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A COMPACT HYDROGEN RECYCLING SYSTEM USING METAL HYDRIDES

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Abstract

A gas recycling system to prevent losses of isotopically enriched hydrogen gas has been developed for the operation of a liquid target (2.7 liter) used by the Radiative Muon Capture group at TRIUMF. The experimental requirements for high gas purity (chemical impurities below 10^{-9}), low operating pressure (below 1 bar abs) and high loading pressure (14 bar needed for a palladium purifier) together with the usual hydrogen safety requirements were satisfied with a metal hydrid storage device in combination with a small pump/compressor system. A description of the complete system together with its characteristic operational data are given in this paper.

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1. Introduction

Liquified hydrogen gas is often used as a target for particle beam experiments. As long as standard grade gas with natural isotopic composition is used in small quantities, recycling the hydrogen gas is not normally done. However, if a large quantity of high purity or isotopically enriched gas is used, gas recycling may be desirable or even necessary. For tritium it is absolutely essential because its radioactivity prohibits venting it into the atmosphere.*

There are various methods to recycle hydrogen gas depending on the experimental setup and its limitations. In this paper we present a recycling system which utilizes the ability of certain metallic alloys to store large amounts of hydrogen by forming hydride compounds. The system was developed to serve the repeated operation of a high purity liquid protium target (isotope ^1H only) used in experiment # 452 at TRIUMF to measure radiative muon capture on hydrogen (RMC(H)). This process $(\mu^- p)_{1s} \rightarrow n + \nu + \gamma$ is known as a promising tool to study the semileptonic induced pseudoscalar interaction [1].

In the next section we summarize the demands of the RMC experiment on the target and the gas handling system. It is followed by a brief listing of the advantages of the hydride method including some data on the alloy we have chosen. Section 4 contains a description of the gas handling system, while its performance is described in section 5.

2. Demands on the RMC liquid hydrogen target

The extremely low rate of RMC on hydrogen (approx. 0.03 s^{-1} in liquid to be compared with 4.55×10^5 s^{-1} for ordinary muon decay) makes the experiment very vulnerable to various sources of background. The important sources of background which affect the design of the hydrogen target are listed below.

- Muons which form $(\mu^- Z)$ atoms in the walls of the hydrogen container will eventually initiate a RMC(Z) process. This may result from direct stops of muons during the passage of the beam through the container walls. In addition, it may result from muons scattering on hydrogen atoms and reaching the wall or diffusion of neutral $(\mu^- p)$ or $(\mu^- d)$ atoms with subsequent transfer of the muon to a wall atom. A rather large cylindrical target container ($16cm$ $\phi \times 15cm$ length, volume approx. 2.7 liter) with 0.25mm thick walls made out of pure gold was found to be a practical solution. The target's size reduces the probability that muons will reach the lateral walls by scattering or diffusion. In addition, the short lifetime of $(\mu^- Au)$ atoms (73 ns) is used to distinguish between photons from RMC(Au) and photons from RMC(H) (2195 ns).

- Muons which are captured on heavy atoms in the target liquid form $(\mu^- Z)$-atoms which eventually initiate a RMC(Z) process. This effect is enormously enhanced by the transfer process $(\mu^- p)_{1s} + Z \rightarrow (\mu^- Z)_{1s} + p$ with a density dependent rate of order 10^{11} s^{-1} in liquid hydrogen[2]. A purity of $\leq 10^{-9}$ parts per hydrogen

*Pure tritium gas at NTP has an activity of 9.7×10^{13} Becquerel/l.

atom was therefore demanded in the target liquid. This level can be achieved in the gas entering the target by means of a palladium purifier (see [3] and our test results in section 5). Good vacuum conditions with small outgassing and leak rates are required in the target cell and all the interconnecting tubing between the palladium purifier and the target cell. The room temperature combined outgassing/leak rate tests are reported in section 5 together with an estimate of the solubility of contaminants frozen on the cell wall in liquid hydrogen at 16 K.

