(CLASSIFICATION)

DE92 006562

HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

DATE May 8, 1959

54-3000-340 (3-37)

ALC-GE HENLAND, WASH

(CLASSIFICATION)
DECLASSIFIED
WITH RECTIONS

MASTER

Classification Cancelled And Changed To

DECLASSIFIED
WITH DELETIONS

DECLASSIFIED

HW-60236 J-DEL

By Authority of CA Berman

10-30-91, CG-PR-2

By TK BURRIS, 11-8-91

Verified By J.E. Savely, 11-18-91

This document consists of
20 pages. Copy No. 13
of 55 copies.

COPY 1 OF 1.

CHEMICAL PROCESSING DEPARTMENT
RESEARCH AND ENGINEERING OPERATION MONTHLY REPORT
APRIL, 1959

Compiled by Members of the
Research and Engineering Operation
Chemical Processing Department

May 8, 1959

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by
General Electric Company under Contract #W-31-109-Eng-52

~~RESTRICTED~~

This document contains Restricted Data as defined in the Atomic
Energy Act of 1954. Its transmission or the disclosure of its
contents in any manner to an unauthorized person is prohibited.

FOR OFFICIAL USE ONLY

J-1

DECLASSIFIED

INTERNAL DISTRIBUTION

-
1. G. J. Alkire	22. R. L. Moore
2. C. R. Anderson	23. J. M. Nielsen
3. C. A. Bennett - E. W. Christopherson	24. D. W. Pearce - R. E. Brown
4. J. G. Bradley	25. O. H. Pilkey
5. R. J. Brouns	26. A. M. Platt
6. C. L. Brown	27. W. H. Reas
7. L. P. Bupp - H. M. Parker	28. E. L. Reed
8. R. E. Burns	29. C. A. Rohrmann
9. V. R. Cooper	30. O. C. Schroeder
10. P. F. Gast - J. E. Faulkner	31. L. C. Schwendiman -
11. A. B. Greninger - O. H. Greager	C. E. Linderoth
12. K. G. Grimm	32. H. P. Shaw - J. B. Fecht
13. K. M. Harmon	33. R. J. Sloat
14. M. K. Harmon	34. R. E. Smith
15. O. F. Hill	35. M. J. Szulinski
16. J. F. Honstead	36. R. E. Tomlinson
17. H. H. Hopkins, Jr.	37. E. E. Yoiland
18. W. P. Ingalls	38. M. T. Walling, Jr.
19. E. R. Irish	39. J. H. Warren - V. R. Chapman
20. R. E. Isaacson - M. H. Johnson	40. 300 Files
21. L. M. Knights	41. Record File

EXTERNAL DISTRIBUTION

- 42. - 44. A. T. Gifford, AEC-HOO
- 45. Union Carbide Nuclear Company (Paducah Plant), Attn: R. W. Levin
- 46. Union Carbide Nuclear Company (ORGD), Attn: D. M. Lang
- 47. Chicago Patent Group
- 48. duPont Company, Aiken - Attn: W. P. Overbeck
- 49. duPont Company, Aiken - Attn: M. H. Wahl
- 50. duPont Company, Aiken - Attn: L. C. Peery
- 51. duPont Company, Aiken - Attn: J. W. Morris
- 52. duPont Company, Aiken - Attn: W. E. Winsche
- 53. duPont Company, Wilmington - Attn: V. R. Thayer
- 54. Goodyear Atomic Corp., Portsmouth, Ohio - Attn: F. E. Croxton
- 55. Savannah River Operations Office, Aiken, South Carolina

CHEMICAL PROCESSING DEPARTMENT
RESEARCH AND ENGINEERING OPERATION

APRIL, 1959

PUREX PROCESS TECHNOLOGY - E. R. Irish

Head End

Irradiated uranium, cooled from 93 to 106 days, was dissolved to form solvent extraction feed. The processing of unclarified feed in the solvent extraction section continued during the month as part of a test to determine if any long-range adverse effects resulted from processing uncentrifuged HAF.

The differential pressure across a plugged silver reactor was reduced from 38 to 2 inches water pressure (at comparable air flows) by flushing with 2 M $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ - 0.2 M NaOH. Since regeneration, the reactor has operated normally. The C-Cell prototype dual-pass silver reactor became inoperable because of plugging and thus is also scheduled for sodium thiosulfate-caustic flushing. Prior to its removal from service, off-gases from approximately 4600 tons of dissolved uranium had been processed through the reactor with only two regenerations; however, one regeneration was on the lower bed only rather than both upper and lower beds. All ammonia scrubbers functioned satisfactorily but no quantitative data as to ammonia recovery have been obtained.

