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OAK RIDGE NATIONAL LABORATORY

Operated By
UNION CARBIDE NUCLEAR COMPANY

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL
CENTRAL FILES NUMBER

57-10-59

DATE: October 15, 1957

COPY NO. 20

SUBJECT: Recovery of Plutonium from Chalk River
Solution, Oxide and Miscellaneous Scrap

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-2-

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CONTENTS

	<u>Page</u>
0.0 Abstract	3
1.0 Summary	3
2.0 Plutonium Recovery from Nitrate Solution	4
2.1 Preliminary Handling	4
2.2 Solution Processing	4
3.0 Plutonium Recovery from Oxide and Scrap Solids	7
3.1 Solids Dissolution and Feed Preparation	7
3.2 Solvent Extraction	10
4.0 Plutonium Product Purity	10
5.0 Plant Material Balance	13

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-3-

0.0 ABSTRACT UNCLASSIFIED

The processing of unirradiated plutonium nitrate solution, PuO_2 , and miscellaneous Pu-Al scrap from Chalk River during the fourth quarter FY-1957, has resulted in the recovery of 3.6 kg plutonium. Processing of irradiated plutonium-aluminum alloy slugs received in the same shipment and containing 1154 g plutonium was delayed pending modifications to increase plant shielding.

1.0 SUMMARY

Approximately 3,618 g of plutonium was recovered as product from the unirradiated plutonium received from Chalk River in shipment EVG-QRL-235. This shipment contained 4,876 g of plutonium and consisted of unirradiated plutonium nitrate solution (1,857 g), plutonium oxide (1,489 g) scrap (377 g) and irradiated plutonium-aluminum alloy slugs (1,154 g). The plutonium nitrate solutions were processed by ion-exchange only; the plutonium oxide and scrap required dissolution, one cycle solvent extraction and isolation by ion-exchange. The irradiated plutonium-aluminum alloy slugs were not processed but are being held in storage pending plant modifications to increase the biological shielding.

The total amount of plutonium measured by ORNL was 75.90 g (2.04 per cent) less than the Chalk River measurements. Process losses were 0.22 per cent and the major loss (0.17 per cent) occurred in the IIBW stream.

Complete dissolution of PuO_2 was obtained in 52 hours using 13.4 M HNO_3 and 0.02 M HF as dissolvent. Acid concentrations of 10 to 13.4 M HNO_3 and 0.01 to 0.03 M HF were tried before the optimum reagent concentration was selected.

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-4-

2.0 PLUTONIUM RECOVERY FROM NITRATE SOLUTION

2.1 Preliminary Handling

The plutonium nitrate solution was shipped to ORNL in 36 flasks, each containing approximately 400 ml, and was transferred to seven polyethylene bottles. By ORNL analysis, the plutonium content of the solution was 1,843 g, 0.80 per cent less than the Chalk River measurement. The solution contained 31 g of uranium by Chalk River measurement. A breakdown of the plutonium and uranium content is presented in Table 2.1.

2.2 Solution Processing

The plutonium nitrate solution was processed through the ion-exchange system only. It was introduced into the system by way of the Waste Recycle Tank (Fig. 2.2.1) where hydroxylamine sulfate (2 g/g Pu) was added to convert the plutonium (IV) to plutonium (III).

Final dilution of the plutonium nitrate solution to flowsheet conditions (0.25 M HNO_3) was accomplished by dilution with a metered amount of water while pumping the solution to one of three parallel resin columns. The flow through the column was 1 ml/min/cm^2 . The resin column raffinate was transferred to a 100-gal tank by means of a submerged centrifugal pump for monitoring before disposal to waste.

After approximately 500 g of plutonium was sorbed on the resin, the feed was diverted to a fresh resin column. The loaded column was then eluted, downflow, with $0.25 \text{ M H}_2\text{SO}_4$ -- $0.05 \text{ M (NH}_2\text{OH)}_2\cdot\text{H}_2\text{SO}_4$ to remove uranium from the column. The elution was stopped after 2 volume changes, 9 liters, because of plutonium breakthrough. The plutonium product was then eluted by pumping 0.8 gal/hr of 5.7 M HNO_3 -- $0.3 \text{ M NH}_2\text{SO}_3\text{H}$ upflow through the unit. The first volume change was diverted to the recycle tank, then 10 liters of product solution was collected in the product storage tank. The product was then dropped by gravity to a 5-in.-dia by 6-ft-long shipping container.

