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Design, safety assessment, and testing of a uranium based hydrogen storage bed

Rupsha Bhattacharyya*, Dibyendu Bandyopadhyay, Kalyan Bhanja, Sadhana Mohan
Heavy Water Division, Bhabha Atomic Research Centre, Mumbai-400085, Maharashtra, (INDIA)
E-mail: rupshabhattacharyya1986@gmail.com

ABSTRACT

A uranium based getter bed for storage of upto 2 gm hydrogen has been fabricated and its qualitative performance with respect to adsorption and desorption of hydrogen has been studied. Several safety measures were incorporated in the design and operation of the storage bed based on potential hazards that can arise in handling hydrogen and uranium. The observed behavior of the bed can be used to obtain design and operating information for future experiments.

KEYWORDS

Hydrogen storage;
Uranium;
Getter bed;
Hydriding;
Reversible storage;
Safety analysis;
Hazard identification.

INTRODUCTION

Solid state storage of hydrogen in the form of a metal or alloy hydride has been proven to be a very effective and compact way of storing hydrogen and its isotopes for both stationary and mobile applications[1]. For storage of hydrogen, a wide variety of different metals and alloys have been extensively studied. Uranium metal is one such material to which several researchers have devoted attention, mainly because of its favorable thermodynamic and kinetic properties with respect to hydriding and dehydriding reactions and because it is relatively easily available in the nuclear industries[2, 3]. In the present work, hydrogen uptake and release by uranium turnings were studied in a storage vessel fabricated in-house. The principal aim of this exercise was to obtain operational experience and to study the feasibility of using uranium as a getter material for rapid uptake and release of hydrogen. Experience in in-house fabrication and testing of the overall behaviour of a compact system for hydriding and dehydriding of uranium and obtaining some design and operating parameters for such systems were other objectives of this work.

DESIGN AND FABRICATION OF THE BED

The initial design of the bed was for storing 0.67 gm of hydrogen gas on uranium, at 100 % of the stoichiometric capacity based on previous experiences of different research groups. The hydriding reaction considered was[4]

$$U + 1.5H_2 = UH_3, \ \Delta H_r = -97.5 \text{ kJ/ mole } H_2 \quad (1)$$

From the above reaction it was calculated that about 52 gm of uranium turnings would be required stoichiometrically. This was rounded off to 60 gm. It is known that solid getter materials undergo significant volume expansion on hydriding[5], thus the storage vessels should have adequate free space in them to accommodate the expansion. For uranium it is known than the hydride volume is 75% more than

the volume of the metal[6]. The volume expansion of uranium on hydriding and change in powder density were considered in estimating the maximum solid volume. The design pressure was selected as 20 bar (a) and design temperature was taken as 800 K. The large value of design pressure was selected for a compact storage system and also for enabling the vessel to withstand stresses and accidental mechanical impact during transportation. At the maximum design temperature of 800 K, the equilibrium dissociation pressure of hydrogen over uranium is estimated to be about 8 bar (a) only[7]. So even at this temperature the pressure will never rise to 20 bar (a) as considered in the design. This determines the gas volume as the number of moles of gas is fixed. The vessel volume thus consists of the solid volume and the gas volume taken together and is about 1.5L cc for the case reported here. The length to diameter ratio of 1:3 was chosen from a preliminary heat transfer analysis so as to provide maximum surface area for free convective and radiative cooling during hydriding, since no other cooling mechanism was proposed to be used for the this test bed.

The vessel design was based on ASME Boiler and Pressure Vessel Code, Section VIII, Division 1. Some pertinent design data are provided in TABLE 1. The vessel was fabricated out of standard Schedule 40 pipe section of appropriate dimension and has an all welded construction. Figure 1 shows a photograph of the vessel without the attached band heater and insulation layer.

TESTING OF THE BED AND RESULTS

Test procedure

The following sequence of operations was followed for the performance of hydriding and dehydriding experiments:

i) Nitrogen was charged into the vessel to a pressure of about 5 bar (g) and all valves were closed.

