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Materials Science and Technology (MST) Division
Nuclear Materials Process Technology Group (MST-12)
Chemical Process Research and Development Report

David G. Clifton

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MATERIALS SCIENCE AND TECHNOLOGY (MST) DIVISION
NUCLEAR MATERIALS PROCESS TECHNOLOGY GROUP (MST-12)
CHEMICAL PROCESS RESEARCH AND DEVELOPMENT REPORT

by

David G. Clifton

Abstract

- A process for the recovery of plutonium and americium from molten salt extraction (MSE) salt residues has been demonstrated. It is based upon a new chloride anion-exchange process at low acidity that eliminates corrosive HCl fumes.

- The Los Alamos americium oxide production line has been improved to give more product with a concurrent lowering of personnel radiation exposure.

- A cost study has been made for the disposal of americium-contaminated calcium metal buttons that were obtained by pyrochemical recovery of plutonium from MSE salts. The waste form used in the study conforms to WIPP-Facility standards and current state-of-the-art radioactive waste disposal. The cost estimate is ~ \$300/g ^{241}Am .

- Plutonium decontamination factors of ~ 300 have been obtained from lead-platinum alloy dissolution experiments carried out in alumina crucibles using lead oxide slag to getter the plutonium.

INTRODUCTION

The Nuclear Materials Process Technology Group (MST-12) currently has the responsibility for five major programs:

- Plutonium Dioxide Production for the Fast Flux Test Facility (FFTF) Reactor
- Plutonium Scrap Recovery
- Uranium Scrap Recovery
- Americium Recovery and Purification
- Uranium Metal Production

The group conducts supporting chemical process research and development (R&D) projects that provide resources for the continual maintenance, upgrading, and innovation that are necessary to keep the major programs current with advanced technology.

This report gives the status of the plutonium R&D projects but does not directly address the position of major programs (e.g., production goals, problems, and outputs). These are reported elsewhere.

I. PLUTONIUM AND AMERICIUM RECOVERY FROM MSE RESIDUE SALTS:

Larry R. Avens and David G. Clifton

The pyrochemical MSE process extracts americium from liquid plutonium metal using a molten mixture of sodium, potassium, and magnesium chlorides. This gives a plutonium metal button with lowered americium content and salt residues containing sodium, potassium, magnesium, americium, and plutonium chlorides.¹ Because of poor physical separation of molten metal from salts, the residues may include small beads of plutonium or plutonium oxide particles resulting from metal bead oxidation.

At Los Alamos over 100 MSE residues containing ~ 12 kg of plutonium and 400 to 600 g of americium are stored in the vaults. This backlog is small compared with ~ 20 metric tons of residues containing 1 metric ton of plutonium and ~ 70 kg of americium stored at Rocky Flats Plant (RFP).

Over the years, RFP has recovered actinides from these high-chloride wastes using several approaches with mixed success.

1. Dissolution of MSE salts in HCl, precipitation of the actinides with KOH, filtration, redissolution of the separated hydroxides in HNO₃, and then separation of the americium from plutonium with hexanitrate-anion-exchange chromatography were accomplished. The eluted plutonium then went

to the main plutonium recovery process, but the feed and wash effluents containing the americium were sent to thiocyanate ion-exchange columns for americium recovery.²

2. Later, the caustic precipitation step (see above paragraph) was replaced with cation-exchange columns.³ The dissolved salts, in very dilute solutions, were loaded onto cation-exchange columns to get rid of the chloride ions, and the actinides were eluted from these columns with 7 N HNO_3 and then passed through anion-exchange columns for americium and plutonium separation. The effluent americium was then precipitated as the oxalate and calcined to oxide.

3. A combination anion exchange with either an extraction-chromatography procedure or a liquid-liquid extraction approach recently has been studied but has not yet been put into production.⁴

4. Present pyrochemical approaches to the problem focus on metallic plutonium recovery that requires subsequent purification to remove americium from the plutonium button. Also, most of the americium ultimately is in a mixed metal alloy that is either buried or requires special processing to obtain pure americium.

A. New Process for MSE Salt Residues

Recovery of both plutonium and americium from MSE salt residues using a new chloride anion-exchange process at low acidities that eliminates corrosive HCl fumes has been demonstrated at Los Alamos. The new process takes advantage of the high-chloride salt content of the MSE residue salts and gives only discardable low-level wastes plus the two products, plutonium dioxide and americium nitrate in nitric acid solution, for the AmO_2 production line.

