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TRITIUM PROCESSING USING METAL HYDRIDES

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by

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TRITIUM PROCESSING USING METAL HYDRIDES

A RESEARCH PAPER

by

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ABSTRACT

E. I. duPont de Nemours & Company is commissioned by the U. S. Department of Energy to operate the Savannah River Plant and Laboratory. The primary purpose of the plant is to produce radioactive materials for national defense. In keeping with current technology, new processes for the production of tritium are being developed. Three main objectives of this new technology are to ease the processing of, ease the storage of, and to reduce the operating costs of the tritium production facility. Research has indicated that the use of metal hydrides offers a viable solution towards satisfying these objectives. The Hydrogen and Fuels Technology Division has the responsibility to conduct research in support of the tritium production process. Metal hydride technology and its use in the storage and transportation of hydrogen will be reviewed.

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TRITIUM PROCESSING USING METAL HYDRIDES

Introduction

New technology is being developed to better accommodate the production of tritium. The main concern for improving the existing process is to update the system using current technology with regards to size, safety, reliability, and economic aspects. This new technology will center on the use of metal hydrides as a means for storing, separating, and transferring tritium. Metal hydrides have been shown to have many applications in industry involved with hydrogen processing, as well as many adaptations to power-type systems. Technical questions to be answered by supporting research refer to the classification of the most suitable metal hydrides for the system and determining the operating conditions of the facility. Also, a procedure for the accountability of the tritium should be considered.

Metal Hydride Technology

A metal hydride is a metal that can directly and reversibly react with hydrogen. It acts as a solid sponge, soaking up hydrogen with a high volumetric packing density. In the process, the reaction liberates

heat as seen by the equation

The exothermic reaction can be reversed at high temperatures, thus desorbing the hydrogen. The term "rechargeable metal hydrides" has been given to those hydrides that can perform the reaction at room temperature and near atmospheric pressure. These hydrides can absorb and desorb great amounts of hydrogen efficiently under simple conditions virtually indefinitely and thus offer an excellent means by which to store and transport hydrogen.

Research has shown that hydrogen can be stored more efficiently with metal hydrides versus compressed gas or liquid hydrogen. This is due to the fact that the H-atoms are chemically bound within the hydride's crystal lattice structure. This bond forms a stable compound which readily exists at low pressures and temperatures. This provides both safety and economic advantages. Another advantage of using metal hydrides is the ability to separate hydrogen from a mixture of inert gases. With the proper choice of a metal hydride, processes are capable of absorbing only hydrogen isotopic atoms at desired temperatures and pressures.

The process of hydrogen storage on metal hydrides and its high packing density can be seen in Figure 1. The graph reflects experimental pressure-composition isotherms representative of the absorption/desorption properties of a metal hydride. To determine these, a storage

vessel is filled with the metal solid and then evacuated of all air present. A pure hydrogen gas is then slowly introduced to the tank. This is done while maintaining a constant temperature in the vessel. The curves are made up of individual points corresponding to the hydrogen to metal atom ratio (H/M) when the system reaches equilibrium at a given pressure. Point A is of interest because beginning at this point rapid absorption begins to take place with very little change in pressure. This region is termed the plateau pressure. At point B and pressures beyond, the sample is completely in the hydride phase and a continued increase in the pressure results only in a small additional absorption of hydrogen. The process is reversed by adding excess heat to the system represented by Eq. 1. The hydrogen will begin to desorb or "outgas" as predicted by the equilibrium curve and the hydride returns to its previous metal phase. Figure 1 also shows the effect of temperature upon the range of the plateau pressure. Isotherms of increasing constant temperature tend to have higher plateau pressures and shorter absorption plateaus.

This metal hydride technology has many applications beyond obvious volume saving storage purposes. Metal hydrides also serve as a means for compressing hydrogen gas as an alternative to mechanical compression. By altering the temperature of a hydride bed, hydrogen gas is compressed without the need for moving parts. Cooling the bed causes an intake of hydrogen gas at a low pressure. The exhaust function is served by heating the bed to drive off the hydrogen gas at increased pressure. The

temperature change required of the process is small between plateau pressures as described by the van't Hoff equation

$$\ln P_p = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

which describes the plateau pressure relative to the reciprocal of the temperature and to ΔH , the enthalpy change of the hydriding reaction per mole of H_2 .

In addition to tritium processing, hydride technology has potential advantages in a variety of applications. Other uses heat pumps for industrial and residential purposes, hydrogen cooled refrigerator systems, and automobiles powered by hydrogen. Two vehicles, a Michigan post office jeep and a West German mass transit bus, have been demonstrated to use hydride beds for storage of their hydrogen fuel (or hydrogen/gasoline mixture) [3].

