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THE PHASE DISTRIBUTION OF PLUTONIUM AND AMERICIUM IN PRODUCTION ELECTROREFINING

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Abstract: Plutonium can be purified by a nonaqueous, electrorefining technique (1).[1] In such a process, most of the plutonium is recovered as pure metal at the cathode, while some remains as an impure anode and some remains in the molten-salt electrolyte. Americium 241, an impurity contained in the original feed plutonium, has high radioactivity. Thus, the removal and concentration of americium pose certain problems.

To investigate the distribution of plutonium and americium in sodium, potassium, and magnesium-chloride salts; in product metal; and in anode; some 31 electrorefining runs were made. The final results are summarized. Briefly, findings show after electrorefining that the average americium content of the feed metal was 960 parts per million (ppm) and of the salt, 1230 ppm. The average americium concentration in the product metal was 267 ppm. An average of 35.2 grams of plutonium per run was found in the salts as plutonium chloride.

In runs where feed anodes depleted to less than 200 grams, impurities other than americium were found in the salts. After electrorefining, an average of 362 grams of plutonium was retained in the salts also as metal globules.

INTRODUCTION

In earlier work with electrorefining processes at Rocky Flats, insufficient data were acquired to determine the distribution of americium and plutonium in the salts produced. Plutonium and americium enter the salt phase by reacting with magnesium chloride (2). After electrorefining, a certain amount of plutonium in the salt phase is found in the form of metal globules.

The objectives of the current work were to investigate the distribution of plutonium and americium in the salt, product metal, and anode. Salts, containing equal molar mixtures of sodium and potassium chlorides with 2.5-weight percent magnesium chloride, were precast to fit the six electrorefining cells used. Feed metal for the experiments included impure gallium-stabilized, delta-phase plutonium. Electrorefining feed anodes were cast in plutonium-foundry furnaces. A series of 31 electrorefining runs were made. Equipment details and results of the electrorefining process used have been given by Long and Schweikhardt (2,3). Results on plutonium purification and process efficiency have been summarized by R. L. Standifer in an internal report.

DISCUSSION

Experimental:

A series of 31 electrorefining runs were made in six production cells to demonstrate the feasibility of a purification technique as a production process. Data were collected to determine the distribution of the americium and plutonium in the various phases. Experimental conditions are described.

FEED METAL – Plutonium feed material was 1-weight percent gallium-stabilized, delta-phase metal containing about 2000 parts per million (ppm) total impurities. The average weight of the plutonium feed anodes was 3227 grams and the average americium content was 960 ppm. The result shows an equivalent of 3.10 grams of americium per run in the feed for the 31 runs.

SALTS – Salt charges were precast and contained 730 grams of potassium chloride, 570 grams of sodium chloride, and 34 grams of magnesium chloride. The salts were mixed in a ball mill for 30 minutes and the salt mixture poured into a quartz crucible. The crucible was placed in a resistance furnace and heated to 800°C until the salts became molten. The molten salts were purged with anhydrous hydrochloric acid (HCl) for 15 minutes to remove any moisture and then poured into a quartz mold to cool. Salt cakes were removed from the mold and placed in a drying oven for storage until used.

At the start of a run, no americium or plutonium was contained in the salt. Average weight of the salt before electrorefining was 1320 grams. After electrorefining, average weight of the salts was 1310 grams.

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[1] See references.

Salts and plutonium metal in the molten state were stirred for about 48 hours during the electrorefining runs. Details of the electrorefining process and experimental conditions for the 31 runs have been fully described in earlier reports (2,3). Plutonium and americium contents in the salts were determined by radiochemical analysis, and impurities in the salt by emission spectrographic analysis.

Plutonium was recovered from the salts, ceramics, and anode heels by aqueous processes. Salts and ceramics were crushed and the plutonium removed by leaching in 7 N nitric acid (HNO_3). The leached ceramics were then washed with water and discarded. The solution, containing some undissolved plutonium oxide, was filtered and the undissolved plutonium oxide washed with water to remove excess chlorides.