TABLE 1 : Design data for the hydrogen storage bed

Design Parameter	Value
Amount of Hydrogen to be stored	0.67 gm
Amount of Uranium	60 gm uranium turnings
Design pressure	20 bar (a)
Maximum operating pressure	5 bar (a) (at ambient temperature, during hydrogen charging to the system.
Maximum design temperature	600^{o}C (during dehydriding or desorption) [Operating range 25-450^{0}C]
Vessel dimensions	15.2 cm (height), 11.4 cm (outer diameter), 5.52 mm (shell thickness)
Vessel closure	Flat head on top, torispherical head on bottom with nozzles for gas entry, exit and liquid drainage respectively
Material of construction	SS 316 L
Total weight of vessel	6 kg
Tubing and fittings	¼'' SS tube and fittings
Filter material	Ceramic sintered disk (20 mm diameter, 3 mm thickness, average pore size 5 μm, porosity grade 4, placed at gas inlet, outlet and regeneration liquid drainage point)
Flange dimensions	4.5'' flange with 1' opening (for thermocouple insertion), pressure rating 150 lb.
Gasket material for flange	SS 304
Screen	100 mesh screen (nominal opening size 150 μm) supported on perforated SS plate and welded to vessel inner wall)
Heating method	Electrical heating by band heater with temperature controller
Heater output power	400 W (maximum)
Insulation	Cerawool insulation, 1" thickness
Support type	Ring and tripod stand welded to vessel outer wall

Figure 1 : Pressure vessel for storage of hydrogen as uranium hydride

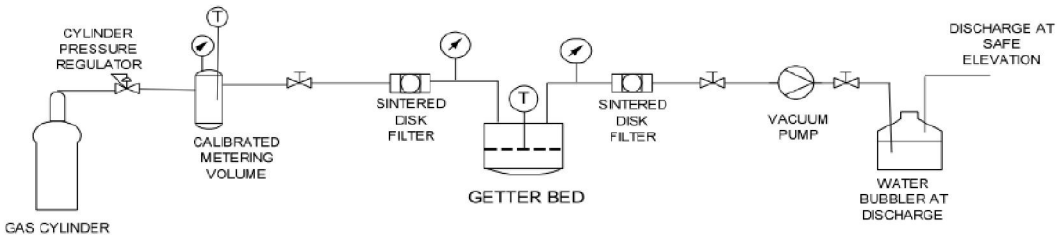

Figure 2 : Schematic diagram of experimental set up for studying hydriding and dehydriding of uranium

The drop in pressure inside the vessel was noted with time to obtain a measure of the global leak rate. Soap solution was applied to all joints to detect any sources of leakage and appropriate tightening of the leaking joints was carried out.

ii) Helium leak test was performed using a sniffer probe to determine the leak tightness of the vessel. A maximum global leak rate of $3.1*10^{-5}$ Torr L/sec was detected, which was low enough to be acceptable.

iii) The bed was pressurized to 115% of the maximum operating pressure (i.e. 21 bar (a)) with helium and the pressure was allowed to be held for 40 minutes in course of which no detectable leak was observed from the vessel. Thus the integrity of the bed was ensured.

iv) To clean the surface of the oxide layers the uranium chips were first rinsed with tap water, then distilled water and finally ultrapure water, then dipped in a solution of concentrated nitric acid of 8(N) strength taken in a glass beaker and stirred with a glass rod for about 20 minutes. They were rinsed off with distilled water and then with acetone and finally dried for 30 minutes in air. Then the turnings were carefully charged into the vessel. The use of uranium turnings for the test runs was motivated by the fact that they are not pyrophoric and can be handled with relative ease in the open as opposed to fine powder or dust which would readily react with air or oxygen even at ambient temperature[7].