Fission Product Recovery

No additional solids removal was experienced when a once-centrifuged batch of IWW was gelatin-treated (addition of 0.002 lb./gal. gelatin and digested for one hour at 80° - 85°C) and recentrifuged. Testing of two feed rates (11 and 26 gal/min.) during recentrifuging indicated markedly less solids removal at the higher rate. The final "clarified" IWW was depleted in zirconium and niobium by factors of 2.5 and 1.4, respectively.

Solvent Extraction

Upon completion of the neptunium recovery run, irradiated uranium processing was initiated; however, because of process upsets and malfunctioning and/or equipment failures a major portion of both products contained high gamma activity and failed to meet product specifications. Specific items which contributed significantly to the subnormal decontamination were as follows:

- a) Bypass of HS Column - The HS Column was bypassed when a leak developed in the bottom disengaging section; thus, the two to three decontamination factor normally attained in this column was no longer available.
- b) High fission product activity in the 3WB - Abnormally high gamma activity was experienced in the 3WB stream when severe entrainment and foaming of acidified IOW refluxing in the

DECLASSIFIED

rework tank added incompletely hydrolyzed waste to the 3WF. The addition to the 200 of solvent recovered from the 20W also appeared to be related to the high 3WB gamma activity.

- c) Low HA Column decontamination - A fluctuating HAF flow rate produced lower-than-normal HA Column decontamination performance by preventing control at the optimum organic uranium saturation until the HAF rotameter and pump were changed. Frequent shutdowns and startups also contributed to the poor HA Column performance.
- d) Crosscontamination - Some crosscontamination of the intercycle solvent extraction product streams occurred when the solutions used for in-cell decontamination of the HS Column were transferred to waste via a common header.
- e) Operation of L-Cell Package - When the Plutonium Ion Exchange Unit equipment did not function properly (see Plutonium Concentration), plutonium concentration was accomplished in the L-Cell Stripper and Concentrator. Thus, the decontamination factor of ten, which can be attained in the plutonium ion exchange unit, was not available.

As a result of the above-mentioned difficulties, both uranium and plutonium productions were curtailed. However, despite the relatively poor plant performance, forty percent of the uranium produced met product specifications, and another 35 percent was acceptable after either blending or processing through silica gel. Twenty-five percent was reprocessed because of high gamma activity or to permit recycling of out-of-specification plutonium. Only fifteen percent of the plutonium product was acceptable for plutonium fabrication without further decontamination; however, twenty percent was accepted by the Finished Products Operation for processing through Recuplex. The remainder of the plutonium required recycling through the Purex Plant before meeting specifications.

At month's end all plant equipment was functioning properly with the HS Column bypassed, and indications are that normal decontamination performance will result. Both the HAS flow and HA Column pulse frequency have been increased ten percent to assist in improving decontamination.

Temporary brief periods of partitioning failure were experienced throughout the month with up to sixty percent of the plutonium measured in the IBU stream. Based on the belief that the nitrite in the 2BW stream (now returned to the IBXF Tank) caused the partitioning loss, the 2AF sodium nitrite addition was decreased twenty percent and the IBX flow increased twelve percent, but neither adjustment corrected the partitioning problem completely. However, preliminary results indicate that the addition of 0.045 M sulfamic acid to the 2BX has returned the IBU plutonium content to a normal 0.4 percent.

Successful bottom interface operation of the IC Column (which increases the column capacity approximately thirty percent) was demonstrated during the month; however, about 700 pounds of uranium were lost via the ICW before the

proper operating conditions for the organic continuous column were firmly established. Normal ICW uranium losses were achieved by increasing the IC Column L/V from 0.92 to 1.15 and increasing the pulse frequency from 42 to 92 cycles per minute.. The major portion of the uranium accumulated in the ICW was segregated for rework.

Neptunium Recovery

The April neptunium run utilized the 2A Column for separating neptunium from fission products and plutonium while processing reduced 3WB. Both ferrous sulfamate and hydrazine were added to both the 2AF (3WB) and 2AS. The 2AP (containing the neptunium and uranium) was processed in the IBX and IBS Columns with the bulk of the uranium going to the IC Column and the ICU Concentrator. The neptunium remained in the IBP stream, was again reduced and then returned to to the 2A Column after all the 3WB had been processed. The final reflux-recycle operation of the 2A - 2B Columns reduced the fission product concentration to an acceptable level and provided additional plutonium decontamination.

Operation of the new flowsheet was quite satisfactory. Gamma decontamination was good ($CF = 20$), considering the low gamma activity of the feed ($\sim 1.5 \times 10^6$ uc/gal), and the 2AW neptunium loss ranged from 0.5 to 1.0 percent. High, but tolerable, uranium concentration resulted from discontinuing 2A - 2B Column recycle prior to completion of the IBX Column stripping. Eight-hundred grams, equivalent to ninety percent of the neptunium in the 3WB processed, were recovered and sent to the purification facility.

