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LA Report 148

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September 27, 1944

This document contains 16 pages

PRODUCTION OF PLUTONIUM BY ELECTROLYSIS

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Per H. F. Carroll July 10, 1958
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Per Phil Lang, FSS-16 Date: 4-4-85
By M Ballegos, CIC-14 Date: 3-25-96

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ABSTRACT

Plutonium has been produced by electrolytic reduction of its trichloride in a solvent of barium, potassium, and sodium chlorides. The $PuCl_3$ is best prepared by a dry method and should be free of oxygen. Electrolyses should be carried out at approximately 800° C, using cathodes of tungsten, molybdenum or tantalum, and graphite anodes. The initial plutonium trichloride concentration may be about 30 percent, and hydrogen or inert gas such as argon should be employed to prevent oxidation.

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PRODUCTION OF PLUTONIUM BY ELECTROLYSIS

INTRODUCTION

Two methods for the production of metallic plutonium were considered by the metallurgy group at Site Y prior to the availability of the material in appreciable quantity. These were bomb reduction and electrolytic reduction, and small scale stand-in work was performed using tuballoy. The stand-in electrolytic investigation is summarized in detail elsewhere1). It was found that uranium could be deposited from a solution of its trichloride in a fused solvent containing 48 percent $BaCl_2$, 31 percent KCl and 21 percent NaCl by weight. The stand-in experiments were performed in small Pyrex cells and recoveries in excess of 50 percent were readily obtained on a 50-mg scale. Accordingly, the same techniques were applied to plutonium reduction as soon as it became available on the same scale.

EXPERIMENTAL

The cells used for 50-mg electrolyses, as well as for most of the larger-scale reductions, consisted of 18/7 semiball Pyrex joints, usually constricted at the base to an internal diameter of 4 to 5 mm. The cathode of tungsten or other wire was sealed through the base exposing only about 1 mm of its length. The cell top carried the anode and an inlet and outlet for inert-gas cover. The gas, either hydrogen or argon, passed from tanks over tuballoy chips, heated to 500° C, into the cell. The effluent gas (argon and chlorine or HCl and hydrogen) flowed through a cold trap, over soda-lime and Drierite to a flow indicator. The line was also connected to a vacuum pump, and prior to heating of the cell, the entire system was evacuated several times and flushed with the gas. The cells were heated by a wire-wound pot furnace and the temperature controlled by a thermocouple shielded by Pyrex tubing, and operating a proportioning controller. Temperatures were constant to

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1) LA-147

± 2° C. Because of the toxic nature of the material, the pertinent portions of the equipment were enclosed in a hood.

The solvent salts were reagent grade, dehydrated at 150° C where necessary, and individually fused and cast in platinum. They were then ground in porcelain, mixed to contain 48 percent $BaCl_2$, 31 percent KCl, and 21 percent by weight of NaCl, and fused, cast, and reground. The mixture was kept in a desiccator and heated to 150° C before use. The plutonium trichlorides were prepared by the chemistry group by a variety of methods and were checked by chemical and X-ray analyses. The methods of preparation are listed below to correspond with the designations in Table I. Details may be found in LA-112.

(a) Hydroxylamine - wet preparation of $PuCl_4$ reduced by hydroxylamine and dehydrated in HCl.

(b) Formaldehyde - wet preparation of $PuCl_4$ reduced by formaldehyde and dehydrated in HCl.

(c) Hydride - metal reduced by lithium, converted to hydride, hydrochlorinated with HCl.

(d) Hydrogen - wet preparation of $PuCl_4$ dehydrated in HCl and reduced by hydrogen.

(e) HCl - PuO_2 ignited from nitrate and reduced by a mixture of HCl and hydrogen.

(f) Oxalate - trivalent oxalate hydrochlorinated by a mixture of HCl and hydrogen.

The trichloride, as received, was transferred to the base of the cell and the powdered solvent superimposed; all filling and opening operations were performed in a closed box. Upon completion of the electrolysis, the cell was cooled under the inert gas and opened in the box. The contents were usually washed with water

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and acetone and examined microscopically at low magnification.

Table I is a chronological summary of the experimental data. The trichlorides prepared by wet methods invariably contained oxygen, probably as oxychloride. They were very dark and difficultly soluble in water. It is likely that metal was produced in runs 1398, 1508, 1556, 1576, and 1590, but was probably coated by oxide which prevented coalescence. $PuCl_3$ prepared from hydride (1549) was light green, soluble in water, and yielded the first coherent electrolytic metal, indicating that the melting point of plutonium was probably below 660° C.