v) The metering tank was charged with hydrogen to a pressure of 20 bar (a). The inlet to it was closed and its outlet was opened to charge the storage vessel with hydrogen to a pressure of about 5 bar (a). From the accurately known volumes of the vessels and with the help of the temperature and pressure readings from each vessel, the amount (i.e. the number of moles) of hydrogen charged into the storage vessel was ascertained.

vi) The reaction of hydrogen with uranium turnings was not appreciable at room temperature, so electrical heating was employed to raise the temperatures. A band heater was used for this purpose. The surface temperature of the solid as well as the

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TABLE 2 : Hydrogen uptake by uranium

Run	Initial Fill Pressure (bar (a))	Fill Temperature (deg C)	Final Pressure (bar (a))	Final Temperature (deg C)	Mass of hydrogen adsorbed
1	4.6	30	0.0	30	0.2560
2	4.5	34	0.5	34	0.2194
3	4.5	34	4.0	34	0.0274

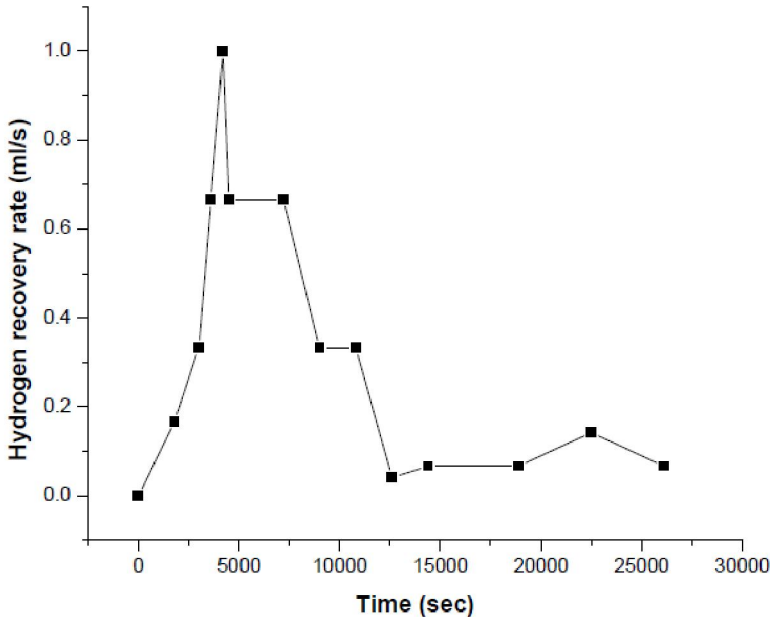

Figure 3 : Cumulative hydrogen release during dehydriding

skin temperature of the vessel wall was sensed using thermocouples. The solid surface temperature was taken as the reaction temperature and it was the input to the temperature controller for adjusting the heater output power. The reaction took place rapidly at about 120 to 140°C and the initial charge of hydrogen was observed to be adsorbed within a few minutes. After adsorption was over the vessel was filled with helium gas to a pressure of 3 bar (a) in order to provide an inert blanket over the uranium.

vii) For dehydriding, the bed was initially evacuated by an oil-free scroll pump at ambient temperature for 45 minutes to 60 minutes to remove the blanket gas. Then the heater was switched on, the temperature was set to about 300°C and evacuation was allowed to continue for a total time of about 7 hours. The hydrogen released by the dissociation of uranium hydride was sent out through a bubbler containing water to wash off any entrained solids. An empty guard vessel was placed before the bubbler in order to prevent suction of water from the bubbler into the vacuum pump. Water displacement method was used to approximately estimate the quantity of hydrogen released upon heating and evacuation. The evacuation rate was found to depend on the temperature and the amount of hydrogen remaining adsorbed in the uranium. Water in the bubbler was kept as a sample to detect traces of uranium in it.

