be lost in the process steams prior to the IWW by carrying on barium sulfate.

A crude batch experiment with the IWW-NS/RC-25 system indicated periods in excess of thirty minutes were required to approach strontium removal equilibrium. The slow flow rates implied and the conservative capacities described above discouraged further effort on this exchanger at this time.

Another measurement of IRC-50's behavior with IWW-NS at pH 9.2 was made because of the reputed selectivity of this carboxylic acid type resin for divalent ions in the presence of monovalent ions. Strontium recovery ranged from only 41 percent initially down to none after passage of ten column volumes.

Previous experiments had indicated the precipitation of alkaline earth carbonates by a carbonate-form anion exchange resin to be a promising method. Capacity measurements were made on two such systems, (1) Dowex 1 x 2 - carbonate and (2) Dowex 1 x 8 - mixed carbonate and oxalate. With IWW-NS at pH 8 passing through Dowex 1 x 2 - carbonate, 60 percent strontium recovery was obtained for the first three column volumes and about 30 percent for the first sixty column volumes. On passing the same solution through Dowex 1 x 8 - mixed carbonate and oxalate, strontium recovery vacillated between 0 to 70 percent for forty column volumes. In view of these poor strontium removals ion exchange investigations have been halted in favor of another look at precipitation processes (barium carbonate or sulfate carrying) and possibly solvent extraction.

Ruthenium Recovery

A nitric acid leach - TBP solvent extraction procedure has been scouted which shows promise of effecting separation of ruthenium from copper sulfide carrier. Fresh homogeneously precipitated copper sulfide from synthetic dissolver solution containing 10^{-4} M ruthenium plus a radio-ruthenium spike was washed with water and carbon disulfide (to remove any free sulfur) and air-dried. Refluxing of this precipitate with 2 M nitric acid for one hour leached out 84 percent of the ruthenium. Recovery of at least 95 percent should be attainable by more extended and/or vigorous treatment.

Isolation of ruthenium from that copper which also dissolves during the nitric acid reflux may be achieved by solvent extraction into TBP as suggested by British work reported in Geneva Conference Paper 413. Extraction is accomplished from a low acid solution salted with sodium nitrate. The organic phase is then stripped with 6 M nitric acid. This method was given preliminary test with traced $K_4 Ru (NO_2)_6$ and produced over 80 percent ruthenium recovery by simple batch extraction and strip. Experiments are in progress to check whether the ruthenium species obtained by refluxing copper sulfide in 2 M nitric acid will behave similarly.

An unsuccessful attempt was made to leach ruthenium from copper sulfide which had been precipitated from full activity level dissolver solution and then had aged for two months. Leaching of ruthenium from copper sulfide freshly precipitated from full level dissolver solution will be investigated to determine whether the difficulty is due to radiation or to aging.

ANALYTICAL DEVELOPMENT

Coulometric Determination of Plutonium

The studies of coulometric titration techniques for plutonium assay continued using cerate and dichromate standards for a study of the indicator electrode system. The error of dilution mentioned last month was found to be caused by inefficient stirring and failure to attain equilibrium conditions in the cell during the course of the titration. While comparing the reaction of the derivative polarographic and conventional potentiometric electrodes during coulometric titrations in very dilute dichromate solutions (0.001 molar or less), it was found that the reduction reaction is slow, and both electrodes have sluggish response, particularly near the titration endpoint. A deliberate overtitration by a fixed amount (e.g., one percent) appears to be advantageous in increasing precision and avoiding low results due to insufficient reaction times. The derivative polarographic endpoint has been yielding high results and is to be studied further. In similar studies with a cerate standard, the reactions were even more sluggish than with dichromate, but these unexpected results may be due to deterioration (hydrolysis) of the particular cerate solution used.

Uranium Isotopic Analysis

A group of low results for uranium-235 in enriched metal samples was obtained recently using the spectrographic method for uranium-235, uranium -238 ratios. Because of this, a reinvestigation of the methods and techniques being applied was made. It was found that the main difficulty was that the method for making plate background corrections was not applicable to the range of some samples received. It was possible to improve the background correction method and the sample excitation conditions using information obtained in the direct reader study mentioned in the January report.

Uranium Fluorimetry

The use of a sodium fluoride flux containing two percent lithium fluoride for the fluorimetric determination of uranium was recommended in a recent report (from the laboratories of the National Lead Company). In a brief experiment a group of six samples were run using the lithium fluoride flux along with a similar group using pure sodium fluoride. The ignitions were carried out using flame fusion. The mixed flux had a slightly reduced sensitivity, but the precision by both techniques was comparable. The mixed flux doesn't offer any advantage when flame fusion is used. A possibility of considerable advantage exists for fusions by induction heating because of nonsticking and improved optical properties claimed for the lithium-containing flux. A test of this in the service laboratories which use induction heating has been recommended.