- Deuterium in the target cell can result in the formation of ^3He, followed eventually by RMC(^3He) with a predicted rate of 0.676 s^{-1} [4]. The ^3He is formed at the end of a series of muon catalyzed reactions. The most important reaction chain† is $(\mu^- p)_{1s} + d \rightarrow (\mu^- d)_{1s} + p$ with a rate of $(1.43 \pm 0.13) \times 10^{10}\ s^{-1}$ [5], $(\mu^- d)_{1s} + p \rightarrow (p\mu^- d)^+$ (rate: $(5.6 \pm 0.2) \times 10^6\ s^{-1}$) and $(p\mu^- d)^+ \rightarrow (\mu^-\ ^3He)_{1s} + \gamma$ (rate: $(0.46 \pm 0.03) \times 10^6\ s^{-1}$). (See ref.[7] for a more comprehensive overview.) Normal grade hydrogen gas contains approx. 70–150 ppm (parts per million) deuterium, a number which varies with the exact source of the hydrogen gas. As indicated by the reaction rates given above a contamination of less than 5 ppm is necessary to keep the background below the 10% level. Only recently has such isotopically clean hydrogen gas become available [8].

The RMC specific demands on the target given above have implications on the gas handling system as well. The expense of isotopically pure hydrogen gas ($3/liter at NTP) makes a recycling system desirable. The use of a palladium purifier requires a high input pressure of about 10 bar to match the refrigerator's condensation capability and the fragility of the gold target cell requires that the gas be recovered by the recycling system at low pressure, less than one atmosphere.

3. The choice of a recycling method based on hydride formation

The formation of hydride compounds in the lattice of various metals in contact with hydrogen gas is well established. In forming the hydride, heat is released which needs to be removed to stabilize the compound. Formation and dissociation of the hydride is reversible, offering use as a hydrogen storage device. In comparison with compressed gas storage the hydride method features several advantages:

- High storage capacity can be achieved, because almost every atom of the metal can combine with a hydrogen atom. Hydrogen densities of approx. 50% of liquid density can be achieved at room temperature and rather low pressure above the metal surface (typ. 2–3 bar).
- The loading pressure depends on the specific metal or alloy chosen, but in general it is lower than 5 bar, as compared to 400 bar for compressed gas bottles of the same volume.
- Nonhydrogenic gases are not stored in the lattice of the metal. Therefore the creation of an H-O explosive mixture in the storage device is practically impossible as the residual free gas volume in the bottles housing the alloy is small. If by accident a large amount of oxygen is pumped into the storage device, it may damage the alloy by slow oxidation, but an explosion is almost impossible.
- Performing a complete gas absorption and supply cycle is simple since changing the temperature is all that is needed to control the gas pressure.

Our selection of a specific metal was based on the following features: a low loading pressure due to the fragility of the target cell, high supply pressure because of the palladium purifier to be loaded and, last but not least, easy handling and availability. Various metals and alloys are known to absorb hydrogen in large amounts. Examples are Uranium, Palladium, Titanium, Vanadium and Zirconium and alloys made out of them, all having different hydrogen concentration and pressure relations. Uranium was considered since it is the best material concerning the loading pressure. The equilibrium pressure of hydrogen above uranium is of the order 10^{-5} mbar at room temperature [9], therefore no pump is needed to evacuate a hydrogen filled volume. However, the supply pressure is limited to normal atmospheric pressure requiring a compressor for loading the target through the palladium purifier. In addition, handling is somewhat difficult, first due to restrictions as a nuclear fuel material and its inherent radioactivity and second, because uranium hydride, once created, is a very reactive powder which burns in air and tends to obstruct mechanical pumps, valves etc.

Disregarding uranium because of these reasons we finally chose a commercially available alloy supplied by HWT‡ with code number 5777.§ This alloy has a loading pressure below 5 bar and a hydrogen storage capacity of 200 l/kg. The alloy was delivered in five small convenient steel bottles (approximate volume 2 l) each containing about 5 kg of the alloy so that each bottle would store 1000 l of hydrogen. Each bottle was equipped with a bellows valve and a relief valve set to 27 bar (The max. possible pressure would be 50 bar given by the container strength). Each storage bottle was placed in a tight-fitting, water-cooled copper sleeve which itself was surrounded by an electrical heater sleeve. A thermocouple was placed in a gap between the bottle and the copper sleeve to provide the input reading of the heater power controlling circuit. Only one unit can be heated at a time, all others being cooled by default. The waterflow is automatically stopped when the unit is selected for heating. Some properties of alloy # 5777 are given in fig.1. They are essentially in agreement with what was known from the data sheets supplied by the manufacturer, giving the equilibrium relations between gas content, pressure and temperature.

