

312
/DESIGN AND TESTING OF A MODULAR HYDRIDE HYDROGEN

STORAGE SYSTEM FOR MOBILE VEHICLES/

by

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INTRODUCTION

Hydrogen is becoming a more popular candidate as a fuel for internal combustion engines. It is desirable as a fuel in heavily polluted areas since the major product of its combustion is water vapor. Recent discoveries of high purity hydrogen fields have sparked much interest for developing potential uses for this promising fuel. Also as atomic power becomes more prominent, hydrogen gas could be manufactured cheaply by many power plants using off-peak power.

The stationary storage of hydrogen is well developed in industry today. Stationary storage of hydrogen is usually accomplished by high pressure vessels which require a great deal of volume and mass to store a relatively small amount of hydrogen. Liquid storage is also common for stationary storage of hydrogen since the cryogenic losses may be mostly recaptured in a refrigeration cycle. However, mobile storage of hydrogen as a liquid or gas does not show much promise. The high container mass and volume of gaseous hydrogen storage makes it infeasible for mobile transport. The cryogenic losses associated with liquid storage would also be undesirable for use in a mobile vehicle on an intermittent basis. The storage of hydrogen in the form of metal hydrides does show much promise for stationary as well as mobile hydrogen storage. The volumetric density of hydrogen storage as a metal hydride is significantly greater than hydrogen stored as a liquid. Hydrides can release hydrogen as a gas at convenient pressures and temperatures so that it may readily be burned by slightly-modified conventional internal combustion engines. The use of metal hydrides as a hydrogen storage medium is the basis for this investigation.

REVIEW OF LITERATURE

CHARACTERISTICS OF HYDROGEN AND ITS STORAGE

Hydrogen as an Energy Source

Hydrogen shows promise as a fuel since it has the highest density of energy per unit mass of any chemical fuel. It is essentially non-polluting with water being the main product of its combustion. The versatility of hydrogen allows it to be used in many energy converters ranging from fuel cells to internal combustion engines. Hydrogen is presently more expensive (per joule) than other forms of energy, however there are possibilities that hydrogen could become economically competitive with the major fuel sources in the future. The most promising method of producing hydrogen at a competitive cost involves a chemical process already used in making liquid synfuels. A first standard step in making liquid synfuels, as shown by Pruett (1981), is reacting coal with steam to make synthesis gas, which is a mixture of hydrogen and carbon monoxide. The hydrogen then could be used directly as a fuel rather than converting it to a liquid, if appropriate storage and distribution arrangements were made. Energetically, this would be a more efficient process than making liquid synfuels, which require additional energy-consuming chemical steps. In the more distant future, when fossil fuels are no longer economical, hydrogen could be separated from water through the process of electrolysis. Electrolysis procedures may be driven by nuclear, solar, or other forms of energy during off-peak hours of electricity demand. This would increase the effectiveness of the electric power utilities by allowing them to produce a higher percent of peak power almost all the time.

Methods of Storing Hydrogen

The present methods of storing hydrogen are suitable and safe for the current industrial uses of hydrogen, but they would not be sufficient for moving vehicles or for special applications where fuel storage space is limited. Table 1 contains a comparison of the three hydrogen storage methods for use in an automobile or a comparable moving vehicle. The comparison is based on the energy equivalent of 54 kg of gasoline (about 76 liters of gasoline or 21 kg of hydrogen).

Table 1. COMPARISON OF HYDROGEN STORAGE SYSTEMS

Storage System	Fuel and Container Weight, kg	Volume m^3	Advantages	Disadvantages
Gas at 136 atm	1021	1.87	Proven Technology	Low Storage Density
Liquid at 20 deg K	160	0.29	High Storage Density	Not Energy Efficient, Safety Problems
Magnesium Hydride (40% voids)	314	0.31	High Storage Density at Room Temperature	High Temperature Required to Dissociate

From Cummings and Powers (1974)

The compressed gas method of storage is extremely heavy and bulky. For example, a storage vessel containing 21 kg of hydrogen at 136 atmospheres would weigh 1021 kg and occupy 1.87 cubic meters. First-order scaling laws from Cohen and Wernick (1981) show that the container mass required to store a certain hydrogen mass is essentially independent of the pressure and container volume. Therefore, little improvement is achieved by deviating from the standard 136 atmosphere storage tanks commonly used. Furthermore, accidental rupture of the container is always a concern because of the wide range over which hydrogen-air mixtures are explosive.

Hydrogen storage as a liquid presents an improvement in weight and volume over the compressed gas method of storage, however the difficulty with this concept is the heat transfer into the storage vessel due to its low temperature storage requirement. Hydrogen is a saturated liquid at one atmosphere at 20.4 degrees Kelvin. Very efficient insulated containers are available but the heat loss rate is still significant. Hydrogen losses on the order of five percent per day are common with state-of-the-art cryogenic low-volume storage systems. This heat flow leak makes it necessary to vaporize a small amount of liquid hydrogen from the vessel and thus creates potential safety problems. Furthermore, it does not appear economically feasible to recover the hydrogen boil-off in a refrigeration cycle for off-road vehicles or automobiles as stated by Cummings and Powers (1974). Consequently, the hydrogen loss caused by the heat leak would drastically reduce the overall efficiency of a vehicle used on an intermittent basis. -

The initial liquefaction of hydrogen is also costly in terms of energy, using substantially more than 30 percent of the energy content of the gas as given by Cohen and Wernick (1981). This cost is not normally retrievable on reconversion to gas. Inadvertent exposure of liquid hydrogen to air results in violent boiling of the liquid as it condenses nitrogen and oxygen out of the air. When liquid hydrogen is released to the environment at standard conditions, it rapidly evaporates expanding its volume approximately 850 times. This hydrogen gas, when mixed with sufficient air to yield the four percent lower flammability limit, forms a combustible hydrogen-air mixture with a volume 21,000 times the volume of the original liquid. This indicates the potentially destructive capability of a small liquid hydrogen spill.

The concept of storing and supplying hydrogen by means of a reversible chemical reaction has been under study for several years. One useful reaction is the formation of metal hydrides. The storage of hydrogen as metal hydrides is attractive due to their ability to store hydrogen compactly and safely at ambient temperatures. For example, the storage of hydrogen as iron titanium hydride achieves a volumetric storage density 1.2 times that possible for liquid storage. Although the density of hydrogen by volume in a hydride is high, the density by weight is less satisfactory when compared with pure liquid hydrogen because of the weight of the associated metal. It is only the high energy density per unit weight of hydrogen as a fuel (approximately three times the energy density of gasoline on mass basis) that makes metal hydrides feasible as an energy storage medium.

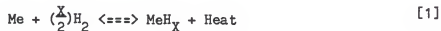
Although not presented in Table 1, the comparison of hydrogen storage systems, a fourth possible means of storing hydrogen is the use of zeolite molecular sieves. The phenomenon of trapping gas molecules in zeolite molecular sieves has been known since 1961 in work with argon and helium gases. The process of trapping or encapsulation relates to cases in which the critical dimensions of the gas molecule (guest) are slightly larger than the effective pore opening of the zeolite (host). Hydrogen is trapped in the zeolite pore structure by heating usually to 200 to 300 degrees C and introducing the gas under extreme pressure. Subsequent quenching of the zeolite to ambient temperature under pressure results in trapping of the gas inside the zeolite pores. Release of the encapsulated molecules can then be achieved by heating the loaded zeolite or by treatment with water which being more strongly sorbed could in some cases displace the guest molecule as stated by Fraenkel, et al (1978). They also found that the main disadvantage of zeolite encapsulates is

the need of very high pressures in order to attain substantial hydrogen storage levels. At the higher pressures, 1000 to 2000 atm, hydrogen capacities of only 1.0 to 1.5 percent by weight can be achieved as compared to 1.75 percent by weight of HYSTOR 102 iron titanium metal hydride alloy. In contrast with the metal hydride formation/decomposition cycle, the molecular sieve encapsulation/decapsulation cycle is not a chemical but a physical process and the two should not be confused.

CHEMICAL AND PHYSICAL PROPERTIES OF HYDRIDES

Basic Chemical Reaction

Most elemental metals will react with hydrogen to form metal hydrides. In the simplest form this reaction involves the formation of hydrogen-metal bonds through the reaction of the elemental metal with hydrogen gas. In many cases the reaction is simple and direct, consisting merely of bringing gaseous hydrogen (H_2) in contact with the metal (Me). The number of hydrogen atoms which may react with a single metal molecule, designated by X in the equation below, may range from zero to seven, depending on the metal's characteristics and the degree of hydrogen association. For example, a single molecule of lanthanum-pentanickel ($LaNi_5$) may associate with seven hydrogen atoms (7H) to obtain the fully hydrided state, lanthanum-pentanickel hydride ($LaNi_5H_7$).



The arrows point in two directions, which means that the reaction is reversible. The reverse reaction can be accomplished by thermal decomposition of the hydride to yield the metal and pure hydrogen. A fundamental property of

metal hydrides is their heat of formation, the heat given off when the hydride is formed by the reaction of hydrogen with the metal. In order to decompose the hydride back into its original elements, metal and hydrogen gas, the same amount of heat must be added to the system. This heat for the reverse reaction is termed the heat of decomposition. This heat can be quite large in some metals and is roughly proportional to the stability of the hydride. The more stable the hydride, the higher the temperature and thus, the more the heat of decomposition will be. The fact that heat is required to release hydrogen gas from the metal hydride is of great practical consequence. It is a primary consideration in the design of systems for storing hydrogen in metal hydrides.

Pressure-Temperature Relationships

As was stated before, the reaction of gaseous hydrogen with a metal hydride is reversible. Its direction is determined by the pressure and temperature of the hydrogen gas. If the pressure is above a certain level, termed the dissociation pressure, the reaction proceeds to the right to form the metal hydride. If the pressure is below that level, the metal hydride decomposes into the metal and hydrogen gas. Therefore at a constant temperature, an increase in the pressure of the hydrogen gas would cause more molecules of hydrogen to react with the metal to form metal hydride. The hydrogen content of the metal hydride can be expressed as the ratio of hydrogen atoms to the total number of metal atoms (H/Me). The dissociation pressure is often plotted against hydrogen content of the hydride to obtain an absorption curve for a particular hydride. An ideal and a typical absorption curve are both shown in Figure 1.

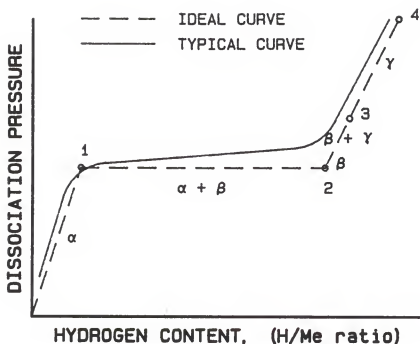


Figure 1. ABSORPTION CURVE FOR HYDRIDES

When gaseous hydrogen is brought into contact with a metal that is capable of forming a hydride, hydrogen molecules (H_2) are absorbed onto the surface of the metal. Some of the molecules dissociate into hydrogen atoms (H), which enter the crystal lattice of the metal and occupy specific sites among the metal atoms. These sites on the metal atoms are called interstitial sites. As the pressure of the gas is increased, a limited number of hydrogen atoms are forced into the crystal. This phase of the hydride requires a great increase of the dissociation pressure to force a relatively small number of hydrogen atoms into the hydride. In this phase, the hydrogen exists as a solid solution of atoms in the metal crystal lattice. This phase is often called the alpha phase of the hydride and is shown as the left portion from the origin to 1 of the absorption curve in Figure 1.