Fission Counter

A measurement of the shape of the curve of counting rate versus discriminator bias was made for the gas scintillation fission counter. An americium-241 alpha source was used to minimize the spontaneous fission count contribution at low counting rates. Although the curve is not linear (even on a semi-log plot), extrapolation from high counting rates is sufficiently accurate to obtain a discriminator bias value suitable for fission counting in routine practice.

Additional fission chamber shielding has been necessary to reduce the neutron background effects when counting plutonium spontaneous fissions, and the chambers located nearest the neutron source will need still more shielding. Two of the five fission counters are now ready for final calibration.

Alpha Standard

Two standard alpha discs of americium-241 were received from UCRL for comparison purposes. The results obtained with the 325 Building low geometry standard counter were 0.62 percent and 0.86 percent higher than the UCRL value. A very similar difference has previously been found in this laboratory using plutonium standards. The bias will be investigated further.

TTA - Separations

Extraction efficiency data of TTA in orthodichlorobenzene as a function of pH have been extended to Zr^{+4}, Pu^{+3}, UO_2^{++}, Ce^{+3}, and Am^{+3}. An interference of ferric ion, due to precipitation, in separations of Pu^{+3} and Pu^{+4} in some Purex-type solutions is being studied. Extraction data obtained to date is given in Table XI. At pH values above the 90 percent extraction value the ion in question is essentially completely extracted into the organic phase.

TABLE XI

pH VALUES FOR 10 PERCENT AND 90 PERCENT EXTRACTION OF VARIOUS IONS INTO 0.1 M TTA IN ORTHOCHLOROBENZENE

	pH Value	
Ion	10 Percent Extracted	90 Percent Extracted
Zr^{+4}	<-1.0	-0.9
Pu^{+4}	-0.3	-0.02
Pu^{+3}	0.2	1.5
Th^{+4}	0.1	0.8
UO_2^{++}	1.9	3.0
Y^{+3}	3.1	3.7
Ce^{+3}	3.3	3.9
Am^{+3}	3.7	4.6
Sr^{++}	6.2	>6.5

Radiography with a Thulium Source

In cooperation with Fuel Technology personnel, a brief investigation of the application of thulium-170 sources for the x-ray inspection of welds on aluminum cans was made. In particular, this would be applied to inner welds (e.g., I and E slugs) not easily x-rayed by conventional means.

An 80-curie Tm-170 source (emitting 550 R/hr at 3/4 inch or 4 R/hr at 8 inches) was used for the tests. Good radiographs were obtained on duPont 502 or 506 x-ray film and Polaroid-Land camera film in two to six seconds. The duPont 506 film gave the best resolution. Voids and metallic inclusions of 0.1 to 0.5 millimeter in aluminum welds were well resolved. The useful life of an 80-curie source would be at least 1.5 years allowing up to one minute exposures and the cost of the source is currently about $900.

An americium-241 source was also tested for such radiography, and it was found that adequate source strength is not obtainable for the desired one minute or shorter exposures.

DECLASSIFIED

Electron Microscopy of UO_3

Several variations of the UO_3 replication technique for electron microscopy were tested, but the method outlined last month remains the most satisfactory one. Additional specimens were photographed at 19,000 X magnification. A Mallinckrodt Pot and HAPO Pot powder had identical appearance. All specimens of continuous calcined powder have less well-defined, and much smaller crystals than pot powders. A high temperature batch (P-108; 440 C) lacked crystal appearance but hydration (hot slurry) plus 395 C dehydration of this material caused very significant crystallization.

IN-LINE ANALYSIS

Determination of Plutonium Valence State

In order to avoid improper plutonium distribution in the Purex 2A column, continuous monitoring for the plutonium valence state after 2AF make-up may be needed. Since indirect analysis may be adequate, several possibilities for in-line analysis in the 2AF make-up exist including: 1) monitor for excess nitrite, 2) monitor for ferrous depletion, 3) monitor for sulfamate depletion, and 4) monitor for plutonium(III) depletion.

