Pyrochemical Processes for the Recovery of Weapons Grade Plutonium Either as a Metal or as PuO₂ for use in Mixed Oxide Reactor Fuel Pellets

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PYROCHEMICAL PROCESSES FOR THE RECOVERY OF WEAPONS GRADE PLUTONIUM EITHER AS A METAL OR AS PuO₂ FOR USE IN MIXED OXIDE REACTOR FUEL PELLETS

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Abstract

We have developed two processes for the recovery of weapons grade Pu, as either Pu metal or PuO₂, that are strictly pyrochemical and do not produce any liquid waste. Large amounts of Pu metal (up to 4 kg.), in various geometric shapes, have been recovered by a hydride/dehydride/casting process (HYDEC) to produce metal ingots of any desired shape. The three processing steps are carried out in a single compact apparatus. The experimental technique and results obtained will be described.

We have prepared PuO₂ powders from weapons grade Pu by a process that hydrides the Pu metal followed by the oxidation of the hydride (HYDOX process). Experimental details of the best way to carry out this process will be presented, as well as the characterization of both hydride and oxide powders produced.

Introduction

Agreements between the USA and Russia to reduce the quantity of nuclear weapons have promoted the continued development of new methods to recover the plutonium from these weapons while minimizing the waste produced and the radiation dose to operators. Lawrence Livermore National Laboratory (LLNL) has developed pyrochemical techniques to recover Pu as a metal using a Hydride/Dehydride/Casting process (HYDEC), or as PuO₂ by alternating Hydride/Oxidation reactions (HYDOX) until all the plutonium metal is converted to the oxide form. These two processes do not produce any liquid or solid waste.

Most of the options being evaluated for plutonium disposition require plutonium oxide, which will be used as feed material for Mixed Oxide (MOX) reactor fuel pellets, glass or ceramic immobilization forms, or a grouting system for boreholes. Metal produced in HYDEC can be either canned for long term storage or used to manufacture new weapons. The HYDEC and HYDOX processes will be incorporated into an Advanced Recovery and Integrated Extraction System (ARIES), along with other supporting technologies, to recover plutonium from the cores or "pits" of nuclear weapons, thus providing the necessary first step for disposition of fissile material from excess nuclear weapons. This demonstration will be performed jointly by Los Alamos and Lawrence Livermore National Laboratories at the Los Alamos plutonium facility.

Large scale hydriding of Pu was first used at LLNL to recover Pu metal from Special Isotope Separation (SIS) components in 1985. This system consisted of separate vessels to perform hydriding, dehydriding, and casting. In 1988 LLNL initiated a project to combine these operations into a single vessel. In 1989 LLNL began adapting this system to recover Pu from weapons.

In this paper we will describe in detail the experimental details of HYDEC and present some of the results obtained. We will also discuss the best way to carry out the HYDOX process and present the characterization of both hydride and oxide powders produced.

Hydride/Dehydride/Casting Process (HYDEC)

HYDEC provides a simple and reliable process to recover plutonium in metallic form from various sources (pits, scrap, etc.). It utilizes the hydriding of plutonium as a way to separate Pu from other materials because Pu undergoes a large increase in volume which spalls off from the reacting front as it hydrides. The hydride particle size is a function of the reaction temperature. Low temperature (<100°C) hydriding produces fine particles; coarse particles are produced at higher temperatures (<200°C). The hydriding reaction is exothermic according to the following equation,

\[
Pu + \frac{x}{2} H_2 = PuH_{2x} \quad \Delta H_f = 39-43 \text{ kcal/mole} \quad (1)
\]

To recover Pu as a metal the hydride is heated in the range of 700-900°C. This heating will decompose the hydride and release hydrogen gas, which is then available to react with fresh Pu metal (hydrogen recycle mode). In the above temperature range Pu is liquid and can be poured into a mold to cast as an ingot. During these operations there is no waste produced, thus the HYDEC process is more efficient than an acid-dissolution process.

For safety reasons, the HYDEC apparatus is mounted inside an argon-flushed glovebox in case a leak develops because plutonium hydride is a very pyrophoric substance. The vertical arrangement of the apparatus requires a rather small glovebox space (15" wide by 31" in length and 43" high). Operation of the equipment requires minimal handling by the operator and this results in low radiation exposures. The system was designed with future automation and remote...
handling in mind to reduce handling and radiation exposure to a minimum in future systems.

**Apparatus and Operating Parameters for HYDEC**

The HYDEC apparatus consists of a vacuum chamber where the hydriding, dehydriding and casting operations are carried out. Figure 1 shows where the corresponding zones are identified.