The oxide was recovered by routine production methods. The solution containing plutonium chloride was passed through anion-exchange columns (using Dowex-1®)[2] for recovery. Anode heels were dissolved in a solution containing 3 N HNO_3 and 0.2 N hydrofluoric acid (HF). The plutonium was recovered by routine production methods.

Results:

Americium is thermodynamically more active than plutonium. Therefore, at equilibrium, it is apparent that americium concentrates in the salts. The chemical reaction (Equation 1) for americium (Am) during electrorefining is:

$$2Am^0 \text{ (in Pu)} + 3MgCl_2 \rightleftarrows 2AmCl_3 + 3Mg^0 \qquad (1)$$

The reaction takes place until the americium approaches equilibrium with the salts, anode feed, and product metal.

Table I shows the americium distribution in the feed metal, product metal, and electrorefining salts for all 31 runs. The average americium content of the plutonium-product metal after electrorefining was 267 ppm or 0.66 grams in 2493 grams (average) of product. This is equal to 21 percent of the americium in the original feed.

During the 31 runs, an average of 74 percent of the americium in the feed material was retained in the salts as americium chloride. This is equal to 1.61 grams of americium in 1320 grams of salt. The total americium content of the salt and product metal, by analysis, averaged 2.27 grams. The average americium content of the plutonium feed material was 3.10 grams. The difference in americium concentration between the feed metal and the salts and product metal was 0.83 grams, and is assumed to be in the anode heels. The anode heels were not sampled for americium.

The chemical reaction (Equation 2) of plutonium with magnesium chloride present in the molten electrorefining salt is:

$$2Pu^0 + 3MgCl_2 \rightleftarrows 2PuCl_3 + 3Mg^0 \qquad (2)$$

The reaction is necessary to produce plutonium ions in the salt solution, prior to electrorefining. It takes place during the 30-minute stirring time prior to electrolysis. At the start of the run, there were 34.0 grams of magnesium chloride in 1320.0 grams of salt. From this, the maximum amount of plutonium as chloride that could be present in the salt is calculated as follows:

$$\frac{(34.0 \text{ grams } MgCl_2) \times 2(239 \text{ molecular weight Pu})}{3(94.3 \text{ molecular weight } MgCl_2)}$$

$$= 57.0 \text{ grams plutonium (Pu) as plutonium chloride } (PuCl_3) \qquad (3)$$

Analysis of the salts indicated an average of only 32.5 grams of plutonium as chloride in the salts after the run. A small amount of magnesium chloride ($MgCl_2$, approximately 1 gram) is consumed by reaction with americium. The evidence thus indicates that all of the magnesium chloride is not consumed during the runs. This is not unexpected, as an equilibrium constant of near unity can be estimated for Equation 2 from free energy of formation data (4). A similar result was observed during earlier work at Rocky Flats (5). Four of the runs have not been included in the average because product metal globules were in the salt samples.

The reactions for electrorefining of plutonium are as follows:

Anode Reaction: $Pu^0 \rightarrow Pu^{+3} + 3e^-$
Cathode Reaction: $Pu^{+3} + 3e^- \rightarrow Pu^0$

The more noble impurities concentrate in the anode and the less noble concentrate in the salt. The amount of less noble impurities in the salts was

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[2] Trademark of The Dow Chemical Company, Midland, Michigan.

TABLE I. Americium in the Feed Metal, Product Metal, and Electrorefining Salt.

