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FINAL REPORT
PRODUCTION TEST 231-10 - SUPPLEMENT B
PROCESS EVALUATION-PRODUCTION OF
CONCENTRATED PLUTONIUM NITRATE SOLUTION
IN BUILDING 231 - TRANSFER TO AND
PROCESSING IN BUILDING 234-5

INVENTORIED

FEB 3 1955

BY

W. B. KERR

TECHNICAL SECTION

ENGINEERING DEPARTMENT

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PRODUCTION TEST 231-10-SUPPLEMENT B

PROCESS EVALUATION-PRODUCTION OF

CONCENTRATED PLUTONIUM NITRATE

SOLUTION IN BUILDING 231

TRANSFER TO AND PROCESSING IN BUILDING 234-5

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By BR/10/85

by

W. B. Kerr
Process Assistance
Separations Technology Unit

October 3, 1951

NUCLEONICS DIVISION
RICHLAND, WASHINGTON

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PRODUCTION TEST 231-10-SUPPLEMENT B
PROCESS EVALUATION-PRODUCTION OF
CONCENTRATED PLUTONIUM NITRATE
SOLUTION IN BUILDING 231
TRANSFER TO AND PROCESSING IN BUILDING 234-5

INTRODUCTION

All of the 231 Building final product was prepared for off-site shipment prior to the startup of the 234-5 Building. The evaporator (S-1) effluent, a solution approximately 10 molar in nitric acid with plutonium concentration of 275 grams/liter, was dried within the shipping container (sample can) to a solid cake. The purpose of this drying operation was to minimize personnel contamination and/or loss of product during shipment. The dried cake was redissolved in water before further purification steps could be performed.

The major steps in the Purification operation were:

1. Reduction of Pu IV and VI to Pu III by 47% hydriodic acid,
2. Precipitation of Pu III Oxalate by 0.67 M Oxalic acid,
3. Washing of the precipitate with 0.1 M Nitric - 0.1 M Oxalic acids solution, and
4. Transfer the oxalate to the Dry Chemistry operation.

Subsequent to start-up, eighty to ninety per cent of the 231 Building final product was routed to the 234-5 Building for Purification by the procedures listed above. The short on-site shipment eliminated most of the shipping hazards. This made it possible to limit the drying operation to supply a liquid for transfer to the 234-5 Building.

Process changes to permit the use of the liquid S-1 effluent (AT solution) as the feed solution for the 234-5 Building would permit:

- a. Savings of at least 35 man-hours processing time/kilogram of plutonium processed,
- b. Retiring the dissolution equipment in the 234-5 Building, and

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- c. Bypassing the drying equipment in 231 Building with all the 231 Building effluent that was processed in the 234-5 Building.

A development program (6) established that, at 30°C., a maximum of 2.0 M nitric acid concentration was allowable in the feed solution. At greater concentrations, the iodide ion supplied by the hydriodic acid was oxidized to iodine by nitric acid. Increased waste losses resulted because the iodide ion was oxidized before the plutonium was reduced.

The procedures for testing the purification of AT solution as recommended by the development group (6) were presented in Production Test 231-10 Supplement B.⁽³⁾ The current report is written to provide a history of:

- a. Work done and data collected during the test, and
- b. Conclusions and Recommendations obtained from studies of the data.

OBJECTIVES

Production Test 231-10 Supplement B was initiated to establish the procedures for the precipitation of Plutonium (III) Oxalate in Plant equipment from AT solutions. It was necessary to demonstrate, with plant equipment, that:

- a. Evaporation in the S-1 Tank in the 231 Building could be arrested within a product concentration range of 350 ± 50 g Pu/liter of solution,
- b. Sample cans containing the standard batch of plutonium could be handled safely in transfers from the 231 to the 234 Building.
- c. Solutions could be completely transferred from Sample Cans to the purification vessels in the 234 Building without dilution or mechanical agitation,
- d. Satisfactory hydriodic acid reductions of Pu(IV) and (VI) to Pu(III) and subsequent oxalate precipitations could be made in the 10 liter reaction vessel in the 234 Building, and that
- e. Comparable waste losses and impurity content resulted from the new process conditions.