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-5-

Table 2.1
Plutonium and Uranium Content of Chalk River Solution

ORNL Flask No.	Chalk River Flasks, Nos.	ORNL* Volume, l	ORNL Pu* Measurement, g	Chalk River Pu Measurement, g	Chalk River U Measurement, g
1	307, 319, 340, 343, 350	1.4067	278.02	255.7	3.54
2	308, 316, 318, 330, 342	2.9595	292.40	307.1	5.26
3	309, 311, 320, 321, 322, 349	3.4833	328.70	318.6	1.90
4	317, 325, 336, 338, 347	2.1885	233.50	243.5	3.53
5	305, 323, 326, 329, 345	2.0916	238.70	242.0	5.39
6	306, 341, 344, 346, 348	2.5948	215.61	231.7	9.27
7	324, 327, 328, 337, 339	2.5426	255.62	258.5	2.27
TOTAL		17.2670	1,842.55	1,857.1	31.16

* Volumes were obtained by solution weight (error + 0.2 per cent) and analytical specific gravity (error + 0.1 per cent); the plutonium content was obtained by the potentiometric ceric sulfate method (error + 0.5 per cent); the total limit of error was 0.55 per cent.

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Fig. 2.2.1 Metal Recovery Plutonium Isolation System

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-7-

After product removal, the resin column was reconditioned by pumping 30 liters of reconditioning solution, 0.1 M HNO_3 -- $0.1 \text{ M (NH}_2\text{OH)}_2\cdot\text{H}_2\text{SO}_4$, upflow through the column to the Waste Recycle Tank. The reconditioning solution and the material resulting from the dilute product cut was then pumped from the Waste Recycle Tank to the resin column which was in a sorption cycle.

The loss of plutonium to the resin column raffinate (IIBPW) during the sorption cycle and uranium elution was 0.045 per cent.

3.0 PLUTONIUM RECOVERY FROM OXIDE AND SCRAP SOLIDS

3.1 Solids Dissolution and Feed Preparation

Plutonium oxide and miscellaneous scrap, mostly reduction crucible slag, billets and chips were shipped from Chalk River in 22 carriers. The plutonium oxide, in fine powdered form, was poured into standard 1-gallon paint cans from 250-cc polyethylene bottles after which the bottles were rinsed with water to remove residual oxide. The scrap material was poured into the paint cans directly from the carriers. All of the transfer operations were accomplished in the plutonium handling facility which consists of a hood equipped with dry box gloves.

After transfer, the paint cans were segregated into batches that contained not more than 450 g of plutonium for criticality considerations. Four plutonium oxide dissolutions and one scrap dissolution were made. For the first oxide dissolution 10 M HNO_3 and 0.03 M HF was used as the dissolvent. From 70 to 100 hr at reflux temperature was required for complete dissolution (Fig. 3.1.1). The third, fourth and fifth dissolvings were made by adding 13.4 M HNO_3 to the dissolver after the paint cans were charged, heating the solution to maximum temperature and then adding sufficient 27 M HF to make the solution 0.01 to 0.02 M with respect to HF.

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-8-

Complete dissolution of the plutonium oxide was accomplished in 52 hr using 13.4 M HNO_3 -- 0.02 M HF. After dissolution, the solution was jetted to the feed tanks followed by a dissolver rinse with water. Aluminum nitrate, which served to complex the fluoride ion, was added directly to the feed tank.

By ORNL analysis of the dissolver solution, the plutonium content of the dissolved plutonium oxide and scrap was 1,757 g, 5.7 per cent less than the Chalk River measurement. The plutonium content of each batch of dissolver solution is presented in Table 3.1.

Table 3.1
Plutonium Content of Dissolver Solution

ORNL Dissolving No.	Chalk River PuO ₂ Container No.	Volume,* l	ORNL Pu* Analysis g/l	ORNL Pu Measurement g	Chalk River Measurement g
MD-1	38, 39	280.1	1.25	350.12	368.6
MD-2	40, 41	249.8	1.28	319.74	369.7
MD-3	42, 43	352.0	1.02	359.04	371.5
MD-4	44, 45, 46	439.1	0.80	351.28	378.1
MD-5	47 - 59	310.4	1.21	375.58	377.0
Heel	---	458.0	0.0033	1.51	--
TOTAL				1,757.27	1,864.9

* All analyses are by the potentiometric method (error $\pm$ 0.5 per cent) except for the heel, where the gross α count was used. The volume of the dissolver was obtained with a liquid level instrument (error $\pm$ 1.0 per cent) and analytical specific gravity (error $\pm$ 0.1 per cent). The total limit of error for the plutonium measurement was $\pm$ 1.12 per cent.