Run No.	Feed Metal Weight (grams)	Product Metal Weight (grams)	Americium in Feed Metal (parts per million)	Americium in Product Metal (parts per million)	Percent Americium Extracted	Americium in Salt by Analysis (grams per gram)
1-F	3340	2865	980	200	80	1.58×10^{-3}
4-B	3400	2336	980	188	81	1.80×10^{-3}
3-D	3381	2858	980	224	75	1.70×10^{-3}
2-E	3300	2636	980	222	78	1.40×10^{-3}
8-C	3228	2754	806	180	78	1.30×10^{-3}
* 7-B	3274	1909	926	*898	* 4	*2.50×10^{-5}
6-A	3350	2414	926	252	73	1.90×10^{-3}
9-D	3272	2778	806	187	77	1.10×10^{-3}
10-F	3275	2844	806	255	69	1.30×10^{-3}
16-F	3345	3157	806	299	63	5.40×10^{-4}
15-E	3252	2697	975	343	65	1.30×10^{-3}
13-C	3214	2871	1069	263	75	3.34×10^{-4}
14-D	3220	2153	1226	632	49	1.30×10^{-3}
11-A	3224	3062	1069	249	77	1.60×10^{-3}
*12-B	3226	1363	1069	*626	*42	*4.5×10^{-4}
17-A	3104	2483	936	218	77	None
23-F	3218	2545	936	167	82	1.60×10^{-3}
26-D	3248	2779	936	390	59	1.50×10^{-3}
25-C	3211	2585	936	181	81	1.40×10^{-3}
18-B	3029	2052	913	148	84	1.10×10^{-3}
21-E	3193	2715	1226	429	75	None
27-A	3245	2324	913	263	71	1.78×10^{-3}
28-B	3096	1785	913	210	77	4.06×10^{-4}
29-C	3187	2622	1028	310	70	1.26×10^{-3}
30-D	3201	2529	1028	216	79	7.1×10^{-4}
31-E	3150	2610	913	431	52	8.9×10^{-4}
32-F	3177	2529	913	237	74	1.20×10^{-3}
5-A	3210	2089	925	42	95	**1.85×10^{-2}
22-F	3054	2659	None	465		None
20-D	3205	1944	935	None		None
19-A	3203	2353	935	None		None
Average:	3227	2493	960	267	74	1.23×10^{-3}

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* The two runs in the B cell were not normal and were not averaged.

** Value was not included in the average. It is a factor of ten higher than the others, and may be due to analytical error.

low, except when the feed anode was depleted to less than 200 grams.

Tables II and III show the distribution of impurities in the salt phase. Analysis of the salts for runs where the anode was less than 200 grams is shown in Table II. Analysis of salts for electrorefining runs in which the anodes weighed more than 200 grams is shown in Table III.

In some of the runs plutonium-product metal appeared as small globules at the salt-metal interface. Table IV shows the amount of plutonium metal retained as globules after electrorefining as determined by analysis and material balance (weight difference).

In general as calculated by weight differences, the plutonium lost from the metal phase minus the plutonium found in the salt by analysis is equal to the amount of plutonium metal globules in the salt. The metal globules would be undetected in the samples taken for salt analysis. The quantity of globules varied from run to run and cell to cell (see Table IV). The amount of globules in the salt was thought to be related to the amount of metallic sodium produced during the run which in turn was caused by abnormally high voltages. Figure 1 shows possible causes for the production of metallic sodium and consequently plutonium globules.

Cell B showed a much greater plutonium loss to the salts by weight difference than any of the other

TABLE II. Impurities in Electrorefining Salts after Runs Where Anodes Weighed Less Than 200 Grams.

Run No.	Anode Weight (grams)	Impurity Concentration (parts per million)					
		Aluminum	Chromium	Copper	Iron	Gallium	Nickel
3-D	157.0	400	200	50	500	<2.5 (percent)	400
9-D	98.0	200	20	100	10	3000	<10
10-F	63.0	500	200	50	50	<2.5 (percent)	50
29-C	129.0	100	200	<10	100	<100	40

TABLE III. Impurities in Electrorefining Salts after Runs Where Anodes Weighed More Than 200 Grams.

