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Using Metal Hydride to Store Hydrogen

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1. INTRODUCTION

Hydrogen is the lightest element. At ambient conditions on a volume basis it stores the least amount of energy compared to other fuel carriers such as natural gas and gasoline. For hydrogen to become a practical fuel carrier, a way must be found to increase its volumetric energy density to a practical level. Present techniques being developed include compressed gas, cryogenic liquid and absorbed solid. Each of these techniques has its advantages and disadvantages. And none of them appears to be satisfactory for use in a hydrogen economy. In the interim all of them are used for demonstration purposes. Metal hydrides store hydrogen in a solid form under moderate temperature and pressure that gives them a safety advantage. They require the least amount of energy to operate. Their stored hydrogen density is nearing that of liquid hydrogen. But they are heavy and the weight is their main disadvantage. Current usable metal hydrides can hold no more than about 1.8% hydrogen by weight. However much effort is underway to find lighter materials. These include other solid materials other than the traditional metal hydrides. Their operation is expected to be similar to that of metal hydride and can use the technology developed for metal hydrides.

The absorption of hydrogen by metal hydride is an exothermic reaction. Heat removal during refueling becomes the controlling factor on refueling time. Metal hydride expands in volume up to 20% that imposes stress on the container wall. How to design metal hydride beds that is low cost, light and effective in heat transfer for mobile applications has been the subject for development since in the 1970's. Over the past several years, the hydrogen technology group at Savannah River Technology Center has developed and demonstrated metal hydride storage beds onboard a transit bus using an internal combustion engine and two utility vehicles powered by fuel cells. The modular design of the beds provides great flexibility in meeting capacity needs. Systems with hydrogen capacities of 2 kg and 15 kg have been demonstrated. This presentation gives an overview on how metal hydride stores hydrogen in comparison with other techniques, and discusses the development and demonstration of metal hydride storage systems for onboard applications.

2. COMPARISON OF STORAGE TECHNIQUES

It has been widely reported that hydrogen will be the fuel of the future, because its abundance on earth, it burns cleanly with water being the only byproduct, and it contains the highest energy on a weight basis. In reality, hydrogen is only a fuel carrier and energy is required to produce elemental hydrogen. In addition, hydrogen contains very small amount of energy on a volume basis, and volume counts the most when fuel is stored and transported. From the point when hydrogen is produced to the point when hydrogen is converted to work, energy consumed in storage, transport and other must be at a minimum to maximize the energy carried to do work. Storage is probably the most important step in this process.

Present storage techniques for hydrogen include compressed gas, cryogenic liquid and absorbed solid (metal hydride and other). To store hydrogen as compressed gas energy must be consumed to reach the high pressure. Compressing hydrogen requires significant amount of energy. To obtain a reasonable estimate, one may use the adiabatic compression equation[2] and add the efficiencies of the electric generator and the compressor. The plot in Figure 1 is constructed by using this equation, and by assuming that fuel cell produces the electricity at 60% efficiency to run a compressor at an efficiency of 85%. This plot shows that compressing hydrogen to 5,000 psi (340 atm) and 10,000 (680 atm) will require 36 MJ/kg and 47 MJ/kg. These correspond to 30 and 40% of the low heat value (LHV) of hydrogen. Storing hydrogen as a compressed gas is quite energy intensive.