Usually at some critical concentration and pressure, the metal becomes saturated with hydrogen and goes into a new phase called the monohydride phase or beta phase of the hydride. If the hydrogen pressure is now increased slightly, much greater amounts of hydrogen are absorbed. As the hydrogen content of the hydride is further increased, the dissociation pressure remains constant and forms a plateau. This pressure is logically called the plateau pressure for the hydride at the given constant temperature. In this portion of the absorption curve, the metal hydride coexists as a solution of hydrogen atoms with the monohydride phase of the hydride. This is the portion from 1 to 2 on the curve in Figure 1. Although thermodynamic reasoning implies that the plateau pressure should be flat over the coexistence range (alpha + beta), as given by Huston and Sandrock (1980), it actually has a slight slope termed the plateau slope. A quantitative measure of the plateau slope $\left| \frac{d(\ln P_d)}{d(H/Me)} \right|$ should be considered in the design and operation of hydride systems. The amount of slope differs from alloy to alloy and usually arises from chemical segregation during solidification. Annealing treatments prior to crushing and activation of the hydride alloy can reduce the slope as stated by Sandrock (1978). There is a direct and strong dependence of temperature on the plateau pressure. The plateau pressure (P_p) is related to the absolute temperature (T) by the familiar van't Hoff equation as modified by Huston and Sandrock (1980).

$$\ln P_p = \frac{2}{X} \frac{\Delta H}{RT} + C = \frac{A}{T} + C \quad [2]$$

The number X is defined in equation 1, ΔH is the enthalpy change (heat) of the hydriding reaction per mole of hydrogen, R is the universal gas constant, and

C is a constant related to the entropy change of the hydriding reaction. An additional constant, A, is introduced into equation 2 to show the functional dependence on temperature and simplify engineering calculations. Van't Hoff curves for the HY-STOR alloys, a commercial tradename used by Erogenics Division for hydride forming alloys, are shown in Figure A1. A wide range of hydrogen pressures and temperatures are conveniently represented on this one graph. Because most of the isotherms are sloping, a H/Me ratio is indicated on each curve in Figure A1 to specify its source. In addition, only desorption curves were plotted. The enthalpy change (ΔH) and other constants of equation 2 are listed in Table A1 of the appendix for the various HY-STOR alloys. The units selected are such that the plateau pressure is given in atmospheres when the temperature is expressed in degrees Kelvin.

As the hydrogen content of the metal hydride reaches point 2 on the adsorption curve given in Figure 1, the hydride is in the monohydride phase (beta). At this point, a slight increase in hydrogen content requires a great increase in dissociation pressure. This is where the hydride starts to enter the dihydride phase or the gamma phase. Both the monohydride phase and the dihydride phase will coexist (beta + gamma) until point 3 of the curve is reached. From this point, the hydride exists only in the dihydride phase (gamma). Since the dissociation pressure does increase sharply for small gains in H/Me ratio, it is not feasible to store much hydrogen in the dihydride phase. The largest storage of hydrogen as one would expect, is from point 1 to 2 of Figure 1 which is the coexistence of the alpha and beta phases. Notice that the typical behavior does not exactly follow the ideal behavior. This minor difference is credited to hydride phases overlapping one another slightly.

When an absorption-desorption curve for a constant temperature of a specific hydride is plotted, the curves do not follow the same paths. This pressure difference between an absorption and desorption isotherms is referred to as hysteresis of the system. The absorption-desorption curve for iron titanium hydride at a constant temperature of 40 degrees Celsius is represented by Figure 2 as given from Reilly and Sandrock (1980).

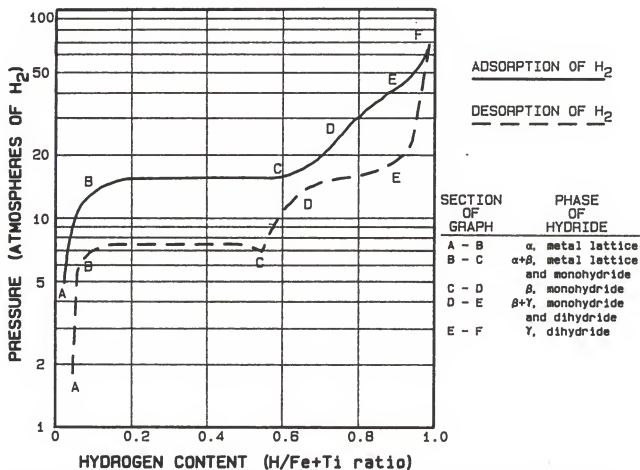


Figure 2. ADSORPTION/DESORPTION CURVES FOR FeTi
(CONSTANT HYDRIDE TEMPERATURE OF 40°C)

The upper curve represents the dissociation pressure measured as hydrogen was added to an alloy of iron and titanium; the lower curve represents the dissociation pressure measured as hydrogen was being removed from the same

system. The amount of hysteresis varies widely from alloy to alloy, and its origin is not fully understood. Hysteresis must be considered during alloy selection especially when different hydride beds are to be coupled in closed cycle operation. The degree of hysteresis can be indicated in two ways: the pressure ratio P_a/P_d , and $\ln(P_a/P_d)$ as given in Table A1. Assuming that hysteresis is largely independent of temperature for a particular alloy, these pressure ratios can be applied directly to the desorption curves in Figure A1 to construct Van't Hoff curves for absorption. The various phases of the iron titanium hydride are also plotted with hysteresis effect on the absorption-desorption curve of Figure 2.

Heat Transfer Characteristics

The thermal conductivity of a metal hydride system has to be considered closely in the design of a hydride storage unit. The thermal conductivity of the hydride and its storage system regulates the heat flow within the storage unit and determines the rate of hydrogen absorption and desorption. The rate of absorption or desorption of a system is often referred to as the kinetic or dynamic response of the storage system. Specific heats of metals and their hydrides are easily determined and typically fall in the range of 0.1-0.2 cal/g deg C as given by Sandrock and Huston (1981). The thermal conductivity is usually more difficult to determine. The thermal conductivity of the metal is usually many times greater than the conductivity of its respective metal hydride. For example, the thermal conductivity of magnesium (Mg) is approximately 124 times the thermal conductivity of the hydride it forms, magnesium hydride (MgH_2), as taken from JANAF Thermochemical Tables (1965) and Ellenger, et al (1955). This difference in conductivity is typical of most hydrides and indicates that the metal hydride would have a specific thermal conductivity

for different hydrogen contents (H/Me ratios). As one would expect, this variable thermal conductivity complicates the problem of expressing heat transfer of the hydride as a mathematical model. The work with the thermal conductivity of hydride beds is very complex and involved. The thermal conductivity of the metal or hydride phase is not sufficient. The effective conductivity of the bed must be calculated and this depends upon the alloy used, particle size, packing, void space, and other factors. Relatively little thermal conductivity data of metals and their hydrides is available. However, some research in the thermal conductivity area has been completed or is in the process of being completed. Some modeling of metal hydride beds has been done by Masamune and Smith (1963), in which they presented a correlation of theoretical and experimental work on the conductivity of beds as spherical particles. Extensive experimental work on bed conductivity of LaNi_5 and FeTi activated hydride was also done by Goodell (1980), and some conductivity work on FeTi hydride by Reily and Wiswall (1974).

The thermal conductivity of the metal hydride bed is not the only factor controlling the rate of absorption or desorption of hydrogen. The total thermal conductivity of the system depends on 1) the thermal conductivity of the hydride or metal powder, 2) the thermal conductivity of the hydrogen gas, 3) the thermal conductivity of the metal in the heat exchanger or storage tank, and 4) the thermal resistance between these various elements of the total system. The thermal conductivity of the hydride or metal powder is greater than the thermal conductivity of the gas by a factor of 2-10, depending on the pressure in the system, and is less than the thermal conductivity of the solid metal by a factor of 100-200. Thus, the thermal conductivity in the storage system must be given proper attention in the technical design stage in order

to ensure good charging and discharging rates. The poor thermal conductivity of the metal hydride may cause problems with systems that need extremely good dynamic response. The thermal conductivity of metal hydrides can be improved in a variety of ways. One such process developed by Daimler-Benz results in the thermal conductivity of the system being increased by as much as a factor of 10 as stated by Toepler, Bernauer, and Buchner (1980). In this process, the metal hydride powder is mixed with five to ten percent (by weight) of an inactive metal powder and is compressed under high pressure. The material is subsequently tempered at 450-500 deg C with continuous hydrogen charging and discharging, thus forming a stable matrix of the inactive metal in which the hydride powder is embedded. Metals suitable for this application include aluminum, magnesium, and copper, or just about any metal with a high thermal conductivity. Since this process of forming a porous metallic-matrix hydride (pmh) can improve the heat transfer characteristics by as much as ten times in some instances, the surface area of the heat exchangers may be decreased to obtain the same kinetics as a system without these metal matrixes. This could ultimately reduce the volume required by the system by reducing the large volume required for the heat exchangers. The heat exchangers of hydride storage systems usually make up a good deal of the volume.

The hydride formation reactions of the various hydrides are all exothermic, but to varying degrees. Thus, it is necessary to remove heat from the hydride storage system during the hydriding process and similarly supply heat to the system during the de-hydriding process. The hydride storage system must provide for this transfer of heat. There are two heat transfer methods, direct and indirect exchange. Direct exchange involves physical contacting of two media exchanging heat and is sometimes termed a convection bed. Indirect

exchange occurs across a boundary impermeable to the exchanging media and is often called a conduction bed.

In a convection bed, the heat of reaction necessary to liberate hydrogen is supplied by circulating hot hydrogen, which is heated externally, through a charged bed. Two advantages of such a system would be that first, heat transfer to the bed would not be limited by poor hydride thermal conductivity as it might be in conduction beds, and second, a much simpler container design would be possible. The main disadvantage of the convection bed model is that it requires that the hydrogen gas be circulated through the hydride and therefore would require a hydrogen pump to be incorporated into the system. A convection bed model is of great interest if a very high dynamic response of the system is required. If this high dynamic response is not necessary, then the conduction bed model may be more practical.

The conduction bed model involves the use of a heat exchanger to transfer the heat to the hydride. The conduction bed has shown greater promise than convection beds in vehicle applications since it requires no auxiliary pumps to transfer heat. The heat is supplied through the exchangers by either the exhaust gases of the engine or by circulating hot radiator coolant heated by the engine. The amount of heat supplied to the hydride storage system must be carefully controlled. If a charged hydride is accidentally heated too much, great pressures may be generated as illustrated by the van't Hoff plot in Figure A1. If these pressures are not controlled by the regulation of heat through the heat exchanger of the system, the extreme hydrogen pressures could easily rupture the hydride container. The main disadvantage of the conduction bed model is that the container design is much more complex than the convection model. In a conduction bed, the heat exchangers must be in direct

contact with the metal hydride. This direct contact may create problems due to the fact that as hydrogen is absorbed by the hydride, the hydride increases in volume. In some hydrides, such as LaNi_5 , the volume increases by about 25 percent during hydriding and contracts an equal amount on de-hydriding as stated by van Vucht, et al (1970). Expansion of the packed bed during hydriding can lead to stresses on the container walls that are many times those from the gaseous hydrogen pressure alone. The expansion property of hydrides complicates the design of hydride storage containers. A complete hydride hydrogen storage system integrated with the vehicle will be discussed later in the complete analysis.

Tolerances to Impurities

The fact that metal hydrides can absorb and desorb hydrogen gas reversibly at convenient pressures and temperatures make them good storage prospects. These metal hydrides may be charged and discharged more than 2000 times if a high purity hydrogen gas is used. If there are even small amounts of impurities, (as little as 32 ppm as found in commercial quality hydrogen gas) the loss of hydrogen storage capacity may be greatly reduced after only a few cycles. Goodell and Sandrock (1979) have done a good deal of research in the area of surface "poisoning" of metal hydrides, especially with LaNi_5 , FeTi , and $\text{Fe}_{.85}\text{Mn}_{.15}\text{Ti}$.

Studies they conducted on these three metal hydrides included the measure of their sensitivity to impurities such as oxygen, carbon monoxide, and water. The effects of room temperature cycling of hydrogen gas containing 300 ppm of an impurity were observed for the three alloys. They found that the oxygen and the water vapor produced very similar effects. FeTi and $\text{Fe}_{.85}\text{Mn}_{.15}\text{Ti}$ show

continuous poisoning in the presence of oxygen and water, but LaNi_5 does not. After an initial partial loss of capacity in oxygen- or water-contaminated hydrogen, LaNi_5 almost completely recovers and then exhibits substantial immunity. In comparison, after only thirty cycles of 300 ppm oxygen or water impure hydrogen gas, FeTi and $\text{Fe}_{.85}\text{Mn}_{.15}\text{Ti}$ lose about half of their initial hydrogen storage capacity. The similar effects that oxygen and water had on the three alloys were attributed to the H_2O molecule splitting on the metal hydride surface, resulting in surface oxidation as was observed in the oxygen contaminated samples.

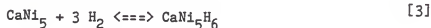
The carbon monoxide was found to be far more detrimental than oxygen or water to all three alloys. $\text{Fe}_{.85}\text{Mn}_{.15}\text{Ti}$ shows at least some resistance to carbon monoxide in comparison to the Mn-free FeTi . After some initial loss of hydrogen storage capacity, $\text{Fe}_{.85}\text{Mn}_{.15}\text{Ti}$ reaches a level where little further damage occurs, whereas FeTi and LaNi_5 soon lose all hydrogen storage capacity in the presence of carbon monoxide.

