Development of Small-Scale Plutonium Electrorefining

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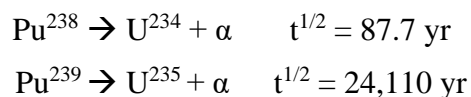
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Abstract

Molten salt extraction and electrorefining of plutonium were successfully conducted with only a 200 g initial charge. Due to the small-scale, the electrorefining cell components were redesigned. The efficiency and yields of this process are comparable to similar processes, even at larger scales. Chemical analysis of the plutonium product and the anode heel is presented. The product was 99.8% pure. The anode heel was able to be depleted beyond the expected freezing point without significant impurity carryover.

1. Introduction

The pyrochemical processing of plutonium metal has been carried out for decades at a scale amendable to production. However, increased interested in the behavior of plutonium as it ages has driven a need to produce plutonium at a scale that is amenable to scientific studies [1–6]. This minimizes the cost and time required to generate new batches of plutonium and provides flexibility for metal to be produced at various chemical compositions, isotopic mixtures, and process conditions. For the intent of studying the effects of aging, a new batch of plutonium must be produced in order to remove all prior defects and in-growth of daughter products. This ensures a well-defined and accurate starting condition from which to measure the effects of aging with time. As the plutonium ages, the decays of isotopes, in particulate Pu^{238} and Pu^{239} produce decay products, as shown below:

$$Pu^{238} \rightarrow U^{234} + \alpha \qquad t^{1/2} = 87.7 \text{ yr}$$
$$Pu^{239} \rightarrow U^{235} + \alpha \qquad t^{1/2} = 24{,}110 \text{ yr}$$

These decay products are "born" with a certain amount of energy causing them to recoil or travel through the metal lattice displacing atoms until their energy has dissipated. Additionally, the alpha particles eventually become helium bubbles within the metal matrix. The rate at which plutonium ages can be accelerated by increasing the amount of Pu^{238} [7–9]. By having a smaller-scale process, the isotopic mixture can be varied without creating excessive waste. Hence, the targeted scale for production is 200-grams of initial charge.

Electrorefining of plutonium has been performed for decades at kilogram-scale levels. However, electrorefining at the sub-kilogram-scale has not been reported since the 1960s. In 1940's, Kolodney first electrochemically produced plutonium metal by electrowinning $PuCl_3$ at the milligram to 1-gram scale [10]. However, due to the successful development of bomb reduction, the development of electrochemically produced plutonium metal was not pursued for some time.

In 1960, Blumethal and Brodsky reported electrorefining plutonium in eutectic LiCl-KCl at 55-gram scale by depositing plutonium as a solid and re-melting deposits into a button after transferring it to another container [11]. In 1960's, Mullins et al. demonstrated that bomb reduced plutonium metal could be electrorefined to purity of 99.98% [12]. The initial anode weight ranged from 287-304 g. The process used NaCl-KCl-PuCl$_3$(10 wt%) molten salt. The design by Mullins et al. was quickly scaled to 3.5 kg and electrorefining at the kilogram-scale has become routine [13]. A thorough review of plutonium electrorefining over the decades has been published by Willit [14]. This marks the first reported attempt to electrorefine plutonium at this scale in molten CaCl$_2$ and the first reported hundred-gram plutonium electrorefining work since the 1960's.

2. Experimental Methods

Two processing steps were used to purify aged, impure plutonium metal: molten salt extraction (MSE) and electrorefining (ER). Each of these setups are sketched in Figure 1. Both processes took place in a resistive furnace well incorporated into the bottom of an inert argon atmosphere glovebox. The furnace was heated to 945°C with a constant flush of argon flowing in the furnace. Yttria-stablized magnesia (MgO) crucibles (99.2%, Tateho Ozark Technical Ceramics, Inc.) were used to contain the molten salts and metals for MSE and ER. An alumina stirrer (99.5%, Ortech, Inc.) with a tungsten rod (99.95%, Midwest Tungsten Service) through the center was used to mix during both MSE and ER.
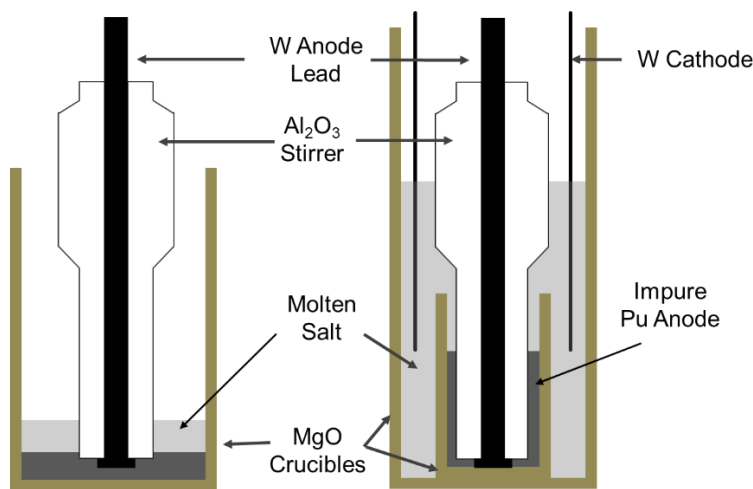