The process flow sheet given in Fig. 1 is as follows: Broken MSE salt cake and crucible pieces undergo dissolution and leaching with HNO_3 until the solution is ~ 1 to 2 N and almost saturated with salt at room temperature. The filtered liquid is collected and appropriate amounts of NaNO_2 are added to adjust the plutonium to Pu IV. Since the solution has high-chloride levels ($\text{Cl} \sim 5$ M) as it flows through a Dowex 1 x 4 resin column in the chloride form, PuCl_6^- is sorbed, and the americium, magnesium, and other salts exit in the effluent. The resin bead-invading

Fig. 1. Flow Diagram: Plutonium and Americium Recovery from Molten Salt Extraction Residues (2 kg MSE Salt Cake Containing 200 g Pu and 20 g Am).

americium, magnesium, and other salts are washed from the column with 1 N HNO_3 - 4.8 M NaCl .

The clean plutonium on the resin is eluted with 0.5 N HCl , precipitated with NaOH as the hydroxide, filtered, washed, dried, and calcined to a PuO_2 product. The filtrate is discardable and the resin is ready for another loading.

The combined feed and wash effluents contain the americium; magnesium; some plutonium; and the hydrogen, potassium, sodium, chloride and nitrate ions. A moderate rate of addition of solid NaHCO_3 to this solution neutralizes it and releases CO_2 without excessive frothing. Further addition of NaHCO_3 to saturation precipitates the americium and plutonium, while the magnesium stays in solution and goes with the filtrate. This occurs because the solution has a pH of 8 to 9 at saturation with NaHCO_3 .

The americium product cake may be redissolved with minimal nitric acid and reprecipitated with NaHCO_3 to lower any magnesium contamination, if deemed necessary. This filtrate is combined with the first one and is discardable.

The final americium cake is dissolved with nitric acid, adjusted to 7 N, and sent to the head-end anion-exchange column of the americium production line, where it is cleaned of any residual plutonium and then converted through the oxalate to americium dioxide.

Two options for filtrate treatment are either cement fixation of the liquid and burial or precipitation of the magnesium as a reasonably filterable carbonate by the addition of sodium or potassium carbonate followed by filtration. This filtrate is discardable as caustic waste, while the wet cake is a low-level contaminated solid that can be stabilized for burial by calcination to MgO .

If it is not desired to recover the americium, addition of sodium or potassium carbonate to the combined feed and wash effluents precipitates americium, plutonium, and magnesium as readily filterable materials. This cake can be stabilized by calcination to a solid form, presumably MgO contaminated with americium and plutonium oxides, for storage as fairly high-level contaminated waste.

B. Experimental Results on MSE Salt Residues

1. Salt Dissolution and Crucible Leach

Two MSE salt residues, XBLP 217 and 143, from vault storage were studied experimentally, with the results shown in Table I.

Gamma radiation levels of 100 to 300 mrad/h were measured for these residues, so shielding precautions were necessary in handling them.

Dissolution of random samples of the broken salt pieces with minimal quantities of 1 N HNO_3 went smoothly with very little gas release, minor heat release, and little residue. Initially, blue Pu III was seen, but it slowly changed to blue green and then to green as presumably it was oxidized to Pu IV. The addition of NaNO_2 ensures that this oxidation takes place. As the chloride concentration increased during dissolution, the red-brown PuCl_6^- complex seemed to form.

Later tests with other MSE salts showed that if appreciable amounts of plutonium metal or oxides are present, they consume the hydrogen ion in reaction; dissolution in 2 to 4 N HNO_3 is necessary to obtain a final feed solution that is 1 to 2 N in hydrogen-ion concentration.

When 4.9 g of XBLP 217 was dissolved in 15 ml of added 1 N HNO_3 , 16.5 ml of a solution 4.15 M in chloride ion was found; it is probably marginal for sorption of the Pu complex on chloride-form anion resin. (Note the liquid volume increase of ~ 10% upon dissolution.) Here, an amount of black residue left on a fine-fritted glass filter after solution clarification by filtration was too small for characterization.

Next, ~ 30 g of broken MgO crucible pieces were leached in 1 N HNO_3 . The gamma radiation of the crucible pieces dropped from 120 mrad/hr to 6 mrad/hr after 3 minutes of leaching and finally decreased to 1 mrad/hr (or background level) after an additional 45 minutes of leaching.

A 21.6-g salt piece dissolved in 55 ml of 1 N HNO_3 gave a volume of 62.7 ml (~ 14% increase) with the temperature increasing from 23 to 26°C in ~ 20 minutes. Solution filtration left ~ 100 mg or ~ 0.5% of black residue. The assay of this solution gave a chloride concentration of 5.4 M, which should provide good anion-exchange sorption. This salt-to-acid ratio corresponds to dissolving a 2-kg salt cake in ≤ 6 l of 1 N HNO_3 and leaving 10 g of black residue.