Another gas which decreases the storage capacity of hydrides is sulfur dioxide. As was illustrated, different compounds have different degrees of tolerance for certain contaminants. If a contaminant is expected in the hydrogen gas, a metal hydride with a fairly high resistance to the impurity should be used. Usually the poisoning damages only the surface of the hydride, and may be reversed by repeating the activation procedure that was followed with the virgin metal.

Chemical Stability

Another problem, which has only recently been discovered, is the chemical breakdown of the hydride. This breakdown is not significant unless

temperatures greater than 100 deg C or hundreds of thousands of absorption-desorption cycles are performed. This chemical breakdown of the original metal is termed disproportionation. Some hydrides are more likely to undergo this chemical breakdown. For example, CaNi_5 is very sensitive if used under high temperatures of 100-250 deg C and the diffusion of the metal atoms becomes significant. The desired reaction for CaNi_5 is:



Under higher temperatures, the irreversible disproportionation reaction is thermodynamically preferred:



LaNi_5 is much more resistant to disproportionation than CaNi_5 , and FeTi appears to be immune to this chemical breakdown as stated by Cohen and Wernick (1981). Therefore, a hydride must be carefully selected if it will be used at high temperatures or under a great number of cycles.

Hydrogen Embrittlement of Steels

Hydrogen embrittlement in high alloy steels is a common and severe problem in handling hydrogen in industry today. A basic difficulty is the fact that high-strength alloys of steel which designers turn to for fabrication of highly stressed parts are those that are most susceptible to hydrogen embrittlement. Alloys not severely effected by hydrogen embrittlement can be selected for environments with extremely high hydrogen content. Thus, for storage vessels of hydrogen such as metal hydride containers, the problems

associated with hydrogen embrittlement may be expected. Proper alloys must hence be used in design of these vessels. Presented in Table 2 is the degree of hydrogen embrittlement of certain classes of metals. These materials may react with hydrogen more severely when used in the fabrication of metal hydride hydrogen storage vessels. The repeated cycling of temperature and pressure as the system is placed under repeated charging/discharging cycles is much more detrimental to a storage vessel than if it were placed under a constant high pressure or temperature. For that reason, the material listed in Table 2 may not perform as well as expected if used as a metal hydride hydrogen storage vessel.

Table 2. RELATIVE DEGREE OF HYDROGEN-ENVIRONMENT EMBRITTLEMENT

Material	Degree of Embrittlement	Characteristics
High strength steels Nickel-base alloys	Extreme	Large decreases in notch strength and notched and unnotched ductility. Some decrease in unnotched strength. Propagation of surface cracks.
Ductile, lower strength steels. Pure nickel Titanium alloys	Severe	Considerable reduction of notch strength and notched and unnotched ductility. No reduction of unnotched strength. Propagation of surface cracks.
Metastable 300 series Stainless steels Beryllium-copper Pure titanium	Slight	Small decrease in notched strength and unnotched ductility. Failure of unnotched specimens from within.
Aluminum alloys Stable austenitic stainless steels. Copper	Negligible	Essentially unembrittled with no surface cracks.

Table from Mathis (1976)

INVESTIGATION

OBJECTIVES

The objectives of the investigation were:

- 1) Design and build a volumetric efficient hydrogen storage module for a tractor using metal hydrides as a storage medium.
- 2) Design and build test facilities capable of adequately evaluating the metal hydride hydrogen storage module.
- 3) Successfully activate and conduct preliminary performance tests on the hydride modular storage system to evaluate possible design problems.

THEORY AND DESIGN

Choice of Hydride

If a material is to serve as a feasible hydrogen storage medium, it must satisfy a number of criteria. The most important criterion is that it should have rapid kinetics for absorbing and desorbing hydrogen. If the dynamic changes of hydrogen consumption of the engine cannot be met by the hydride storage system, the system would be useless for mobile hydrogen storage. Other important criteria that are of lesser importance, but need careful consideration are that the hydrogen storing material must be abundant, inexpensive, and should have a reasonable charging/discharging life. A system that requires frequent replacement or reactivation would not be feasible, considering the current cost of most metal hydrides. The hydrogen storage medium should also be able to store large quantities of hydrogen reversibly at

convenient pressures and temperatures. These temperatures of desorption should be reasonably close to ambient if possible. If the temperatures of hydrogen desorption can not be met at room temperature, the temperature should be easily obtained by use of the waste heat from the engine so that auxiliary heat is not necessary. Another important consideration in designing a hydrogen storage system is that the medium should have a low atomic weight. The low storage medium weight is of great importance in the design of light weight mobile vehicles such as automobiles. The weight factor of a storage medium is of lesser consequence in the design of storage systems for large traction vehicles such as tractors or earth moving equipment. Such implements often require additional weights for ballast. The final major consideration of a hydrogen storage system is that it should be adequately safe. Since hydrogen is extremely explosive when released into air, the concept of a moving hydrogen storage system is potentially hazardous. The hydrogen stored in metal in the hydrided and de-hydrided state should be at least as safe in ordinary service as common fuels such as gasoline and diesel fuel.

It is a challenging problem to meet all of the criteria of hydrogen storage simultaneously. These criteria eliminate all known binary metallic hydrides, consisting of hydrogen and one metal, from consideration due to their extremely high dissociation temperatures. A borderline possibility is magnesium hydride since it has one of the lowest dissociation temperatures of the binary hydrides. The major drawback of magnesium hydride is that the temperature for decomposition at one atmosphere is 289 degrees C which could not easily be drawn from waste engine heat. Although binary hydrides do not seem practical, the formation of a compound metal hydride containing two or more metals and hydrogen has shown much promise. Hydrides containing two metals

combined together are known as ternary hydrides. Almost all the hydrides that are of interest for storing hydrogen are ternary hydrides or higher composition hydrides. Table A2 lists a few additional properties of HY-STOR metal hydrides not included in Table A1, such as percent weight usable capacity of hydrogen, plateau slope, and current hydride costs. These properties along with the properties listed in Table A1 and Figure A1 make the decision of a hydride choice easier.

Most metal hydrides can easily meet the fluctuating rate changes of hydrogen consumption in engines so long as the hydride temperature is maintained above its dissociation temperature. The storage system heat transfer limitations are almost always the rate controlling factor of the kinetics in the metal hydride system. Therefore, it would be advantageous to select a hydride with good heat transfer properties. As it turns out, the heat transfer properties of hydrides do not vary significantly. To obtain the needed rapid kinetics of the system, a hydride that does not require a great deal of externally supplied heat would be preferred. In addition, a constant hydrogen gas pressure in the system of at least one atmosphere would be desirable so that a pressure boost to the engine would not be required. Therefore, to allow initial engine start-up, the dissociation pressure should be at least one atmosphere at ambient temperature. If an ambient temperature of 25 degrees C is assumed, any hydride to the right of LaNi_5H_3 in Figure A1 would satisfy the one atmosphere dissociation pressure. If start-up in colder climates is required, a hydride towards the upper right corner of Figure A1 would be preferred. The seven alloys that meet the required one atmosphere dissociation pressure at 25 degrees C are HY-STOR 101, 102, 203, 204, 205, 208, and 209.

Since tractors are often refueled in remote areas, it would be desirable for the metal hydride storage system to absorb hydrogen gas from a refueling tank at a pressure under 10 atmospheres (147 psi). This would allow a lighter weight refueling tank to be used, thus reducing the investment. Of the seven alloys listed above, only four would fall below an adsorption pressure of 10 atmospheres at 25 degrees C. The other alloys would require cooling of the hydride storage system for the adsorption pressure to be reduced. This cooling could be accomplished by use of a refrigeration unit either on the tractor or on the refueling tank, but this would require an additional undesirable energy input. The four alloys which fall under the 10 atm association pressure and above the one atmospheres dissociation pressure criteria at 25 degrees C are HY-STOR 101, 102, 205, and 208, as can be seen from Table A1. These four alloys have the most practical adsorption and desorption pressures at an ambient temperature of 25 degrees C.

A major design parameter of metal hydrides is their maximum hydrogen storage density that they may acquire. The size and cost of the hydride system depends in part upon the storage density of the alloy selected. Reversible hydrogen capacities (useable capacity) of the HY-STOR alloys are given in Table A2. These values are for a pressure change of $10P_d$ to $0.1P_d$ (where P_d is dissociation pressure) at 25 degrees C. The useable capacity will vary somewhat depending upon the desired pressure range, making comparisons between alloys difficult. However, since the pressure ranges for the four alloys listed above are approximately the same, Table A2 will give a good estimate of the alloy's hydrogen capacity. From the table, it can be seen that HY-STOR 101 and 102 have significantly more hydrogen capacity than HY-STOR 205 or 208. Also shown in Table A2 is the current price listing for the various HY-STOR

alloys. Notice that HY-STOR 205 costs more than twice that of HY-STOR 101, 102, or 208, which all cost about 28.50 \$/kg. Also, since HY-STOR 208 has a hydrogen capacity of 1.2 percent (by weight) and HY-STOR 101 and 102 have capacities of 1.75 and 1.79 percent respectively, HY-STOR 101 and 102 would have a hydrogen storage costs of about 1600 \$/kg of hydrogen and HY-STOR 208 a cost of 2350 \$/kg of hydrogen. Therefore, HY-STOR 101 and 102 provide a cheaper storage cost than HY-STOR 208.

As was mentioned earlier, the weight of a hydride storage system is not as important as the volume of the system when it comes to large traction equipment such as tractors. Even though HY-STOR 101 and 102 have the greatest storage density on a weight basis, it does not necessarily follow that they would be the most volume efficient hydrides. Shown in Table 3 on the following page is the hydrogen density of various storage mediums on a weight basis and a volume basis, including liquid and gaseous hydrogen.

Table 3 shows that even though Mg_2Ni (HY-STOR 301) has a higher energy density (hydrogen capacity) per unit weight, FeTi (HY-STOR 101) has a higher energy density per unit volume. The only hydride listed in Table 3 with a higher energy density on a volume basis than HY-STOR 101 is magnesium hydride. As was stated earlier, magnesium hydride is not a preferred hydride because of its high dissociation temperature (298 degrees C) at one atmosphere. HY-STOR 101 or 102 seem to be the most practical hydride for hydrogen storage in a tractor. HY-STOR 102 is the preferred alloy over HY-STOR 101 for two reasons. First, HY-STOR 102 is much easier to activate than HY-STOR 101. The activation of HY-STOR 101 requires that it be heated to 300 degrees, evacuated for a period of time and then slowly cooled. After it has been cooled, hydrogen gas can then be added over a fairly long period of time, sometimes up to three to

Table 3. HYDROGEN DENSITY OF VARIOUS STORAGE MEDIUMS

HY-STOR Equivalent	Storage Medium	Hydrogen Storage Capacity		Energy Density	
		By Weight (percent)	By Volume (gm/ml)	By Weight (cal/gm)	By Volume (cal/ml)
	Magnesium Hydride (MgH_2)	7.0	.101	2373	3423
HY-STOR 301	Magnesium-Nickel Hydride (Mg_2NiH_4)	3.16	.081	1071	2745
	Vanadium Hydride (VH_2)	2.07	.095	701	3227
HY-STOR 101	Iron-Titanium Hydride ($FeTiH_{1.95}$)	1.75	.096	593	3254
HY-STOR 205	Lanthanum-Pentanicel Hydride ($LaNi_5H_7$)	1.37	.089	464	3017
	Liquid Hydrogen (H_2)	100.0	.07	33900	2373
	Gaseous Hydrogen (H_2)	100.0	.008	33900	271

Figures taken from Rilly and Sandrock (1980)

four weeks. HY-STOR 102, on the other hand can be activated at room temperature and requires only about eight to ten hours of hydrogen gas addition to become fully activated. The second and more important reason that HY-STOR 102 is preferred over HY-STOR 101 is HY-STOR 102 contains small amounts of manganese, which gives it a much greater resistance to carbon monoxide poisoning due to hydrogen impurity. Possible carbon monoxide poisoning of HY-STOR 101 would greatly reduce its hydrogen storage capacity, as compared to similarly contaminated HY-STOR 102.

Packing of Hydride in Vessel

A critical factor in the design of an efficient metal hydride based hydrogen storage system is the manner in which the hydride is contained within

the storage vessel. Since the main reason for using metal hydrides over compressed gas is to decrease the storage volume needed, a volume efficient metal hydride system needs careful consideration. Also, it is essential to take into account that as hydrogen gas is absorbed into a hydride, the hydride must expand to accommodate this gas absorption. Therefore, a metal hydride storage system must maximize its volumetric efficiency and yet allow for the expansion which will take place.