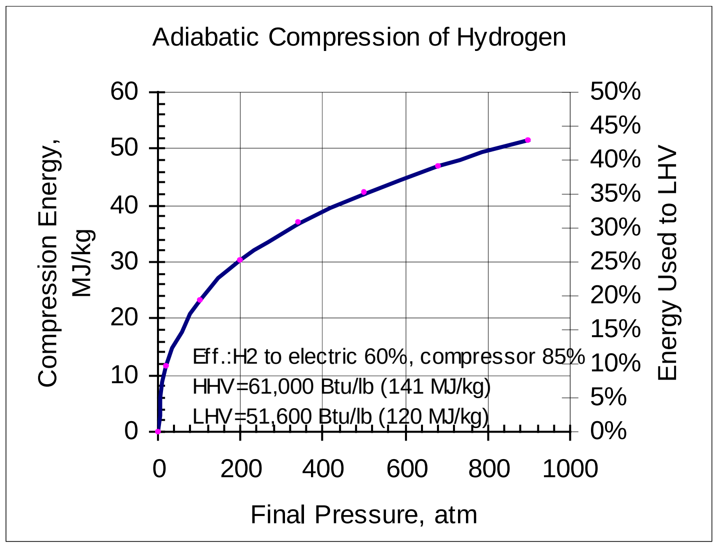

Figure 1. Energy consumption of compressing hydrogen.

To store hydrogen as a liquid, the energy required to cool hydrogen to the liquid state is critical. Theoretical heat to cool hydrogen from 25 ^oC to 20 ^oK and condense it to liquid is about 3.4 MJ/kg (2.94 sensible and 0.45 condensation). But the actual required energy is much higher due to the inefficiency of refrigeration at the extremely low temperature. The minimum required energy may be calculated using an ideal refrigeration cycle, the reversed Carnot cycle[3]. The efficiency of this cycle depends on the temperatures at which heat is added and rejected, and is equal to T1/(T2-T1), where T1=evaporator temperature=20 ^oK, T2=condensing temperature=298 ^oK. Therefore the efficiency in our case is 20/(298-20)=7.2%. To generate 3.4 MJ to liquefy one kg of hydrogen will require 47 MJ (3.4/0.072=47). This is 39.2% of the LHV. The actual required energy can be significantly more because the refrigeration cycle will be less than ideal. Heat will also be required to evaporate the liquid and warm up the gas before feeding it to the energy conversion device such as a fuel cell. This may require an additional of 3.4 MJ/kg. This makes the total required energy to store hydrogen as a liquid to be 50.4 MJ/kg. This is 42% of the low heat value of hydrogen. Liquid hydrogen storage is as energy intensive as the compressed hydrogen.

Using metal hydride to store hydrogen requires an absorption step and a desorption step. A typical absorption step requires a supply of 20-atm hydrogen and the removal of about 7 kcal/mol (14.6 MJ/kg) heat of absorption. It has been shown in Figure 1 that energy needed to compress hydrogen to 20 atm is about 12 MJ/kg (10% of LHV). The heat of absorption is removed by coolant at temperatures of about 10 ^oC. At this temperature the coefficient of performance of a cooling system is about five[4]. The energy required for the cooling will be

14.6/5=3 MJ/kg that is 3/120=2.5% of the LHV. Similar amount of heat would be needed to desorb the hydrogen, but this can be provided by the waste heat of the energy conversion device (fuel cell or internal combustion engine) and is practically free. The total energy required to operate a metal hydride storage system is therefore about 15 MJ/kg, or about 12.5% of LHV. This is the lowest operating energy compared to those of compressed hydrogen and liquid hydrogen. Therefore, metal hydride for hydrogen storage has the advantage of low operating energy, moderate pressure and temperature, and high volumetric density.

3. THE DESIGN AND OPERATION OF METAL HYDRIDE STORAGE SYSTEMS

A large group of metal alloys can react with hydrogen reversibly to form metal hydrides[5]. But only a few of them are suitable for hydrogen storage. The alloy must react and release hydrogen readily at moderate pressure and temperature, and must be stable to maintain its reactivity and capacity over thousands of cycles. This special group includes materials from the AB_5, AB_2 and AB types, where A and B are metal elements. Examples are $LaNi_{5-x}Al_x$, $TiV_{2-x}Mn_x$ and $FeTi_{1-x}Mn_x$, where x is a variable for adjusting the equilibrium pressure and stability of the material. Low levels of other elements are often added to improve the overall performance. Metal hydride vessels for hydrogen storage are more like heat exchanges. They must have thermal jackets or conduits for heat transfer medium to cool and heat the material. During discharge waste heat from the fuel cell coolant or engine is used to supply the heat. The heat desorbs the hydrogen and generates a pressure to feed the fuel cell. During refueling the bed is connected to a supply of hydrogen gas and is cooled by the same or external coolant. High pressure and quick cooling are needed for fast absorption and quick refueling.

