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A PROTOTYPE HYDRIDING APPARATUS
(APPLICATION FOR PLUTONIUM RECOVERY)

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**A PROTOTYPE HYDRIDING APPARATUS
(APPLICATION FOR PLUTONIUM RECOVERY)**

Robert P. DeGrazio

Chemistry Research and Development
PROCESS CHEMISTRY

SUBJECT DESCRIPTORS

Plutonium Recovery
Plutonium Hydrides
Plutonium Oxides
Plutonium Metal
Safety
Oxygen
Hydrogen
Inert Atmosphere
Pressure Vessels
Pyrophoric Materials

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A PROTOTYPE HYDRIDING APPARATUS (APPLICATION FOR PLUTONIUM RECOVERY)

Robert P. DeGrazio

Abstract. The major components and the operation of an experimental hydriding prototype apparatus are described. The apparatus was designed to recover plutonium from metallic substrates.

INTRODUCTION

A prototype apparatus was constructed for recovering plutonium, as plutonium hydride, from various types of metallic substrates. The plutonium recovery operation is based on the plutonium-hydrogen reaction as shown in Equation 1 (see Reference 1).

Equation 1.

Throughout this report the above reaction will be described as "hydriding."

Since plutonium hydride is a pyrophoric powder, it is air oxidized to plutonium dioxide. This change permits safe handling of the material during additional processing.

Oxidation of the hydride to oxide is based on Equation 2 (see Reference 2) as shown below.

Equation 2.

The design criteria of the hydriding prototype apparatus was based on the reactions shown in Equations 1 and 2. Design emphasis was placed on the safe handling of plutonium hydride and gaseous hydrogen in the apparatus. An addition design

criterion was that the apparatus have the capability to operate under relatively high temperatures ($\sim 400^\circ\text{C}$).

During the hydriding cycle, gaseous hydrogen reacts with plutonium in an oxygen-free reactor to produce plutonium dihydride (PuH_2). It is possible to produce other plutonium-hydrogen compounds having different hydrogen-to-plutonium ratios, depending on operating parameters.³ For this type of recovery process, however, the formation of non-stoichiometric plutonium hydride compounds is not significant.

As plutonium hydride is produced during a hydriding operation, it spalls free from the metallic substrate and drops into a tray. Since plutonium hydride is a pyrophoric powder, it is converted to plutonium dioxide by "burning" (oxidation) in an air atmosphere as illustrated by Equation 2. The oxide form of plutonium is the final product recovered by the hydriding prototype.

Acid leaching is the primary method used at Rocky Flats for plutonium recovery; however, hydriding does not damage certain types of reusable substrates, so it was more advantageous to use hydriding than acid leaching for these reusable substrates. Hydriding also eliminates the use of large volumes of leaching acid solutions and the need for subsequent removal of plutonium from these solutions.

The Hydriding Laboratory is shown in Figures 1 and 2. Figure 1 shows the east side of the laboratory; Figure 2 shows the laboratory's west side. Glove boxes in which related hydriding work is performed are also shown. The function of work in these glove boxes is not included in the scope of this report, but will be described in future reports.

FIGURE 1. East Side of Hydriding Laboratory.

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FIGURE 2. West Side of Hydriding Laboratory.

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FIGURE 3. Hydriding Prototype Apparatus.

DESCRIPTION OF PROTOTYPE EQUIPMENT

Prototype Hydriding Apparatus

The hydriding apparatus was designed to convert plutonium metal to plutonium hydride and to convert the resulting hydride to plutonium oxide. The apparatus consists of five major sections: (1) an argon-inerted glove box, (2) two reactors, (3) a master control console, (4) a master instrument panel, and (5) a hydrogen burning system. A schematic of the apparatus is shown in Figure 3.

The schematic also illustrates the flow pattern of the material processed. It is not the purpose of this report to describe the operation of the mechanical components of the apparatus, but rather to present a brief description of the five primary sections.

Inert Glove Box

Hydriding and oxidizing operations are performed in reactors located in an argon-inerted glove box.

FIGURE 4. Gloveport Covers Installed on the Glove Box.

15157-3

FIGURE 5. Exterior View of the Hydriding Reactor.

FIGURE 6. Interior of the Hydriding Reactor.

FIGURE 7. Exterior View of the Oxidation Reactor.

FIGURE 8. Interior of the Oxidation Reactor.