Run No.	Anode Weight (grams)	Impurity Concentration (parts per million)					
		Aluminum	Chromium	Copper	Iron	Gallium	Nickel
5-A	701	<10	<10	<10	<10	<10	<10
6-A	448	<10	<10	<10	<10	<10	<10
27-A	467	<10	<10	40	40	<10	<10
30-D	648	<10	<10	<10	<10	<10	<10

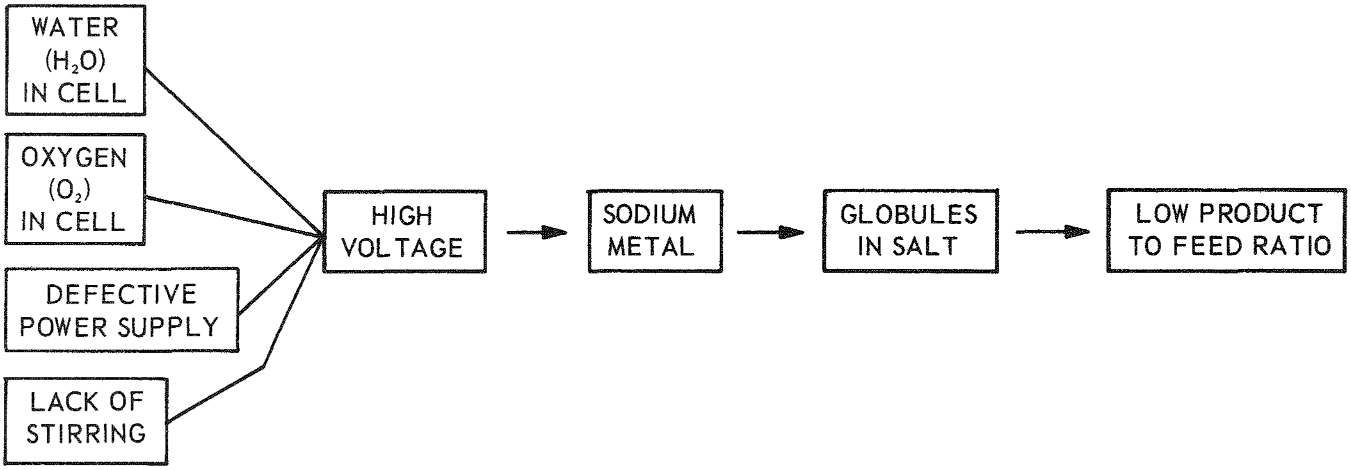
TABLE IV. The Amount of Plutonium Retained in the Salts as Calculated by Weight Difference and as Determined by Analysis. (All amounts are in grams.)

Cell A		Cell B		Cell C		Cell D		Cell E		Cell F	
Weight Difference	Analysis	Weight Difference	Analysis	Weight Difference	Analysis	Weight Difference	Analysis	Weight Difference	Analysis	Weight Difference	Analysis
483	24	581	*345	355	39	332	58	444	34	135	47
488	57	654	39	223	34	396	41	110	41	431	*163
44	33	837	21	231	30	427	*132	407	None	100	26
444	None	741	56	436	4	853	None	335	15	327	None
322	None	683	*522			291	44			336	51
454	36					197	5			268	43
Average:											
371	37	699	39	311	27	416	37	324	30	266	42
**Metal Globules:											
334		660		284		379		294		224	

* These analyses were not averaged because plutonium metal was found in the salt samples.

** The weight difference minus the analysis data equals the gram weight of the metal globules.

FIGURE 1. Possible Causes of Metallic Sodium Production.