Special attention was paid to the question of how much gas remains in the alloy after evacuating it at a certain temperature. This question is related to the isotopic purity required for the RMC experiment. Usually the alloy is tested using normal hydrogen in which case 6.7 liters of normal hydrogen with a deuterium content of 150 ppm will contaminate a 1 m^3 charge of deuterium free hydrogen to about 1 ppm deuterium.

In order to determine the residual gas in the alloy after extracting gas at 330°C over 8 hours until no outgoing hydrogen flux was measurable, we added 9 liters (NTP)

†All rates are normalized to liquid hydrogen density ρ_0, if appropriate. $\rho_0 = 4.25 \times 10^{22}\ nuclei/cm^3$

‡Address of supplier: HWT, D–4330 Mülheim a.d. Ruhr, Germany. Since HWT has recently quit the manufacturing of these alloys we enclose the address of another supplier of similar alloys: ERGENICS Inc., 247 Margaret King Avenue, Ringwood, N.J. 07456, USA.

§The composition of the alloy is proprietary of HWT.

of deuterium gas to the unit to mix with the hydrogen remainder¶. This mixed gas was then extracted under careful control of the gained gas volume. Samples of the extracted gas were analyzed by mass spectroscopy to determine the hydrogen/deuterium content. A steady increase of the equilibrium constant $K = p^2_{HD}/(p_{H_2}\ p_{D_2})$ with p_{xx} the partial pressure of gas xx was measured for samples taken at later times and at higher alloy temperatures until it reached K = 3.44 which is very close to the equilibrium value of K = 4 [10]. Assuming equilibrium had been reached, the residual gas content was calculable by knowing the total amount of extracted gas (11 liter at NTP composed of 26% H and 74% D). The final result was that, after heating the alloy at 330°C for 8 hours, about 3.4 liter of gas remained bound as a hydride. This could only be regained by going to higher temperatures. At 400°C the inaccessible amount of gas was about 1.6 liter.

4. The gas handling system:

The schematic layout of the gas handling system is shown in fig.2. All five hydride storage tanks were hooked up to a single gas supply and gas recovery line respectively, but they remained individually controllable by independent valve connections. Gas is provided by heating a selected storage unit such that a minimum of 5 bar output pressure is maintained. The gas is brought to the inlet of the palladium purifier where a small fraction of the gas is used to flush the surface of the purifier for cleaning purposes ("bleeder"). This flushing gas is returned to the recovery gas line to be recovered by the previously emptied storage units after passing through a liquid nitrogen trap for removal of water vapour. Finally, the throughgoing purified gas enters the target cell where it is cooled and condensed into liquid. Once the pressure in the supply unit drops below 5 bar and the temperature reaches 250°C the unit is regarded as exhausted. It is then closed off from the supply line, cooled down to room temperature and connected to the recovery line to be ready to absorb gas eventually evaporated from the liquid target.

The collection of gas is improved over the alloy's basic capabilities by using a pump/compressor system which allows the maintenance of a lower target pressure (4 mbar) and a higher alloy loading pressure (3 bar). The vacuum reached is sufficient to pump on the target (which is below atmospheric pressure) as well as to evacuate storage units in transfering gas from one module to another. The output pressure of 3 bar is sufficient to load the storage units up to 100% of their capacity in about 1 hour, a limitation given mainly by the cooling efficiency.

In the case of an electrical power failure a bypass allows gas recovery by the storage units, although at a somewhat reduced rate. As an emergency safeguard against gas loss, breaking disks and relief valves were added in-line and connected to an evacuated dump volume capable of storing the entire gas inventory. Fortunately, its use was never required.