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Figure 3.1.1 .DISSOLUTION OF CHALK RIVER PuO_2 IN METAL RECOVERY PLANT
420 grams PuO_2 per BATCH

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-10-

In the feed tank, the solution was chemically adjusted to approximate Purex second plutonium cycle feed specifications. The composition of the feed was:

Pu	0.40 g/l
HNO ₃	6.0 <u>M</u>
U	0.13 mg/l
Al	0.05 <u>M</u>

3.2 Solvent Extraction

One cycle of solvent extraction (Fig. 3.2.1) which consisted of an extraction column and a strip column was required to purify the plutonium. The plutonium was extracted from the feed with 30 per cent tributyl phosphate in kerosene diluent (Amsco), scrubbed with 0.5 M nitric acid, and then stripped from the solvent with 0.05 M nitric acid - 0.10 M hydroxylamine sulfate.

Solvent extraction losses from the extraction column (IIAW) and strip column (IIBW) were 0.005 and 0.17 per cent respectively.

The plutonium product stream (IIBP) flowed from the strip column by gravity to a Dowex-50 resin column for isolation. The resin column was loaded, eluted, and reconditioned in the same manner as that described in Sect. 2.2. A plutonium loss of 0.045 per cent occurred in the resin column effluent (IIBPW).

4.0 PLUTONIUM PRODUCT PURITY

Five product carriers containing a total of 3,617.59 g of Chalk River plutonium were shipped to Rocky Flats, Colorado. The concentration of the solutions ranged from 18 to 54 g/l plutonium.

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Figure 3.2.1 METAL RECOVERY FLOWSHEET FOR RECOVERY OF PLUTONIUM FROM CHALK RIVER OXIDE AND SCRAP

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-12-

The uranium content of the product was 0.78 per cent, which represents a separation of the plutonium from the original uranium by a factor of three.

The composition of the product is presented in the following table:

Product No.	Volume, ^a l	Plutonium ^a Content, g/l	Uranium Content, g/l	HNO ₃ <u>M</u> ³	Total Plutonium, g	Total Uranium g	Product Cylinder No.
PP-1	18.51	49.09	0.169	4.48	908.66	3.13	N-31 ^b
PP-2	18.24	44.38	0.487	4.84	809.49	8.88	N-21 ^b
PP-3	16.64	44.27	0.940	4.61	736.65	15.64	N-37
PP-4	17.60	53.97	0.028	4.61	949.87	0.49	N-51
PP-5	17.83	18.07	0.017	5.23	212.92	0.30	N-41

- a. Volumes of product cylinders were obtained by solution weight as measured by Metal Recovery Strain Gage (error $\pm$ 0.1 per cent) and analytical specific gravity (error $\pm$ 0.1 per cent); plutonium content was obtained by the potentiometric ceric sulfate method (error $\pm$ 0.5 per cent); the total limit of error for the plutonium measurement was $\pm$ 0.52 per cent.
- b. Product in cylinders N-31 and N-21 was primarily from the plutonium nitrate solution and the other three contained plutonium from the oxide and scrap.

The isotopic concentration of the plutonium product is given in the following table:

Plutonium Isotopic Composition in Atom Per Cent

Product No.	Pu- 239	Pu- 240	Pu- 241
PP-1	95.138	4.558	0.304
PP-2	95.390	4.358	0.252
PP-3	96.800	3.010	0.190
PP-4	96.670	3.170	0.160
PP-5	96.730	3.100	0.170

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-13-

5.0 PLANT MATERIAL BALANCE

Based on ORNL measurements, an over-all plutonium balance of 101 per cent was obtained for the program. Losses from the system totaled 8.01 g (0.22 per cent). The total amount of plutonium measured by ORNL was 75.90 g (2.04 per cent) less than the Chalk River measurements. The material balance is presented below:

Plutonium Material Balance

Material	Plutonium weight, g	
	Chalk River Measurement	ORNL Measurement
Plutonium nitrate solution	1,857.10	1,842.55
Plutonium oxide and scrap	<u>1,864.90</u>	<u>1,757.27</u>
TOTAL	3,722.00	3,599.82
Difference		122.18
Product shipped, g		3,617.59
Product on hand, g		11.42
Samples shipped, g		1.00
Samples on hand, g		8.08
In waste disposals, g		<u>8.01</u>
TOTAL, g		3,646.10
ORNL feed measurements, g		<u>3,599.82</u>
TOTAL GAIN, g		46.28
Difference between ORNL and Chalk River measurements, g		122.18
Net difference, g		75.90

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