Tritium Processing

Metal hydrides are readily applicable to tritium processing. Each hydrogen isotope exhibits a different plateau pressure characteristic of its absorption/ desorption properties. Examples of the plateau pressures for hydrogen and deuterium on vanadium metal are shown in Figure 2. The two distinct pressures allow for fractionally separating deuterium from natural hydrogen. By proper selection of the base metal, these properties can be used to accomplish tritium separation. Another element of interest is helium-3, a decay product of tritium. However, metal hydrides do not react with atoms other than hydrogen isotopes. This permits the

purification of the stream by vacuuming off helium and any other inert gases present while the tritium is absorbed on the bed.

The two metal hydrides of primary interest at the Savannah River Laboratory are palladium and alloys of lanthanum, nickel, and aluminum (LANA). Palladium is coated on kieselguhr, an earth substrate with high surface area. Higher storage capacity for the LANA alloys have dedicated them to tritium storage beds, whereas the reduced pressure drop through beds of palladium/kieselguhr reserve its use for hydride pumps. The LANA alloys will provide a more efficient volumetric packing density for hydrogen than the palladium. Also, by altering the aluminum concentration, the LANA alloys will be more adaptable to the varied absorption/ desorption properties desired.

Economics

The use of the metal hydrides for storage and processing purposes provides for a considerable economic savings. This is due mainly to the high efficiency of the metal hydride beds which eliminates the need for large storage tanks. This reduces the size of tritium storage an overall processing facilities. Thus the economic savings results from the land, building construction, and operating costs associated with the more efficient facility.

Safety

Safety aspects are enhanced by the design as well. The reduced size of the facility permits the containment of the tritium equipment in

nitrogen circulated hoods. The nitrogen gas in the hoods can be continuously stripped to recover any tritium that otherwise would have been lost to the environment. Also, the operating conditions for the storage beds are room temperature and subatmospheric pressure. This provides a safer and more convenient working environment to operate the facility.

Reliability

A reliable process for accountability of the tritium on a metal tritide bed is necessary. One method associated with hydride research involves desorbing the gas to a calibrated volume and measuring isotopic composition. This requires considerable time to do as well as a large calibrated tank, a feature opposing the design objectives. Also, the accuracy is limited by residual amounts of tritium that may not have been fully desorbed from the bed. This implies the need for a new approach, i.e., an "in-bed" accountability method. Tritium decay produces a known value of heat per mass of material. By measuring the heat radiating from the bed, the mass of tritium stored can be calculated.

A prototype bed used to experimentally simulate a metal hydride bed loaded with tritium is shown in Figure 3. The heater in the bed's center outputs wattage simulating the amount of tritium in the bed. The metal hydride bed is enclosed in an insulated jacket through which nitrogen circulates. The simulated decay heat will be absorbed by the nitrogen in the jacket. Two methods by which to measure the heat loss have been

considered. One procedure is to valve closed both nitrogen ports and watch for a rise in the temperature of the jacket as shown in Figure 4.1. This poses an unsteady-state heat transfer problem. The solution to this problem will require that careful material balances be performed on both the storage bed and the nitrogen jacket. A second method circulates nitrogen through the jacket as shown in Figure 4.2. By controlling the flow rate, the decay heat released can be predicted using a simple steady-state heat balance only on the jacket.

Summary

The use of metal hydrides satisfies all of the design objectives for an improved tritium process. Use of this technology should improve safety and reliability as well as reducing the size of the facility. The new technology also offers an economic savings and improved operating conditions. Continued research will determine the best qualified method for tritium accountability.

FIGURE 1. HYDRIDE ABSORPTION CURVES

FROM: "Hydrogen Storage", G.D. Sandrock, May, 1981.

**FIGURE 2. HYDOGEN VS. DEUTERIUM
PLATEAU PRESSURES**

FROM: "How Metals Store Hydrogen", E. Lee Huston and G.D. Sandrock, December, 1981

FIGURE 3. SIMULATED STORAGE BED

FIGURE 4.1. UNSTEADY STATE ACCOUNTABILITY **FIGURE 4.2. STEADY STATE ACCOUNTABILITY**

EQUATIONS

2. van't Hoff equation

$$\ln P_p = \Delta H / RT + C$$

P_p : plateau pressure

ΔH : enthalpy change of hydriding reaction per mole of H_2 .

R : universal gas constant

T : absolute temperature

C : constant related to the entropy change of the hydriding reaction

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