A higher percentage of virgin neptunium has been accumulated in the 3WB during the April uranium processing than has been previously experienced. This has been achieved by better control of nitrite concentration in the HA Column since the 2BW was rerouted into the IBXF instead of the HAO. Consequently, the neptunium losses in the HAW, as well as the 2DU, are near the lower analytical limits of detection; however, at the present time these limits represent a HAW loss of ten to fifteen percent and a 2DU loss of one to two percent.

Plutonium Concentration

Because the resin pushes were extremely erratic and frequent plugging of the resin receiver occurred, the 2BP was routed to the L-Cell Package during the first part of the month. After a defective gasket in the equalizing line was changed, a new teflon sleeve installed in the three-way valve, the resin replaced, and minor adjustments made in the operating techniques, the unit functioned satisfactorily. Attempts to improve decontamination in the unit by increasing the XAS to 300 percent of flowsheet and the XAF from 6 M to 7 M HNO_3 did not change the decontamination significantly.

Testing of two modified Corley Magnaflo XAF pumps, installed together in parallel with the existing Lapp Pulsafeeder XAF pump, was started, but one pump developed a severe vibration after about six hours of operation. When correction of a metal-to-metal contact failed to improve operation of the pump, the only remaining cause of vibration appeared to be the carbon thrust bearing loose in its housing. Since facilities are not yet available for replacement of the bearing, the spare pump is being installed.

Solvent Treatment

The gamma activity of the IOO and 200 increased seven and three-fold, respectively, above normal when high intercycle gamma activity was experienced in the solvent extraction section. However, doubling the frequency of batch washing aqueous changes and the potassium permanganate, IOC and 20S rates for 24 hours plus a general drop in gamma activity levels throughout the remainder of the plant reduced the gamma activity to normal.

Incremental additions to the 200 of 500 gallons of solvent recovered from the 20W over a 24-hour period had no apparent effect on the operation of the 2D Column but correlated with a five-fold increase in the 3WB gamma activity. Approximately 800 gallons of solvent were discarded, after batch washing to reclaim plutonium and uranium, to the organic crib because of high residual gamma activity.

Waste Treatment and Acid Recovery

Frequent plant shutdowns and startups coupled with waste and uranium rework operations precluded optimum operation of the waste treatment and acid recovery equipment and low IWW volumes. Consequently, the waste sent to the underground storage tanks averaged 107, 551, 157 and 4 gallons per ton of uranium for neutralized IWW, solvent washes, cell drainage and centrifuge cleanouts, respectively. The coating waste sent to storage remained at 231 gallons per ton of uranium. Over-all plutonium and uranium losses for the month were 0.47 and 0.14 percent, respectively. Coating waste losses for plutonium and uranium accounted for 11 and 8 percent of the over-all losses, respectively.

Other items of interest in the waste treatment and acid recovery operations were:

- a) A bottoms transfer from the No. 2 Acid (Waste) Concentrator equivalent to five flows was initiated to reduce corrosion resulting from accumulated corrosion products in the here-to-fore stagnant bottoms.
- b) After peaking in the 5000 to 10,000 uc/gal. range during the previous month, the gamma activity of the Purex recovered acid declined to 1000 - 1500 uc/gal. (Normal activity = 500 - 1000 uc/gal.).
- c) Thirty-five hundred gallons of miscellaneous wastes were re-worked with no adverse process effects after 35 days of refluxing.
- d) Gelatin treatment of IWW prior to centrifugation produced no significant reduction in the rate of bed plugging when the treated solution was processed through the IWW anion exchange equipment.

Self-concentration in Tanks 241-A-101, 102, and 103 continues at boil-off rates of 2.9, 19.6, and 1.0 gallons per minute, respectively. Recent calculations indicate temperature excursion in TK-241-A-101, during which the sludge temperature increased from 136°C to 156°C before the trend was reversed by dilution of the tank contents and increased air flow to the recirculators, may have been caused by overconcentration (greater than 8 M sodium concentration). After receiving process wastes for fourteen months, TK-241-A-102 now contains 64 percent of the terminal 8 M sodium concentration at the hydrostatic head limit.