The two means by which the heat necessary for hydrogen dissociation may be supplied to the system are by convection (heat transferred to hydrogen gas and the gas used to heat the hydride) and conduction (heat transferred by direct contact between exchangers and hydride). The conduction bed model will be used in this design for reasons stated in an earlier section. Since the conduction bed model requires direct contact between the heat exchangers and the hydride, the hydride expansion during hydrogen adsorption creates some special problems. Either the heat exchanger must be allowed to deflect with the hydride, or the hydride must expand around a stationary heat exchanger. The first means of allowing the heat exchanger to deflect with the hydride is most common when a porous metallic-matrix hydride (pmh) is used. As stated earlier, a pmh is a stable matrix of an inactive metal in which the hydride powder is embedded. It is a solid which cannot flow around heat exchangers, so the heat exchangers must expand or contract with the pmh.

A fine hydride powder not contained within a pmh can flow around heat exchangers. Most conduction bed models that have been used for mobile hydrogen storage have been a finely ground hydride powder instead of a pmh. Therefore, most designs have required the powder to flow around the heat exchangers and any other obstacles in the hydride, such as hydrogen collection and

distribution tubes. Problems have been encountered in many reaction bed designs due to stresses that arise when the hydride powder does not flow around obstacles (heat exchangers, hydrogen tubes). After a number of charging-discharging cycles have been performed, the repeated swelling and shrinking of the powder as it absorbs and desorbs hydrogen leads to packing under the action of gravity and the volumetric expansion.

There are a number of ways in which the expansion problem encountered in conduction beds may be reduced or eliminated. To completely avoid the expansion problem, Sandrock and Huston (1981) have developed an encapsulation scheme of packing a metal hydride in a container. The expansion is accommodated by the loosely packed individual capsules, preventing any stress on the main container walls. Each capsule is a thin-walled aluminum tube containing the hydride and capped on one or both ends with a porous metal filter. Such a design also eliminates the long-distance gas impedance problem of a packed bed. The major drawback to this method of approaching the expansion problem is that the aluminum encapsulated hydride would cost a great deal more than the already expensive metal hydride.

As the hydride powder settles toward the bottom of a container, it is increasingly compacted. Eventually, the swelling during adsorption of hydrogen begins to stress the container excessively. This can lead to rupture of the container after extensive cycling. A possible solution is to use horizontal tanks which have a small diameter or contain small subcompartments so that the volume increases can be relieved by vertical expansion. This is the basis for our design of a hydride system for a tractor. Figure 3 on page 29 illustrates how the metal hydride is to be packed into the system. Seven subcompartments, each encircling a heat exchanger, will be filled approximately 80

percent full so as to have room for hydride expansion. Each subcompartment shell is constructed of a stainless steel porous metal filter. The metal filter, supplied by Mott Metallurgical Corporation, has a length of 89.5 cm, diameter of 12.7 cm, wall thickness of 1.194 mm, and a pore size rating of 0.5 micron grade. Hydrogen gas can then pass through the porous stainless steel filter to react with the metal hydride. This design makes an efficient use of space, allow for easy expansion of the hydride, and provide for a maximum heat transfer distance or hydrogen flow distance of 44 mm or less. If the diameter of the subcompartments was decreased, an unreasonable number of heat exchangers would be needed to transfer heat to the system. If the diameter of the subcompartments was increased, the hydrogen gas would have higher hydride impedance and the heat would have to flow a greater distance through the hydride. The proposed design is a compromise which allows the heat or hydrogen to flow through the hydride a reasonable distance. Figure 8 on page 50 presents a photograph of the 0.5 micron grade porous stainless steel filter.

CROSS SECTIONAL VIEW OF VESSEL

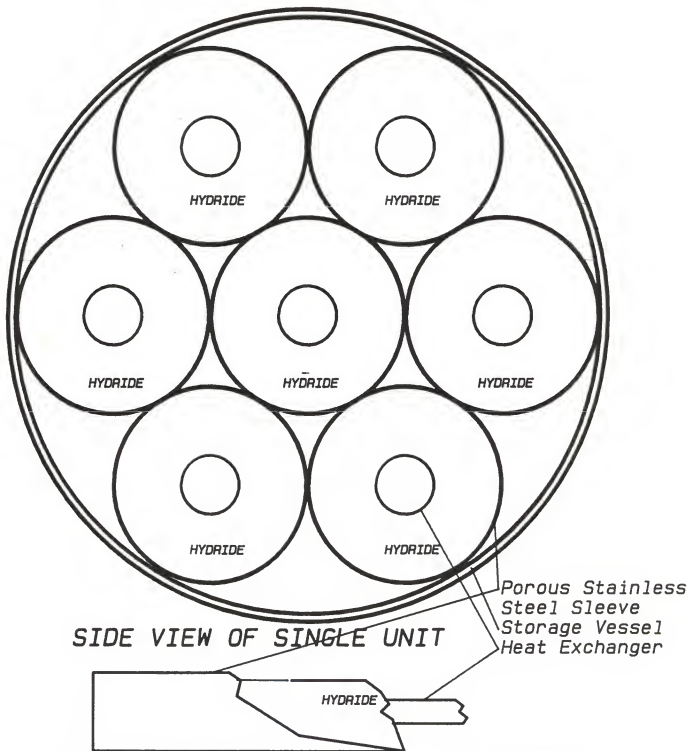


Figure 3. PACKING OF HYDRIDE IN VESSEL

Heat Exchanger Design

Fast dynamic response of a metal hydride hydrogen storage system is necessary to meet the hydrogen consumption fluctuations of an internal combustion engine. Since the kinetics of a storage system almost always depend upon heat transfer limitations of the system, the heat exchangers need careful and complete analysis so that the best design may be obtained. Most hydride systems in the past have used the conventional once-through heat exchanger design such as the one in Figure 4 on page 33. This type of heat exchanger complicates the assembly of a metal hydride hydrogen storage system. Since the heat exchanger tubes must go completely through the storage vessel and be sealed up to 50 atmospheres in most cases, the tubes must be welded on both ends of the storage vessel. This makes the vessel difficult to load with hydride and nearly impossible to disassemble should it become necessary. Also, because this conventional design requires that tubes be rigid and sealed on both ends of the storage vessel, the tubes are placed under great compressive and bending stresses when the hydride expands during hydrogen adsorption. These additional stresses have probably been a contributing factor to the failure of many metal hydride hydrogen storage systems. A common way to offset these stresses has been to increase the strength of the heat exchanger tubes by increasing their wall thicknesses. Increasing the tube wall thickness does usually solve the failure problem of the storage system, but at the expense of a decrease in heat transfer capacity.

For use in metal hydride hydrogen storage systems, a more practical design than the conventional once-through heat exchanger is the bayonet tube heat exchanger. An illustration of a typical bayonet tube heat exchanger, also called a re-entrant tube heat exchanger, is presented in Figure 4 on page

33. The heat exchanger consists of a tube, capped at one end, in which is placed a second tube. By leaving a gap between the bottom of the inner tube and the cap of the first tube, a fluid path is created by which heat transfer may occur between the primary fluid (water or exhaust gasses) flowing through the annulus and a secondary medium (metal hydride) outside of the first tube. The primary fluid can be made to flow either down the center tube and up the annulus or in the reverse direction.

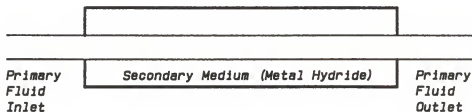
A bayonet tube heat exchanger has a number of advantages over more conventional once-through designs. Since the tube requires only one penetration through the pressure vessel, it can be assembled entirely outside of the vessel and then clamped to it in one operation. This allows for easy assembly as well as disassembly. Furthermore, since only one end of the exchanger is fixed to the storage vessel, the tube is not subjected to significant bending or axially compressive stresses. Given the absence of these stresses, the wall thickness of the heat exchanger tubes can be decreased and therefore result in greater heat transfer capacities than the conventional once-through design. Because the heat transfer capacity of a system can be increased by the decrease of tube wall thickness, bayonet tube exchangers can transfer more heat than conventional once-through exchangers of the same tube thickness and diameter. The convective heat transfer coefficient of a bayonet tube exchanger is approximately 10 percent greater than a conventional design as calculated by Baum (1975) using the Dittus-Boelter equation. While the 10 percent increase is well within the uncertainty of the Dittus-Boelter equation, McAdams (1954) also suggest that the heat transfer for an annulus can be as much as 17 percent above the value for a tube. If the heat transfer improvements of using an annulus instead of a tube are considered and if it is

taken into account that the tube thickness may be decreased, the performance of the bayonet tube exchanger can be significantly superior to that of a once-through design.

To gain the full heat transfer advantages of a bayonet tube heat exchanger, it must be designed properly. Baum (1975) has presented some criteria which will optimize the design of a bayonet tube heat exchanger. In his conclusions to the experiments he performed, he states that to optimize the design, the inner tube should have about three-fourths the diameter of the outer tube. The inner tube should also be about two to three times thicker than the outer tube. These values are approximate and present some tradeoffs between pressure drop through the exchanger and the heat capacity of the exchanger. These design criteria for bayonet tube heat exchangers were followed in our design of a metal hydride hydrogen storage system. If the pressure drop across the exchangers is not acceptable, the ratio of the diameters (D_2/D_4) will be decreased to obtain a reasonable pressure drop. A photograph of the bayonett heat exchanger is presented in Figure 11 on page 53.

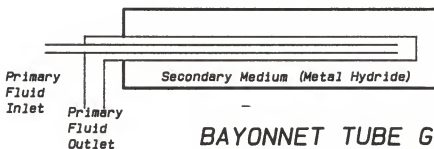
SINGLE-PASS HEAT EXCHANGER

Cross Sectional View



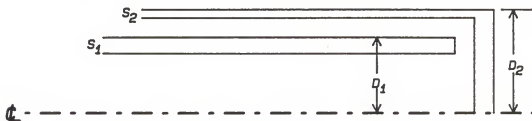
BAYONNET TUBE HEAT EXCHANGER

Cross Sectional View



BAYONNET TUBE GEOMETRY

Half Cross Sectional View



DESIGN CRITERIA:

$$S_1/S_2 = 2$$

$$D_1/D_2 = .75$$

Figure 4. HEAT EXCHANGER COMPARISON

Metal Hydride Systems Integrated With Tractor

There are an infinite number of designs in which a metal hydride hydrogen storage system can be integrated into a tractor's fueling system. Of all the possibilities, some will operate more efficiently than others under given specifications. The design of a hydride storage system will fall into one of three categories: 1) the single metal hydride system, 2) the dual metal hydride system, or 3) a metal hydride system combined with a fossil fuel system. Each system type has specific design advantages and disadvantages which will be discussed.

Single Metal Hydride System

The single metal hydride system is a storage system which uses only one alloy of metal hydride for hydrogen storage. This single alloy is generally a low temperature hydride alloy (LTH alloy is an alloy which dissociates at low temperatures) but doesn't necessarily have to be. A low temperature hydride, LTH, is usually selected so that there will be adequate hydrogen pressure in the system at ambient temperature to allow for engine start up. As the hydrogen gas is consumed by the engine immediately after engine start up, the metal hydride hydrogen storage system begins to cool off rapidly due to the endothermic reaction that takes place when a metal hydride decomposes into the metal and hydrogen gas. To maintain an adequate hydrogen pressure, the heat from combustion of hydrogen (in the form of hot engine coolant) is supplied to the metal hydride hydrogen storage unit. An electronic controlling device is constructed such that the amount of heat supplied to the metal hydride hydrogen storage vessel is inversely proportional to the hydrogen pressure at the storage vessel. A small decrease in hydrogen storage vessel pressure from the

pre-set minimum (about two to three atmospheres) would result in a small increase in heat supplied to the storage vessel: a large decrease in hydrogen storage vessel pressure would result in a large increase in heat supplied to the storage vessel. The design of the heat regulating device will be performed after basic tests have been completed on the metal hydride hydrogen storage system. Figure 5 on page 37 shows the complete single metal hydride system design integrated with the tractor components.

The refueling of the single metal hydride hydrogen storage system does not require that it be as critically controlled as the depletion of hydrogen from the storage system during consumption by the engine. In refueling the system it is desirable for hydrogen to be adsorbed into the system as quickly as possible. Since the adsorption of hydrogen into a metal to form a metal hydride is an exothermic reaction, the heat of adsorption must be removed from the storage vessel. The rate of hydrogen adsorption is regulated by the rate in which heat may be carried away from the storage vessel. Therefore, to provide for quick refueling, the rate of heat removal must be maximized. Refueling a hydrogen storage system is performed by circulating large quantities of water at ambient temperature (or cooler if feasible) through the storage vessel as hydrogen is added.

