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Small-Batch Plutonium Metal Creation

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Disclaimer

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Abstract

Small-batch processes were used in the early days of Pu research into the properties of the element primarily because of the scarcity of the material. Baker (Baker, 1946) described a process that has been used as a basis for the current project. High purity ^{242}Pu was purchased from the Oak Ridge National Laboratory for this purpose. The thermo-metallic bomb reduction process is used to create up to 1g of Pu metal. The excellent reference by Cleveland (Cleveland, 1979) serves as a basis for the chemical processing of the plutonium. The complete process includes the recycling of by-product material created during target fabrication.

Background

An experimental campaign to determine fundamental physical and thermodynamic properties of Pu metal has been undertaken at the laboratory. For these purposes 13.5 g of high isotopic purity ^{242}Pu oxide was purchased from the Oak Ridge National laboratory. Originally begun in 2004, the program was mothballed in 2006 due to a redirection of experimental priorities. Restarted in 2013, the program is current today.

The source material as received contains at the very least decay products that must be removed prior to experimental use. Chief among these is ^{241}Am, the decay product of beta-emitting ^{241}Pu. Any other impurities, i.e. anything that is not plutonium, are also removed to the best of our ability prior to the creation of metal. The experimental campaign is interested in Pu properties and not properties of eutectics or other intermetallic species formed due to impurities in the source material.

Processes Involved

Dissolution of Oxide

The dissolution of Pu oxide is fairly straightforward, as long as the material isn't high-fired. Modified fume-hood operational limits permit the dissolution of 1g of oxide. The simplest process involves heating the material in con HNO_3 / 0.005 M HF in a Savillex® vessel, typically overnight, at ≈ 90C to produce a brilliant emerald green solution. The process can be carried out either in a sealed or open-topped vessel. To prevent excess acid fumes from going up the fume hood exhaust a two-stage condenser is used to recover evaporated fumes. The resulting solution is too concentrated to be run through a subsequent anion exchange column, so it is diluted with 4N HNO_3 to produce one ≤ 10N HNO_3.

Purification Chemistry

A prepared plutonium solution is passed through an 18mm ID x 150mm long AG-1-X8 anion resin bed in a glass column. The column design has a 150 ml reservoir on the top and a buret-style tip bent at 45

degrees to eliminate splashing of the column effluent while draining into a collection vessel. The resin is treated with 8N HNO_3 prior to introduction of the feed material. As long as there is not plutonium polymer present in the solution, the plutonium will form a very dark green band in the upper half of the resin column. The polymer form of Pu is not retained by the resin and can be seen visually as a bright green band streaming off the column with the load solution. The sample container is rinsed with 8N HNO_3, which is then run through the column. The column is then rinsed with additional 8N HNO_3 to remove the ^{241}Am daughter of the ^{241}Pu in the material. It will also greatly reduce the level of uranium decay daughters present in the material as well. The column is then converted to the Cl^- system using at least 50ml of 10M HCl. Sufficient HCl must pass through the column to remove all traces of HNO_3, otherwise a rather vigorous bubbling reaction will occur with the introduction of the subsequent HI solution. During this step the band of plutonium may all but disappear depending on the color of the batch of resin used, as the hydrated $PuCl_6^{-2}$ ion is brown.

Next a solution of 1:10 con HI / 10N HCl is warmed for a few minutes during the HCl wash step on a hot plate set to 100C. This solution is then introduced into the column and the collection vessel switched to collect the plutonium as it is reduced to Pu^{+3} and no longer retained by the resin. As the Pu band moves down the resin bed the brilliant blue color of Pu^{+3} is observed. Collection continues for several ml beyond the last visible blue color coming off the column.

The collection vessel is again switched and any residual plutonium is stripped off of the column with 1N HCl.

The eluted plutonium solution is evaporated to near dryness with the addition of 8N HNO_3 to oxidize the plutonium back to Pu^{+4} as well as eliminate residual iodine and HCl. This step is performed regardless of whether the material is to be passed through the anion column a second time or is ready for oxalate precipitation.

The prepared solution is diluted to a nominal 3N acid concentration, then heated on a hot plate to 50C. A precipitating solution containing peroxide (for valence adjustment) and 1M $H_2C_2O_4$ is added slowly over a period of several minutes with manual agitation of the resultant solution. The mixture can be allowed to stand overnight on the hot plate. Typically the total solution volume is less than 100ml, so the solution can be equally split between two 50ml plastic centrifuge cones. The solution is centrifuged and the supernate collected for further processing. The precipitate is washed first with 2M HNO_3 / 0.05M $H_2C_2O_4$, then twice with water. All washings are added to the supernate for later processing.