Runs 1612 through 1639 were performed with a dry preparation of $PuCl_3$, which, although it contained approximately 0.5 percent of oxygen, yielded appreciable amounts of metal upon electrolysis. These experiments indicated that for a given current density the recovery was reduced by an increase in temperature, but was increased at constant temperature by increase in current density. This effect is in accord with expectations, for the cathode efficiency is diminished almost entirely by reaction of anode products with the metal. The low current densities employed in the early experiments resulted from the belief that the melting point of the metal was high and that it would be deposited as a solid. Having determined that the metal was liquid at the electrolysis temperature, a run (1661) was made at 900° C, but probably at too low a current density to secure reduction. At 600° C mainly powder was obtained (1671), indicating that the melting point was between 600° and 660° C (the melting point by thermal analysis appears at present to be about 630°).

At this point, a new method of $PuCl_3$ preparation was introduced, resulting in a superior product. Using the trichloride prepared by hydrochlorination of the dioxide, it was determined that high-density metal (run 1677) was produced by

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TABLE I. ELECTROLYTIC PRODUCTION OF PLUTONIUM

Run	$PuCl_3$ Type	Charge Pu mg	Charge ($PuCl_3$ Wt. %)	Operating Conditions	Result
1398	Hydroxylamine	65	24	Tungsten cathode 0.030" diam., Tungsten anode 0.040" diam. 650°C, 0.025 amp, 60 minutes, hydrogen cover	Dark nodular powder. Reacts vigorously with dilute HCl.
1508	Formaldehyde	49	21	Same as 1398, 640°C	Fine dark powder. Reacts with water and dilute HCl.
[illegible]	Hydride	53	11	Same as 1398, but 660° C, 3/4" electrode spacing, 0.030 amp, 60 minutes, argon cover	Fine dark powder with 10 small metallic spheres weighing approx. 5 mg. Assay 95% Pu.
1556	Hydrogen	61	12.7	0.040" tungsten anode and cathode, 3/4" separation, 660°C, 0.015 amp, 120 minutes, argon cover.	Dendritic powder. $PuCl_3$ dark and difficultly soluble in water.
1576	Hydrogen	56	12	Same as 1556, but 0.030 amp, 60 minutes	Dendritic powder. Reacts vigorously with dilute HCl.
1590	Hydrogen	54	11.5	Same as 1556, but 0.050 amp, 30 minutes	Fine brown powder. Reacts vigorously with dilute HCl.
1612	Hydrogen ($0.5\%\ O_2$ in chloride)	53	11.2	Same as 1556, but 0.030 amp, 60 minutes.	Many small metal spheres in addition to fine powder. Metal malleable. Assay 100 ± 5% Pu.
1620	Hydrogen ($0.5\%\ O_2$ in chloride)	50	10.8	Same as 1612, but 710°C	Fewer metal droplets than in 1612.
1629	Hydrogen ($0.5\%\ O_2$ in chloride)	51	11.0	150 mg Zn as cathode. Tungsten anode 0.040" diam, 660°C, 0.050 amp, 30 minutes, argon cover.	Brittle cathode alloy. Some fine powder. 16.5 % Pu in upper portion of alloy.

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TABLE I (CONTINUED)

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Run	$PuCl_3$ Type	Charge Pu mg	 $PuCl_3$ Wt.%	Operating Conditions	Result
1639	Hydrogen (0.5% O_2 in chloride)	99	33	Tungsten anode and cathode 0.040" diam, 3/8" separation, 660°C, 0.050 amp, 60 minutes, argon cover	Very many Pu droplets, larger than in previous runs. Assay 95% ± 5% Pu.
1661	Hydrogen	51	11	Quartz cell, 5 mm ID, tungsten anode and cathode 0.040" diam, $\frac{1}{2}$" separation, 900°C, 0.20 amp, 30 minutes, argon cover	No reduction.
1666	Hydrogen	51	19.7	Same as 1639, but 0.20 amp, 25 minutes	Fairly large Pu beads; approximately 20% recovery.
1671	Hydrogen	51	19.7	Same as 1666 but 600°C	Mainly fine powder. Reacts with water slowly. Reacts vigorously with HCl.
1677	HCl	52	20	Same as 1666	Over 50% recovery of droplets weighing 3-4 mg. Density 19.1. Best yield.
1631	HCl	50	19.2	Identical with 1677, but 5 minutes only.	Many small Pu spheres.
1688	HCl	1020	33	Pyrex cell, 7 mm ID, tungsten cathode 0.040" diam, tungsten anode 1/8"diam, anode to cathode 1", 660°C, 0.50 amp, 75 minutes, argon cover	Large spherical deposit on cathode. Numerous droplets, larger weighing 15 mg. (Fig.1) Density cathode sphere 19.1 Density droplets 16.7. Microscope shows eutectic phase (Fig.2).