Because of the hydride being a pyrophoric powder, the oxygen content within the glove box is maintained at <1.0 vol %. To minimize air diffusion through the gloves, gloveport covers were installed on the glove box as shown in Figure 4. The covers are vacuum sealed to the gloveports when the gloves are not in use. An argon gas purge is used to break the seal, which permits use of the gloves.

Hydriding Reactor

An exterior view of the hydriding reactor is shown in Figure 5. The reactor is shown with the door in a closed position. The door is secured with six latches against a neoprene "O" ring. Figure 6 shows the interior of the hydriding reactor. The material to be hydrided is placed above a tray that is located near the bottom of the reactor. Hydrogen and argon inlets, in addition to thermocouple inlets, are located at the rear of the reactor. Thermocouples monitor the temperature of the plutonium-hydrogen reaction and the temperature of the reactor's atmosphere.

Oxidizing Reactor

Figure 7 is an exterior view of the oxidation reactor with the door in the closed position. The door is secured with four latches against a neoprene "O" ring. The interior of the oxidation reactor is shown in Figure 8. Inlets for argon, air, and thermocouples are located in the rear of the reactor (not shown). Figure 8 shows the tray in which plutonium hydride is oxidized and the stirring bar used during oxidation. Both the oxidizing reaction temperature and the reactor atmosphere temperature are monitored during an oxidation operation.

Master Control Console

Hydriding and oxidizing operations are controlled from the Master Control Console shown in Figure 9. The Console incorporates the following controls:

FIGURE 9. Master Control Console.

Legend

1 - Pressure Gauges	4 - Switch Controls
2 - Pressure Controllers/Recorders	5 - Warning Lights
3 - Temperature Recorder	6 - Exhaust Valve

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1. Pressure gauges—These gauges register pressures within the reactors during hydriding and oxidizing operations.
2. Pressure controllers/recorders—These instruments control and record pressures in the hydriding and oxidizing reactors.
3. Temperature recorder (6-point)—Hydriding and oxidation reaction temperatures are recorded with this instrument. Atmospheric temperatures in the hydriding and oxidizing reactors are also measured and recorded with this recorder.
4. Switch controls—Operation switches are also located on the Master Control Console for hydriding and oxidizing operations.
5. Warning lights—These lights will glow, and an alarm will sound if abnormal operating condition occur during hydriding or oxidizing operations.
6. Exhaust valve—Air from the oxidizing reactor is exhausted through this valve.

Instrument Control Panel

The Instrument Control Panel, shown in Figure 10, contains hydrogen and oxygen detectors. These detectors monitor the glove box during hydriding and oxidizing operations for possible leakage of hydrogen or oxygen or both. A mass flow meter, also located on the panel, records the volume of hydrogen consumed during a hydriding operation. Rotameters on the panel control flow rates of hydrogen, argon, and air during hydriding and oxidizing operations.

Hydrogen Burning Apparatus

Residual hydrogen that is not used in hydriding operations is pumped from the reactor to an apparatus where the hydrogen is burned in a natural gas flame. The hydrogen-burning apparatus is located in a separate glove box as shown in Figure 11. Figure 12 shows the components of the hydrogen-burning apparatus located inside the glove box. These components consist of (1) a flame-burning housing, (2) flame trap, (3) flame

arrestor, and (4) a water condensate trap. The purpose of the flame-trap is to prevent a flame "flash-back," if one should occur, from traveling down the exhaust line to the reactors. In the event natural gas leaks into the glove box, the gas will flow through the flame arrestor and be cooled below its autoignition temperature prior to being exhausted to the building exhaust system. The purpose of the condensate trap is to collect water produced when hydrogen is burned. The volumes of burned hydrogen have usually been small, however, and no water, to date, has been collected in this trap.

The equipment shown on top of the glove box in Figure 13 consist of the following: (1) rotameters, which control the flow rate of natural gas and air to the flame, (2) water jacket, which is located near the center of the glove box in Figure 13 and is used to cool the exhaust gases prior to the gases being exhausted in the building's exhaust system, and (3) a continuous air monitor, which detects contamination that may have escaped the four traps located between the reactors and the hydrogen-burning glove box.