Figure 1: Setup for Molten Salt Extraction and Electrorefining

2.1. CaCl$_2$ Salt Preparation

99.0-105.0% calcium chloride dihydrate (CaCl$_2$·H$_2$O) was received from Thermo Fisher Scientific Chemicals, Inc. CaCl$_2$·H$_2$O was dehydrated by drying at 200°C for 72 hrs under

vacuum in stainless steel trays. After drying, the salt experienced a weight loss of 25.52% (theoretical water loss: 24.51%). The salt was rapidly transferred into an inert nitrogen glovebox located next to the vacuum ovens. The dried $CaCl_2$ salt was then loaded into a Pt(80%)/Rh(20%) crucible with CaF_2 added as a binder to constitute 0.1 wt%. The salt was heated to 850°C and sparged with argon for 6 hours. Then the molten salt was vacuum transferred from Pt/Rh crucible through a Pt/Rh siphon tube into a chilled aluminum mold to form a casted salt cake. The drying process and characterization of the dried $CaCl_2$ is reported in greater detail elsewhere [15].

2.2. Molten Salt Extraction

MSE was performed using 199.9 g of an aged Pu-Ga alloy in a 2.25" OD (2.0" ID) MgO crucible. 7.4 g of $MgCl_2$ (99.9%, ultra-dry, Thermo Fisher Scientific Chemicals, Inc.) was added to serve as the extractant along with 26.1 g of a casted $CaCl_2$ salt cake. Once molten, the salt and metal were mixed with the alumina stirrer at 50 RPM with incremental increases up to 150 RPM over the course of 15 minutes. Then the stirrer was stopped and raised from the melt. The furnace was shut-off and allowed to cool naturally overnight.

2.3. Electrorefining

 The resulting ingot from MSE was casted into an anode using a tantalum funnel and MgO crucible (1.0" OD, 0.76" ID). The anode was added into the inner crucible (1.25" OD, 1.0" ID, 2.0" H) of concentric MgO crucibles. On top of the anode, 7.4 g of $MgCl_2$ (99.9%, ultra-dry, Thermo Fisher Scientific Chemicals, Inc.) were added to seed the electrochemical process. 246.5 g of the same casted $CaCl_2$ salt cake were added to serve as the bulk of the electrolyte. The same combined alumina stirrer/tungsten rod from MSE served as the anode lead. The cathode was a tungsten ring (99.95%, Midwest Tungsten Services). The cathode was positioned so that it was suspended more than an inch above the bottom of the outer crucible (2.25" OD, 2.0" ID, 5.0" H) within the annulus between the inner and outer crucible so that molten plutonium would deposit and drip off into the annulus.

Once molten, the electrodes were lowered into the melt and a constant potential was applied to the cell using a Sorenson DCR10-80B power supply. The alumina stirrer was rotated at 80 RPM for duration of ER. The open circuit potential (OCP), also referred to as back electromotive force (Back EMF), was sampled every 30 min by interrupting the power to the cell for 3 sec. then recording the potential between the anode and cathode.