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SUMMARY

It was demonstrated that satisfactory Plutonium III Oxalate precipitate can be obtained from 231 Building AT solutions containing 350 ± 50 grams/liter plutonium in 8.8 to 10.7 M nitric acid solutions. Processes established by this test permit the elimination of the final concentration in the 231 Building and subsequent dissolution in the 234 Building for all internal processing at Hanford Works. This results in the saving of approximately 37.5 man hours operating time/kilogram of plutonium processed.

RECOMMENDATIONS

Based on the results of this test, the Process Section has recommended to the Manufacturing Division that:

- a. The evaporation in the S-1 Tank be arrested at a plutonium content of 350 ± 50 g/liter,
- b. The concentrated solution from S-1 Tank be transferred to Sample Cans, as currently practiced, in lots containing 160 gram of plutonium,
- c. The final elevated-temperature evaporation of plutonium solutions be eliminated for that material to be processed at Hanford Works, and,
- d. Material from the Sample Cans be processed in the 234 Building in accordance with procedures supplied by the Process Section. (These procedures are identical to those outlined in Production Test 231-10 Supplement B.)

EXPERIMENTAL

Procedures

231 Building

Approximately 4.5 kg of plutonium was prepared in Cell 3 as a solution with plutonium concentration of 300 to 400 grams/liter solution, and 8.8 to 10.7 M nitric acid. (HNO_3 concentration was not a control item but was to be used only as an aid in evaluating any part of the test which appeared off standard.) Each 231 Building run was sampled for plutonium assay and then

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divided into batches containing 160 grams of plutonium. These batches were transferred to the 234 Building.

After the completion of the 231 Building program, a flush was made of the still (S-1) and concentrate lines and vessels to determine if the processing of the more concentrated plutonium solution had resulted in excessive holdup in the system. The flush recovery was normal, 6.5 per cent of a run compared to routine process flush recoveries of 7.5, 3.9, and 14.9 per cent of a run.

234 Building

The plutonium solution, as received in sample cans in the 231 Building, was sampled for plutonium assay and purity determinations and then transferred to the purification reactor. The solution was then diluted with distilled water. The quantity of water added was sufficient to reduce the nitric acid concentration from 11 M to less than 2 M for any batch within the specified concentration range.

The plutonium solution was reduced by 47% hydriodic acid and then precipitated with 0.80 instead of 0.67 M oxalic acid. The increase in oxalic acid concentration was made to maintain a maximum volume of 7.5 liters in the 10 liter reaction vessel. Further processing was normal with no changes in material or procedures through the precipitate washing, dry chemistry, and reduction operations.

Sampling

The liquid wastes, the supernate and wash solutions, were sampled for plutonium assay and the metal buttons were sampled for impurity analyses.

Controls

Control materials for evaluating this test were normal production materials explained in the tables.

Discussion of Results

Conclusions from Table I are:

- a. The controls on the S-1 concentration operation are adequate

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to produce plutonium nitrate solutions between the concentration limits of 300-400 g/Pu/liter solution, and

- b. The Hydrogen Ion content of the AT solution is between 8.8 and 10.7 g/liter. This is equivalent to molarity as nitric acid.

The data in Table II indicates that AT solution can be processed in 234 Building without undesirable results. This is shown by:

- a. Waste losses from the test batches were comparable to the losses from the controls.
- b. The decrease in AT-oxide deviation (difference between plutonium content of a batch of AT solution and the plutonium oxide produced from this batch) indicated some small improvement in the ease of transferring the oxalate precipitate.
- c. Comparable material balance between 231 and 234 Building. This is a further indication of normal hold-up in the AT tank to sample can equipment in 231 Building.

Table III shows slight increase in the impurity level of some elements (Bi, Ca, Cd, In, Mg and P) when compared with the controls. These elements would not be removed from the material during the drying operation, so it was concluded that these increases in impurity were not a function of the test and did not influence the decisions regarding the test.

The metal produced from the test material is of comparable quality to that used as control material. This is shown in Table IV. Any differences in the impurity level between test and control materials are considered to be insignificant.