For practical and economical reasons, the moderate pressure mentioned above usually mean a hydrogen supply pressure of less than about 400 psia (27 atm), and a discharge pressure of higher than about 30 psia (2 atm). Moderate temperature means no colder than about 10 ^{o}C for absorption and no hotter than about 100 ^{o}C for desorption. Going outside this range of pressure and temperature would mean increased requirement of energy and supporting equipment, and is highly undesirable.

4. ENGINEERING ISSUES OF METAL HYDRIDE STORAGE VESSELS

<u>Fines confinement</u>

Metal hydrides break up to fine powders with sizes in the micron range (Figure 2). The fine particles if not confined can migrate and interfere with the operation of moving parts such as valves. Filters with proper pore size and area must be used to prevent the migration of the fines but minimize resistance to gas flow.

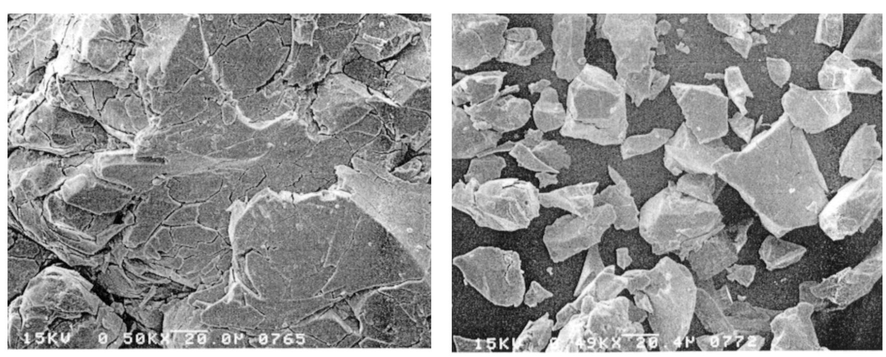

Figure 2. Metal hydride ($LaNi_{4.25}Al_{0.75}$) broke up to fine powder after repeated hydrogen absorption and desorption, 1 cycle (left) and 10 cycles (right).

Expansion and contraction

Metal hydride expands when absorbing hydrogen and contracts after releasing the hydrogen. This expansion and contraction must not be overly restricted. If the bulk of the metal hydride powder is unable to expand due to restriction or lack of space, stress will build up on the container wall and could eventually deform or damage the container. Tests conducted with La-Ni-Al hydride in a 3-inch diameter, horizontal container showed that the wall stress increased dramatically when free space is less than 15%[6]. See Figure 3. It is utmost important that the metal hydride powder can expand and contract in the container without causing damage.

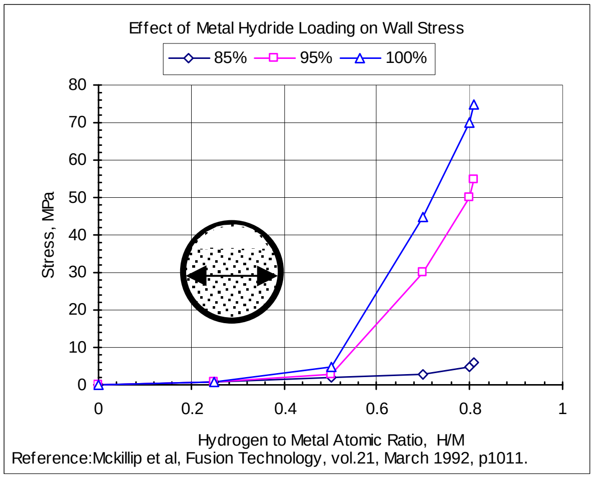

Figure 3. Effect of metal hydride loading on container wall stress.