Test results

Hydriding operation

The entire quantity of hydrogen that could be adsorbed by 60 gm of uranium was not charged all at once but was distributed over three pulses, designated as runs 1 to 3 in TABLE 2. The total amount of hydrogen adsorbed by uranium was evaluated as the sum of the hydrogen adsorbed in each run. The bed thus acts like a batch reactor with an initial charge of hydrogen and uranium. To ensure consistency in calculation, the temperature during charging of hydrogen and the temperature after cooling the bed to that initial temperature and ensuring that there is no further change in pressure inside the bed were taken

TABLE 3 : Hazard identification and preventive measures for uranium based hydrogen storage system

Hazard Category	Hazard Identification	Hazard Prevention
Fire/flammability hazard from hydrogen	Hydrogen leak or accidental release into surrounding air from the hydrogen cylinder along with presence of ignition source (sparks due to static electricity discharge, welding operations etc)[10] Assuming entire hydrogen from the vessel was released into the room and assuming it to be well mixed with the air, the average percentage of hydrogen is expected to be $100*1.5*10^{-3}$ m3/75 m3 = 0.002 % which is much lower than the lower explosive limit of hydrogen in air at STP (4% by volume)	i)Use of hydrogen gas area monitors ii)Elimination of ignition sources iii)Provision of proper firefighting equipment (dry chemical powder extinguisher) made at the site of experiments iv)Well ventilated site of experimentation for quick dilution of leaking gas v)Storage of no flammable gases or liquids in the vicinity of the test set up vi)Prevention of heating of the hydrogen cylinder by any other means.
Fire/flammability hazard from uranium	Exposure of finely powdered uranium to air and moisture leads to explosive reactions and fire, liberating large amounts of heat [8]. Uranium turnings do not present such hazards. The metal oxide or hydride is also toxic and the hydride also is pyrophoric [6].	i)Bed leak tightness was checked thoroughly ii) The bed was not opened in air directly, but only under inert gas blanket iii) Filters (ceramic sintered disks) were provided at all inlet and outlet ports of the vessel to confine fine dust and powder within the bed itself iv) Dry chemical powder extinguisher, other personal protective equipment were provided at the set up.
Chemical toxicity of uranium	Depleted uranium is a highly toxic substance affecting the kidneys, lungs, bones [11]. Assuming entire amount of uranium ws released into the room on pressure vessel failure and assuming it to be well mixed with the air, the average concentration of uranium in air is expected to be 60 gm/75 m3 = 0.8 gm/m3. Since this amount is above the lower permissible exposure limit of uranium (0.25 mg/m3) [12, 13], safety in design has been stringently incorporated. The pressure vessel was designed for 60 bar (a) pressure and the integrity of the vessel and piping system was tested and established at 21.5 bar(a) while the maximum operating pressure during testing was 5 bar (a).	i) Face masks and Comfo respirators and gloves used for preventing any accidental inhalation or ingestion or contact with uranium ii) The Material Safety Data Sheet for uranium and first aid measures were displayed at the site of experiments. iii) Water and sodium bicarbonate solution were provided at site for decontamination iv) Design was carried out as per ASME code (ASME Boiler and Pressure Vessel Code, Section VIII, Division 1) iv) Guard vessel containing water was placed in the gas outlet path to remove uranium fines from recovered hydrogen during dehydriding

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Hazard Category	Hazard Identification	Hazard Prevention
Radiation hazard from uranium	Uranium is an alpha emitter [11].	i) 60 gm uranium presented no criticality hazards. ii) Periodic monitoring of surface dose rate on the storage vessel was carried out. iii) The steel vessel wall thickness was sufficiently large to stop the passage of the emitted alpha particles.

to calculate the number of moles of hydrogen adsorbed.

Amount of uranium turnings charged into vessel: 60 gm

Total mass of hydrogen adsorbed: 0.5028 gm

Mass of hydrogen that can be adsorbed in 60 gm uranium: 0.67 gm

Percent of stoichiometric loading attained: **0.5028*100/0.67 = 75.04%**

Thus under the given conditions of hydriding, the entire amount of uranium could not be used for uptake of hydrogen. This may be due to partial oxidation of the uranium turnings during charging into the bed, which makes it unavailable for reaction with hydrogen.