3. Results

The resulting product of MSE is pictured in Figure 2. There was a dark gray salt on top of a metallic phase with a distinct interface. The salt was broken off and removed from the metal. A qualitative gamma dose rate measurement was performed at the top of the salt, top of the metal and bottom of metal with results of 1480 mR/hr, 620 mR/hr and 135 mR/hr. This was a positive indicator that most of the americium had been extracted into the salt phase.
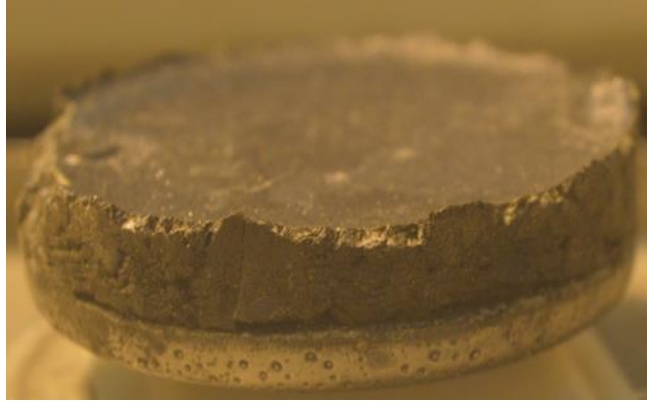
Figure 2: Americium rich salt on top of plutonium metal ingot after molten salt extraction

The metal ingot pictured in Figure 2 was casted into a geometry to fit into the inner cup of ER concentric crucibles. The resulting anode weighed 187.3 g. After loading the anode and salt into the crucible, the crucible was loaded into in a furnace well in an inert argon glovebox. The furnace was ramped to 945°C over 4 hrs. The electrodes were lowered and electrorefining commenced by applying a constant potential. While electrorefining, the current and OCP (back EMF) were recorded. The values for each variable recorded are displayed in Figure 3. Initially, the current started at 2.3 A and rose slightly to 2.4 A, then gradually decreased to 1.1 A at the end of the run. The OCP started initially at 0.013 V and rose slightly until the end of the run where a sharp rise occurred up to 0.412 V. This sharp rise indicated the end of run and the electrodes were raised out of the molten salt. Mullins et al. demonstrated that processing beyond this sharp rises results in contaminating the product and correlates to the theoretical point of solidification of the anode [16]. Overall, the ER process ran for 37.35 hours with a cumulative charge of 2.5×10^5 C (69 A·h).
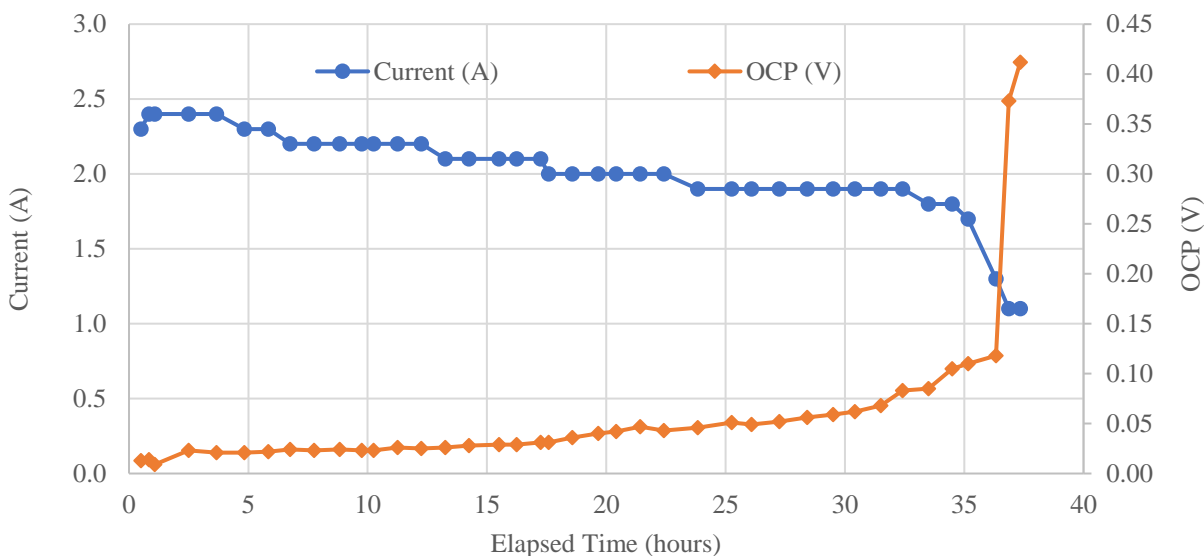
Figure 3: Process data collected while electrorefining