Hydrogen density

How to increase the stored hydrogen density is the most critical issue. Density must be considered both in weight and volume. A high weight fraction of hydrogen will do no good if the weight per volume is small. One most obvious example is hydrogen gas. It is 100% hydrogen but its weight per volume is uselessly small at ambient conditions. To put metal hydrides in perspective with other hydrogen containing materials, the hydrogen content in several common metal hydrides are shown in Figure 4, together with that of methane, propane, methanol, gasoline, gas and liquid hydrogen. Note that bulk density, which is about half of theoretical density for a solid is used to calculate the volumetric density of hydrogen. The reason is obvious. One can in practice fill a tank to the bulk density of the material not to the theoretical density of the material. This figure brings out two very significant points. First, the present practical metal hydrides contain about 0.06 g/cc of hydrogen compared with 0.07 for liquid hydrogen and about 0.1 for the liquid hydrogen carbon fuels that include gasoline, methanol and ethanol. Second, the light solids such as magnesium hydride and the sodium aluminum hydride increase the hydrogen weight ratio significantly but not the volumetric density. The volumetric density of sodium aluminum hydride is actually decreased. This information implies an important point: the bulk volumetric density of hydrogen storage is not likely to be more than 0.07 g/cc, certainly not 0.1 g/cc.

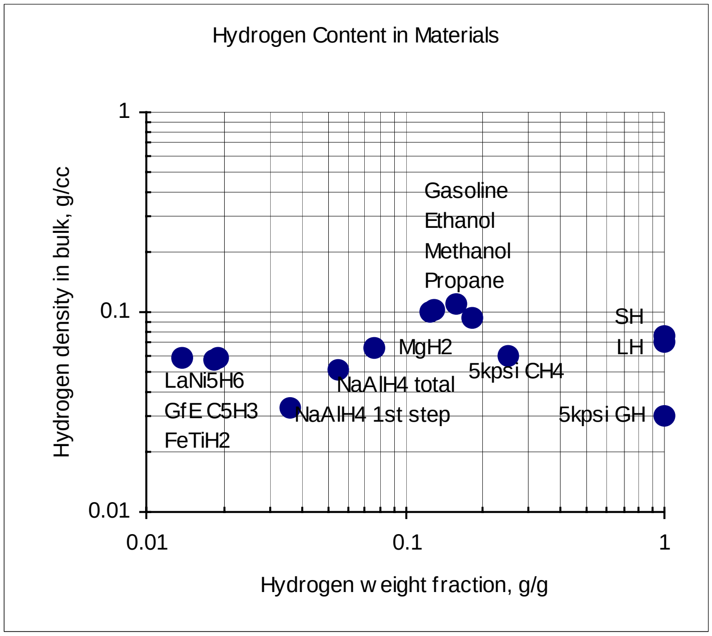

Figure 4. Hydrogen density in materials.

Heat transfer and refueling rate

Using metal hydride to store hydrogen is a heat driven process. Heat needs to be removed during refueling and supplied during discharging. Heat transfer during refueling is more demanding than discharging, because refueling time needs to be short while discharging time extends several hours. Heat transfer aspects of a hydride container must be considered carefully. According to the general heat transfer equation:

$$Q = q\,t = U\,A\,\Delta T\,t \quad \text{or} \quad t = Q / (U\,A\,\Delta T)$$

Where Q is total heat required to remove, q is heat/time, t is time, U is the overall heat transfer coefficient, A is heat transfer area and ΔT is the temperature difference between metal hydride and coolant. To decrease the time t, U, A and ΔT must be increased. High coolant circulation increases U, and low coolant temperature increases ΔT. High hydrogen pressure increases the equilibrium temperature and therefore increases ΔT. The heat transfer area A is increased by decreasing container diameter and by adding fins or metal foams. For a given design, the supply pressure of hydrogen and the coolant rate control the refueling time. Figure 5 presents the refueling time of a 3.5" diameter metal hydride container under different coolant rates and hydrogen supply pressures. The data indicate that for 90% full, the time increased from 27 minutes to 38 and to 90 minutes as the coolant rate decreased from 17 liter/min to 3 and 1 liter/min. At 17 liter/min coolant rate the time for 80% full increased from 18 minutes to 27 minutes when the hydrogen pressure decreased from 400 psig to 200 psig. High pressure and efficient cooling are essential for a short refueling time.