TABLE I

MSE SALT AND CRUCIBLE RESULTS

<u>CHM-1 SOLUTION ASSAY RESULTS</u>										<u>RESULTS</u>
<u>MSE RESIDUE</u> <u>I.D.</u>	<u>SALT</u> <u>WT</u> <u>g</u>	<u>FINAL</u> <u>SOLN VOL</u> <u>ℓ</u>	<u>SOLN</u> <u>CONC</u> <u>g salt/ℓ</u>	<u>SAMPLE</u> <u>NO.</u>	<u>Pu</u> <u>g/ℓ</u>	<u>Am</u> <u>g/ℓ</u>	<u>CHLORIDE CON</u> <u>g/ℓ</u> <u>M</u>		<u>RATIO</u> <u>Pu/Am</u>	
XBLP 217	4.9	0.0165	297.	234	11.2	0.881	147	4.15	12.7	A wt loss of 1.2 g was seen leaching 30 g of crucible
XBLP 217	1.2	0.110	10.9	235	3.12	0.253	1.6	0.045	12.3	
XBLP 217	21.6	0.0627	344.	237	15.0	1.09	192.	5.4	13.8	Powder from bottom of MSE container was dissolved.
XBLP 217	12.7	0.037	343.	246	14.1	1.10	185.	5.2	12.8	
XBLP 217	10.1	0.047	215.	255	33.6	0.81	95.	2.68	41.5	
XBLP 143	9.2	0.0265	347.	256	22.1	5.96	180.	5.08	3.71	
XBLP 143	5.5	0.0155	355.	264	21.0	6.60	195.	5.5	3.18	

The XBLP 217 salt was black but also some green powder, suspected to be rich in PuO_2 , was in the bottom of the container. This may have resulted from oxidation of finely divided plutonium metal. Dissolution in 1 N HNO_3 was rapid with grey froth formation; only blue Pu III color was seen after several hours at 23°C, and considerable residue that looked like PuO_2 was found. This residue needs further study.

Table I shows that random samples of XBLP 217 salts gave a fairly constant Pu-to-Am ratio of ~ 13 except for the powder in the can bottom, which was richer in plutonium. The table also shows that the attained salt concentrations for the solutions are high enough for good resin sorption of the plutonium.

Another vault-stored MSE salt residue, XBLP 143, was examined and found to be analogous to XBLP 217. Dissolutions in 1 N HNO_3 went smoothly, giving solutions above 5 M in chloride-ion concentration. Crucible pieces were effectively leached in dilute HNO_3 , and only small amounts of residues remained after filtration. One residue that remained from a dissolution in 10 N HNO_3 -0.05 N HF was assayed as having 5.03 g Pu/l, 0.0088 g Am/l, and 0.000127 g chloride/l, so the plutonium has only 1750 ppm Am and less than 30 ppm chloride; therefore, it can be added to regular plutonium-process streams.

Table I shows the plutonium-to-americiuim ratio to be different for the two cakes; however, this is to be expected as it is a function of the cakes' previous history.

Estimates from the acquired tabulated data for XBLP 217 give ~ 41 g Pu and ~ 3 g Am per kg of salt, while XBLP 143 gives ~ 61 g Pu and ~ 18 g Am per kg.

2. Process Tests on MSE Salt Residues Using Fig. 1 Flow Sheet

Portions of salts from XBLP 217 and 143 were dissolved in 1 N HNO_3 , filtered, and the valence adjusted to Pu IV by the addition of NaNO_2 . These solutions were passed directly through a column of chloride-form Dowex 1 x 4 anion-exchange resin and processed as shown in the Fig. 1 flow sheet. Table II lists the experimental data obtained.

Only a portion of the solution that was obtained by the dissolution of 12.7 g of salt was used in Experiment 17 to avoid column overload.