REDOX TECHNOLOGY OPERATION - M. K. HarmonSolvent Extraction

Testing of the behavior of boric acid in the extraction system was continued in conjunction with evaluation of an acidic flowsheet for the first extraction cycle. One HAF batch was processed using the following HA Column flowsheet:

HAF:HAIS:HAS:HAX = 124:55:25:375

Stream	Molarity						Hexone
	UNH	ANN	HNO ₃	NaNO ₃	Na ₂ Cr ₂ O ₇	H ₃ BO ₃	
HAF	1.62	0.43	•0.28	0.59	0.1	0.05	
HAIS	0.05	2.5	-0.2	0.81	0.06	•	
HAS	-	1.3	•0.2	-	0.1	•	
HAX	-	"	+0.1	"	"	"	100%

Samples of the HAF and other process streams, taken while employing this flowsheet, indicated the boron concentration to be below the detection limit of 20 parts boron per million parts of solution. Spectrographic analysis of the uranium product stream showed the boron to be less than the detection limit of one part boron per million parts uranium. Interference in the spectrographic analysis of the plutonium product stream prevented accurate determination of the boron concentration below 20 parts boron per million parts plutonium.

Neptunium losses in the HAW stream during the test were below the detection limit, which corresponded to a 2 percent instantaneous loss. Approximately 70 to 80 percent of the neptunium in the feed appeared in the HAF stream indicating the reflux to be considerably less than that encountered in earlier tests.

The fission product activity of the LAFS stream increased approximately five-fold as a consequence of the acidic HA flowsheet. This increase in activity, primarily ruthenium, persisted throughout the plutonium cycles but did not necessitate the rework of any plutonium product. The acid-deficient uranium cycles, particularly the 2D Column, removed the additional ruthenium, giving a uranium product stream well below the specification limit for fission product activity.

Laboratory inspection of a few agitated HAW samples revealed the presence of a precipitate, even during the use of the acidic HA Column flowsheet, which had not been noticeable in un-agitated samples. The precipitate, which appears similar to that encountered previously in the LAW stream and the HAIS concentrator, may be the major cause of the precipitate problem encountered during the recycle of the HAW stream to the HAIS concentrator. Further investigation is planned to determine the factors affecting the precipitate formation and the point in the process at which the precipitation occurs.

Operation of the extraction system at rates low enough to conform to the E-Metal dissolution rates necessitated a 40 percent increase in the 2DS flow, to approximately 40 gallons per hour per square foot, to provide adequate sodium removal in the 2D Column. The following flowsheet,

2DF:2DIS:2DA:2DX = 88:16:35:400,

reduced the sodium content of the product stream from 160 to 25 parts sodium per million parts uranium. Despite the reduction in the 2DW salt strength to 0.36 M aluminum nitrate, the uranium recycle averaged only 10 percent.

Cribbed Waste

Diversion of the feed oxidation condensate to the high activity waste system reduced the beta activity of the cribbed condensate to approximately 2 percent of the average for the preceding three years. Following the diversion of the ruthenium-contaminated condensate, the fission product activity spectrum of the cribbed waste was similar to that encountered in the waste concentrator, predominantly zirconium-niobium.

Waste Storage

Sampling of the non-boiling 241-S wastes, which are 5 to 7 years old, has been initiated in a program aimed at evaluating drying and permanent storage of these wastes in the bismuth phosphate waste storage tanks. Samples of the 112-S tank, taken at six different levels, showed the gamma activity, 0.2 curie per gallon, to be essentially all cesium. Specific analyses revealed the strontium activity to be approximately 200 micro curies per gallon. Factors to be investigated for the wastes in this and other non-boiling tanks include the maximum feasible concentration and the thermal characteristics of the dried waste.

FINISHED PRODUCTS TECHNOLOGY - R. E. SmithURANIUM CONVERSION OPERATIONProcess Performance

All UO_3 shipped met product specifications. Two containers failed to meet the particle size specifications and required remilling.

Nine hundred thirty three (933) pounds of nitric acid per ton of uranium processed (88.5% of theoretical) were recovered at an average concentration of 47%.

The average operating rate of the calciners was 7.16 tons uranium per unit for each day on the line. The overall calciner operating efficiency was 97.9%. Calcination of enriched metal in the G calciner was continued and averaged 8.4 tons uranium for each day on the line.

Marginal milling performance with the enriched UO_3 was traced to an improperly installed deflector plate in the hammermill.

Process Improvement

Automatic start-up and shut-down controls were installed on the remaining two concentrators. In addition, one concentrator control system was modified to allow the calciner feed tank weight factor to start up and shut down the concentrator as needed.

The condensate piping from the evaporator vapor condenser was revised to prevent the build-up of condensate in the condenser.

The H calciner powder bed was removed for inspection of the agitator. Three hinge pins were found to be broken and two 3/4-inch shear pins, having 5/8-inch shear diameter, were cracked. All notched hinge pins were replaced with solid pins. All shear pins in the hubs with broken hinge pins were also replaced.

One broken thermowell was replaced during the month.

The performance of K calciner, equipped with magnetic flowmeters, was excellent.