The most promising method found is to determine the ferrous-ferric ratio by a simple potential measurement. It was found that a 300 millivolt potential difference (platinum or gold electrode) exists between a 6 M nitric acid solution containing a trace of ferrous and one containing ferric but no ferrous. The electrode appears to be very stable. The 300 mv potential change is observed when ferrous ion is titrated with nitrite. An in-line monitor based on the simple potential measurement would be a go no-go device simply indicating the presence or absence of ferrous but giving no measure of the amount of excess nitrite or ferrous. Monitoring the 1BP stream by this method to insure excess ferrous is another likely application.

A nitrite concentration analyzer would be much more desirable because excessive nitrite addition is to be avoided in order to minimize solvent degradation. This type of analyzer may be based on an automatic titration principle in which a reducing agent (ferrous) is added to a measured sample to an endpoint, which is detectable by the above potentiometric method. More simple (mechanically) methods have been investigated. The potential at a dropping mercury electrode was found to be a linear function of nitrite concentration from 0.002 to 0.05 M in a nitric acid solution. Good precision was obtainable up to 0.01 M.

Another technique which looks promising involves separation of the nitrite from the sample by gas sparging (as NO), absorption in a pH cell containing a neutral electrolyte, and relating the pH decrease with the amount of nitrite in the sample. This method requires a knowledge of the volumes of sample and absorbing reagent.

The direct determintion of plutonium valence state by remote methods has not been attempted experimentally. Colorimetry is not sufficiently precise, but solvent extraction followed by an alpha count is possible.

DECLASSIFIED

[redacted]

Liquid Contact Alpha Counting

Alpha sensitive scintillation screens having protective plastic films which are resistant to process solutions (primarily nitric acid and TBP-kerosene solutions) can now be produced at will. The screens, fabricated as outlined last month, have about a 75 percent counting efficiency and about 65 percent modal pulse height compared to a good, commercial GE zinc sulfide screen.

An in-line analysis unit (sample cell and sensing unit) using the liquid contact scintillation alpha screen has been designed, and a prototype for testing purposes is being built. Cost of the sensing unit is about $500. Considerable work remains on the problem of high background due to screen contamination.

Acidity Monitoring

A prototype sensing unit for determining nitric acid and uranium concentrations simultaneously in Purex feed streams (primarily HA and 1A) has been constructed for additional laboratory studies. The uranium concentration is determined colorimetrically, and the acidity is determined conductimetrically with a correction for the uranium contribution. The experimental studies reported in the past two months provided the design basis. The unit appears to give reliable estimates of the two concentrations within ± 5 percent. Sufficient data has been collected to design a controller containing a data analyzer (analog computer) so that both ionic concentrations can be recorded directly.

Laboratory studies indicate that the conductimetric method for nitric acid will apply quite well to the Redox 3BP sample and also to the Redox 3AF if the aluminum nitrate concentration is known to within ± 5 percent.

Gamma Absorptometer

A gamma absorptometer with a Tm-170 source for a Purex plutonium concentrator sample has been completely assembled and calibrated. It will be installed by operations' forces in the near future.

Oxygen Monitor

The electrochemical method for continuous determination of oxygen in pile gas is undergoing a plant test. The research and development results are being issued as subject report HW-42636.

Miscellaneous Instrumentation

A integrating circuit for the multiplier phototube output of the direct reading spectrograph attachment has been designed, and a prototype is being made.

A resistance heater with the elements bonded to glass by means of the printed circuit technique has been developed, and several heaters are being used on small laboratory apparatus. The advantages are compactness, excellent thermal conductivity, convenience in using magnetic stirrers and in seeing the vessel contents during heating.

The radiation monitor alarm for the Cobalt-60 source was redesigned to increase speed of response and sensitivity.

LABORATORY SERVICES

Laboratory Services activities may be summarized as follows: 150,000 gallons of crib-level waste was transported to 200 West Area for disposal. Average plutonium analysis was 2.0 x 10^{-4} uc/ml. Average gross beta analysis was 5.4 x 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 x 10-7 uc/ml. Average beta analysis was less than 8.0 x 10-7 uc/ml.

Decontamination personnel made seven trips to the 300 North Burial Ground with hot waste from the 327 Building. Readings on the "Gunk Catcher" were approximately 5 rads plus 5 r at a distance of six feet. Four barrels, containing hot waste, were concreted and hauled to the 300 North Burial Ground. Cement fill was added to the burial pipes to reduce the field readings.

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

CONTACT ENGINEERING UNIT - R. E. TOMLINSON

Operations proceeded routinely throughout the month.