Dehydriding operation

The evacuation rate was measured at different times during the entire evacuation operation by a water displacement method. Measurements were continued till no bubbling was seen in the water after about 7 hours. This is only a crude method of estimation and liable to errors but it outlines a principle of getter bed testing. In future tests, digital flow meter system at the exit line from the bubbler vessel is proposed to be used. The results are shown in Figure 3. The total amount of hydrogen released was then calculated by the area under the curve. The maximum bed temperature attained during dehydriding in this system was about 275°C. Better insulation of the system will allow higher temperatures to be reached in this system.

From the area under the graph 1, the total quantity of hydrogen released is determined to be 6286 ml at 1 atm (a) pressure at 34 deg C. Therefore the number of moles released by heating and evacuation is 0.2495. The recovery (on molar basis) is thus calculated as

$$\%\ H_2\ \text{recovery} = \frac{0.2495}{0.2512} * 100 = 99.3\ \%$$

HAZARD ANALYSIS AND SAFETY CONSIDERATIONS IN DESIGN AND OPERATION

The storage of hydrogen in the form of uranium hydride involves the handling of two hazardous substances viz. hydrogen and uranium. Thus in the design of the bed and in formulating its operating procedure, some possible hazard inducing scenarios were considered and appropriate provisions were made for their prevention and if required, mitigation.

Safety provisions in design and operation

a) When a fissile substance like uranium is used for the getter bed care must be taken that in a single bed the quantity of uranium is such that it never exceeds the critical mass of uranium (which is about 48 kg for a bare, unreflected sphere and about 15 kg for a water or steel reflected sphere) [9]. Further to prevent criticality hazards, the storage bed should also not be surrounded by water which acts as a reflector. In the present experiments, only 60 gm of natural uranium turnings were used at a time, thus eliminating all possibility of a criticality hazard.

b) Only clean, dry metallic uranium turnings were charged into the vessel and the vessel was purged by helium before introduction of hydrogen gas. This was done to avoid any possible reaction with air or moisture. Further, the turnings charged into the bed were of sufficiently large dimensions (about 1 inch length) that these were safe to handle in the open and were not pyrophoric [8].

c) The mechanical design of the bed was for 20 bar (a) pressure and 600°C temperature whereas in actual operation the maximum fill pressure was be 5 bar (a) and maximum temperature was about 300°C. The helium leak testing (by MSLD technique) for the vessel was performed prior to the experimental runs and the maximum leak rate detected was $3.1*10^{-5}$ Torr. L / sec. Integrity testing of system was done using nitrogen at 21 bar (a) pressure at ambi-

ent conditions with no detectable leakage from the vessel over a period of 40 minutes. Thus leak tightness and mechanical integrity of the bed were assured.

d) Use of ceramic sintered disks at gas inlet and outlet to contain fines was made. Also portable area monitors for hydrogen were used in the experimental area to detect any accidental release of hydrogen during the experiments. Periodic assessment of surface dose rate on the vessel was made to ascertain if there was any accidental exposure of the operating personnel to harmful radiation.

Possible hazards in getter bed operation and preventive steps

The possible hazards (chemical and radiological hazards were most relevant for the present study) and prevention steps are described in Table 2.

SUMMARY AND CONCLUSION

A pressure vessel was fabricated for storage of upto 2 gm of hydrogen using uranium as the getter material with initial hydrogen fill pressures of the order of 5 bar (a). Preliminary testing of the bed was carried out by performing both hydriding and dehydriding steps. The dynamic behaviour of the bed was observed and that is expected to help in the formulation of a sound operating policy for a getter bed based hydrogen storage facility. Extensive safety provisions were made in design and operation of the storage bed. The same set up will be used for more extensive and thorough quantitative testing and data thus obtained will be compared with results reported in literature.

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