FUTURE WORK

Further studies relating to the concentration and transfer of plutonium nitrate at Hanford Works are not anticipated. Further work will be done to permit off-site shipment of AT solution. This would retire the final concentration equipment.

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REFERENCES

1. HW-15907, Production Test 231-10. Determination of Optimum Sample Can Load Weight to be delivered to the 234 Building. W. B. Kerr, SECRET
2. HW-18659, Production Test 231-10 Sup. A, Increase in Sample Can Load Factor, W. B. Kerr, SECRET
3. HW-19254, Production Test 231-10 Sup. B, Purification of Undried AT Solution, W. B. Kerr, SECRET
4. HW-18617, Production Test 231-10 Interim Report, Optimum Sample Can Load Factor, W. B. Kerr, SECRET
5. HW-18877, Production Test 231-10 Sup. A. Interim Report, Optimum Sample Can Load Factor, W. B. Kerr, SECRET
6. HW-18738, Summary Report, Use of AT Solution without Evaporation, 234-5 Development Group - W. L. Lyon and J. F. Facer, SECRET

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TABLE I
OPERATIONAL DATA (1)

<u>231 Building Data</u>		<u>234 Building Data</u>				
<u>234 Batch</u>	<u>Assay(2)</u>	<u>Assay</u>	<u>(234 Assay X 100)</u> <u>231 Assay</u>	<u>Acidity Feed</u> <u>Solution</u>	<u>Supernates</u>	<u>AT-Oxide(5)</u> <u>Deviations</u> <u>(% of batch)</u>
X-10-12-80	395.1	406.3	102.8	10.09	0.0309	0.37
81	394.0			9.67	0.130(3)	3.29
82	387.2	386.6	99.8	10.27	0.0187	1.00
83	392.0			9.83	----(4)	2.42
84	398.3	399.8	100.4	8.88	0.0222	4.72
85	368.4			9.33	0.0237	0.48
86	356.2	359.2	100.8	9.11	0.0389	2.20
87	384.3			10.68	0.0167	1.38
88	381.1	385.5	101.2	10.13	0.0202	0.13
89	366.5			10.21	0.0367	0.88
90	375.3	370.3	98.7	10.06	0.0315	2.01
91	339.7			10.12	0.0634	0.19
92	346.8	346.1	99.8	10.12	0.0569	1.81
93	375.1			10.43	0.0272	0.93
94	364.6	378.5	103.8	10.50	0.0615	0.00
95	361.6			10.63	0.0211	1.01
96	385.1	388.5	100.9	10.45	0.0192	2.19
97	377.7			10.74	0.0417	0.25
98	353.1	367.5	104.1	10.68	0.0381	2.00
99	346.7			9.84	0.0259	1.44
100	332.3	342.1	102.9	10.42	0.0448	6.25
101	332.0			10.45	0.0294	0.63
102	331.8	355.8	107.2	10.33	0.0262	0.37
103	361.6	386.6	106.9	10.62	0.0425	0.20
104	366.8			10.52	0.0321	1.06

1. All quantities grams Pu/liter solution unless otherwise identified.
2. Calculated from Assays of solutions into Sample Can.
3. Non-Standard operation. Results not averaged nor used in evaluation.
4. Sample spilled.
5. AT-Oxide deviation is the difference between Pu loaded to Sample Can as calculated from 231 Assay and Pu calculated to be in the weighed oxide. This is an indication of ease of transfer.

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TABLE II
OPERATIONAL COMPARISONS

<u>Item</u>	<u>Test Batches</u>			<u>Controls</u>		
	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>
Supernates (grams Pu/liter solution)	0.0335	0.0634	0.0167	0.0311 ⁽¹⁾	0.136 ⁽¹⁾	0.0077 ⁽¹⁾
M.B. (%)	102.25	107.2	98.7	99.78 ⁽²⁾	109.6 ⁽²⁾	84.0 ⁽²⁾
M.B. outside limits ⁽³⁾ (%)		23%			10.2 ⁽²⁾	
AT Oxide deviation ⁽⁴⁾ (% of Batch)	1.4	6.3	0.0	1.9 ⁽⁵⁾	8.6 ⁽⁵⁾	0.0 ⁽⁵⁾

1. 127 Batches in December 1950.
2. 194 Batches, June and July, 1950.
3. Reproducibility of the chemical analysis is $\pm 2\%$. If the material balance is between 96% and 104% when calculated by this formula, $MB = \frac{234 \text{ Assay} \times 100}{231 \text{ Assay}}$, the results are within expected limits.
4. See (5) Table I.
5. Same as 2 above excluding 6 non-standard batches.