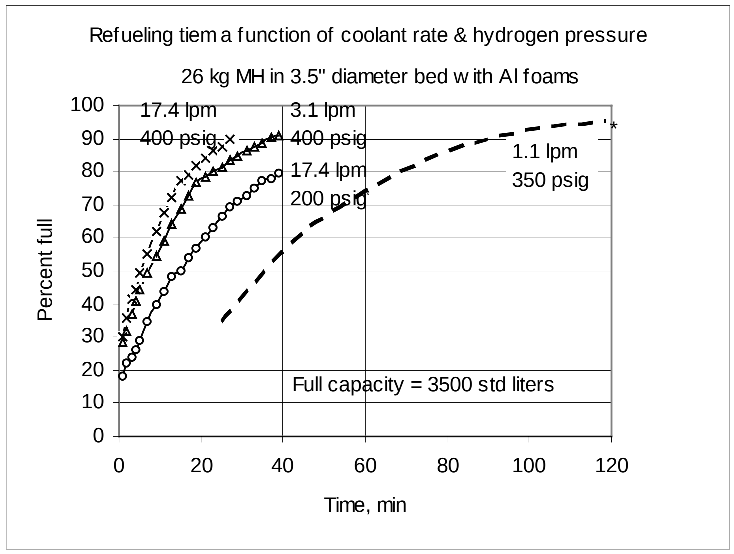

Figure 5. Refueling time of a metal hydride storage bed.

5. STORAGE SYSTEM DEMONSTRATED ONBOARD VEHICLES

With the above engineering issues in mind, a patented design for metal hydride hydrogen storage was developed. The basic feature of this design is a horizontal vessel divided into compartments by metal plates, filled with metal foams and fitted with a porous metal filter and a U-shape coolant tube. The foam material occupies about 6% of the space, leaving about 94% space open. Metal hydride powders occupy about 80% of the open space saving 20% for expansion. The

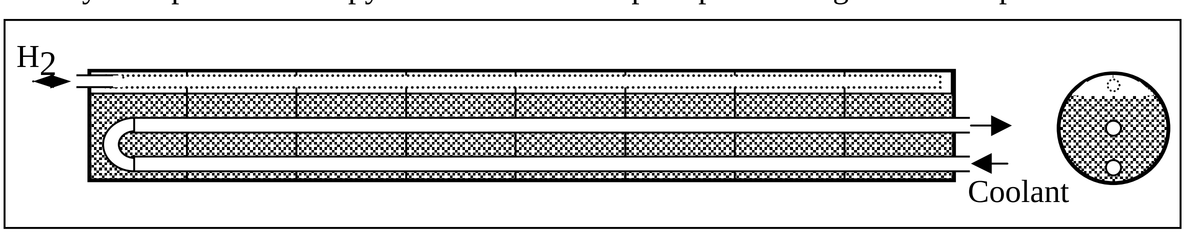

Figure 6. The design of a patented metal hydride hydrogen storage vessel.

arrangement of these components is shown in Figure 6. The length, diameter and the number of vessels are variables that are chosen to suit a particular application.

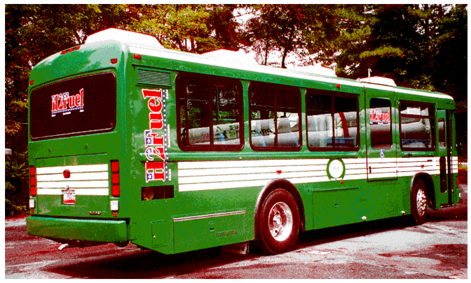

Figure 7. The hydrogen powered bus.