METAL FINISHING OPERATIONRecuplex

Forty-five runs, consisting of crucibles, fragments, powders, and clean-outs were processed through the S & C Hood. Slurry losses to crib averaged 0.12 percent of the recovered plutonium. The average number of

crucibles per Task III crucible run was increased from six to eight, with an associated reduction from 3.5 to 2.8:1 in the Al to F mol ratio. Solvent extraction processing of this feed appears to be satisfactory.

The SE Hood processed 1230 liters per day at 66 percent operating efficiency, for an average instantaneous rate of 1860 liters per day. Waste losses to crib averaged 0.0065 g/L (0.25% of the feed plutonium). The low throughput was probably caused by silaceous scale on the column walls.

The Task I supernatant evaporative heat kill test was completed. Evaporative heat kill produces a concentrated supernatant equivalent to chemical kill, provided about 10 parts of Dow-Corning A-F emulsion per million parts of supernatant are added to the supernatant feed prior to concentration to prevent foaming and short circuiting in the concentrator.

Task I - II

One hundred thirty seven (137) runs were processed with an average filtrate recycle of 4.33 percent.

Operation of the continuous unit was intermittent during the month due to variances in the feed supply. The frequent start-ups required, and a wide variation in feed product concentration contributed to the above normal recycle.

A chemical flush of the drum filter was carried out which proved to be approximately 90 percent effective. A small amount of manual fiddling was subsequently required. This was the first clean-out of this type required in the nine months since start-up.

Task III

On a test basis, one reduction was attempted without mixing the calcium with the tetrafluoride. The calcium was placed in the bottom of the crucible and a small amount of iodine booster (0.2 mls) was used. Very little chemical reaction took place, and 87.8 percent of the tetrafluoride powder was recovered and reduced using standard mixing procedures.

DECLASSIFIED

PROCESS CHEMISTRY - K. M. HarmonREDOX PROCESS ASSISTANCE

For several months, a laboratory investigation of the use of 0.7% ozone in air for the removal of fission product ruthenium (as the volatile RuO_4) from Redox 2BP (plutonium product) has been under way. The results indicate that successful ruthenium volatilization from this type solution, at least with this low an ozone concentration, requires that an auxiliary oxidizing agent, or catalyst, be used, that the solution be free of oxidizable organic materials, and that the solution be nearly boiling. In the most successful tests, satisfactory ruthenium removal rates were achieved at 98 C for samples of air-sparged, plant 2BP which had been made up to a composition of 0.5 M HNO_3 , 0.7 g/l Pu, 0.001 - 0.003 M cerium(IV) nitrate, and 1.0 M $\text{Al}(\text{NO}_3)_3$. The system is complicated by these factors: 1) any additives must be compatible with subsequent processing steps; 2) the plutonium apparently must be hexavalent to permit ruthenium volatilization; and 3) although cerium(IV) appears to be the most suitable auxiliary oxidant, it tends to precipitate from solution under the ozonation conditions. The best method found for preventing the formation of insoluble cerium compounds in these solutions is the addition of aluminum nitrate.

NEPTUNIUM PROCESSINGNeptunium Purification

Nine hundred and ten grams of Np^{237} were processed through the anion exchange facility during the month. The material consisted of 110 grams recovered from fluorination ash at Paducah and 800 grams of new material from the Purex plant. A high ratio of natural thorium to neptunium in the Paducah material (1.3/1) and a high uranium to neptunium ratio in the Purex material (20/1) caused poor adsorption of neptunium on the resin, with resulting high column waste losses (about 10%).

While recovering plutonium from neptunium processing wastes, the four-inch diameter, four-foot high anion exchange column shattered. The conclusion reached from investigating the incident was that the rupture occurred as a result of the internal pressure to which the glass pipe was subjected. It is not known if the column broke under the normal operating pressure of 25 to 30 p.s.i., or if an abnormal pressure which exceeded the safe working limits of the glass had developed, through sudden, excess gas evolution.

Neptunium Oxalate Precipitation

Investigations of neptunium oxalate precipitation conditions were continued. Oxalate precipitations were carried out in which the neptunium concentration, neptunium valence state, nitric acid concentration, and temperature of the slurry were varied.

In the present process, in which neptunium(IV) nitrate is added to 1 M oxalic acid, a light-gray, very difficult-to-filter precipitate is formed. This

material gradually changes to a bright green, readily filterable material when left in contact with the mother liquor. It was found that the rate at which the light-gray precipitate turns to a green, filterable precipitate increases with increasing temperature. The rate did not appear to be materially affected by the nitric acid concentration or the neptunium concentration of the slurry. It did appear, however, to be dependent on the particular batch of feed used. In dilute strikes in which the anion exchange eluate was precipitated directly (without evaporative concentration or pre-reduction), a rate difference of a factor of four was observed between batches. When feed material eluted from old resin (resin which had been used for a number of runs) was used, a filterable material was obtained in 30 minutes with hot strikes ($\sim 50^\circ\text{C}$) and in 60 minutes with cold strikes ($\sim 25^\circ\text{C}$). In contrast, when material eluted from new resin was used, a two hour contact period was required before a filterable precipitate was obtained with hot strikes and 4 - 6 hours with cold strikes.