The precipitate is transferred with water into a 15ml glass scintillation vial, topped with a watch glass, then a beaker is placed over the vial, all on top of a hot plate. The temperature is set to 80C and the solution allowed to stand until it is dry, a process that can take days to complete. When the cake appears dry, then the temperature is slowly raised until all water of hydration has been removed from the solid material, as evidenced by the elimination of any condensation from the inverted beaker. The temperature is then set to 400C and calcination of the oxalate begins. Over a period of about 2 hours the precipitate will turn to a khaki-green color seen in Figure 1 indicative of the conversion to PuO_2.

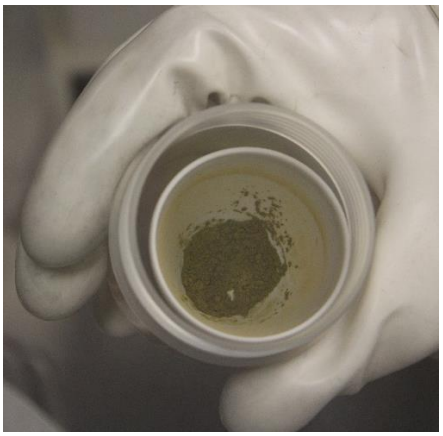

Figure 1 PuO_2 inside the glovebox

The material is transferred into an inert-atmosphere dry box for handling purposes where it is then weighed into a reaction cell for hydroflourination. Using HF as the fluorinating agent, the PuO_2 is converted to PuF_4 over a period of a few hours. Upon removal from the reaction cell, there are occasionally evidence of PuF_3, which is a blue-purple color, mixed in with the predominantly pink-brown color of PuF4 as seen in Figure 2.

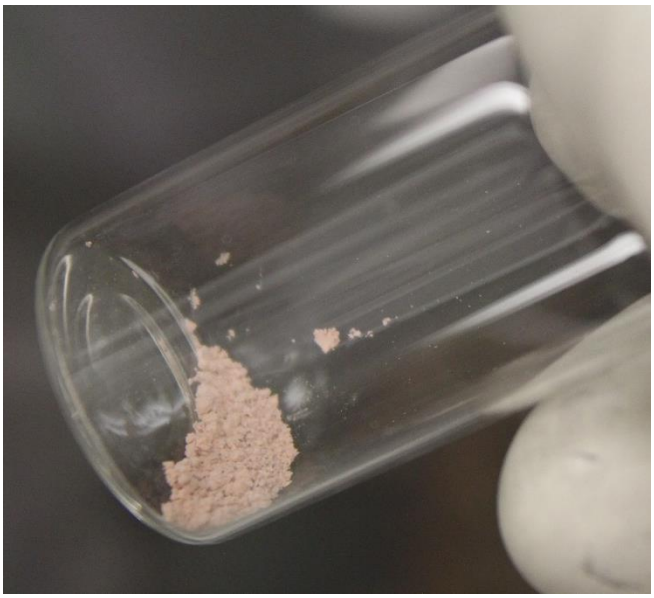

Figure 2 PuF_4 ready for conversion to metal

Conversion to Metal

PuF_4 is converted to metallic Pu by a thermo-metallic process using Ca metal. Basically, PuF_4 is mixed with a 25% excess of Ca metal. Elemental iodine (25 mole % of the Pu in the reduction cell) is added to the mix to provide two functions: adding additional heat to the reaction mixture and lowering the melting point of the resultant CaF_2 slag. Baker (Baker, 1946) also reported that the reaction worked best with a top and bottom cap of Ca + I_2, 20mg and 150mg respectively for the 1g scale used. The materials are loaded into a MgO crucible, shown in Figure 3 which is then inserted into a stainless steel reaction

cell. The cell is suspended in the center of an induction furnace coil using a rod attached to the cap of the cell.