TABLE 11
PROCESS TESTS ON DISSOLVED MSE SALTS

<u>STREAM</u>	<u>Pu (g/l)</u>	<u>Am (g/l)</u>	<u>Mg (g/l)</u>	<u>Vol (l)</u>	<u>Pu (g)</u>	<u>Am (g)</u>	<u>Mg (g)</u>	<u>ppm Am</u>	<u>ppm Pu</u>	<u>ppm Mg</u>
<u>EXPERIMENT 17 (XBLP 217 SALT)</u>										
Feed	14.1	1.10	-	0.0265	0.374	0.0291	-	78,000	-	-
Effluent and Wash	0.0151	0.327	-	0.0925	0.00140	0.0302	-	-	46,200	-
Eluate	5.22	0.000957	0.011	0.081	0.423	0.0000775	0.000891	180]	-	2,100
Bicarb ppt Dis- solved	0.0676	1.68	0.033	0.021	0.00142	0.0353	0.000693	-	40,200	19,600
Bicarb ppt Filtrate	0.000805	0.00144	-	0.117	0.0000942	0.000168	-	-	-	-
2nd Bicarb ppt Dissolved	0.0404	1.54	0.012	0.0165	0.000666	0.0254	0.000198	-	26,200	7800
2nd Bicarb ppt Filtrate	0.00512	0.00581	-	0.0235	0.000120	0.000137	-	-	-	-
Eluate ppt Dis- solved	17.7	0.00372	0.034	0.022	0.389	0.0000818	0.000748	210]	-	1923
K ₂ CO ₃ ppt Filtrate	0.000727	0.000166	0.012	0.110	0.0000800	0.0000183	0.00132	-	-	-
<u>EXPERIMENT 18 (XBLP 143 SALT)</u>										
Feed	22.1	5.96	-	0.0265	0.586	0.158	-	270,000	-	-
Effluent and wash	0.121	1.71	-	0.085	0.0103	0.145	-	-	70,000	-
Eluate	9.73	0.00624	0.009	0.081	0.788	0.000505	0.000729	641]	-	925
Bicarb ppt Dissolved	0.406	6.28	0.052	0.022	0.00893	0.138	0.00114	-	64,650	8260
Bicarb ppt Filtrate	0.00513	0.0000048	-	0.101	0.000518	0.00000048	-	-	-	-
2nd Bicarb ppt Dissolved	0.239	4.29	0.020	0.029	0.00693	0.124	0.00058	-	55,700	4677
2nd Bicarb ppt Filtrate	0.0159	0.00258	-	0.038	0.000604	0.0000980	-	-	-	-
Eluate ppt	21.4	0.0146	0.048	0.032	0.685	0.000467	0.00154	682]	-	2248

The plutonium product contained ~ 200 ppm Am vs a value of 78,000 ppm for the feed and it had ~ 2000 ppm magnesium. The plutonium yield was calculated and found to be greater than 100%, indicating assay problems. An americium yield of ~ 87% is based upon data for the feed and the solution obtained by dissolution of the second bicarbonate precipitate. Again, scattered assay results are a problem. The americium product had ~ 41,000 and ~ 27,000 ppm plutonium after the first and second bicarbonate precipitations, respectively.

In Experiment 18, the plutonium product had ~ 700 ppm vs ~ 270,000 ppm americium in the feed, and again the calculations give a yield greater than 100%. The americium yield after the second bicarbonate precipitation was ~ 78% and contained ~ 56,000 ppm plutonium.

The present americium dioxide production line uses feeds that contain up to ~ 200,000 ppm or 20% plutonium; therefore, it can handle the americium product stream shown in the flow sheet.

The magnesium results in Table II show that the americium product contains magnesium levels above specifications of 5000 ppm. A second precipitation with the bicarbonate lowers magnesium by about a factor of 1/2. It is assumed that further magnesium decontamination will occur during the americium oxalate precipitation; in fact, it should obviate the second bicarbonate precipitation.

These two tests using actual MSE salt residues gave excellent and easy plutonium recovery with high yields and quite acceptable product purity. Americium yields are acceptably high, although scattered assay results preclude firm yield figures; however, high yields are supported by the very low concentrations found in the discardable filtrates. Plutonium contamination of the americium product stream requires that it be processed through the americium dioxide production line hexanitrate-anion-exchange system.

3. Additional Experiments

Los Alamos MSE salt residues contain ~ 8 wt% magnesium chloride, so most simulated tests to date were done at this level. Residues at RFP can run as high as 30 wt% $MgCl_2$; therefore, additional experiments, one at ~ 25 wt% and a couple at ~ 5 wt% magnesium chloride, were performed with simulated MSE salts.

At the higher magnesium chloride level, better separation of plutonium and americium was observed, presumably because of the overall increase in chloride concentration. The americium product contained only ~ 6% plutonium vs values of ~ 10 to 20% that occurred in some lower magnesium chloride tests. Also, the plutonium seemed to sorb more tightly on the column (i.e., in a narrower band) and yield figures were ~ 99% for plutonium and $\geq 90\%$ for americium. The americium product obtained from only one bicarbonate precipitation contained ~ 33,000 ppm magnesium; this is considered to be high.

Tests with lower magnesium chloride concentrations and consequently lower chloride ion levels gave lower plutonium product yields because of losses to the americium fraction. A plutonium yield of ~ 98% with ~ 440 ppm americium in the plutonium fraction and an americium yield of ~ 98% with ~ 11% plutonium in it are typical results for a low-magnesium chloride test. The magnesium levels in the products are not yet known because of delays in receiving assay results.