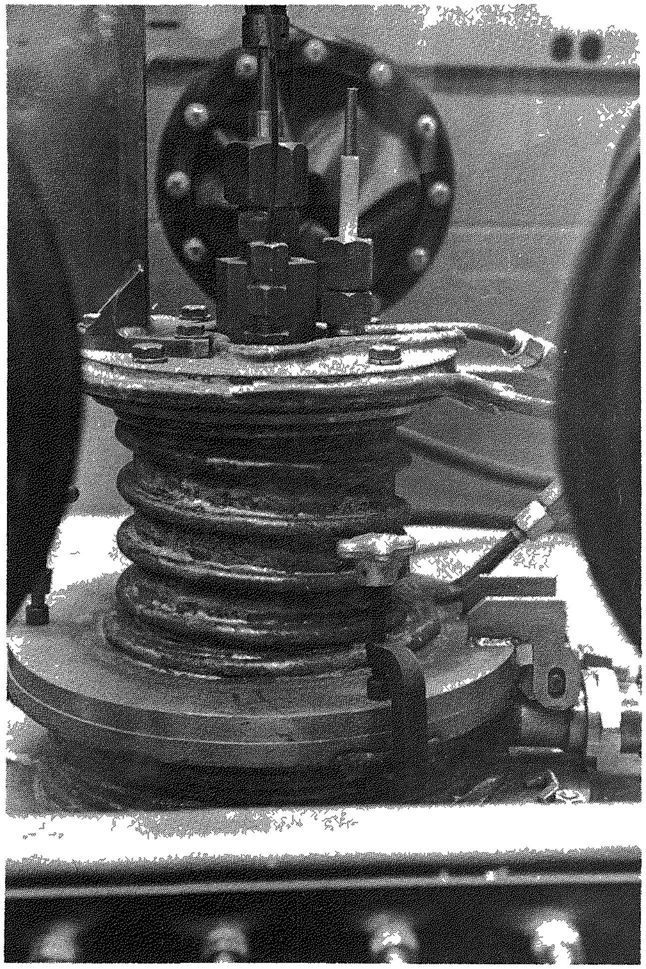


cells. At the end of the runs, when Cell B was opened, evidence was always given of metallic sodium. The direct-current electrolysis power supply was a possible cause of the metallic sodium generated in Cell B. Run conditions and equipment were the same for all cells, with the exception of the electrolysis-power supplies which differed for each cell.

Plutonium loss to the salt in Cell F was less than in the other cells, averaging only 266 grams by weight difference. A commercial Regatron[3] direct-current power supply was used on the two runs in Cell F in which the least amount of plutonium was lost to the salts. The results indicate that the power supplies are a significant factor in making efficient electrorefining runs.

In Figure 2, one of the cells used in the experiments is shown.

FIGURE 2. One of the Electrorefining Cells Used in the Experiments.



SUMMARY AND CONCLUSIONS

Phase distribution of americium and plutonium was determined in a series of 31 electrorefining runs. It was found that an average of 74 percent (1230 ppm) of the americium was retained in the salts as americium chloride. An average of 21 percent (267 ppm) of the americium was found in the plutonium product. An average of one percent or 32.5 grams of plutonium was retained in the salts as plutonium chloride. An average of 11.2 percent or 362.0 grams of plutonium was retained in the salts as finely divided, plutonium-product metal.

Impurities other than americium appeared in the salts from electrorefining runs in which the feed anodes were depleted to less than 200 grams.

REFERENCES

1. L. J. Mullens, Jr. *Plutonium Electrorefining Cell.* U. S. Patent No. 3,098,028 filed by the U. S. Atomic Energy Commission, Washington, D. C. February 16, 1961.

2. J. L. Long and R. D. Schweikhardt. *Electrorefining of Plutonium.* U. S. Patent No. 3,282,806 filed by the U. S. Atomic Energy Commission, Washington, D. C. November 1, 1966.

3. Jack L. Long and Robert D. Schweikhardt. *Plutonium Electrorefining at Rocky Flats.* RFP-871. Rocky Flats Division, The Dow Chemical Company, Golden, Colorado. April 17, 1967.

4. A. Glassner. *The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K.* ANL-5750. Argonne National Laboratory, Argonne, Illinois. 1962.

5. J. L. Long. Private Communication. 1964.

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[3] Electron Measurements Company, Eatontown, New Jersey.