The cause of the high filtrate losses (filtrate neptunium values ranging from 50-140 mg/liter) that had been experienced was found to be the incomplete reduction of neptunium(V). In all cases in which the initial filtrate neptunium values were high, the addition of ferrous ion (to a final concentration of $\sim 0.01\text{ M}$ ferrous ion) produced further precipitation, giving neptunium filtrate values ranging from 12-27 mg/liter. It was also found that the reduction of neptunium(V) during the precipitation step was very slow. When neptunium(V) nitrate was added to a solution containing 1 M oxalic acid and reducing agent to give a final slurry of 0.15 M oxalic acid, 8 g/l semi-carbazide, 10 g/l neptunium, 3.2 M HNO_3 , and 0.006 M ferrous ion, reduction to the Np(IV) state was only 80% complete in 60 minutes at room temperature.

Neptunium Filtrate Recycle

Various ways of recovering the neptunium from the oxalate filtrates were tested. Concentration, reduction, and reprecipitation with oxalic acid gave excellent neptunium recovery, but poor quality product which was contaminated with iron, calcium, and silica. The most attractive scheme appears to be treatment of the filtrate to destroy oxalate, followed by anion exchange recovery. To date, the oxalate destruction has been accomplished on a large scale by concentration of the filtrate to a nitric acid concentration of about 10-12 molar. However, laboratory scale tests indicate that a permanganate kill would also be satisfactory.

ANALYTICAL ASSISTANCE

E-5 Uranium Bias

Analytical investigations were carried out to determine the extent to which the present analytical method used for the Purex E-5 (dissolver solution) uranium assay is biased by the presence of extraneous process constituents - constituents other than uranyl nitrate and nitric acid. Preliminary tests were made using an E-5 composite sample representing the February and March production period. The present non-specific method (uranium calculated from

solution density) was compared to a specific method for uranium (controlled potential-coulometric titration) using standard solutions to compensate for normal analytical biases. Data obtained from these tests indicate that E-5 uranium results were biased high during the test period by one per cent or more, due to process impurities. Because of the limited nature of the study and the magnitude of the indicated bias, more extensive tests are planned for the future.

Carrier Distillation Studies

Recent work with the carrier distillation method used for the spectrographic determination of metallic impurities in plutonium shows that certain impurity results are dependent on the original form of the sample and the method of sample preparation. The normal practice is to convert the various forms of plutonium (metal, nitrate, fluoride, etc.) to PuO_2 and determine the impurity levels in the oxide by the carrier distillation method. It was found that iron, chromium, and nickel values as measured for a given material varied with the bulk density of the oxide, with oxide of lower bulk density giving higher impurity values. The bulk density of the oxide, in turn, was found to be dependent on the ignition temperature and the form of the material before ignition. Of the sources of oxide studied to date, metal and nitrate, the low temperature ($\sim 500^\circ\text{C}$) ignited nitrate gave the highest measured impurity values.

As a result of these findings, a program was initiated to develop a common sample preparation procedure to eliminate this source of variation.

QUALITY CONTROL AND STANDARDS

The Quality Control Program for the Chemical Processing Department analytical laboratories was maintained as usual. The "Quarterly Analytical Control Quality Report - January-March, 1959", HW-60024, was issued. The results of the plutonium metal sample exchange - Group XIII were submitted to the Rocky Flats Plant in document HW-59922.

A program to investigate the use of plutonium dioxide as a primary standard continued during the month. It has been found that the oxide is readily dissolved by fusion in sodium bisulfate, in an erlenmeyer flask. The mix is heated to $550-600^\circ\text{C}$ for 45-90 minutes, giving a melt which, when cooled, is readily soluble in water.

234-5 DEVELOPMENT OPERATION - H. H. Hopkins, Jr.Task I

Several determinations were made of the particle size distribution of plutonium oxalate in a laboratory-prepared Task I slurry. Although the data are somewhat scattered, the upper and lower limits have been fairly consistent. The results are summarized in the table below.