5. Results:

The gas purity of 10^{-9} (for heavy contaminants) is not measurable by means of a mass spectrometer. Therefore, it was checked in an indirect way by measuring the palladium purifier's leakage and the leakage rate in the target flask respectively. The palladium purifier was tested twice by supplying nitrogen, argon and neon instead of hydrogen on its input side and noting the pressure change on the output side by means of an ion gauge. The pressure change measured was 2.7×10^{-7} mbar. That pressure increase was translated into a gas flow of 2.1×10^{-7} mbar liter/sec using the calculated conductance from the ion gauge to the turbopump (0.8 liter/sec). The mean gas flow of hydrogen during the target filling procedure was 59 mbar liter/sec resulting in a transmission ratio of heavy gases and hydrogen of 3.6×10^{-9}. The initial contamination of hydrogen with heavy gases was low (order 10^{-5} or better) and so the contamination of the hydrogen with heavy gases after passing the purifier was less than 10^{-13}.

The leakage and outgassing rate of the target cell including the pipes downstream of the palladium purifier was determined before each experimental period, after pumping on the cell for 2 to 3 weeks, by isolating the cell from the pump and measuring the pressure rise over 24 hours. In addition, the gas accumulated during this day was analyzed with a mass spectrometer to determine the nonhydrogenic component. The critical pressure is 8.1×10^{-4} mbar as the contaminations would then equal 10^{-9} of the hydrogen filling. The times extrapolated from the 1 day measurements to reach the critical pressure varied significantly. Averaging 10 measurements we obtain a value of 26.0 $\pm$1.7 days, roughly the length of a data-taking run. One has to keep in mind, however, that this number gives a rather conservative estimate, as it is taken at room temperature. During the run, at 16 K, heavy gases are frozen to the wall of the target. With no liquid hydrogen in the target cell, the density of nitrogen in the target cell is equivalent to a vapour pressure of 9.3×10^{-17} mbar. The solubility of nitrogen in liquid hydrogen raises this density to a vapour pressure equivalent of 8×10^{-12} mbar [11] but the density is still far below that corresponding to the critical pressure of 8.1×10^{-4} mbar.

In order to maintain the isotopic purity of the hydrogen gas, which was produced by electrolysis of the ultrapure H_2O, all 5 storage units were heated to 400°C and pumped over 1 day before flushing them with a few liters of protium and heating them again. The 4 m^3 of protium gas were then loaded into the storage devices. The deuterium contamination was checked many times by taking samples directly from the target during the experiment. The samples have been analyzed for their deuterium content by the Environmental Isotope Laboratory at the University of Waterloo and Metabolic Solutions Inc., resp.[12]. Fig.3 shows the quoted results. The drop in the contamination after June '91 is due to a replacement of the entire gas inventory by a new charge. Obviously, the second charge had a much lower deuterium contamination[13].

The filling time for the target ($\approx$ 18 hours) is determined by the cooling capacity of the refrigerator (10 W @ 20 K) and the throughput of the palladium purifier (5 standard liter/min @ 200 psi input pressure). The recovery time for emptying the target completely was typically 5 hours. This time was controlled by an electrical heater on the target which was set to keep the target warm-up under control rather than to give maximum recovery speed.

In general, very little user interaction has been required to handle the gas system in all respects. An unforeseen test of the ability of the gas handling system occured once

¶The particular storage unit used to perform this test has not been used for the RMC experiment to avoid any possible source of deuterium contamination.

when the vacuum shell of the target collapsed and the hydrogen boiled away rapidly, although not explosively. The entire volume of gas was totally gathered by the storage units without any loss.

Acknowledgements

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[12] Dept. of Earth Sciences, Univ. of Waterloo, Waterloo, Ontario, Canada N2L 3G1 and Metabolic Solutions Inc. Acton, MA 01720, U.S.A., resp.

[13] This water was purchased directly from AECL Commercial Products, Chalk River, Ontario K0J 1J0.

Figure Captions

1. Measured properties of a HWT hydride storage unit. Nominal storage volume 1 m^3. Alloy code no.: 5777.
(Connecting lines for eye guidance only.)
a) Hydrogen absorption rate in l/min vs. time for a loading pressure of $\approx$ 2 *bar* at 17°C. The irregular behaviour at short times reflects the difficulty of keeping the pressure and temperature constant during periods of intense hydride formation with strong heat production.
b) Equilibrium pressure of a fully charged HWT storage unit (Q = 100 %) as a function of temperature.
c)Equilibrium pressure in a storage unit measured at 95°C for various hydrogen charges (in percent of full charge).