After allowing the material to cool naturally overnight, the electrodes and crucible were removed from the furnace. Pictures of their condition after the ER run are shown in Figure 4. The anode heel solidified and adhered to the anode stirrer. It was easily chipped off and sampled for chemical analysis. The bottom of the cathode was coated in a thin layer of plutonium metal. After breaking off the bottom of the outer crucible, a ring of plutonium metal was visible in the annulus between the inner and outer crucible. However, the ring did not completely coalesce into a single piece. The plutonium metal deposits dripped into the annulus and formed a partial ring with the open space between the ends of the ring being filled with metal shot. The total weight of the ring and shots was 146.4g resulting in a yield of 78.2%. The cathodic efficiency (η) was calculated to be 71.4% using equation (1):

$$\eta = \frac{nFm}{A \cdot Q} \tag{1}$$

where n is the number of electrons exchanged (3 for the deposition of plutonium), F is Faraday's constant, m is the actual mass of the deposit collected, A is atomic mass of plutonium, Q is total charge passed. The inner crucible was also broken open to search for any remains of the anode. No metal was observed in the inner crucible. The partial ring was also sampled by extracting a sample from the core of the ring. The major impurities (>5 ppm in product, >100 ppm in anode) along with Am and Ga from the chemical analysis of the anode heel and ring sample are displayed in Table 1. The purity of product was 99.83% with tungsten as the main contaminate. The anode mainly contained the more noble metals of Al, Fe, Ga and U.
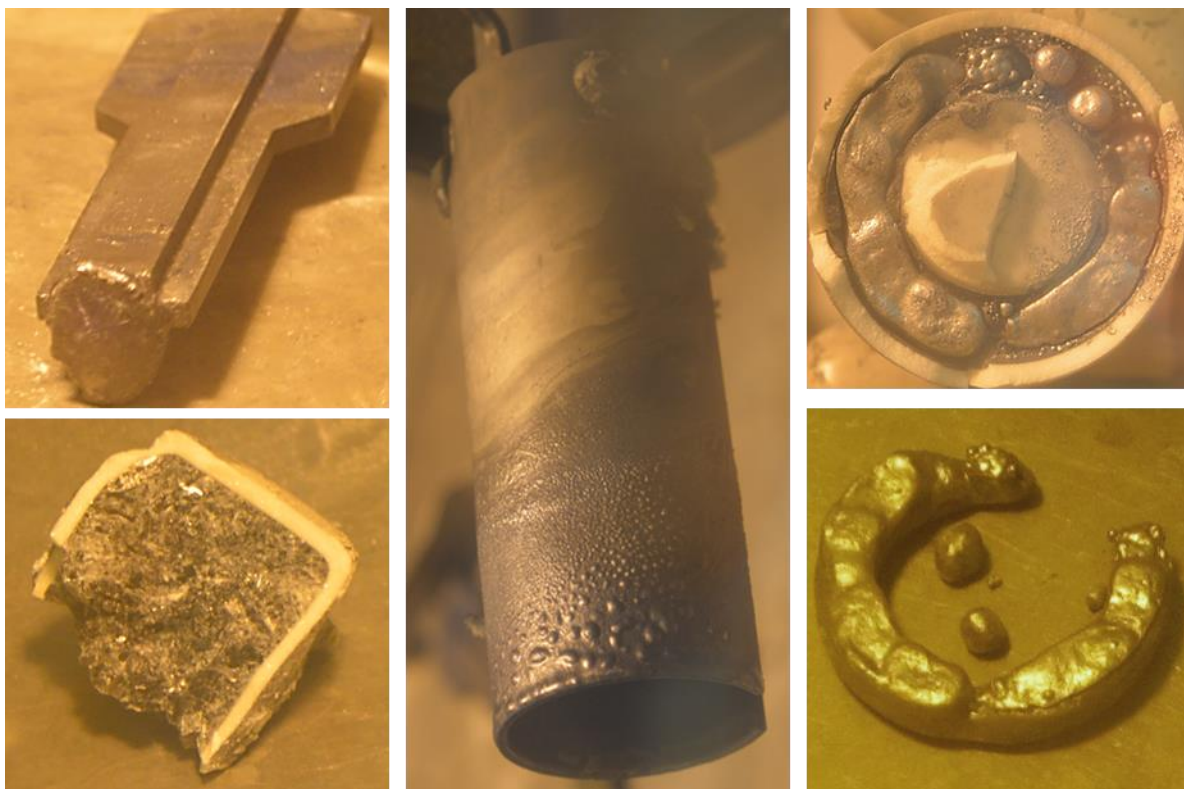
Figure 4: Breakout of electrorefining cell: anode lead and stirrer with anode heel attached (top left), cross-section of anode crucible (bottom left), cathode coated with plutonium metal (center), partial ring and shots of pure plutonium in annulus between the inner and outer crucible (top right), and bare partial ring and shots of plutonium product (bottom right).

