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HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

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MONTHLY REPORT
CHEMICAL PROCESSING DEPARTMENT
RESEARCH AND ENGINEERING OPERATION
MAY 1962

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AUTHOR

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CHEMICAL PROCESSING DEPARTMENT
RESEARCH AND ENGINEERING OPERATION MONTHLY REPORT
MAY 1962

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

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June 7, 1962

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract #AT(45-1)-1350
between the Atomic Energy Commission and the General Electric Company

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CHEMICAL PROCESSING DEPARTMENT
MONTHLY REPORT

MAY, 1962

II. ACHIEVEMENTS (Continued)

G. RESEARCH AND ENGINEERING OPERATION

1. Purex Process Technology - B. F. Judson

a. Solvent Extraction

During the month solvent extraction performance continued to show improvement in all portions of the plant except the 2D Column of the Final Uranium Cycle. Decontamination and recovery performance of the First Cycle was excellent. Superior performance in the Final Plutonium Cycle produced plutonium with only 20 - 25 per cent of the gamma activity permitted by the product specifications. Large volumes of supernatant solutions from plutonium precipitation operations in the 234-5 Building were successfully processed through the Purex Plant.

Uranium losses in the 2EW stream from the 2E Column were reduced from a peak of 1.5 to approximately 0.03 per cent by using 5 vice 2.5 per cent sodium carbonate solution for solvent washing and adding a batch contact step in the No. 2 Solvent System. The 2EW losses were further reduced to <0.002 per cent with normal flow ratios and solution temperatures after installation of a new 2E Cartridge containing graded nozzle plates interspersed with 3/4-in. thick plastic plates. The operable pulse frequency of the new cartridge is 63 cycles per minute compared to 38 for the previous nozzle-plate cartridge.

b. Neptunium Recovery

Neptunium accumulation in the Backcycle Waste System was below normal because 30 - 50 per cent of the neptunium in the virgin feed escaped via the final uranium product. (This material is recovered during subsequent uranium processing at Paducah.)

c. Plutonium Concentration

Resin movement in the plutonium ion exchange unit intermittently became very difficult near mid month after the resin had been in the unit approximately 45 days. During the periods of poor pushing, plutonium recycle increased sufficiently to raise the plutonium concentration appreciably throughout the plant. Using a special procedure for changing resin, including appropriate critical mass controls, the resin in the unit was replaced without a shutdown. Operation of the unit was smooth subsequent to the resin change.

[redacted]

d. Solvent Treatment

Solvent losses from the No. 2 System increased a factor of four to 400 gallons per day, after inauguration of a five per cent sodium carbonate wash in the feed tank to the 20 Column (TK-R1). However, the "lost" solvent was segregated from the washes and stored for future recovery. The batch washing in TK-R1 was discontinued when the 2E Column uranium losses returned to normal after installation of the new 2E Column cartridge. In addition, the concentration of sodium carbonate was reduced from 5 to 2-1/2 per cent in the organic wash solutions throughout the plant.

e. Waste Management

After the installation of new flow controls, the prototype for denitration of high activity waste (IWW) operated smoothly at a formaldehyde flow of fifty per cent flowsheet. Decontamination performance of the recovered acid system appeared to remain low, possibly due to sampler and receiver cross contamination.

f. Fission Product Recovery

Batch size for strontium recovery from high activity waste (IWW) has been increased to 60 kilocuries of Sr 90 per sulfate precipitation. Overall recovery continues to be 50 - 60 per cent with the major loss occurring in the sulfate step.

Aged rework material was successfully purified at the Strontium Semiworks using a batch contact with di(2-ethyl hexyl) phosphoric acid. The strip contact was made with nitric acid under careful pH control to avoid the use of citric acid and its attendant decomposition problems.

Campaign operation of the HA-HC purification columns in the Strontium Semiworks was underway at month's end with preliminary data indicating low HAW losses and excellent cerium decontamination.

2. Redox Process Technology - R. G. Barnes

a. Plutonium Anion Exchange

Leak checking and operability testing of the anion exchange system installed in the 233-S Building was completed at mid-month. Modifications to the facility recommended by the Hazards Review Task Force, which included replacement of the XAS Feed Tank (L-1) with one of favorable geometry and poisoning of the XCX Addition Tank (L-1-A) with Pyrex Raschig rings, were also completed and processing of plutonium requiring rework was started on May 20, 1962. Mechanical difficulties in the extraction system caused frequent shutdowns and changes in the processing rate, so that stable operation of the anion exchange facility was not attained. Preliminary data indicated that an arithmetic decontamination factor of 5 or more was readily attained, and all final plutonium product met shipping specifications.