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TABLE I. (CONTINUED) [redacted]

Run	$PuCl_3$ Type	Charge		Operating Conditions	Result
		Pu mg	$PuCl_3$ wt. %		
1707	HCl	50	19.3	Tantalum cathode 0.030" diam, graphite anode 1/8" diam, $\frac{1}{4}$" separation. 660°C, 0.20 amp, 20 minutes, argon cover	Plutonium spheres show microscopic globular inclusions (Fig. 3).
1711	HCl	49	19.1	Same as 1707 but 0.040" tungsten cathode	Approx. 50% yield of droplets. Very few inclusions No eutectic (Fig. 4).
1720	HCl	74	26	Same as 1711, but 3/8" electrode separation, 0.5 amp, 13 minutes	Larger droplets. Few inclusions. (Fig. 5).
1740	HCl	71	14.5	Pyrex cell with 2 mm ID base, tungsten cathode, 0.040" diam, graphite anode, 1/8" diam, 1" separation, 660°C, 0.30 amp, 10 minutes, argon cover	$PuCl_3$ partially hydrated. Small droplets, 17% recovery. Almost single microscopic phase (Fig. 6).
1784	HCl	1000	33	Tungsten cathode 0.040" diam, graphite anode 1/8" diam, cell flushed with dry HCl during heating, 660°C, 1.0 amp, 35 minutes, argon cover	Water liberated during HCl flushing. $PuCl_3$ incompletely converted. Very little massive metal. Mainly brown powder completely soluble in HCl with gas evolution.
1844	HCl	50	10.7	Same as 1784, but 0.20 amp, 16 minutes	Low yield of droplets. $PuCl_3$ only 93% converted.

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TABLE I. (CONTINUED)

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Run	PuCl$_3$ Type	Charge		Operating Conditions	Result
		Pu mg	PuCl$_3$ Wt.%		
1856	HCl	52	11.1	Same as 1844, 12 minutes	Fresh PuCl$_3$. Good yield of Pu metal.
1857	HCl	1200	37	Same as 1784, but 0.3-0.5 amp, 71 minutes	Good yield of large Pu droplets. Water wash omitted. Salt crushed and 460 mg of metal collected as large pieces. Remainder flux-melted with no success.
[illegible]	Oxalate	995	35	Molybdenum cell cathode, conical shape, in Vycor jacket swept by purified hydrogen, graphite anode $\frac{1}{4}$" diam, 800°C, 2.0 amp, 20 minutes	Well-collected single button. Recovery approximately 75%. Density 19.1. No microscopic evidence of alloying at molybdenum-plutonium interface.

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electrolysis, and (run 1681) that the reduction was electrolytic and not the result of secondary chemical reaction with sodium or barium.

Having achieved some measure of success on the 50-mg scale, a 1-gram reduction was carried out using the new trichloride (1688). A large bead of metal weighing almost 400 mg was obtained on the projecting tungsten cathode in addition to the usual droplets (Fig. 1). Microscopic examination of these droplets showed the presence of an eutectic phase and the presence of free cubes of a phase taken to be tungsten (Fig. 2). The experiments which followed were designed to determine whether the tungsten was derived from the cathode by alloying, or from the anodes by solution followed by electrolytic deposition. Alloying of plutonium with tantalum had been reported as negligible even at 900°C, and so an electrolysis (1707) was carried out in a cell with tantalum-wire cathode and graphite anode. The metal showed nonmetallic inclusions, but no evidence of a second metallic phase (Fig. 3). A tungsten cathode was substituted and the run repeated (1711, 1720). No evidence of free tungsten or of the eutectic was found (Figs. 4, 5). It may be concluded, then, that the tungsten present in the metal of run 1688 was obtained by anodic solution and subsequent electrodeposition. This belief is confirmed by the deposition of tungsten crystals under similar conditions in earlier electrolyses. Experience in uranium deposition employing hydrogen as a cover gas had been that virtually no tungsten was transferred from the anodes. The difference in behavior may be attributed to considerably greater attack by chlorine than by HCl. It will be noted that hydrogen was used in the first experiments, but argon was substituted to avoid the possibility of hydride formation. However, a return to hydrogen (5008) demonstrated that the fears were unfounded.

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The failure to deposit coherent metal from wet-preparation trichlorides was attributed to the presence of oxychlorides. Similarly, $PuCl_3$ which was slightly hydrated by storage (1740, Fig. 6) or incompletely converted (1784, 1844) produced low yields. On the other hand, freshly prepared trichloride resulted in satisfactory recoveries (1856, 1857). This phenomenon is not unusual and is encountered in many fused-salt processes, notably the production of magnesium and calcium.