PARTICLE SIZE DISTRIBUTION OF $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ IN TASK I SLURRY

<u>Stoke's Diameter</u> <u>Microns</u>	<u>Percentage Of Particles Less</u> <u>Than Given Diameter</u>
5	0
10	1
20	10
50	80
100	95

Two samples of what would be considered good dry plutonium oxalate cakes were taken from the continuous Task I prototype to determine moisture content. Portions of these samples were calcined to PuO_2 and then back-calculated to obtain initial moisture content of the cake. The values obtained were 50 and 37 percent (on wet basis), including water of hydration. Air drying a portion of one sample at room temperature for three days reduced the moisture from 37 to 13 percent.

Continuous Chlorination

Operation of the large Hastelloy demonstration chlorinator reached a rate of 295 grams per hour (as plutonium) for a three-hour run.

Equipment changes have included installing 1/4" Hastelloy C tubing through the furnace as a phosgene preheat line, increasing phosgene valve temperature to 110 - 120 C to prevent phosgene liquification, and increasing the vibrator intensity for better powder flow.

The formation of lumps of plutonium trichloride has become an annoyance by plugging the valve to the chloride receiver. This caking is due in part, at least, to frequent interruptions of operation. No efforts have been made to empty the chlorinator prior to shutdown.

Plutonium Trichloride Reduction

First material from the large-scale continuous chlorinator was reduced on a 30-gram scale. Good yields were obtained and reduction temperature and pressures were normal.

Task III

The calcium and iodine reaction was carried out in a tantalum crucible in a pressure vessel. This was the first in a series of tests to determine feasibility of using tantalum as a material for reusable reduction liners. The crucible was pretreated by heating in air to oxidize the surface.

The crucible changed from light-grey to black. Some roughness on the inside near bottom was noted, as well as some flaking of oxide coating. It lost approximately one gram in weight. Other than surface reaction, the crucible seems to be unchanged.

Calcium Iodide - Calcium Chloride System

Calcium Iodide - Calcium Chloride System, HW-60151, Unclassified, was issued. The temperature-composition relationships for calcium iodide and calcium chloride were studied between 400 and 800 C, and between 5 mole percent and 100 mole percent calcium chloride.

Dissolution Of Massive Metal In Sulfamic Acid

Tests made in cooperation with Finished Products Technology personnel corroborated that massive metal can be dissolved rapidly in a saturated sulfamic acid solution. One hundred grams from a three hundred-gram piece of metal was dissolved at a rate of 160 grams per hour. If the dissolution rate is proportional to the surface area, this would indicate a nominal 1400-gram piece as charged to the continuous dissolver might dissolve 3-1/2 - 4 times the rate now achieved by the nitric-hydrofluoric acid method. Concentrations of nearly 100 g/l have been made, and high concentrations appear feasible as long as the temperature of the dissolution is controlled and the solution kept saturated in sulfamic acid. The reactor must be kept cool for rapid dissolution.

The product from the dissolution is plutonium(III) sulfamate, plus a black residue which dissolves in hot concentrated nitric acid. Oxidation of the concentrated plutonium(III) sulfamic mixture with nitric acid and heat results in a violent reaction difficult to control. Controlled dilution with nitric acid and heating of the resultant large volumes to complete the oxidation has not been tested. Direct oxidation with sodium nitrite produces a vigorous reaction, but one which can be controlled by proper techniques. The oxidation of sulfamate ion results in the formation of sulfate.

When concentrated solutions are oxidized to the (IV) state, plutonium sulfate precipitates; and without nitric acid addition, it is probable that polymer would form. Close control of dilution is required. The solubility of plutonium in 4 M HNO₃ at 25 C is 60 g/l at a sulfate concentration of 0.12 M, and 18 g/l at a sulfate concentration of 0.36 M.

Research and Engineering

~~CONFIDENTIAL~~

HW-60236 J-DEL

**DECLASSIFIED
WITH DELETIONS**

~~CONFIDENTIAL~~

J-17

• ORGANIZATION AND PERSONNEL

Personnel

On April 1, 1959 L. F. Lust returned to the Hanford Laboratories after completing assignment with the 234-5 Development Operation.

On April 13, 1959 F. J. Sobeck transferred from the Purex Operation to the Purex Technology Operation.

Trips

V. R. Cooper attended the annual meeting of the American Chemical Society to chairman the Nuclear Technology Subdivision. This meeting was held in Boston, Massachusetts April 6 through April 9, 1959.

V. R. Cooper visited F. P. Baranowski of the Atomic Energy Commission, Washington, D.C. on April 10 to discuss fission product recovery and Non-Production Fuels Reprocessing.

C. L. Brown attended the 5th Nuclear Congress in Cleveland, Ohio April 6 through April 8, 1959.

C. L. Brown visited C. L. Schuske of the Dow Chemical Company, Rocky Flats Plant, Denver, Colorado on April 9 and 10 to confer on weapon component manufacturing procedures and practices pertaining to nuclear safety.