From these tests, it is concluded that high-magnesium chloride levels in the MSE salts enhance the plutonium-americium separation.

a) Tests of magnesium cleanup from the americium product have given mixed results, as is evident in Table II. Difficulties experienced in obtaining reliable magnesium assays have contributed to these ambiguities.

One series of tests of magnesium cleanup from americium product by a second bicarbonate precipitation showed decreased magnesium values ranging from 13,000 - 21,000 ppm Mg in the first product to values of ~ 1700 - 4500 ppm, respectively, in the second product; magnesium was reduced by a factor of ~ 0.2 vs the value of ~ 0.5 seen in Table II.

Further magnesium-decontamination studies are necessary to substantiate cleanup of the americium by both bicarbonate and oxalate precipitations.

b) Filterability tests were made of magnesium precipitates obtained from nonradioactive solutions simulating the filtrates that are shown in the Fig. 1 flow sheet. Precipitants used to form filterable

magnesium compounds were KF , NaOH , K_2CO_3 , Na_2HPO_4 , and $\text{K}_2\text{C}_2\text{O}_4$. A comparison of filtration times and the per cent of original magnesium precipitated under ambient conditions indicated that K_2CO_3 gave the best precipitate. Therefore, for final magnesium cleanup of filtrates, it is recommended that it be precipitated as the carbonate, dried, calcined to MgO , and then buried as a contaminated, stabilized solid.

REFERENCES

1. J. B. Knighton, R. G. Auge, and J. W. Berry, "Molten Salt Extraction of Americium from Molten Plutonium Metal," Rockwell International, Atomics International Division, Rocky Flats Plant report RFP-2365 (March 1976).
2. F. J. Miner, "Chemistry Research and Development Annual Progress Report, Nov. 1, 1979 to Oct. 31, 1980," Rockwell International, Atomics International Division, Rocky Flats Plant report RFP-3180 (August 1981), p. 21.
3. S. G. Proctor, "Cation Exchange Process for Molten Salt Extraction Residues," Dow Chemical, Rocky Flats Division report RFP-2347 (March 1975).
4. L. L. Martella, J. D. Navratil, and M. T. Saba, "Recovery of Plutonium and Americium from Nitric Acid Waste Streams," in Actinide Recovery from Waste and Low-Grade Sources, J. D. Navratil, W. W. Schulz, and A. E. Talbot, Eds., Proc. of the Intern'l. Symp. Co-sponsored by Div. of Ind. and Eng. Chem. and Nuclear Chem. and Tech. of the Amer. Chem. Soc. in NYC, August 24-25, 1981 (Harwood Academic Publishers, New York, 1982), p. 27.

II. AMERICIUM OXIDE PRODUCTION AT LOS ALAMOS: Thomas W. Blum, John L. Parker, Marvin K. Romero, and Deidra D. Yearwood

Los Alamos National Laboratory supplies kilograms per year of high-purity americium dioxide to Oak Ridge National Laboratory for distribution through the isotope pool. Figure 2 shows the flow sheet for this production.

Within the past year, studies of the process have resulted in the considerable achievements shown in Figs. 3 and 4; namely, the output quantity was increased 2.5 times and concurrently worker's radiation dosage was reduced by a factor of $1/4$.¹

These accomplishments (detailed in Ref. 1) resulted from the following:

- All input and output streams were systematically sampled and the contents assayed. From these results and appropriate mass balances, the necessary operational changes were made to successfully optimize the process.

- Considerable modification and redesign of equipment were done to increase shielding from radiation and to decrease the operator's exposure time by reducing the number of manual operations. This included use of Teflon-coated lead sheets wrapped around columns and tanks for shielding, a new design for a closed filtering system that eliminated a significant amount of operator attendance, and a smaller closed anion-exchange column with simpler flow controls that required fewer manipulations.

REFERENCES

1. Thomas W. Blum, John L. Parker, Marvin K. Romero, and Deidra D. Yearwood, "Americium Oxide Production at Los Alamos National Laboratory: Recovery Up--Exposures Down," Los Alamos National Laboratory document LA-UR-83-2962 (November 1983). Presented at American Nuclear Society Meeting, San Francisco, California, October 30 to November 4, 1983.

Fig. 2. Los Alamos Americium Oxide Production

Fig. 3. Americium Production at LANL for Fiscal Years 1979 - 1983.