Table 1: Composition of impurities in anode heel and plutonium product ring

Element	Anode Heel (ppm)	Product ring (ppm)
Al	10,800	54
Am	6.9	0.31
Ca	820	21
Cr	1245	42
Cu	503	6.3
Fe	11,000	211
Ga	13,630	2.5
Mg	753	70
Mn	1323	6.3
Mo	358	<2
Ni	1940	23
Np	2038	48
Pb	163	<5
Ta	130	11
U	32,553	6.2
W	5070	1200

4. Discussion

The efficiency and yield of 71.4% and 78.2%, respectively, compares well to similar previous work. Mullins et al. reported a cathodic efficiency of 71.4 % and process yield of 73.5% in their first hundred-gram scale experiment with a Pu-Fe alloy which is the most comparable run to this work [12]. All other runs were unalloyed, bomb reduced Pu. Later from 1967-1971, Mullins et al. performed 20-g and 100-g electrorefining of medical-grade Pu-238 with an average product yield of 75.8% [17]. More recently, researchers from AWE in the United Kingdom reported their results for ER using molten $CaCl_2$ at a larger-scale [18]. Their efficiencies ranged from 62.0-93.6% with an average of 82.7% and their process yields ranged from 66.9-94.7% with an average of 85.4%. The researchers at AWE used lower initial $MgCl_2$ concentrations of 1.9 wt. % to seed their ER process, compared to 3 wt. % in this work. Additionally, a new, bare tungsten cathode was used in this work which resulted in some plutonium metal being held up on the cathode. These differences may explain the discrepancies in efficiencies and yields. Regardless, the efficiency and yield at the smaller scale for a single run are comparable to the trials at the larger scale.

The high amount of tungsten in the product is surprising especially because it is almost 10x the solubility limit of W in liquid plutonium at 850°C, which is the approximate processing temperature [19,20]. Historically, the temperature difference between furnace temperature (945°C) and the molten salt temperature has been 90-100°C. It is possible under certain conditions to have W dispersed as a separate phase within the α-plutonium matrix. The elevated amount of tungsten may be unique to this run because a new, bare W electrode was used.

Loosely adhering W particles may have initially become entrained in Pu metal deposits. The possibility of greater W contamination earlier in the run is supported by analysis of the top of the product ring which contained less (1050 ppm) W. Alternatively, the small-scale may have resulted in a greater contact area to deposited Pu ratio increasing W content, but Mullins et al. found <20 ppm W in their Pu product [12]. Another possible source of W is anode lead, but this is unlikely because it was sheathed by the alumina stirrer and potential required to oxidize tungsten is much higher than Pu.

Lastly, based on the composition of impurities in the anode, the Pu content in the anode heel was 69.6 wt. %. Based on the phase diagram for Pu-Ga and Pu-Fe alloys, the anode heel should have solidified well before (89.8 wt. % Pu for Pu-Ga and 91.7 wt. % Pu for Pu-Fe) reaching that low of concentration of Pu [20,21]. No ternary phase diagram was found for Pu-Fe-Ga. Mullins et al. observed the spike in OCP being delayed until the Ga:Pu atomic ratios in anode were greater than 0.32 (85.4 wt. % Pu) when iron was present as an impurity [16]. This was also observed in this work producing atomic Ga:Pu ratio of more than double at 0.68. It is postulated that iron may have suppressed the freezing point of the anode and the smaller anode size may have significantly reduced diffusion resistance upon solidification. Regardless of the reason, this run was able to deplete the anode of Pu more significantly than previously reported without significant carryover of iron or gallium.

5. Conclusion

Molten salt extraction and electrorefining were successfully conducted with only a 200 g initial charge. The efficiency and yields of this process are comparable to similar processes, even at larger scales. This enables an adaptable process to provide pure, defect-free plutonium metal for smaller campaigns and scientific programs. The process is currently being used to produce multiple batches of plutonium spiked with varying amount of Pu-238 to accelerate the study of aging effects on plutonium properties. The plutonium feed contained a high level of iron which enabled the anode to be depleted to more than twice as much as a typical run without impurity carryover.

6. Acknowledgements

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