As stated before, when hydrogen is burned in pure oxygen, the main product of its combustion is water vapor. Since air is combined with hydrogen in an engine instead of pure oxygen, NO_x can also be a product of combustion. This NO_x level can often be quite high and unacceptable. A water injection system into the intake manifold can be designed to reduce the NO_x formation as stated by Billings (1976). The water used to inject into the intake manifold could be condensed from the exhaust gases and recycled through the engine. A

simplified water injection system is presented in Figure 5 on page 37.

The major advantage of using a single low temperature hydride is that the system and its integration with the tractor components is the most simple possible design. A good LTH for hydrogen storage is HY-STOR 102 as stated in an earlier section. Since the hydrogen storage cost of HY-STOR 102 is still very expensive, and would be a major drawback to fueling a tractor on hydrogen, it is important to look for ways to bring down the initial investment costs. One such way would be to use a dual fueling system, the first hydride system to start the tractor and the second system to supply hydrogen when the tractor has reached operating temperature. This would allow an efficient use of the hydrides with the high dissociation temperatures such as the magnesium base hydrides. Hydrogen storage cost are about 1600 \$/kg of hydrogen for HY-STOR 102 and would be only 640 \$/kg for HY-STOR 301. This would reduce the investment cost of a hydride storage system by as much as 50 percent.

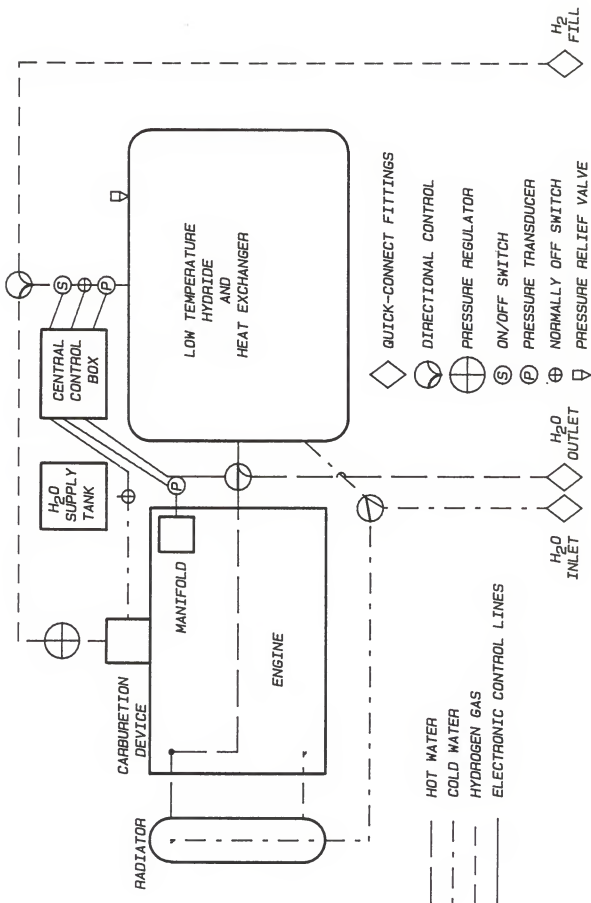


Figure 5. SINGLE METAL HYDRIDE HYDROGEN STORAGE SYSTEM

Dual Metal Hydride System

The second possible design of a metal hydride hydrogen storage system utilizes a dual metal hydride hydrogen storage system. This design involves the use of two separate metal hydride systems, a low temperature hydride (LTH) to start the engine, and a high temperature hydride (HTH) to supply most of the hydrogen to the engine once operating temperature has been reached. The hydride with the low dissociation temperature (HY-STOR 102) would be used to start the engine and supply it with hydrogen since the hydrogen gas pressure would be 2.65 atmospheres at 25 degrees C. This low temperature hydride would be heated by the hot engine coolant should the hydrogen pressure drop below 2.65 atmospheres. The hydride with the high heat of decomposition (HY-STOR 301) would be heated by the exhaust of the engine. As the temperature of the HY-STOR 301 bed reached 290 degrees C the hydrogen pressure would be approximately 2.65 atmospheres. Since hydrogen pressure in the HY-STOR 301 bed would then be adequate to fuel the tractor, the heat supplied to the HY-STOR 102 bed would be shut off, thus preventing further hydrogen liberation from the bed. The HY-STOR 301 bed would handle all the fuel demands of the engine as long as the temperature of the bed remained above the dissociation temperature (290 degrees C). If the temperature of the HY-STOR 301 bed dropped below the dissociation temperature, heat would again be released into the start-up system (HY-STOR 102) and it would take over the hydrogen demand of the engine. Once the dissociation temperature of the HY-STOR 301 bed was met again, the heat to the start-up system would be shut off, ceasing hydrogen liberation. Such dual hydride systems would be more efficient than single systems for the large hydrogen volumes required by a tractor operating at full load.

The control of heat regulation would be accomplished by using two components similar to the electronic components used in the single hydride hydrogen storage system. Refueling would be performed the same as the single hydride storage system except that the cooling water would be directed to either the HTH system or the LTH system depending upon which system was being refueled.

The water injected into the intake manifold to control NO_x formation could be supplied by the HTH system since the exhaust is cooled by this system resulting in water condensation. The dual metal hydride hydrogen storage system integrated with the tractor components is presented in Figure 6 on page 40.

Although the dual metal hydride system is more complicated than the single metal hydride system, the main advantage is the reduction in initial investment of the system. Typically, LTH cost about 2.5 times as much as HTH for the same hydrogen storage capacity. Also HTH usually weighs much less than LTH, therefore the weight ratio of metal hydride to hydrogen capacity is much less. This allows for a more weight efficient design of the system.

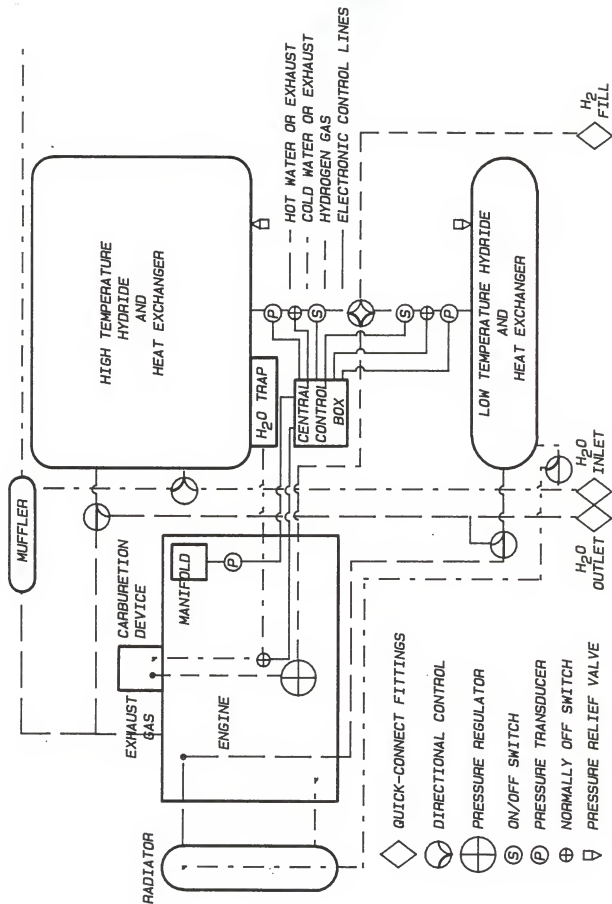


Figure 6. DUAL METAL HYDRIDE HYDROGEN STORAGE SYSTEM

Multifueled System

The third possible design of a metal hydride hydrogen storage system is the use of a hydrogen storage system to supply hydrogen to be burned with fossil fuels (multifueled system). The metal hydride hydrogen storage system could be either a single hydride or a dual hydride hydrogen storage system. A single hydride design is more likely to be used since the main reason for using a dual hydride system is to allow for engine start up. The fossil fuel could be used instead of the LTH for engine start up. The metal hydride hydrogen storage system design would be identical with the previously discussed designs. A separate carburetion device would be necessary for the liquid fuel and the gaseous hydrogen but it would not need to be unreasonably complicated.

There are several advantages of using a multifueled system over a single fueled system. First, the amount of hydrogen burned by the engine is greatly reduced as compared with a purely hydrogen fueled engine so a much smaller metal hydride hydrogen storage system could be used. This would decrease the investment cost of the hydride system incredibly. Another advantage is the efficiency of an engine which burns both fossil fuels and hydrogen gas is significantly increased over that of a purely fossil fueled engine.

EXPERIMENTAL TEST FACILITIES

Safety Aspects

Hydrogen is potentially a very dangerous fuel to handle, therefore safety precautions have to be built into any system which handles it. For hydrogen to become hazardous two conditions must exist. First, sufficient quantities of hydrogen must come in contact with oxygen and secondly, a means of starting combustion must be present. Our test facility has strived to eliminate both of these conditions to reduce chances for an accident. All hydrogen gas is enclosed in its own environment which has been thoroughly checked for leaks. This hydrogen system is leakproof not only to prevent hydrogen from escaping but also to prevent atmospheric contaminants from entering the extremely high purity hydrogen (99.999 percent pure) used in the tests. The entire hydrogen system is sealed off from all electrical components (except pressure transducers) of the test facility and constantly ventilated. If a leak should develop it should be sufficiently diluted so that it remains at a harmless hydrogen-air mixture and vented outside. Even if the leak is large enough to produce flammable hydrogen-air mixtures, all electrical components which might start combustion (switches, motors, and relays) are completely separate from the vented hydrogen system.

Test Module

The test facility consists primarily of the test module, the hydrogen control system, the water control system, and the data acquisition system.

The design parameters of the test module have already been discussed in an earlier section. The measurement devices used to evaluate the performance

of the test module include 3 pressure transducers and 24 copper-constantan thermocouples. Their placement is illustrated in Figure 7 on page 49. Two Omega pressure transducers, one with a 0 - 500 psia range (PX500-500A5V), the other with a 0 - 2000 psig range (PX500-2KG5V), are used to measure the hydrogen gas pressure in the test module. A quarter turn on-off valve protects the 0 - 2000 psig transducer from vacuum pressures which would damage the transducer diaphragm. A 500 psig pressure limiting snubber valve automatically protects the 0 - 500 psia pressure transducer from extreme overpressures. The use of two pressure transducers to measure hydrogen pressure allows more accurate reading in the lower pressure ranges. The other pressure transducer with a range of 0 - 50 (PX105-50G5V) is used to measure the water inlet pressure of the test module heat exchanger to determine the pressure required for different water flowrates through the heat exchanger.

As was stated earlier, 24 copper-constantan thermocouples are used in the test module, of which 21 measure hydride temperatures and 3 measure heat exchanger water temperatures. The 21 hydride thermocouples are constructed of 30 gauge copper-constantan wire to give a reported time constant of approximately 0.9 seconds according to Omega specifications. These thermocouples are spaced in groups of three at seven locations throughout the hydride bed as shown in Figure 7 on page 49. In each of the groups of three, one is at the heat exchanger, the second is at the porous metal filter and the third is midpoint between heat exchanger and the filter. A photograph of the thermocouple spacing tree is presented in Figure 9 on page 51.

The three heat exchanger thermocouples are also constructed of 30 gauge copper-constantan wire with the same time constant as above. The first thermocouple measures water inlet temperature of the inner tube, the second

measures water midpoint temperature at the cap, and the third measures water exit temperature of the annulus formed by the two tubes.

Hydrogen Control System

All valves and gauges used in the control of hydrogen from one component to another are centrally located in the hydrogen control panel as shown in Figure B1 and B2 of Appendix B. A flow diagram illustrating how the various components are connected is shown in Figure B3 of Appendix B. The various components are connected with stainless steel fittings and all gauges, regulators, valves, and pressure transducer diaphragms are constructed of stainless steel. Hydrogen operation should therefore not significantly affect their performance over time. The calibration tanks used to determine how much hydrogen passes to or from the test module are the original tanks used to supply the ultra high purity (UHP) hydrogen and have a volume of 0.04102 cubic meters. The supply tanks are constructed of carbon steel and contain 466 grams (197 standard cubic feet) of UHP hydrogen gas at 136 atmospheres upon delivery. The two stage vane vacuum pump used to initially evacuate all systems is rated at 150 liters per minute (5.3 cfm) and has an ultimate vacuum capacity of 0.1 microns of mercury. A 1.0 cubic meter (250 gallon) propane tank was converted to handle hydrogen gas and is used to store low pressure hydrogen up to 225 psig when needed.