A new plutonium recycle unloading and monitoring system was installed and put into service by month-end. Plutonium-bearing wastes from the Task I operation of the 234-5 Building are transferred into a new geometrically favorable glass tank (L-22) containing a BF_3 neutron counter. There the plutonium concentration and quantity are determined from calibration data and checked against shipper statements before the solution is added to the recycle tank (L-16) for transfer to the metal solution oxidizer (H-4). The neutron counter gave excellent correlations with laboratory analyses at high plutonium concentrations and is adequate for recycle monitoring to one gram of plutonium per liter. Some additional evaluation of background effects at low concentrations will be required.

b. Solvent Extraction

The modified neptunium accumulation process, which employs the HS Column for retention of the neptunium inventory, appears to be operating efficiently. Neptunium has accumulated in the 1AFS Concentrator System and the HSF tank to give a feed to the HS Column of 0.3 - 0.5 gram per gallon. The neptunium concentration in the HS Column waste samples is at or near the lower detection limit of $< 2.0 \times 10^{-4}$ grams per gallon.

At the time of the adoption of ferrous sulfamate as the reductant for the 1BX and 3DS streams in July 1961, the use of sulfamic acid as a nitrite suppressant was continued. Elimination of the sulfamic acid from the 1BX and 3DS salt streams was initiated, on a test basis, in February, 1962. Since no adverse effects were noted, sulfamic acid-free 1BX and 3DS streams are now standard and a chemical savings of $2 per ton has been realized.

c. Waste Storage

The initial attempt to obtain a sludge core sample from the 108-SX tank, using equipment similar to that used by the Purex Operation in January, 1962, was unsuccessful. Plugging of the flushing holes in the cutter head allowed penetration of only 14 inches of the 38-inch sludge layer. Inspection of the core sample, one week later, found that the solids, presumably mainly sodium nitrate, had been dissolved by the 24 inches of seal water trapped in the sample tube above the solids. A second attempt to obtain a sludge core sample from this tank will be made in June following transfer of the non-boiling supernatant solution and dissolution of the top 15-20 inches of sludge.

During June, 1961, an attempt was made to insert a chisel-pointed probe, equipped with seven thermocouples, into the 108-SX tank sludge to measure the temperature of the sludge at various depths. Repeated attempts to penetrate the sludge layer finally bent the 30-inch-long lower section of the probe. A satisfactory probe for inserting thermocouples into the sludge layer, without disturbing the sludge, has not yet been designed. Thermocouple-carrying probes were installed in the 110-SX and 115-SX tanks during the month. These tanks have 0 inches and 3.5 inches of measurable sludge at present. These thermocouples, located at 4-inch intervals on the bottom 2 feet of the probe, will permit temperature measurements as the sludge builds up in these tanks.

3. Finished Products Chemical Technology - L. M. Meeker

a. Metal Finishing Operation

1. Button Line

The button line started up on May 18, 1962, following a six-week shut-down. During the shut-down, equipment modifications were made to permit treating and loading out the supernates for recycling to the separations plants (Redox and Purex) for recovery, as the normal recovery facilities in Recuplex are not available. $KMnO_4$ is now added to the filtrate solution to decompose any oxalate, and the resulting solution treated with $NaNO_2$ to eliminate any excess $KMnO_4$ prior to filtering, sampling, and loading out. Button line operations have been satisfactory; however, rates, dependent on the volume of aqueous recycle generated, are about half those normally obtained when recycle was coupled to the Recuplex process. Aqueous waste generation during the first week of operation exceeded the expected rate due to erratic feed flows. Improved control of chemical additions and elimination of the drum filter cake wash has reduced the waste volume to an acceptable level ($\sim$ 110 - 125 percent of calculated volume).

2. Recuplex

On April 7, 1962, a nuclear excursion occurred in the Recuplex facility in the organic wash receiver (K-9 tank) during a system flush. By April 27, 1962, steps had been completed for making the facility secure against a resumption of the chain reaction. All operations in the Recuplex facility have been suspended for an indefinite period of time. All work in the Recuplex facility has been directed toward "deactivating" the facility in a proven, safe manner. To date procedures have been written and completed for sampling most of the vessels and sumps in the solvent extraction (SE) and reception and blending (R & B) hoods, for checking the status of all valves, and for obtaining special samples from parts of the system.

An AEC-HAPO committee is conducting an investigation of the incident and will issue a report on completion of the investigation.

b. Uranium Reduction Operation

An accidental transfer of UNH solution from the storage tank (X-1) to the 221-U Building, through a transfer line formerly used in the shut down TBP process, resulted in UNH solution ultimately being routed to the waste system. Approximately seven tons of uranium (as UNH) were recovered from the 361-U catch tank, and transferred to a storage tank (301) in the 211-U area on May 11 and May 12, 1962. The material recovered has been sampled to determine purity and subsequent method for reprocessing.