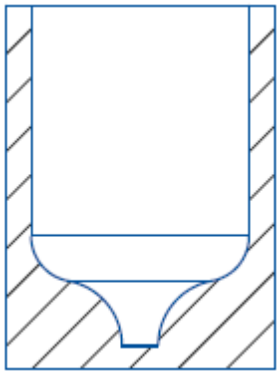

Figure 3 MgO crucible drawing

Our setup uses an optical pyrometer for control of the heating process with a threshold temperature of 300C. Operationally, a 'warm up' period of 30s is used to slowly ramp up the temperature from 300C to 325C. This allows the Ambrell Ekoheat furnace to solve the necessary power equations of the work piece, such that during the next phase where the temperature is ramped to 1000C in 30s the furnace can perform this operation without fault. After reaching 1000C the reaction cell is held at this temperature for three minutes as seen in Figure 4. There is a cool-down ramp in the program, but in actuality the system is shut off at this point and the cell allowed to cool naturally in the glove box atmosphere.

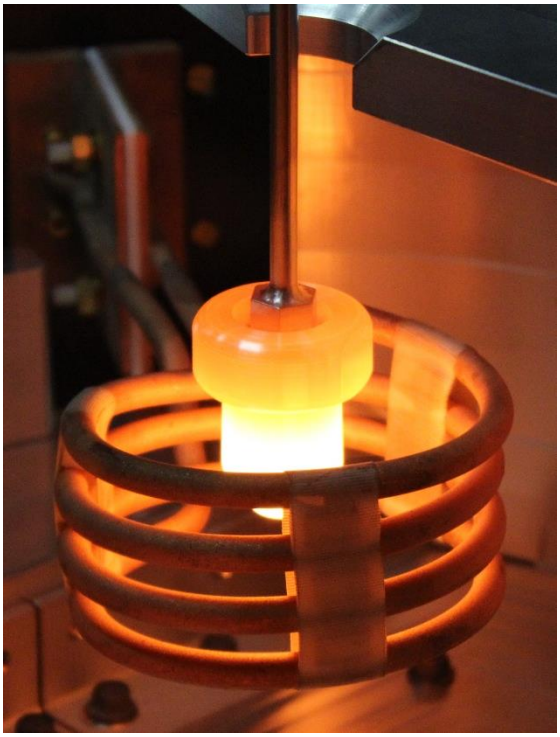

Figure 4 Reaction cell at 1000C

When the cell has cooled to ambient temperature the lid is removed and the MgO crucible taken out of the cell. Due to the change in volume of the Pu metal as it goes through several phase changes while cooling, the MgO crucible is quite often found to be split in half at the location of the button. The button is removed from the surrounding CaF_2 slag and weighed. At this point the as-cast metal still has adhered slag on it and needs to be cleaned as seen in Figure 5. One approach would be to clean off the residue with con HNO_3, but in order to maintain the atmosphere as inert and dry as possible I have chosen an alternative approach, and that is to remelt the metal under a blanket of $CaCl_2$. The button is placed into a MgO thimble, coated with a blanket of $CaCl_2$, then lowered into the bottom of a tube furnace where it is taken to 875C and with gentle stirring heated for about 2 hours. The MgO stirring stick is lifted from the melt prior to turning off the furnace, then the contents are allowed to cool, generally overnight, at which point the crucible is removed from the furnace.

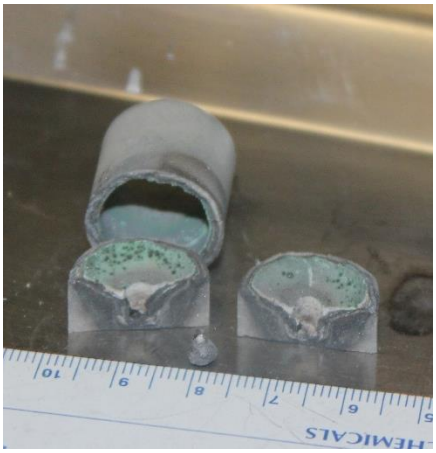

Figure 5 Pu metal as cast

In this instance the crucible is not conveniently split by the cooling Pu metal, so it is instead crushed using pliers. The resulting $CaCl_2$ salt residue is combed through to locate the cleaned Pu metal, shown in Figure 6, which typically has a fine greenish sheen to it, and quite often has been separated into a few pieces of Pu shot as seen in Figure 7. Why this occurs sometimes is not understood.