2. Simplified schematic drawing of the gas system. Pipes necessary for evacuating the system are not shown.
AV1, AV2 .... air pressure operated valves, activated by cell pressure transducer.
AV1 opens, if cell pressure goes below 9 psia. Fresh purified gas is supplied to the target.
AV2 opens, if cell pressure raises above 10 psia. Gas is purged into the recovery system.
The use of the pump/compressor stage is described in the text.
The palladium purifier leakage rate and the target outgassing rate has been determined with the ion gauge (see text).

3. Deuterium content in gas samples taken directly from the target during the various running periods. The units are parts per million. After July 1991 the whole gas inventory was exchanged with a new protium charge. The deuterium content of this new charge was obviously much smaller than the first charge and below the sensitivity of the measurement[13].

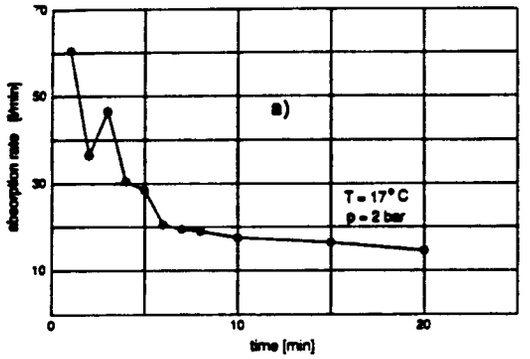

Fig. 1a

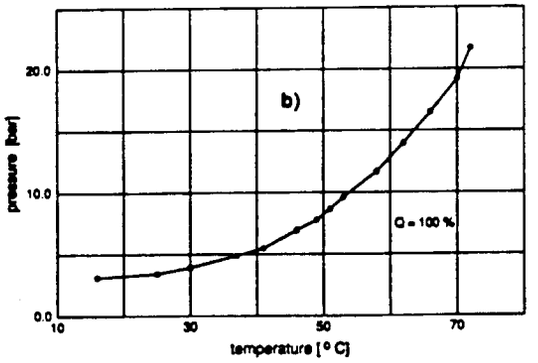

Fig. 1b

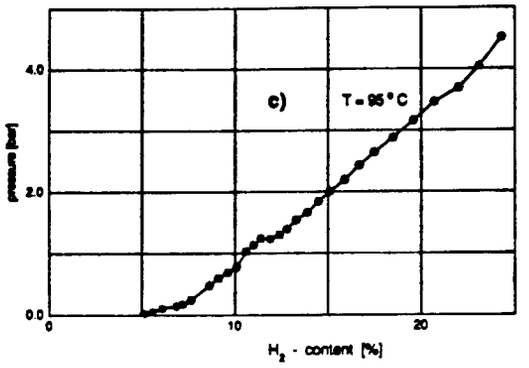

Fig. 1c

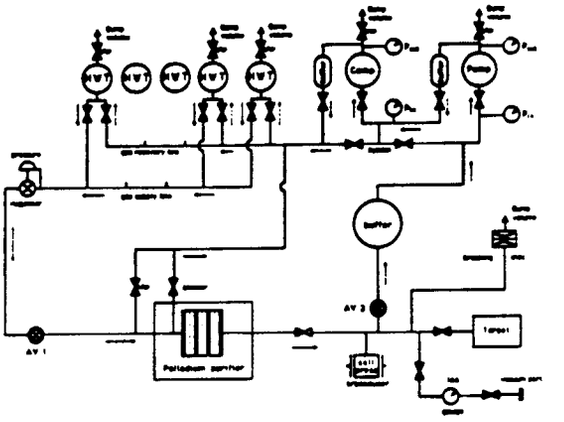

Fig. 2

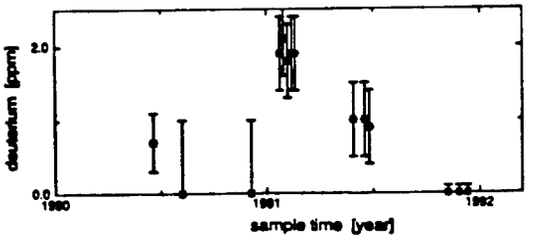

Fig. 3