A hydride hydrogen compressor was designed and constructed to move hydrogen from a low pressure source to a higher one. This hydrogen compressor is a necessity if the same UHP hydrogen is to be used repeatedly as planned. The hydride compressor prevents the UHP hydrogen gas being pumped from being contaminated as would be the case if a mechanical pump was used. In fact, the

hydride hydrogen compressor actually purifies the hydrogen gas as it is pumped. Specifications and a schematic diagram of the compressor are given in Figure B4 of Appendix B.

Water Control System

The temperature of the test module is controlled by conduction of heat through a bayonet heat exchanger to the hydride bed. Heat may be supplied to the hydride bed, as in the case of hydrogen desorption or removed from the hydride for hydrogen absorption. This heat transfer is accomplished by passing hot or cold water through the bayonet heat exchanger. Therefore it is necessary that the test facilities provide a means of both heating and cooling this water supplied to the heat exchanger. The hot water is provided from a 2000 watt electrical heater controllable from 37 to 100 degrees C. Cold water is supplied from a freon 12 refrigeration system capable of cooling a water-antifreeze mixture below zero degrees C. Tap water in the range of 13 to 17 degrees C is also available. The water flow through the test module (hot, tap, or cold) is controlled by a centrally located water control panel as presented in Figure B1 and B2 of Appendix B. A schematic water flow diagram is also presented in Figure B5 of Appendix B. The flow of water through the test module is controlled by electrically operated solenoid valves and a mechanical two way valve. Electrically operated solenoid valves are used so that an automatic water cycling device, which has been designed and constructed, may control water temperature through the test module. This automatic water cycler uses the TTL output of the computer to operate the solonoid valves and the TTL input constantly monitors the system status. If failure of the automatic device occurs or if power is lost to the computer, the system is automatically shut down. This automatic cycling device should

prove valuable for extensive cycling tests so that they do not need to be constantly monitored.

As stated earlier, the hydrogen control system uses a hydride hydrogen compressor to move hydrogen gas from one component to another. Compressor action of a hydride is accomplished by absorbing low pressure hydrogen at a low temperature, heating the hydride to raise the gas pressure (according to the Van't Hoff equation), and releasing this higher gas pressure into the desired component. Therefore, it is required that the hydride hydrogen compressor have a water control system similar to that of the test module. A 1000 watt electrical water heater provides heat up to 100 degrees C to the compressor. Tap water is also available to cool the compressor to the range of 13 to 17 degrees C. For colder compressor temperatures (0 - 5 degrees C), a freon 12 refrigeration system is used. This compressor refrigeration system utilizes the same freon 12 compressor and condensor as does the test module but uses a separate evaporator. Since the test module and the hydride hydrogen compressor use separate evaporators, their temperatures can be controlled independently of one another but using a single freon 12 compressor and condensor system. The evaporator of the hydride hydrogen compressor is 10 meters of tubing coiled around the compressor as shown in Figure B4 of Appendix B.

Data Acquisition System

Data from experiments are collected on a software altered ADAC LSI-11 data acquisition system. The LSI-11 has been modified to use a UNIX base system to allow more than one terminal to be used simultaneously. Many other advantages of UNIX are also available on the system. The data collection programs directly address the ADAC boards therefore they are all written in C.

The transducers used to collect pressure data include three pressure transducers already discussed that have conditioned outputs of 0 - 5 volts. Water flowrates through the test module heat exchanger were measured by a 1.27 cm turbine flowmeter with magnetic pulse output. This flowmeter pulse output was then converted to a 0 - 5 volt signal by a Datronic 3240 frequency converter. All temperature measurements were performed using copper-constantan thermocouples. All thermocouples in the test module (21 hydride and 3 water) were 30 gauge with time constants of approximately 0.9 seconds. All other thermocouples were constructed of 24 gauge copper-constantan wire with an estimated time constant of two seconds.

TEST PROCEDURES

Assembly of Test Module

The ideal metal hydride hydrogen storage system is one that has good heat transfer properties and yet is simple to provide for easy assembly. The design of the test module proposed is of simple concepts but the actual assembly becomes complicated with addition of performance measuring devices. Using 21 thermocouples logically located throughout the hydride bed gives good insight on the heat flow through the hydride bed but also presents the challenging problem of sealing these wires from hydrogen leaks.

Actual assembly of the test module began with inserting the 0.5 micron porous metal filter into the pressure vessel. Since the outer tube of the bayonet heat exchanger is part of the pressure vessel (extending down the center of the pressure vessel), the heat exchanger slips inside the filter as it is inserted. This part of the test module assembly is illustrated in Figure 8 on page 50. After the filter was in place, the thermocouple spacing

tree, presented in Figure 9 on page 51, was slipped over the heat exchanger and inside the porous metal filter. A cross sectional view of the test module including the thermocouple tree is shown in Figure 8 on page 49. Once the hydride thermocouples were in place, the cap to the pressure vessel was bolted off to one side of the filter opening. This prevented the thermocouple wires from being torn from the wire inserts in the vessel cap. The test module was then stood on one end and filled 75 to 80 percent full of hydride to allow for hydride expansion (28 kilograms of HY-STOR 102 hydride). The pressure vessel cap was then bolted in place. Care had to be exercised to make sure that both the O ring (seals hydrogen in vessel) and the flat rubber gasket (seals hydride in filter) were in place before cap bolts were torqued. Figure 10 on page 52 illustrates the above procedure. After the hydride system was sealed, the test module was turned on one side for assembly of the bayonet heat exchanger as shown in Figure 11A on page 53. The bayonet heat exchanger was assembled by simply inserting the inner tube (connected to the cap) into the outer tube (part of the pressure vessel). The inner tube was automatically centered by prongs extending from the end of the heat exchanger outer tube. With the water seal in place, the cap was then bolted to the pressure vessel. The completely assembled test module is presented in Figure 11B on page 53.

Activation of Hydride

After the completely assembled test module was mounted in the test facilities, activation of the metal hydride was begun. The test module was first outgassed by evacuation with a vacuum pump while heating the hydride bed. The test module was considered totally evacuated after pumping at least an hour below 0.005 mm of mercury at 80 degrees C. The hydride bed was then cooled to room temperature and the ultra high purity (UHP) hydrogen gas was released

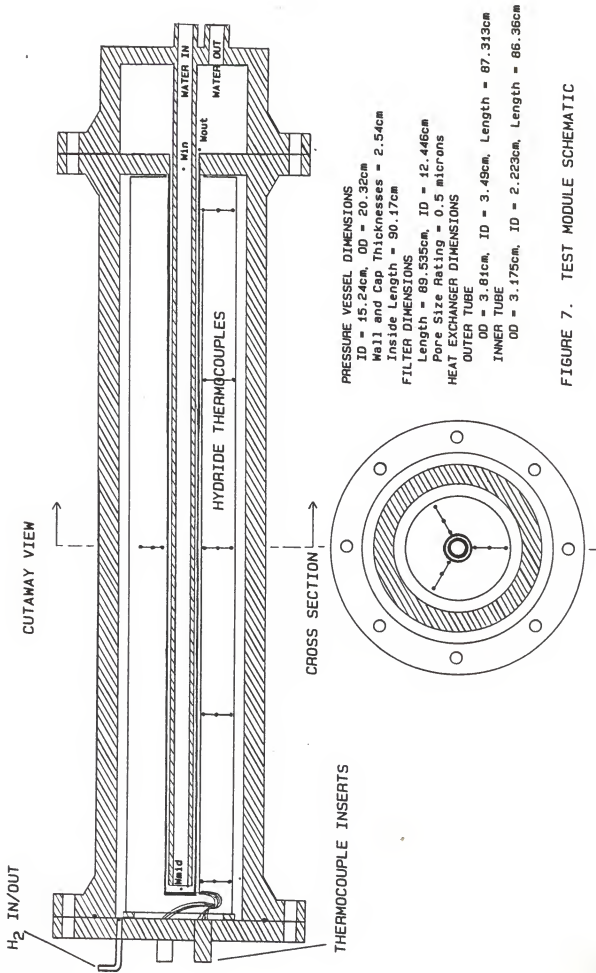


FIGURE 7. TEST MODULE SCHEMATIC



Figure 8A. Porous Stainless Steel Sleeve



Figure 8B. Inserting Sleeve into Pressure Vessel



Figure 9A. Thermocouple Spacing Tree



Figure 9B. Inserting Spacing Tree Over Heat Exchanger

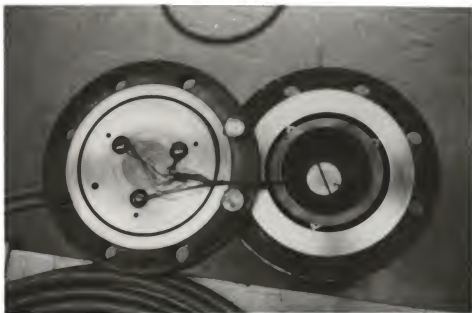


Figure 10A. Porous Sleeve Filled With Hydride



Figure 10B. Pressure Vessel Cap Bolted in Place

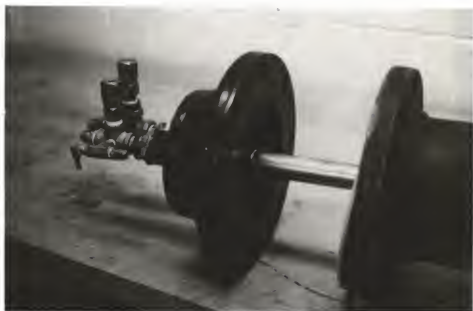


Figure 11A. Assembly of Bayonet Heat Exchanger



Figure 11B. Completely Assembled Test Module

into the test module under 68 atmospheres of pressure. Absorption of hydrogen began after four to five hours and was very slow at first. Absorption of hydrogen continued for three days. At that time the hydrogen was desorbed by heating the hydride bed to 80 degrees C. Absorption-desorption cycles are to be performed until the hydride bed becomes fully activated.

Several factors may prevent the hydride from ever reaching its full activation potential. One factor detrimental to full activation is the use of impure hydrogen gas. Any impurities present in the hydrogen gas tend to collect on the metal hydride surfaces after a number of absorption-desorption cycles. These impurities may be present in even UHP hydrogen gas so all hydrogen bottles used for hydride experiments should be tested for impurities. These impurities may also be present in the system due to inadequate evacuation before hydrogen gas was ever introduced or leaks in the system which may develop over time.

Van't Hoff Tests

After the HY-STOR 102 hydride had been forced through four absorption-desorption cycles, some experimental pressure-temperature relationships were developed. These pressure-temperature properties are also known as the Van't Hoff properties as stated in an earlier section. The Van't Hoff experiments began with absorbing hydrogen into the test module until a H/Me ratio of approximately 0.5 was reached. The test module was then sealed to maintain a constant H/Me ratio. The temperature of the hydride was lowered to approximately ten degrees C and the hydrogen gas pressure was recorded. The hydride temperature was incrementally increased, allowed to stabilize for approximately four hours, and the hydrogen gas pressure was recorded. As the tem-

perature was incrementally increased, hydrogen was desorbed from the hydride and formed the desorption Van't Hoff data. Once the maximum hydride temperature of 86 degrees C was reached, the absorption Van't Hoff data was collected as the hydride temperature was incrementally decreased back to ten degrees C. Both the desorption and absorption Van't Hoff procedures were repeated to obtain two data sets for the same H/Me ratio.

HEAT STEP TESTS

Basic heat step data for the heat exchanger and hydride bed was taken under two conditions. In the first set of conditions, the H/Me ratio was held constant which prevented hydrogen from reacting with the hydride. The second set of conditions were identical to the first except hydrogen was permitted to react with the hydride which varied the H/Me ratio.

In the first set of conditions, hydrogen was absorbed to approximately 0.5 H/Me ratio and the hydride temperature was brought down to 17 degrees C. At that time hot water at 90 degrees C was pumped through the heat exchanger in an attempt to heat the hydride bed as quickly as possible. These conditions of water temperature and flowrate were similar to those which would occur under actual operation in an engine. Several data readings, including water flowrate, temperature differential across heat exchanger, average hydride temperature, and hydrogen pressure were recorded with respect to time. In addition, hydride temperature profiles were recorded for the heat step up to determine the direction of heat flow through the hydride bed. Data was taken for a period of eight hours or until maximum average hydride temperature of 86 degrees C was reached.

Data for the heat step down to 17 degrees C was taken in the same manner as the heat step up. Tap water at 17 degrees C was circulated through the heat exchanger instead of hot water. Hydride temperature profiles were also recorded to gain insight on the direction of heat flow through the hydride bed as it is cooled.