Figure 6 Pu metal after $CaCl_2$ salt bath

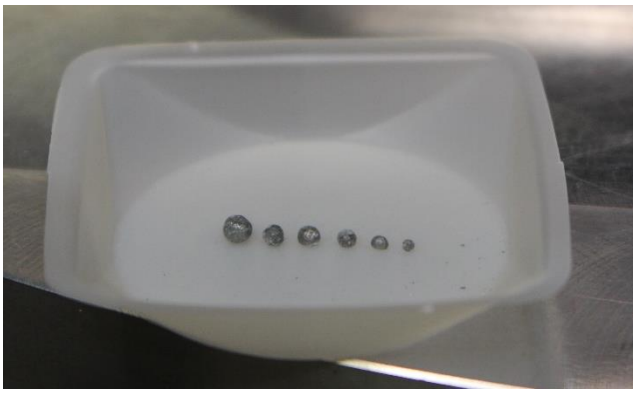

Figure 7 Pu shot after $CaCl_2$ salt bath

At this point the resulting material is again weighed for transfer to the Target Fabrication group and subsequent processing into desired target forms.

Recovery From Slag

The crucibles utilized for the production of purified metal are all collected in the inert atmosphere glovebox and periodically removed for processing. These contain potentially unreacted Ca metal, CaF_2, CaI_2, potentially unreacted I_2, PuF_4, Pu metal, $CaCl_2$, and the crucible material itself, MgO. The material can be brought into solution using a two stage process (Dukes & Prout, 1961) using ≥ 10 N HNO_3 followed by 10 N HNO_3 / 0.8 N $Al(NO_3)_3$ and heat. The MgO slag doesn't dissolve particularly rapidly, but it does go into solution over a period of several hours, and also as long as there is sufficient solution volume present to keep it from salting out. Once in solution a few ml of H_2O_2 is added to the mix for valence adjustment of the Pu. Following this treatment the solution is nominally ready to be put through an anion column and start the chemical purification process.

Ion-exchange Solution Treatment

All column effluent is retained and processed for potential recovery of Pu that didn't behave as expected during the separation process. The initial loading and wash solutions will mostly contain Am and U, however if any Pu polymer is present, it will not be retained by the resin and appear in these solutions. Treatment with H_2O_2 has been found to be effective with respect to eliminating any polymeric form present. Solutions that follow the main fraction of the Pu elution from the column may also have significant Pu present. The general process of dealing with solutions is to evaporate them to minimum volumes and then repeat the process after a significant amount of 8N HNO_3 has been added to affect conversion of any Pu present to the hexanitrato $Pu(NO_3)_6^{-2}$ form. In this final form the resulting solution is sufficiently prepared to be run through the anion column again for impurity removal.

Recovery from Target Fabrication processing waste

The generation of target forms results in the near complete use of Pu metal sent from the metal production lab. As a figure of merit, 500mg of virgin Pu metal ultimately produces 6-10 0.5mg targets, with the remainder of the material now spread over a collection of Kimwipes, lapping papers, cotton-tipped swabs, and the occasional nitrile glove. These materials are all collected in the target production glovebox and periodically bagged out and returned for processing.

The returned materials are carefully loaded into a 2-liter Savillex digestion vessel. The objective of the treatment process is to completely destroy all of the organic matrix present leaving ideally only the entrained Pu. Thermal treatment in a furnace would certainly help, but the uncontrolled nature of the combustion process is far from ideal from a contamination control standpoint, therefore wet digestion techniques are employed. Treatment usually begins with con HNO_3, but also includes aqua regia, 3:1 con HNO_3 / H_2O_2, and con HNO_3 + 0.005 HF. Over a period of several weeks the material is repeatedly heated to incipient dryness and the next treatment solution added after the container has cooled to ambient temperature. At some point the matrix reduction process has diminishing returns, and the resulting mixture is filtered through a 1.5 um glass fiber filter to remove undigested non-descript organic material. Depending on the volume and matrix of the filtrate, it is most likely to be evaporated to a low volume, however not so low that solution components start salting out, then adjusted to near 8N HNO_3 to make a starting solution for the anion exchange process. Valence adjustment is also carried out prior to column loading to ensure that the Pu is in the +4 oxidation state.

References

Baker, R. D. (1946). *Preparation of Plutoniumm Metal by the Bomb Method, LA-473.* Los Alamos: Los Alamos Scientific Laboratory.

Cleveland, J. M. (1979). *The Chemistry of Plutonium.* La Grange Park, IL: American Nuclear Society.

Dukes, E. K., & Prout, W. E. (1961). *Recovery of Plutoniumm From Metallurgical Reduction Residues.* Savannah, Georgia: Savannah River Laboratory.