TECHNICAL SHOPS UNIT - L. J. LUCAS

Mechanical Shops

The work backlog remained at the 10,000 hour level which is near optimum for this shop. Terminations and transfers resulted in the craft personnel complement being one below the desired number. The annual physical inventory of material in caption 5930 was completed and a dollar value established which was 44% in excess of the book value for the material. This profit will be returned to the customers by temporarily eliminating the 20% service charge.

Buildings and Grounds

IR-200, Graphite Machining Facilities. Bids for construction were opened on April 17. Frank H. Lohse was low bidder at $12,655. A.E.C. fair cost estimate was $15,500.

ER-3133, Alterations of 325 and 326 Buildings. The project proposal is being routed for GE approval.

WO-A-15613 (CC-8826) Construction of Cylinder Loading and Storage Dock. No work was done during this month because of the strike against J. A. Jones Co.

Technical Shops Safe Procedures Forum - Paints and Protective Coatings. Arrangements are being made with the General Electric Company Plant at Anaheim, Calif. to obtain the services of J. Albert Seneker who is recommended as an expert in the painting and coatings field. Mr. Seneker will appear on the safety forum and will also be available to assist with other H.A.P.O. problems in this field.

Drafting and Design

To supplement the regular drafting crew, four persons were secured on loan, two from the Graphics Unit and two from the Design Section. The work load continued heavy, the regular work being augmented by the charts and graphs utilized to present the research and development picture to visiting officials.

Glass Shop

A light work load prevailed throughout the month with no overtime work required. Routine laboratory glassware made up the bulk of the work with one complex reaction vessel being fabricated for the Plant Processes Sub-Section.

Photo Laboratory

An increase in service requests has resulted in a 10 day backlog for this facility. The increase was attributed to the number of illustrations required in conjunction with plant visits by G.E. and A.E.C. management officials and the Metallurgy Conference held in Ames, Iowa.

ANALYTICAL LABORATORIES UNIT - E. W. CHRISTOPHERSON

General Chemical Laboratory

Recent backlog was eliminated by month end. Chemical Development and Chemical Research support represented 70% and 20% of the load.

National Lead suggests a 2% LiF - 98% NaF flux for flurimetric uranium determination (The Flurimetric Determination of Uranium. WIN-34). Experiments performed in cooperation with Chemical Research revealed insufficient advantage to warrant use of that flux instead of conventional 100% NaF.

Radiochemical Laboratory

Major effort was represented by support given to Chemical Research studies. Overtime was utilized to reduce a backlog resulting mainly from one inch profile column studies.

Requested by the Process Chemistry Unit, was the detection of 10^{-4} molar aluminum in scavenged Metal Recovery plant waste. Various direct methods, including the aurin tri-carboxylic acid method, failed. However, the latter was effective after pre-treating the acidified sample with "Dowex A-1" anion exchange resin. Satisfactory spike recoveries obtained for most samples.

Interest increased in the verification of the presence of Co-60 in Metal Recovery waste. An effective separation was found for Co-60 when present in amount as low as 0.1% of the total sample gamma activity. Ammonium hydroxide scavenging followed by cobalt precipitation as the oxine was utilized. Qualitative information is presently available. With further study, quantitative Co-60 results should be possible.

Hydrogen in aluminum was satisfactorily determined by vacuum extraction. Operating temperature was 600°. Added bath material was unnecessary.

Spectrometry Laboratory

One mass spectrometer was down for one week due to electronic failures.

Fuel Technology requested analysis of gas contained in voids between slugs and cans. As in the past, cans were drilled under vacuum. The released gas was fed to a mass spectrometer for normal analysis.

Emission spectrographic work was steady. Several plutonium samples were evaluated.

The Water Quality load decreased sharply due to reduced 1706-KE activity.

[redacted]

Work volume statistics are as follows:

	MARCH		APRIL	
	No. of Samples	No. of Determinations	No. of Samples	No. of Determinations
Research & Development				
Pile Technology				
Metallurgy Research	115	395	65	403
Physics Research	68	69	15	23
Pile Materials	761	2709	318	1387
Fuel Technology	50	655	34	380
Pile Engineering	-	-	13	65
Separations Technology				
Chemical Research	921	1696	1277	1873
Chemical Development	534	1257	720	1567
Plant Processes	5	35	14	59
Process Technology	384	1090	944	1652
Other Customers	194	962	188	1036
Totals	3032	8868	3588	8445

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 April, 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
T. R. Cartmell	"A Method for Making Electrically Heated Glass or Ceramic Vessels with Heating Elements Bonded Directly to the Surfaces of the Vessel".

R. B. Richards
Manager, Separations Technology
ENGINEERING DEPARTMENT

RB Richards:khs