The heat step up for the second set of conditions, which allowed the H/Me ratio to vary, was performed after all hydrogen absorption had stopped. At that time the H/Me ratio was 0.744. Heat in the form of hot water through the heat exchanger was applied and the same data was taken as in the first set of conditions. The heat step up lasted for the full eight hours and at that time the hydride bed had reached an average temperature of 81 degrees C.

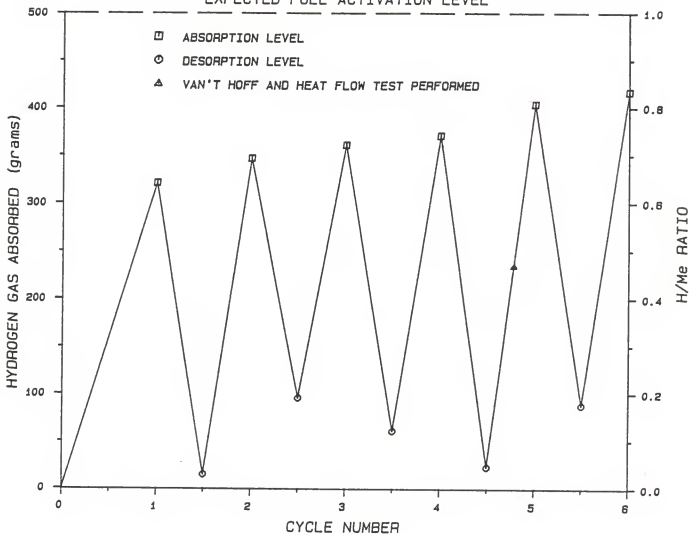
The heat step down for the varying H/Me ratio was performed in the same manner as the heat step up. This test also lasted the full eight hours when an average hydride temperature of 20 degrees C was reached. Hydride temperature profile data was not taken for the varying H/Me heat step tests.

TEST RESULTS

Activation of Hydride

Full activation of the hydride has not been accomplished at this time. The hydride currently has a hydrogen capacity of 1.489 percent by weight as compared to the expected 1.79 percent. The hydride has therefore reached approximately 83 percent of its full hydrogen carrying capacity. On each absorption-desorption cycle, the hydride absorbs about 15 to 20 grams more hydrogen than the previous cycle as can be seen in Figure 12 on page 57. At this rate the hydride can be at full activation level in about six more

----- EXPECTED FULL ACTIVATION LEVEL -----



HYSTOR 102 HYDRIDE ACTIVATION DATA

CYCLE NUMBER	ABSORBED TO (grams H ₂)	DESORBED TO (grams H ₂)
1	321	15
2	347	96
3	361	61
4	371	23
5	404	88
6	417	61

FIGURE 12. HYSTOR 102 HYDRIDE ACTIVATION PROGRESS

absorption-desorption steps. The level of desorption is not of great significance during activation since it can be easily reached by heating the hydride while evacuating the test module.

Van't Hoff Relationships

To obtain the 0.5 H/Me ratio desired for pressure-temperature relationship comparisons, 235 grams of hydrogen was absorbed into the hydride. This would give a H/Me ratio of 0.47 if all the metal hydride atoms were available for reaction. Hydrogen pressure as a function of average hydride temperature is presented in Figure 13 on page 59. As the figure shows, the absorption and desorption curves follow essentially the same path. Trial two data has a slightly lower hydrogen pressure than trial one for the same average hydride temperature.

When the pressure-temperature data is plotted in the form of a typical Van't Hoff curve as shown in Figure 14 on page 60, the experimental data becomes very linear. Also plotted with the test data is reference absorption and desorption lines for HY-STOR 102 as taken from Table A1. The lines formed by experimental trial one and trial two data fall between the reference absorption and desorption lines in most cases but with a slightly flatter slope. In addition to trial two data having a slightly lower hydrogen pressure than trial one for a given temperature, trial two data also has a slightly steeper slope which is more comparable to the reference lines. Table 4 on page 61 lists the best fit regression equation constants for the experimental data as well as the reference lines for the Van't Hoff plots.

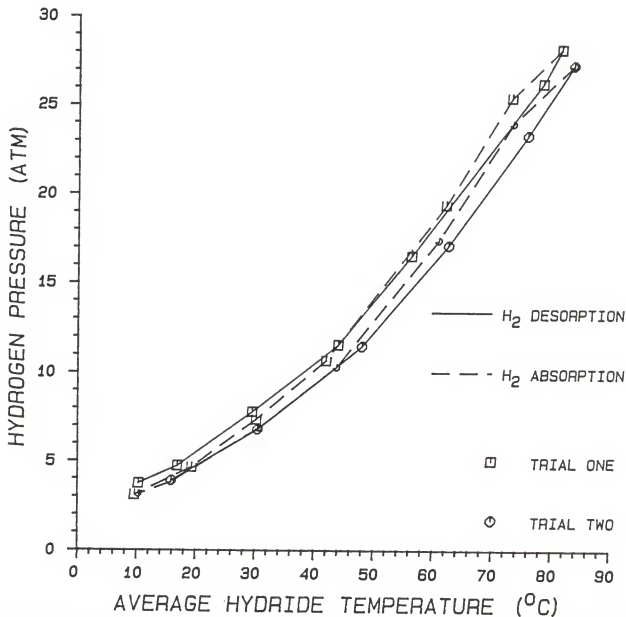


FIGURE 13. TEMPERATURE - PRESSURE RELATIONSHIPS FOR HYSTOR 102 (H/Me = 0.582)

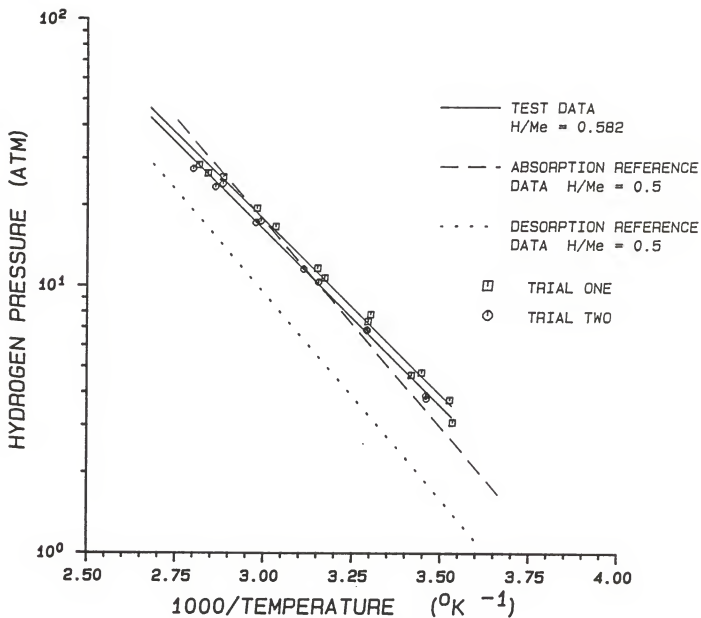


FIGURE 14. VAN'T HOFF PLOTS
 FOR HYSTOR 102 ($H/Me = 0.582$)

TABLE 4. COMPARISON OF EXPERIMENTAL AND REFERENCE VAN'T HOFF CONSTANTS

	Slope Constant A	Intercept Constant C
absorption reference line	-3545	13.49
desorption reference line	-3545	12.87
experimental trial one	-3002	11.87
experimental trial two	-3026	11.86

VAN'T HOFF EQUATION

$$\ln P = \frac{2 \Delta H}{X R T} + C$$

$$\frac{2 \Delta H}{X R T} = \frac{A}{T}$$

for H/Me ratio of 0.5
(X = 1.97)

Heat Step Tests

Four heat step tests were performed, two with a constant H/Me ratio of .582 (heat step up and heat step down) and two with varying H/Me ratios (heat step up and heat step down).

Heat Step Up

Comparison of the two heat step up tests is presented in Figure 15 on page 63. Figure 15A represents the heat flow into the test module when the hydride is not allowed to react with hydrogen (constant H/Me). This test lasted only five hours since the maximum average hydride temperature of 86 degrees C was reached. Heat flow is large at first, as much as 5 kilowatts, but drops off quickly to around 0.5 kilowatts. Figure 15B represents the heat flow into the test module when the hydride is allowed to react with hydrogen (variable H/Me). This test lasted the full eight hours with a maximum average hydride temperature of 81 degrees C. Heat flow was also large at first but stabilizes at a higher heat flowrate than does Figure 15A. The average hydride temperature increased more rapidly in the constant H/Me tests (Figure 15A) than in the tests where hydrogen was allowed to react (Figure 15B). Figure 15C displays the differential heat flow rate between the two tests. On the average, the hydride heat step that was allowed to react consumed 0.2 kilowatts more than the hydride heat step that was held at a constant H/Me. Figure 15C also presents the hydrogen mass of the test module over time.

Temperature profiles of the hydride were performed for the heat step up with a constant H/Me ratio. These profiles presented in Figure 16 on page 64 show a cross sectional half view of the hydride bed from the centerline of the heat exchanger down to the filter. As time increases, the temperature wave

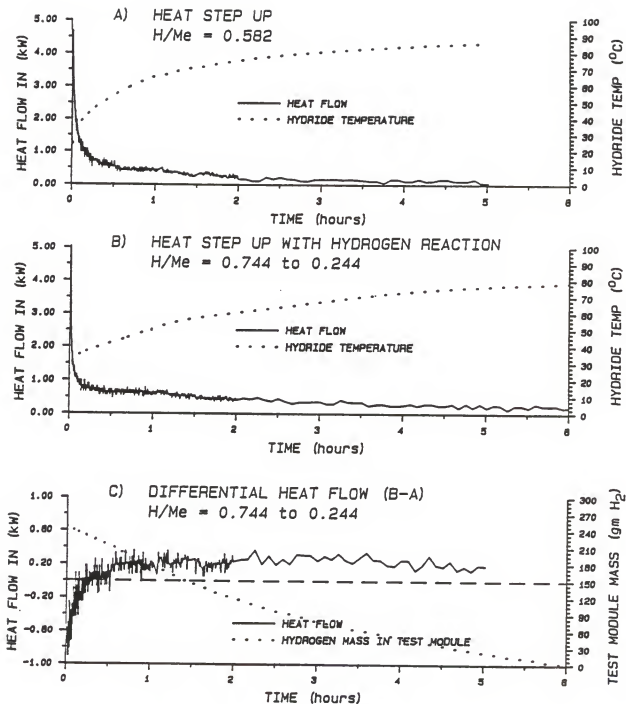
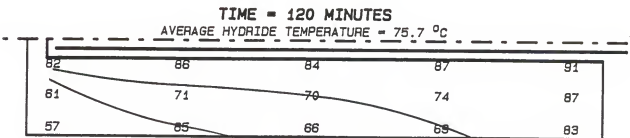
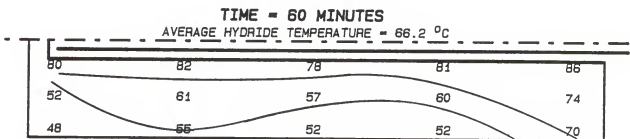
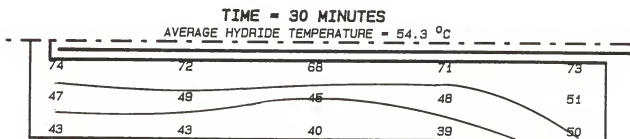
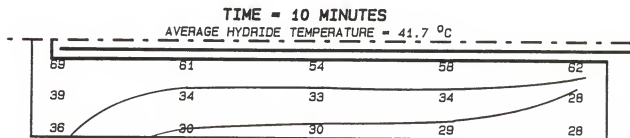
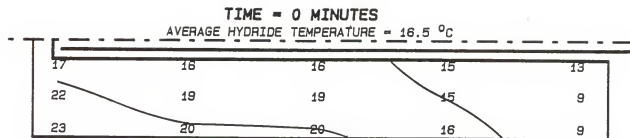


FIGURE 15. HEAT FLOW INTO TEST MODULE
FOR HEAT STEP UP (17° to 83°C)



HALF CROSS SECTIONAL VIEW
FIGURE 16. HYDRIDE TEMPERATURE PROFILES
Heat Step Up

generally progresses radially out from the left end of the heat exchanger where the hotter water enters the annulus formed by the bayonet heat exchanger. The temperature profile then distributes itself more evenly throughout the hydride bed with slightly more heat transfer through the right cap of the test module. Hot heat exchanger exit water is exposed to the right cap (see Figure 7 on page 49) which provides the heat to be transferred through this cap. The left cap is exposed to the external environment and therefore conducts heat out of the hydride bed. This accounts for cooler hydride temperatures at the left as compared to the rest of the bed as the average hydride temperature increases.