One of the obvious drawbacks of the electrolytic method as described, is the formation of individual droplets rather than a single massive piece of metal. While it is probable that operation on a considerably larger scale would remedy this defect, it appeared likely that an increase in the temperature of electrolysis would aid collection of the metal. An attempt to remelt the small droplets in the presence of the electrolysis bath met with no success (1857). Reduction at high temperatures can not be performed in Pyrex, and after considerable stand-in testing, a conical cell of molybdenum was finally selected. This cell rested on a graphite platform and was enclosed in a Vycor jacket. The tube was swept by purified hydrogen, and the electrolysis carried out at 800°C. The metal collected as a single coherent button in the base of the cone. Microscopic examination showed no evidence of alloying at the molybdenum-plutonium interface.

A number of spectroscopic analyses have been made on electrolytic plutonium, but the early analyses are not reliable because of the small quantities involved and because the analytical methods have since been improved. Table II lists the results of two later analyses on larger samples. It will be noted that the sodium content is fairly high, but it is almost certain that even were the sodium not eliminated during remelt,

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it could be reduced to tolerable values by omission of NaCl from the solvent salts.

Table II. Analyses of Electrolytic Plutonium

Impurity	Sample 1688 ppm	Sample 5008 ppm
Li	ND < 1	
Be	ND < 1	ND < 2
Na	20, 80	
Mg		20
Al		ND < 400
K	20, 40	
Ca	< 5, < 10	40
Fe		< 400
Ba	ND < 40	
La		ND < 400
Th		ND < 2000

ND - not detected

CONCLUSIONS

The electrolytic method of reduction was discontinued when it became evident that high purity was no longer a consideration. Sufficient experimental work has been performed, however, to allow several definite conclusions.

1. Plutonium may be prepared by electrolytic reduction of its fused trichloride in a solution of chlorides of more electropositive metals.

2. The $PuCl_3$ is best prepared by a dry method and the oxygen and

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moisture content should be low.

3. The electrolysis is best carried out at approximately 800°C and at high current densities. A suitable $PuCl_3$ concentration appears to be approximately 30 per cent by weight. Cathodes may be of tungsten, tantalum, or molybdenum, and anodes of graphite, although tungsten anodes may serve when a hydrogen cover is used. Access of air to the fused salt must be prevented.

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Fig. 1. Plutonium Beads and Cathode (1688)

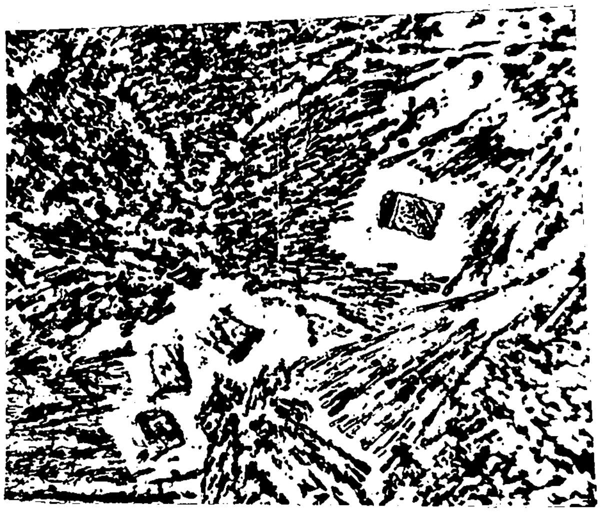

Fig. 2. Eutectic and Free "Tungsten" (1688)

500 x

[redacted]

Fig. 3. Deposit from Tantalum Cathode (1707)

250 x

Fig. 4. Deposit from Tungsten Cathode (1711)

250 x

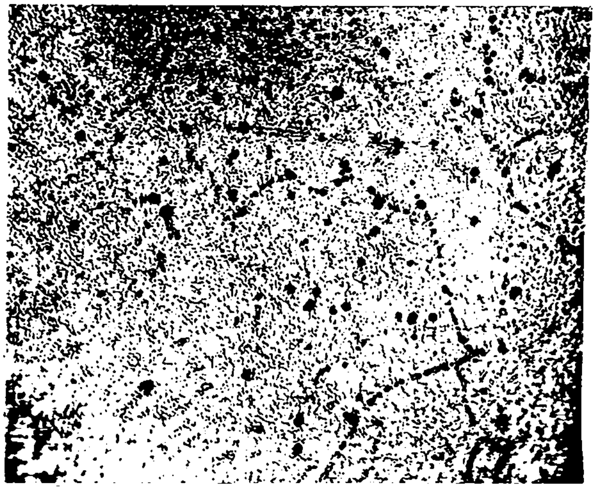

Fig. 5. Deposit from Tungsten Cathode (1720)

250 x

[redacted]

Fig. 6. Deposit from Tungsten Cathode (1740)

250 x

[redacted]