OPERATIONAL PROCEDURES

Hydriding

Hydriding procedures vary with the type of substrate being processed. Generally, however, the procedure is as follows:

The substrate that contains plutonium is placed into the hydriding reactor. The quantity of plutonium that may be hydrided is limited by Nuclear Safety to three kilograms per batch. The reactor is then evacuated to ~ 1 torr of pressure and backfilled with hydrogen to a pressure of ~ 500 torr. As hydrogen is consumed, more is automatically added by a pressure recorder/controller to maintain the desired preset pressure. Completion of the hydriding operation is determined by the termination of hydrogen demand with a simultaneous decrease in reaction temperature.

FIGURE 10. Instrument Control Panel.

Legend

1 - Rotameters	4 - Oxygen (Glove Box) Detector
2 - Hydrogen (Glove Box) Detector	5 - Hydrogen (Room) Detector
3 - Mass Flow Meter	

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FIGURE 11. Hydrogen-Burning Apparatus.

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Legend

1 - Flame Burning Housing	3 - Flame Arrester
2 - Flame Trap	4 - Water Condensate Trap

FIGURE 12. Components of the Hydrogen-Burning Apparatus.

FIGURE 13. Equipment Located Atop Hydrogen-Burning Glove Box.

Legend

1 - Rotameters
2 - Water Jacket
3 - Continuous Air Monitor

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Oxidizing

Conversion of hydride to oxide is accomplished by placing hydride in the oxidation reactor and passing air through the reactor. The hydride is heated and stirred simultaneously as air flows through the reactor.

Oxidation normally occurs at 300 °C. Completion of the oxidizing operation is determined by a decrease in reaction temperature, reactor atmosphere temperature, and by visual observation of material.

To ensure that all hydride is converted to oxide, the material is reburned in a glove box containing an air atmosphere at a temperature of ~500 °C.

SUMMARY OF PROCESS APPLICATIONS

Plutonium has been selectively removed from metallic substrates that do not form hydrides with hydrogen. Plutonium has also been removed from metals that absorb hydrogen (i.e., tantalum) but do not produce a hydride under the hydriding-operating conditions used. The hydriding apparatus is used to recover plutonium from (1) reusable equipment, (2) plutonium scrap, (3) plutonium-coated tools, and (4) plutonium melts from tantalum and tungsten crucibles. The hydriding apparatus is also used to oxidize such pyrophoric material as skull material, plutonium chips and turnings, mixtures of plutonium hydride and plutonium oxide, and plutonium hydride that is generated elsewhere on the plant site. The processing of these materials will be described in future reports. A primary advantage of recovering plutonium as oxide through the hydriding process is the small amounts of solid and liquid wastes generated. The disadvantages of the process is handling hydrogen and plutonium hydrides.

SAFETY FEATURES

Both hydrogen and plutonium hydride present a potential safety hazard. In air, hydrogen in concentrations of 4.1% to 74.2% by volume⁴ forms an explosive mixture. Plutonium hydride is a pyrophoric material and will burn in an air

atmosphere. These facts were considered in the design of the prototype hydriding apparatus. Safety features of the system include (1) locating both the hydriding and oxidizing reactors in the same argon-inerted glove box, (2) continually monitoring the glove box for both oxygen and hydrogen leakage, and (3) only one hydrogen cylinder (220 cubic feet) is on stream at any one time and that cylinder is located outside the building.

Additional safety features of the apparatus include the following: (1) The electrical design makes it impossible to perform a hydriding operation and an oxidizing operation simultaneously; (2) It is electrically impossible to reignite the flame immediately after a flame-out; and (3) the entire system was designed not to exceed 12 psi pressure. If the pressure exceeds this value, relief valves will open, exhausting the reactor gases through the hydrogen-burning system.

The hydriding prototype apparatus has been in operation for approximately three years without significant problems occurring. Only minor modifications and maintenance work have been performed on the apparatus.

REFERENCES

1. R. N. R. Mulford and G. E. Sturdy, "The Plutonium-Hydrogen System. I. Plutonium Dihydride and Dideuteride." *J. Amer. Chem. Soc.* 77:3449-3452. December 1954.
2. Franklin L. Oetting. "The Chemical Thermodynamic Properties of Plutonium Compounds." *Chemical Review* 67:261. 1967.
3. R. N. R. Mulford and G. E. Sturdy. "The Plutonium-Hydrogen System. II. Solid Solution of Hydrogen in Plutonium Dihydride." *J. Amer. Chem. Soc.* 78:3897-3901. February 1956.
4. National Fire Codes. Compilation of NEPA Codes, Standards, Recommended Practices, and Manuals. Gases, Vol. II. 1973-74. Page 50A-4.