Process Test 62-1-T, designed to determine methods for improving the reactivity of UO_3 at the Paducah Plant of Union Carbide Nuclear Company, has been temporarily suspended. The test had been conducted with E-metal to minimize the inventory of UO_3 in test batches, however, this material has recently been routed to the Fernald Plant of the National Lead Company of Ohio for isotopic blending and direct conversion to metal as part of the program for increasing neptunium production. The test will be revaluated and resumed using the depleted uranium system.

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4. Process Chemistry - O. F. Beaulieu

a. Purex Process Assistance

Laboratory investigations on the second sludge sample from Purex Tank A-103 is underway with the results closely parallelling those on the first sludge sample.

	1st sample	2nd sample
H_2O Soluble	67%	64%
HCl Soluble	18%	14%
Residue	1%	3%
Pu g/g sludge	2.1×10^{-5}	3.2×10^{-5}
Np "	2.8×10^{-5}	5.6×10^{-6}
U "	0.006	0.018
Na "	0.281	0.346

Investigation into the process problems around the Purex K-cell is continuing. The effort centers more around the 2D column since performance of 2E was substantially improved with the new column cartridge. Filters from the water system have been obtained and organic extractions on the filter disclosed the presence of resin or other organic material. Water leaching of the filter as well as 1CU leaches of the filter disclosed the presence of surfactants and also a reduction of 1CU extraction rates by a factor of two or more in the presence of the leached material. Subsequent transfer rates of the 2DU during stripping with 0.01 $\underline{M}$ HNO_3 also appeared to be slower.

Thirty-five liters of water were concentrated to 100 ml and laboratory tests indicated that the concentrate foamed on agitation, had little effect when used in a 2E type contact, and increased the disengaging times when incorporated in synthetic 2DF. Additional work will be performed before conclusions are reached. This will include gas chromatographic and infrared analysis of Purex solvent samples from which TBP has been stripped plus diluent extractions of cold stream used in K cell.

b. Redox Plant Assistance

The Redox effort since the May start-up has been concerned with development of procedures and training which would permit control laboratory application of the DK-2 spectrophotometer to Redox process samples on a routine basis.

[redacted]

c. Hot Semiworks Plant Assistance

The recovery of approximately 150 curies of strontium from Tank 54 waste solutions by batch extraction was successfully piloted in the laboratory.

Laboratory studies have shown that hydrogen peroxide will oxidize the citric acid used as a buffer in HCX at a ratio of 10 moles of peroxide for each mole of citric acid in a boiling solution of 2 M HNO_3. Scouting runs to determine the feasibility of substituting tartaric acid or maleic acid for the citric acid in HCX have indicated the following: 1) Better than 99 per cent of the strontium can be precipitated as the carbonate from solutions 1.6 M tartaric acid, 0.7 M maleic acid, or 1.41 M maleic acid. Only 97 per cent of the strontium will precipitate from a solution 2 M citric acid. 2) Titration curves indicate that 0.75 M tartaric acid or 0.5 M maleic acid will have about the same buffering capacity as 1 M citric acid. 3) Undesirable precipitates of sodium and strontium hydrogen maleate are readily formed.

d. Laboratory Assistance

1. The DBP analysis described last month was further modified to provide application to all Purex sample types. By adding an initial 5 g/l uranium contact and a 20% sodium oxalate strip, spike recoveries of 99% ± 6% were found down to 40 ppm DBP.

2. The following tests are being performed to find and eliminate the difficulties currently being experienced with the Pu/U ratio method.

    a. The plutonium found by a precision extraction method confirmed that found by the corrected AT technique using the Purex D-5 composite for April.

    b. No bias was found between a 5×10^4 c/m mount (L-6 count rate) and a 2.5×10^3 c/m mount (H-7 count rate) on the ASP counters.

    c. Initial tests indicate a D-5 composite could have a lower Pu/U ratio when stored in a glass container than if it were stored in a plastic container. There appears to be some selective plutonium absorption on glass.

Distribution ratios were run on scrubber samples from the Z plant incinerator and gave a particle range of 2 to 22 microns. Samples of UO_2 powder from ceramic fuels (HLO) were also analyzed on the counter and were found to have a range of particle size of from 6 to 55 microns. The Coulter counter has been transferred to the Redox Control Laboratory where it will be available for customer work in the future.

The 400 channel RIDL analyzer has been received and placed in service using the gamma detector system belonging to the Redox Analytical

Control Laboratory. An acceptable compliance to the response efficiency of the Control Lab's RCL analyzers has made it possible to operate all of these instruments interchangeably. Specifically, calibration of the Control Lab's gamma analyzing system is being carried out with the RIDL analyzer.

Calibration data has been taken on Sb^{124}, In^{116m}, Cr^{51}, Ce^{141}, Na^{22}, $ZrNb^{95}$, Ru^{103}, and Fe^{59} making a total of 18 isotopes for which the Redox gamma analyzing system has been calibrated. The activity level of the calibration sources of In^{116m} and Fe^{59} were drawn from the efficiency plot of total photopeak area per microcurie versus Mev. The activity levels of the remaining standards have been independently determined and have verified the efficiency curve.