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TABLE III

234 FEED SOLUTION SPECTROGRAPHIC ANALYSES

(ppm based on Pu)

<u>Impurity</u>	<u>Test Material⁽¹⁾</u>			<u>Controls⁽²⁾</u>		
	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>
Ag	1.2	2	L1	2	10	L1
Al	43	100	L20	43	200	L10
As	L50	L50	L50	L50	L50	L50
Ba	L20	L20	L20	L20	L20	L20
Be	L0.02	L0.02	L0.02	L0.02	L0.02	L0.02
Bi	825	G1000	200	380	1000	L2
Ca	145	500	10	55	200	L10
Cd	90	200	L20	40	500	L10
Ce	L200	L200	L200	L200	L200	L200
Co	L20	L20	L20	30	200	L20
Cr	3250	5000	1000	2500	5000	40
Cu	25	50	10	45	100	10
Fe	8000	10,000	2000	7000	G10,000	2000
Hg	L200	L200	L200	L200	L200	L200
In	50	L100	L2	3	10	2
K	Not Determined			250	1000	L20
La	G2000	G2000	G2000	1840	G2000	200
Li	L2	L2	L2	3	L10	L2
Mg	80	200	10	L20	200	4
Mn	290	500	100	375	1000	100
Na	65	200	10	125	1000	L10
Ni	1135	2000	1000	2750	G5000	1000
P	3550	5000	2000	1000	G5000	L100
Pb	80	200	20	45	200	2
Sb	120	200	L50	65	500	L50
Si	36	100	10	100	500	L50
Sn	13	20	2	10	50	L2
Sr	L4	L4	L4	L4	L4 ⁽³⁾	L4
V	270	500	L200	200	500 ⁽³⁾	L200
Zn	L100	L100	L100	L100	L100	L100
Tl	L100	L100	L100	L100	L100	L100

G: Greater Than⁽⁴⁾

L: Less Than

1. 25 Batches X-10-12-80 through X-10-12-104; 21 with complete analyses, 4 not complete because of insufficient sample.
2. 50 batches X-10-9-110 through X-10-11-90.
3. One of 50 batches with value other than L200.
4. For any report "greater than" or "less than", that figure is used in obtaining the average.

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TABLE IV

234 BUTTON SPECTROGRAPHIC ANALYSES ⁽¹⁾

(ppm based on Pu)

<u>Impurity</u>	<u>Test Material</u> ⁽²⁾			<u>Control Material</u> ⁽³⁾		
	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>
Al	L19	L20	L10	13	L20	L1
Be	L0.02	L0.02	L0.02	L0.02	L0.02	L0.02
Ca	24	40	10	18	40	4
Cr	26	50	10	28	50	10
Fe	800	1000	200	580	1000	500
La	97	200	40	420	G2000	20
Li	L2	L2	L2	L1.1	L2	L1
Mg	370	500	200	340	500	200
Mn	145	200	20	122	500	50
Na	L15	L15	L15	17	L100	L10
Ni	96	200	20	140	500	20
Si	29	50	L20	29	50	20

G: Greater Than ⁽⁴⁾

L: Less Than

1. The required impurity determinations have been reduced from the number given on Table III for buttons.
2. Analytical results were requested on only 7 of 13 buttons containing test materials. Two of the seven buttons were made up of half test material and half normal material. Y-10-12-39 through Y-10-12-52.
3. Thirty buttons of normal production series Y-10-12-56 through Y-11-1-57.
4. For any report "greater than" or "less than", that figure is used in obtaining the average.

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