NOTE: RADIATION DATA FOR PRODUCTION YEAR 1983 IS CURRENT THROUGH 7-1-83. DATA POINTS STANDARDIZED BY DIVIDING THE AVERAGE WORKER DOSAGE BY THE TOTAL GRAMS AMERICIUM PRODUCED.

Fig. 4. Dosage Rate per Gram Am Produced.

III. DISPOSAL COST ESTIMATE FOR AMERICIUM-CONTAMINATED CALCIUM METAL
BUTTONS RESULTING FROM PYROCHEMICAL RECOVERY OF PLUTONIUM FROM
MSE SALTS: C. L. Foxx

A detailed study has been completed that gives an updated americium disposal cost estimate that reflects the requirements imposed by the Waste Isolation Pilot Plant--Waste Acceptance Criteria (WIPP-WAC).¹

Certain initial assumptions were needed for this study. One of the first, for disposal of americium-contaminated calcium metal buttons, was to eliminate their potential pyrophoricity with controlled calcination to stable oxides; second, any dispersible powders formed were immobilized by cement fixation of these oxides. Other than this head-end treatment for calcium buttons, the considerations of the study apply to any americium-containing cement disposal.

The packaging requirements for shipping were examined for two waste categories: Remote Handled Transuranic Waste (RH TRU) and Contact Handled Transuranic Waste (CH TRU).

Within each category, a number of factors such as curie limit, number of shipments, gas generation limit, surface dose rate limit, and weight limits were considered.

Calculations showed which of the above became the limiting factors for each mode of shipment. The RH TRU option was eliminated because the number of canister shipments necessary to accommodate the canister curie limits was unacceptable.

It was concluded that the CH TRU category would apply to shipments from Los Alamos, and the limiting factor for these shipments was the gas generation limit. This imposed an americium value of 16.4 g/drum. Calculations based on this gave a cost of disposal of ~ \$300/g americium.

Characteristics of a typical americium waste drum, detailing some aspects of drum pressurization and potential hydrogen evolution, are also presented.

An overall estimate was given that disposal of approximately 43 kg of americium would require ~ 2600 55-gallon drums.

REFERENCES

1. C. L. Foxx, "Cost Estimate for Disposal of a Calcium Metal Concentrate Enriched in Americium-241, Resulting from Pyrochemical Recovery of Plutonium from Molten Salt Extraction (MSE) Residues," Los Alamos National Laboratory Internal Memorandum, MST-12, Symbol MST-12-PS-83-114, to Carolyn A. Mangeng, S-4, MS F611 (October 26, 1983).

IV. PLUTONIUM DECONTAMINATION FROM PLATINUM: R. S. Day and D. G. Clifton

A. General Discussion

Two categories of plutonium contamination of platinum and its rhodium alloys are considered: first, a surface and/or near-surface type; second, a more deeply penetrating or diffusive type.

The first type of contamination can usually be cleaned off by chemical leaching, with or without electrolytic assistance.

The diffusive or more penetrating type of contamination requires more extensive chemical processing.

A literature search for platinum decontamination procedures revealed a patent (U.S. Patent No. 3,841,863, C. E. Caldwell and A. C. Ficklin, October 15, 1974), granted for the cleanup of uranium from platinum, that might apply to the plutonium case.

By this method, molten lead and platinum are alloyed by heating. The alloy is solidified by cooling, selective dissolution is performed with an acid solution, and then upon filtration, the platinum is isolated as the precipitate. Rhodium alloys should behave similarly.

Figure 5 shows a binary phase diagram for the lead-platinum system. Also shown in Fig. 5, as a point of interest, is a horizontal dotted line at 1161K, the melting point of lead oxide (PbO).

The phase diagram shows lead with a melting point of 600.6K, forming a low-lying eutectic at 563K between lead and the intermetallic compound, Pb_4Pt , so if enough lead is present and the temperature is high enough, the melt interacts with the platinum and forms a liquid phase.

The fate of a third element, such as plutonium in this type of a system, is contingent upon its chemical form. Conceivably, as metal it may enter the molten phase and alloy, or as an oxide, it may preferentially migrate to any oxide slags or refractories present.

B. Experiment

1. Exploratory Tests

Radioactively "cold" experiments were conducted to explore the proposed process. Lead-to-platinum ratios, crucible materials, heating

Fig. 5. Pb-Pt Phase Diagram.

temperatures and times, furnace-atmosphere effects upon alloy button formation, and subsequent separation upon cooling were investigated. Also, button dissolution, platinum precipitation, and lead cleanup of the precipitate and its filterability were examined.

2. Procedures

A recipe that minimizes some experimental problems encountered and seems to optimize alloy button formation, subsequent selective dissolution, filtration, and lead disposal is shown as a flow sheet in Fig. 6. This diagram also incorporates minor procedural changes resulting from later "hot" experiments. These changes are being used in the current process.