![Figure 1. Schematic of the Hydride/Dehydride/Casting (HYDEC) reactor](image)

The upper chamber of the vacuum system is the hydriding zone where a plutonium containing object is mounted (a plate in this case) to react with hydrogen and form plutonium hydride flakes that will fall into a heated crucible in the dehydriding/melting zone. We usually maintain the plutonium object at about 250-300°C, using both the furnace heat "shine" and the heat of reaction of hydriding because in this temperature range interlocking Pu hydride flakes >>100 μm are formed that easily fall into the crucible. At temperatures between 25 to 50°C very fine particles (5-10 μm) are formed that cling to the walls and windows of the apparatus by static charge and are very hard to convey into the crucible (see HYDOX sections). In the apparatus shown in Fig.1 there is an infrared scanner that is used to measure the temperature of the reacting plutonium through a sapphire window. In addition, a television camera documents the entire process through a sapphire window adjacent to that for the infrared scanner. Because these cameras have a "wedge shape" view of the object being hydrided it is necessary to rotate the object to get a complete picture of it. A stepper motor attached to a ferrofluidic rotary feedthrough is used to rotate the basket or holder for the Pu part, as shown in Fig. 1. Hydrogen gas is introduced initially into the upper part of the reactor at pressures that vary from 10 to 300 torr.

The middle section of the vacuum system is where dehydriding of Pu hydride takes place accompanied by melting of the plutonium metal. The main component of this zone is a carbon-saturated tantalum crucible, which has an outer Ta₂C layer and an interior microstructure consisting of continuous grain boundary carbides and finely distributed carbide particles within the grains (1, 2). This material has been shown to be capable of containing liquid plutonium for long periods of time without deterioration (1), which we have also observed in this work. The lower part of the crucible consists of a tapered cylinder of carbon-saturated tantalum lapped to mate with an orifice in the crucible bottom, which forms a metal-to-metal valve seat ("hot finger") capable of containing molten plutonium. The hot finger is opened or closed by means of a mechanical linkage operated by an argon-actuated piston outside the vacuum system. When all of the plutonium is removed from the upper chamber and converted to liquid plutonium in the crucible, the hot finger is opened and the liquid plutonium is poured into a large mass copper mold where it rapidly solidifies into an ingot as shown in Fig. 2. The mold is not cooled externally by any fluid. At this point the chamber is evacuated and the system flushed with argon several times. The chamber is then filled with argon to 1 atmosphere and allowed to cool down to less than 50°C.

![Figure 2. Photograph of a plutonium ingot produced by the HYDEC process.](image)

The copper mold is mounted onto a "shuttle mechanism" (see Fig. 1) whose function is to decouple the mold from the vacuum system after an ingot is cast and move the mold to an unloading station. The shuttle lowers the mold, moves it sideways to clear the main structure of HYDEC, and then raises it above the glovebox floor for removal. To release the Pu ingot the mold is turned upside down, and because its sides are tapered, the ingot falls out easily.

The hydride, dehydride, and casting steps take approximately 1.5 hours per kilogram of Pu.

**Hydride/Oxidation Process (HYDOX) to Produce PuO₂**

HYDOX is a process designed to recover Pu from weapon components and other sources (Pu scrap, manufacturing residues, etc.) in the form of PuO₂ powders suitable for use in mixed oxide (MOX) fuel pellets for nuclear reactors, glass or ceramic immobilization forms, or for incorporation into boreholes. HYDOX can also separate Pu metal from other nuclear and non-nuclear materials.
Our main objectives in this work were to define the most efficient process to carry out the above conversion, and to determine the effect that preparation temperature has on the particle size and morphology of Pu hydride and oxide. We evaluated two processes to convert Pu metal into PuO₂: 1) hydriding of the metal/dehydriding of the PuH₂⁺ produced/oxidation of the metal powder into PuO₂; and, 2) hydriding of the metal/direct oxidation of the PuH₂⁺ produced into PuO₂. In both cases we used Ar/O₂ instead of N₂/O₂ mixtures to avoid the nitriding reaction of Pu that begins at 150°C and becomes fast at 250°C.

Hydriding/Dehydriding/Oxidation Process

This process was evaluated using a different vessel for each step, which was a definite disadvantage. The dehydriding step was very slow because the temperature of the powder had to be maintained below 400°C to prevent sintering of the metal particles, whose sintering temperature we found to be ≈ 400°C. We oxidized 400 g of PuH₂⁺ powder, prepared at 100-150°C, with a 4 v/o O₂-Ar gas mixture at ≈ 150°C in a batch reactor. It took about 110 hours to complete the oxidation because, when all the oxygen from the gas mixture was consumed, the residual argon had to be pumped out every time the reaction vessel was refilled with the O₂-Ar mixture. We concluded that this process was inefficient and too slow, so we carried out further experiments by the direct oxidation of the hydride in a flow system at higher temperatures.

Hydriding/Oxidation Process

A. Preparation and Characterization of PuH₂⁺

A large batch of PuH₂⁺ powder was prepared at 100-150°C and the temperature was kept in this range by controlling the hydrogen pressure. It took 7.83 hr. to hydride 2 kg of Pu at this low temperature. Approximately 200 g of this hydride was dehydrided and subsequently rehydrided at 400°C. Thus we could evaluate the effect of temperature on the particle size of the hydrides. The particle size distribution of these powders was carried out by sieve analyses and the results obtained are summarized in Table I.