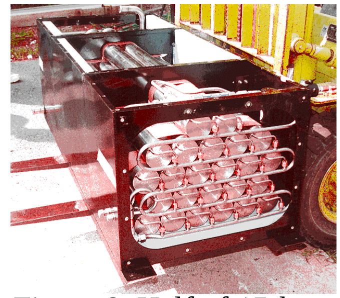

Figure 8. Half of 15-kg storage bed.

A 15-kg hydrogen capacity storage system using this design was demonstrated onboard a 33-ft long, 27-passenger city transit bus in 1998[7]. See Figure 7. The power train was hybrid consisting of a 70-kW internal combustion engine-generator, a 60-kW battery set and a 170-kW AC motor. This hybrid arrangement permitted a small IC engine to support a much higher power AC motor. The result was that energy efficiency was twice that of a diesel engine powered bus. This 15-kg capacity storage system consisted of 48 5-ft long 3.5-inch diameter vessels. Each vessel contained 26 kg of $LmNi_{4.96}Al_{0.04}$, where Lm stands for lanthanum rich mischmetal. The vessels were assembled into two stacks inside two aluminum boxes (Figure 8). The boxes were mounted on the chassis under the floor. Engine coolant at 70 ^{o}C provided the heat to discharge the hydrogen. Each box had no problem to supply hydrogen at a required maximum rate of 6 kg/hr. During refueling either tap water or chilled water was used to cool the vessels. Using 20 atm hydrogen pressure refueling needed 2 hours. This hydrogen storage system performed as expected and met all demonstration requirements.

A second storage system was demonstrated onboard a modified commercial John Deere Gator™ utility vehicle[8]. The original gasoline engine power train of the vehicle was replaced by a hydrogen fuel cell electric motor system. The new power system consisted of the fuel cell stack, the hydrogen storage system, the coolant loop, the water loop and the air loop. The arrangement of these components is shown in Figure 9. The hydrogen storage system used the same vessel design as that of the bus, except that the length was reduced from 5 ft to 3.5 ft to fit the space on the vehicle. Two bundles of 7 vessels were mounted on the sides of the vehicle as shown in Figure 10. Two metal hydrides, $Lm_{1.06}Ni_{4.96}Al_{0.04}$ and $Fe_{0.9}Mn_{0.1}Ti$, were

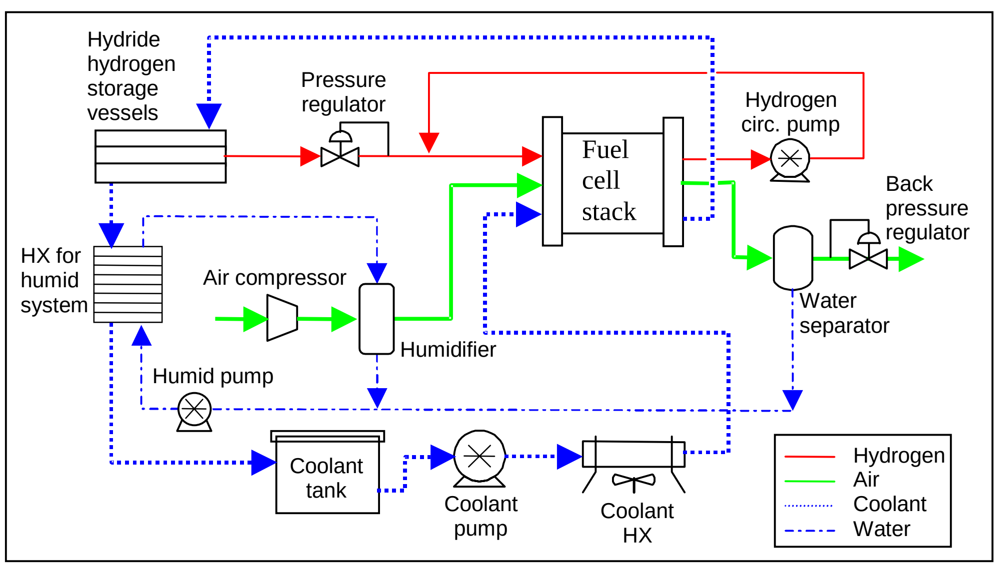

Figure 9. Hydrogen fuel cell power system for Gator™ utility vehicle.