The procedure uses a 65:35 weight ratio for Pb:Pt as a reasonable compromise to lower the quantity of lead needed and yet to allow good melting below 1000°C (1272K); other higher ratios are useable and may provide some mixing advantages, but these have not been studied extensively.

High-purity, high-fired Al_2O_3 crucibles are used for sample containment in a muffle furnace fitted with a tube through the door so it can be continually flooded with a slow stream of air, nitrogen, or argon. The sample is taken to 1000°C and held for at least 1 hour. After removal and cooling, the button is separated from the crucible and any slag and placed in a beaker for selective dissolution in 3-5 N HNO_3 . The platinum forms a finely divided black precipitate that is collected by filtration, thoroughly washed with ~ 1-3 N HNO_3 , and then dried. The filtrate containing the lead and any dissolved plutonium is treated by any of several options before disposal.

3. Comments

Several very important features were defined in the initial "hot" tests:

- It is absolutely necessary to have relatively "cold" facilities such as a hood or glove box in which to perform the decontamination experiments. The original contaminated material is first cleaned of swipable contamination by leaching in ~ 10 N HNO_3 containing a few drops of concentrated HF, rinsed, and dried. It is then moved to the "cold"

Fig. 6. Plutonium Decontamination from Platinum.

hood where a sample is taken to determine its original contamination level, and the subsequent procedures are then carried out.

- Experiments showed that mullite and graphite crucibles for holding samples did not give good alloys and decontamination, even in argon atmospheres, because of container and sample interaction.

- Determination of initial and final contamination of samples was best made by submitting appropriate samples for wet chemical analyses where the samples were heated to a constant weight, sampled, dissolved, and then assayed for plutonium and americium.

- A series of aliquot samples were taken of (1) the initial button-dissolution solution, (2) the plutonium black combined wash solutions, and (3) the combined solutions that were obtained from leaching slags and crucibles. These were placed on glass cover slips, evaporated, and α -counted. The results showed unequivocally that the contamination was going to the slag and/or crucible. This result led to the use of added PbO to serve as a getter-slag in later experiments.

4. Results

A number of decontamination experiments were performed using plutonium-contaminated platinum items taken from the storage vault.

Table III lists the experiments, lead-to-platinum weight ratios used in alloying, initial and recovered weights of plutonium, percentage change of the platinum weight, weight per cent of added lead oxide, initial and product platinum contamination as obtained by assays from CHM-1, comments, and decontamination factors found.

The decontamination factor (DF) is defined as the initial contamination of the platinum divided by the product contamination; both are expressed as grams of Pu per grams of Pt. This factor is considered a measurement of the success of decontamination efforts; the higher the factor the better the decontamination efficiency.

The first three experiments of Table III had 3.5, 7.3, and 15 wt% addition of lead oxide (PbO) added to the lead and platinum mix before melting. These experiments were designed to examine the effects of varying slag quantities on decontamination efficiency. There is no obvious trend shown between the DFs and quantities of PbO added. Upon reflection, this might be expected because only a small absolute value

TABLE III
DECONTAMINATION EXPERIMENTS

EXPERIMENT	^a Pb:Pt wt% Pb: wt% Pt in alloy button		INITIAL Pt wt (g)	RECOVERED Pt wt (g)	% CHANGE Pt wt (%)	wt% PbO added	INITIAL CONTAMINATION, Pu g/Pt g	PRODUCT CONTAMINATION, Pu g/Pt g	DECONTAMINATION FACTOR (DF) ^b	COMMENTS
APPR-2d	60	40	7.65	8.0	+ 4.7	3.5	4.01×10^{-5}	$7. \times 10^{-8}$	573	
APPR-2b	59	41	6.2	6.6	+ 6.5	7.3	3.32×10^{-4}	1.5×10^{-6}	221	
APPR-2c	64	36	4.8	5.2	+ 8.3	15.0	4.01×10^{-5}	$< 1. \times 10^{-7}$	> 401	
APPR-2eA	63	37	8.56	9.15	+ 6.9	10.0	6.9×10^{-5}	$< 5. \times 10^{-8}$	> 1388	
APPR-2eP	63	37	8.46	9.23	+ 9.1	0.0	6.9×10^{-5}	3.4×10^{-7}	204	
PT-1a4A	57	43	6.43	7.62	+ 18.3	10.0	2.5×10^{-4}	$5. \times 10^{-7}$	500	
PT-1a4P	60	40	6.37	7.29	+ 14.4	0.0	2.5×10^{-4}	1.0×10^{-6}	250	
PTF-1A	60	40	8.0	9.11	+ 14.0	10.0	1.2×10^{-4}	2.08×10^{-6}	57	
PTF-1P	61	39	8.0	8.53	+ 6.7	0.0	1.2×10^{-4}	5.65×10^{-6}	21	
MPT-1A	61	39	8.19	8.51	+ 3.9	10.0	8.35×10^{-3}	7.82×10^{-4}	11	
MPT-1P	63	37	8.00	8.62	+ 7.7	0.0	8.35×10^{-3}	1.82×10^{-2}	≤ 1	No appreciable decontam.
APPR-2f	64	36	61.6	81.6	+ 32.5	10.0	4.7×10^{-5}	6.2×10^{-5}	≤ 1	Note: Excessive product wt gain; no decontam.
APPR-2h	64	36	60.6	64.7	+ 6.8	10.0	1.92×10^{-3}	9.5×10^{-7}	202i	
MPT-2	63	37	60.2	63.1	+ 4.8	10.0	1.87×10^{-3}	1.31×10^{-5}	143	
APPR-2g	60	40	40.0	43.8	+ 9.5	0.0	4.7×10^{-5}	1.8×10^{-6}	26	
APPR-2i	68	32	49.4	52.6	+ 6.5	10.0	1.34×10^{-4}	1.2×10^{-5}	11	Graphite crucible test. Data not used in averages.