A. E. Smith visited Kenneth Hupp of Whitman College, Walla Walla, Wash. on April 9 for technical recruiting.

L. E. Bruns visited John Pringle of the Dow Chemical Company, Rocky Flats Plant, Denver, Colorado on April 14 and 15 to discuss plutonium processing and technology.

L. E. Bruns visited R. D. Baker and W. J. Maraman of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico on April 16 and 17 to discuss plutonium processing and technology.

R. E. Van der Cook visited Henry Boppel of the Sheffield Corp., Dayton, Ohio on April 14 and 15 to check progress on measuring machine being manufactured for the Research and Engineering Operation.

R. E. Van der Cook visited W. C. Mullen of the Pratt & Whitney Co., West Hartford, Connecticut on April 16 and 17 to check progress on 6-Coordinate Gage being manufactured for the Research and Engineering Operation.

R. G. Geier visited Robert Hartwell of the Power Reactor Development Company, Detroit, Michigan from April 20 through April 22 to discuss power fuels reprocessing.

Trips (Continued)

W. G. Browne attended the Hot Laboratory Conference in Cleveland, Ohio April 6 through April 10 because of interest in use of hood concepts in the processing of Pu on a production scale.

B. F. Judson visited Dr. Gammill of the Michigan Chemical Company, St. Louis, Michigan on April 6 for consultation on promethium separation process methods.

B. F. Judson attended the 5th Nuclear Congress in Cleveland, Ohio April 7 through April 10. He attended sessions on fission product market forecasts.

R. L. Stevenson visited C. L. Schuske of the Dow Chemical Company, Rocky Flats Plant, Denver, Colorado from April 8 through April 10 to discuss and observe critical mass control practices associated with weapon component manufacture.

E. R. Irish delivered an address before the Idaho District II Science Fair, Lewiston, Idaho on April 4. Contact was made with D. S. Caine.

E. R. Irish delivered an address before the Columbia School District #400, Burbank, Wash. on April 13. Contact was made with D. T. Coates.

E. L. Dunkin contacted G. T. Austin of the State College of Wash., Pullman, Washington on April 17 to set up model of pulse column and waste tank for HAPO display at Engineering Open House.

H. H. Hopkins, Jr. visited A. H. Daane and O. N. Carlson of the Ames Laboratory, Iowa State College, Ames, Iowa on April 13 and 14 to discuss plutonium chloride process and repurification procedures.

H. H. Hopkins, Jr. visited I. B. Venable and J. W. Pringle of the Dow Chemical Company, Rocky Flats Plant, Denver, Colorado on April 15 to discuss plutonium chloride processes and repurification procedures.

H. H. Hopkins, Jr. visited E. Christensen, J. W. Anderson and H. Paxton of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico on April 16 and 17 to discuss plutonium chloride processes and repurification procedures.

R. S. Rosenfels visited B. H. Bieler, L. A. Matheson and J. F. Willging of the Dow Chemical Company, Rocky Flats Plant, Denver, Colorado on April 14 and 15 to discuss ceramic development.

R. S. Rosenfels visited S. D. Stoddard and J. W. Anderson of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico on April 16 and 17 to discuss ceramic development.

Trips (Continued)

J. S. Buckingham presented a paper at the annual meeting of the American Chemical Society in Boston, Massachusetts April 6 through April 9.

J. S. Buckingham visited C. H. Ice of E. I. duPont de Nemours, Savannah River Plant, Aiken, South Carolina on April 7 and 8 to discuss Palm.

Visitors

D. J. Pflaum of the Atomic Energy Commission, Washington, D.C. visited M. K. Harmon on March 24 to discuss problems of declassification.

D. Musser and D. George of the Atomic Energy Commission, Washington, D.C. visited K. M. Harmon on April 7 and 8 to discuss accountability.

E. F. Greenleaf of the Atomic Energy Commission, Division of Production, Washington, D.C. visited R. E. Smith and A. E. Smith on April 8 to discuss plutonium radiation problems and Hands-Off Program.

H. W. Chandler of Radiation Applications, Inc., New York, New York visited V. R. Cooper, E. R. Irish, W. H. Swift and R. E. Tomlinson on April 16 and 17 to discuss fission product recovery and waste disposal.

C. Pierce of the Brookhaven National Laboratory, Upton, New York visited E. R. Irish and W. H. Swift on April 28 to discuss Purex process and tour the Purex Plant.

J. Evans of E. I. duPont de Nemours and Company, Wilmington, Delaware visited E. R. Irish and W. H. Swift on April 28 to discuss Purex process and tour the Purex Plant.

Inventions

None

Manager
Research and Engineering

END

**DATE
FILMED**

2 / 26 / 92