An investigation was made of the process sampling and analytical system used for the 234-5 incinerator off-gas scrubber system. As a result of this investigation, the process sampling was shown to be good and an improved analytical method gave very good checks between samples. Smaller samples may now be analyzed with better precision and accuracy.

A chromium target tube has been installed in the X-ray fluorescence spectrometer. This new tube will facilitate the analysis of low atomic weight elements. Current efforts are directed towards developing a chloride method for $PuCl_3$ product.

5. 234-5 Development - H. H. Hopkins, Jr.

a. Plutonium Recovery From Fabrication Oil

Experiments show that a contact with 5 M HNO_3 for 10 minutes is an effective method of removing plutonium from fabrication oil.

A stock solution of process fab oil (mixture of lard oil and carbon tetrachloride) was black and had a large volume of solids. Separate analyses showed 0.4 - 0.7 g/l Pu, 0.2 - 0.6 percent solids (by volume), 0.01 M Cl^-, SpG of 1.01, and pH of 1.5 - 12.1. After centrifuging for 10 minutes in a clinical centrifuge, the solution contained 0.2 - 0.4 g/l Pu. The stock solution described above was butted to a SpG of 1.2 with CCl_4 (resulting in 44 percent CCl_4).

Samples of this solution were then contacted with the following reagents: H_2O, 0.1 M HNO_3, 5 M HNO_3, 10 M HNO_3, 5 M HNO_3-0.1 M HF, 5 M HNO_3-1 M HF, 10 M HNO_3-1.0 M HF, 0.1 M FS (0.1 M ferrous ammonium sulfate-0.1 M sulfamic acid), 0.1 M FS-0.05 M HF, 1.0 M FS-0.05 M HF, 1.0 M FS, and 10 percent TBP (in the fab oil) with 10 M HNO_3-1.0 M HF. An L/V of one and a contact time of five minutes were used. Three reagents were able to strip the plutonium to 0.05 g/l or less (throw-away value). These reagents are 5 M HNO_3, 10 M HNO_3, and 5 M HNO_3-1 M HF.

A second test series was made using the five best stripping agents from above. The organic used in this run was from the same stock solution as described above, except that it was filtered through an 0.25 micron filter. This material contained 0.17-0.18 g/l Pu. Results of this series showed that use of fluoride did not result in improvement.

A third run series was made to determine the effect of contact time on stripping efficiency. The oil used for this run was samples of the filtered oil described above. Stripping agents used in this were 5 M HNO_3 and 5 M HNO_3-1.0 M HF. Contact times used with each of the two stripping agents were 3, 10, and 30 minutes. The run using HF was ineffective, stripping 43 percent of the Pu in 30 minutes. It appeared in both runs that equilibrium is attained slowly. A 10-minute contact time appears to be effective with 5 M HNO_3.

Samples of fab oil were also tested to determine how much plutonium was present as solids in the oil. Daily samples of oil were received. Half of each sample was filtered through an 0.25 micron filter. The other half was let stand for five days. Five samples showed little ($<$ 5 percent) change in plutonium concentration on filtering or on standing. A sixth sample showed a 50 percent decrease in plutonium on both filtering and on standing for four days.

b. Electrorefining Of Plutonium Metal

Current-efficiency relationships are under study.

The ratio of cathode current density (amp/cm^2) to the concentration of plutonium (%) in the electrolyte was plotted against the cathode for six batch runs. The correlation shows that high current density is favorable as long as the plutonium concentration is high enough. This is to be expected from the work of others who have found that high current density improves efficiency. From this plot, it should be possible to predict optimum conditions for high efficiency.

A run was designed to fill in a point in the 90 percent efficiency region. However, the results did not fit. One explanation of this may be the lower amperage (40 amps). Previous runs had indicated that 50 amps gave better results. This indicates that there is a minimum desirable current density.

One electrowinning run and one electrorefining run in an LiF-NaF-PuF_4 system were attempted to obtain a comparison with the chloride system. Electrowinning was difficult because the anode effect prevented drawing more than seven amps. Apparently the fluorine is held on the anode surface tighter than chlorine.

The electrorefining run performed smoothly except that the decomposition potential of NaF and PuF_3 are so similar that considerable amounts of sodium metal were released. Very little consolidated plutonium was found. There were some "black solids" that appeared to be the same as those found in the chloride system. There was no ceramic corrosion noticed in either case.

c. Critical Mass Control

The critical mass control program of the 234-5 Development Operation has been reviewed. All hood limits have been updated. Emphasis is being directed toward minimizing chances of water flooding, and improved plutonium storage facilities in the glove boxes.

DF Judson

for Manager
Research and Engineering