Table I. Comparison of the Particle Size Distributions of PuH₂⁺ as a function of Temperature

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>100-150°C PuH₂⁺</th>
<th>400°C PuH₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;105</td>
<td>38.3</td>
<td>93.8</td>
</tr>
<tr>
<td>75-105</td>
<td>20.9</td>
<td>3.2</td>
</tr>
<tr>
<td>60-75</td>
<td>23.5</td>
<td>0.4</td>
</tr>
<tr>
<td>43-60</td>
<td>5.3</td>
<td>0.8</td>
</tr>
<tr>
<td>30-43</td>
<td>6.3</td>
<td>1.0</td>
</tr>
<tr>
<td>20-30</td>
<td>4.3</td>
<td>0.6</td>
</tr>
<tr>
<td>&lt;20</td>
<td>1.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The data in Table I clearly show that the hydride particle size increases drastically as the temperature is raised from 100-150°C to 400°C. We did not study the morphology of plutonium hydride particles because our SEM is not equipped to handle this material.

B. Preparation and Characterization of PuO₂ Powders

The direct oxidation of the plutonium hydrides prepared was carried out in a quartz flow-through reactor that had a frit on the bottom to hold the hydride powder and permit the flow of a 4 v/o O₂-Ar mixture, as shown in Fig. 3. The reactor was equipped with a furnace around its lower section to perform the oxidation of the hydrides at ≈ 350°C.

Figure 3. Photograph of the flow-through reactor used for the oxidation of PuH₂⁺ to PuO₂ showing a partial oxidation of the hydride. Note the sharp boundary between the oxide (lower layer) and the hydride (upper layer).

The oxidation of the hydride proceeded according to the following reaction, assuming that at 350°C the hydride has a composition of PuH₂:

\[
\text{PuH}_2 + \text{O}_2 = \text{PuO}_2 + \text{H}_2
\]  

Thermodynamic calculations indicated that water formation does not take place significantly at 350°C, and we did not observe water condensation on the exit lines of the reactor that were at room temperature.

The particle size distributions for PuO₂ prepared by the oxidation of plutonium hydrides is shown in Table II. We have also included in this table the ASTM specification for MOX fuel (3).

Table II. Particle size distributions for PuO₂ made from PuH₂⁺ prepared at 100-150°C and 400°C.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Prepared from 100-150°C Hydride</th>
<th>Prepared from 400°C Hydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;105</td>
<td>12.3</td>
<td>59.4</td>
</tr>
<tr>
<td>75-105</td>
<td>18.5</td>
<td>23.8</td>
</tr>
<tr>
<td>60-75</td>
<td>14.9</td>
<td>10.4</td>
</tr>
<tr>
<td>43-60</td>
<td>10.1</td>
<td>2.8</td>
</tr>
<tr>
<td>30-43</td>
<td>17.1</td>
<td>1.0</td>
</tr>
<tr>
<td>20-30</td>
<td>14.9</td>
<td>0.6</td>
</tr>
<tr>
<td>&lt;20</td>
<td>12.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The ASTM specification for MOX fuel (3) is also included in this table.
The oxide prepared from 100-150°C PuH$_{2+x}$ underwent a significant change in particle size distribution, which almost meets the ASTM specification (3). We feel that this oxide could probably be used directly for MOX pellets because after it is mixed with uranium oxide and other components, the mixture must be ground and blended. On the other hand, PuO$_2$ derived from hydride prepared at 400°C did not change enough in particle size distribution to be used directly in MOX. All of the oxides produced were verified to be PuO$_2$ by x-ray diffraction analysis of the powders and the particle morphologies were studied by SEM.

To simplify the HYDOX process the use of a single reaction vessel is being examined. In a single vessel reactions (1) and (2) are performed in a continuous manner until all the Pu metal is converted to PuO$_2$. The process will be initiated by introducing into the reaction vessel a small amount of hydrogen (10 to 20 liters-STP) and letting it react with Pu until the pressure is below a few Torr. At this point oxygen at low pressure (<100 Torr) will be introduced to decompose the hydride formed and liberate hydrogen to form PuO$_2$, and this sequence will be repeated again until all Pu is reacted. We can use a small amount of PuH$_{2+x}$ containing the same amount of hydrogen as above to start the process with the introduction of oxygen. We will shortly perform this experiment and define the experimental sequence in more detail.

Conclusions

- We have studied the effect that preparation temperature has on the particle size distribution of PuH$_{2+x}$ and PuO$_2$. For the hydride we have found that the particle size increases drastically going from 100-150°C to 400°C.

- For PuO$_2$ formed at = 350°C from hydrides prepared at the two temperatures used, we have found that the particle size distribution of PuO$_2$ tends to shift to lower values than the parent hydride. The oxide prepared from hydride made at 100-150°C nearly meets the ASTM specification for MOX, but the one prepared at 400°C does not and must be ground to size.

- We have proposed a new approach to produce PuO$_2$ from Pu metal based on a continuous cycle of hydriding/oxidation, that is carried out until all of the Pu is converted to PuO$_2$.

References


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