tested. Both materials worked well. But the second material reduced the cost from about \$3/g to \$1/g hydrogen stored. During operation, the coolant of the fuel cell stack heats the metal hydride system to generate a discharge pressure between 2 and 20 atm. A drive test of 50 hours traveled 340 km. At an average speed of 11.5 km/hr, each refuel lasted about 7 hours covering a range of 80 km. The fuel to wheel efficiency was 25% versus 16% for an equivalent vehicle powered by a gasoline internal combustion engine. Key specifications of the power system and vehicle are given in Table 2. The demonstration was a success, but cost reduction is still a key issue before a vehicle of this type can be commercialized.

Figure 10. Picture of the Gator™ hydrogen fuel cell vehicle.

Table 2. Specifications of Hydrogen Fuel Cell Gator™ Utility Vehicle

Vehicle chassis mfr./type	Deere & Co. / Gator™ Utility Vehicle
Fuel cell type	NG2000™ 60 cells
Fuel cell operating pressure	150 kPa (122 to 308 kPa)
Fuel cell operation temperature	60 ^{o}C
Hydrogen / air flow rates	1.5x / 2.5x stoichiometric
Fuel cell power @ 163 kPa	8.3 kW at 38 V
Hydride material	$Fe_{0.9}Mn_{0.1}Ti$
Storage system weight	244 kg
Hydrogen storage capacity	2 kg
Hydrogen discharge temp./ pressure @ 50% loading	50 ^{o}C / 756 kPa
Refueling pressure / time	2170 kPa / 60 minutes
Vehicle weight	~ 900 kg
Operating range	7 hours, or 80 km @ 11.5 km/hr avg.
Maximum cruising speed	19 km/hr

6. SUMMARY

Hydrogen storage is a key issue on the road to a hydrogen economy. Present methods that include compressed gas, cryogenic liquid and solid metal hydrides do not appear practical though feasible. In the interim metal hydrides have advantages in the requirements of operating temperature, pressure and energy. They are heavy but weight should not be an issue for stationary and some other niche applications. Once their weight is reduced by the discovery of new materials, their use in mobile application will be practical. Development effort at Savannah River Technology Center has demonstrated a patented design that solved critical engineering issues associated with using metal hydride to store hydrogen. This design is applicable to both stationary and mobile applications.

REFERENCES:

1. R. S. Irani, "Hydrogen Storage: High-Pressure Gas Containment", MRS Bulletin, September 2002, p680.
2. Unit operation of Chemical Engineering, McCabe, Smith and Hrriott, 4th ed, 1985, p188.

3. Perry's Chemical Engineer's Handbook, 6th edition, p12-24, 1984.
4. Encyclopedia of Chemical Technology, 3rd ed.
5. G. Sandrock and G. Thomas, IEA/DOE/SNL Hydride Database, http://hydpark.ca.sandia.gov.
6. S. T. McKillip, C. E. Bannister, and E. A. Clark, "Stress analysis of hydride bed vessels used for tritium storage", Fusion Technology, vol. 21, Marcy 1992, p1101.
7. L. K. Heung, "On-board hydrogen storage system using metal hydride", in T. O. Saetre (editor), Hydrogen Power: Theoretical and Engineering Solutions, 251-256, 1998.
8. L. K. Heung, T. Motyka, W. A. Summers, "Hydrogen Storage Development for Utility Vehicles", Proceedings of HYPOTHESIS IV, 9-14 September 2001, 336-340, Stralsund, Germany.