^a Estimated Pb:Pt in button;

Estimated Pb wt = Button wt - Initial Pt wt

$$\text{wt\% Pb} = \frac{\text{Pb wt}}{\text{Button wt}} \times 100$$

$$\text{wt\% Pt} = 100 - \text{wt\% Pb}$$

^b Decontamination Factor = DF

$$\text{DF} = \frac{\text{Initial Contamination}}{\text{Product Contamination}}$$

of plutonium is expected to be present as contaminant; hence, addition of slag beyond the minimally required amount for gettering would not necessarily increase the decontamination.

In the course of further experimentation, a value of 10 wt% addition of PbO was arbitrarily selected for testing; this was before assay results of the above experiments were obtained.

The next four experiments tabulated consist of two companion experiments in two sets. The only difference between the companion tests is that one had 10 wt% PbO added. Examination of these four DFs shows higher DFs when PbO is added.

The next group of four tests, PTF-1A and -1P, and MPT-1A and -1P, were to test the reproducibility of the decontaminations seen in the previous two sets. However, included as starting materials in the PTF case were platinum frit pieces similar to the earlier material but sampled from a different location; and in the MPT tests, platinum from a flatware beaker was used. In both experimental sets, one each had 10 wt% PbO added. The DFs were lower than those previously found but still correlate with larger values occurring when PbO is added.

Experiments APPR-2f, -2h, and -2g were tests with scale-ups of from about 6 to 10; APPR-2f and -2h had 10 wt% PbO added and APPR -2g had no added PbO. Discounting APPR-2f as a bad experiment because of its excessive weight gain of ~ 33%, we again see a higher DF for the case of added PbO.

Experiment MPT-2 was designed to reproduce APPR-2h in which a DF greater than 2000 was obtained; however, the DF for MPT-2 was only 143.

Experiment APPR-2i was a scaled-up test performed in a graphite crucible with 10 wt% PbO added and was run in an argon atmosphere. Even though PbO was added, very little slag was evident after the button was cooled and removed, so presumably a considerable amount of PbO was reduced by the carbon; however, some decontamination occurred. (Data for APPR-2i are excluded from the discussion and conclusions given below.)

All experiments in Table III show a weight gain of the product platinum over the initial sample. Gains of about 4 to 9% are assumed to occur because of absorption of gases or moisture on the extremely high-surface area of the powdered product material. Higher weight gains

presumably are due to incomplete cleanup of the lead or possibly insufficient drying.

5. Conclusions

Reasonable decontamination was obtained in these experiments even though reproducibility was poor. The use of lead-oxide slag raised the decontamination factor in most cases. The problem in reproducibility is attributed to the difficulty in obtaining representative samples of the starting and product materials, thus causing less reliable assays.

In order to establish some numerical value for decontamination factors, the following averages are cited:

- a) A straight average of all DFs gives DF = 338.
- b) An average obtained after dropping the two highs (1388 and 2021) and the two lowest (1 and 1) DFs gives DF = 219.
- c) An average obtained by dropping the two highest and lowest (as per b) and all values obtained when no PbO was added gives DF = 272.
- d) An average obtained by dropping all DFs obtained when no PbO was added gives DF = 531.

Case c) with DF = 272 is considered a conservative estimate for results to be expected in routine application of the process of Fig. 6.