Heat Step Down

The hydride heat step down tests are presented in Figure 17 on page 66. The results are similar to those found for the heat step up. As would be expected, the heat step down for the varying H/Me ratio requires more heat to be taken away since the hydriding reaction releases energy.

The hydride temperature profile for the heat step down is presented in Figure 18 on page 67. The hydride bed is cooled the most quickly from the left at first, and then cooling proceeds from both ends towards the middle. As the hydride temperature gets nearer to ambient, less heat is transferred out of the left cap into the external environment. The temperature wave then proceeds from the right cap as is the case in the heat step up hydride temperature profile of Figure 16.

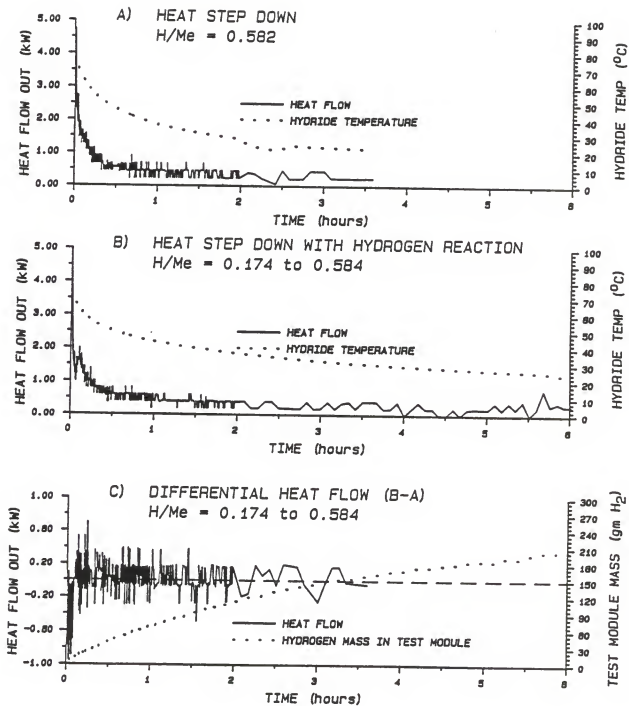
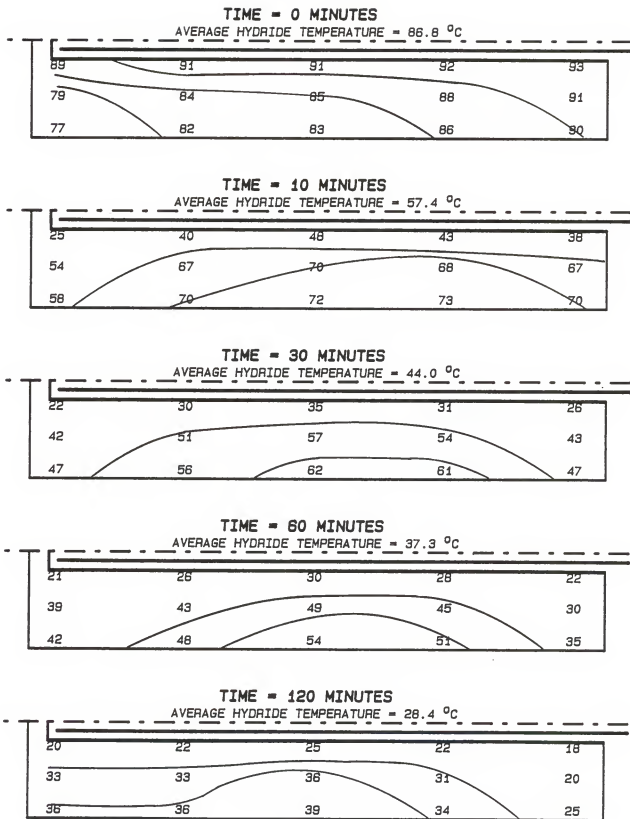


FIGURE 17. HEAT FLOW OUT OF TEST MODULE
FOR HEAT STEP DOWN (83° to 23° C)



HALF CROSS SECTIONAL VIEW
FIGURE 18. HYDRIDE TEMPERATURE PROFILES
Heat Step Down

DISCUSSION

Activation of Hydride

As a hydride becomes fully activated, the metal particles become brittle, split, and provide more surface area in which the hydrogen-hydride reaction may take place. This is apparently the stage which the test module is in at this time. Full hydrogen activation cannot be expected until all the metal molecules are physically exposed to hydrogen gas. By extrapolating on Figure 12, full activation can be expected in six to ten more absorption-desorption cycles. If this is the case, then it requires 12 to 15 absorption-desorption cycles to fully activate HY-STOR 102 from virgin alloy.

Van't Hoff Plots

When considering the Van't Hoff equation on page 9, the H/Me ratio of the hydride greatly affects the slope of the Van't Hoff plot. This is assumed to be the major difference between the experimental slopes and the reference slopes in the Van't Hoff plot of Figure 13. Since the hydride reaches only 83 percent of the complete activation hydrogen level, it seem reasonable to assume that only 83 percent of the metal molecules are available for reaction. The metal molecules available for reaction should then be the only ones considered when calculating the H/Me ratio. The H/Me ratio then becomes 0.582 instead of 0.47. The slope (constant A) of the Van't Hoff plot as calculated from the equation on page 9 then becomes -3050 and compares well with the experimental results of -3002 and -3026 in Table 4.

Every time the hydride is heated and then cooled, more metal molecules become available for hydrogen absorption. With this in mind it seems safe to

assume that the H/Me ratio of trial two would be slightly less than trial one. This difference in H/Me ratios can be observed in the difference of Van't Hoff slope constants of the experimental data.

Separate absorption and desorption Van't Hoff lines are not apparent in the experimental data of Figure 14 on page 60. Since the hydride bed is a range of temperatures forming an average, the hydride will be a mixture between absorption and desorption. A single absorption or desorption line cannot be expected unless the hydride bed temperature is more accurately controlled.

Heat Steps

Since the hydride is not fully activated, the heat flow data presented in Figures 15 and 17 have to be carefully considered. The properties of the hydride are changing rapidly while it becomes activated and therefore these figures should only be used to recognize general trends. A more complete heat balance should be performed after the hydride activation level has stabilized.

One property which should not change drastically between now and full activation is the direction of heat flow through the hydride bed. From Figures 16 and 18 it is easily recognizable that there is a good deal of heat transfer from the heating or cooling fluid through the right cap (as seen in Figure 9) of the test module. There is also a significant transfer of heat through the left cap to the surrounding environment. The bayonet heat exchanger seems to efficiently transfer heat to the outer surface of the heat exchanger, but the transfer of heat from the heat exchanger surface to the hydride is poor. Since heat transfer through the hydride is equally poor, inadequate hydride heat transfer may prove to be a design problem.

CONCLUSIONS

Activation of HY-STOR 102 is an involved and lengthy process. For full activation of the hydride, the particle size must be sufficiently reduced. Full activation of the HY-STOR 102 alloy used in the proposed test module should be obtained in twelve to fifteen absorption-desorption cycles unless unexpected problems arise.

Properties of the HY-STOR 102 plateau pressure seem to be described very well by use of the proper constants in the Van't Hoff equation.

The general design of the test module proposed is structurally and functionally sound. The porous metal filter used to contain the hydride allows gases to easily pass through it and yet the pore size should be small enough to prevent clogging even as the metal hydride particles deteriorate in size over thousands of absorption-desorption cycles. The geometry of the porous metal filter and bayonet heat exchanger seem to provide the necessary expansion when hydrogen is absorbed into the hydride.

A factor which may prove to be of some significance is the poor heat transfer property of HY-STOR 102 hydride. The bayonet heat exchanger design provides good heat transfer to the surface of the heat exchanger, but the heat exchange from the heat exchanger surface to the hydride and through the hydride is poor. More complete dynamic tests need to be performed after full hydride activation has been achieved.

If inadequate heat transfer of the hydride restricts the test module from meeting the dynamic demands of an internal combustion engine, a possible design modification would be the addition of radial fins attached to the outer

tube of the bayonnet heat exchanger. This would effectively increase the surface area of the heat exchanger with a minimum increase in design complication. The addition of radial fins would slightly increase the complexity of module assembly but seems to be the most practical solution to inadequate hydride heat transfer.

SUMMARY

A modular metal hydride hydrogen storage system has been designed and built. The module consists of a 0.5 micron porous stainless steel sleeve and a bayonet heat exchanger. Metal hydride is contained within the porous sleeve with the bayonet heat exchanger extending through the center of the sleeve. Hydrogen gas freely flows through the porous sleeve to be easily collected from the pressure vessel. The use of small diameter modules provide for expansion of the hydride material and the capability for making larger systems by adding additional modules. Although $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Ti}$ hydride is currently being used, other metal hydrides would work equally well in the modular system.

Activation of the HY-STOR 102 hydride is currently being completed. Full activation of the hydride is expected after twelve to fifteen absorption-desorption cycles.

Plateau pressure-temperature relationships of the hydride may be accurately predicted with use of the Van't Hoff equation so long as the hydrogen content of the hydride is known.

Limited heat transfer and temperature profile data has been collected. Analysis of this data indicate that the proposed modular system may have problems meeting the dynamic demands of an internal combustion engine due to poor hydride heat transfer. Further heat transfer tests need to be performed after the HY-STOR 102 hydride has been fully activated.

SUGGESTIONS FOR FURTHER RESEARCH

Complete activation of the HY-STOR 102 hydride should be accomplished before any further testing of the modular storage system. Once the hydride is thoroughly activated and several absorption-desorption cycles have been completed (15 to 20 cycles past activation), it is recommended that the hydride be mapped by performing several isotherm and Van't Hoff cycles. After the characteristics of the HY-STOR 102 hydride are known, dynamic heat transfer properties of the hydride may be determined. If the hydride heat transfer does not prove adequate to meet the dynamic hydrogen flowrates for an internal combustion engine, modular design changes may have to be made. A possible first design change would be the addition of radial fins to the bayonet heat exchanger to increase surface area contact between the hydride and heat exchanger.

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APPENDIX A. PROPERTIES OF HY-STOR HYDRIDES

FIGURE A1. Van't Hoff Plots (Desorption) for Various Hydrides

TABLE A1. Van't Hoff and Hysteresis Constants for HY-STOR Alloys

TABLE A2. Additional Properties of HY-STOR Alloys

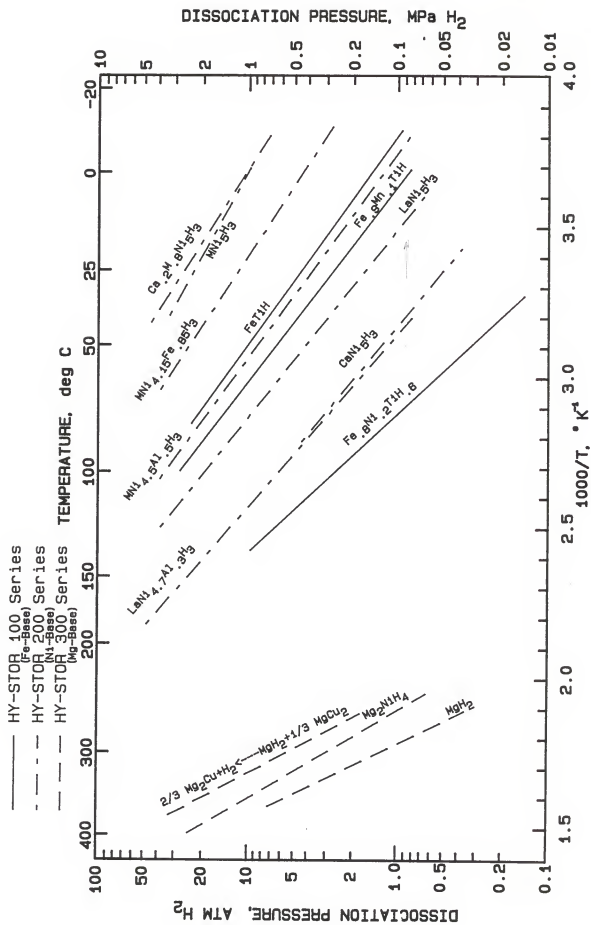


FIGURE A1. VAN'T HOFF PLOTS (DESORPTION) FOR VARIOUS HYDRIDES

Table A1. VAN'T HOFF AND HYSTERESIS CONSTANTS FOR HY-STOR ALLOYS

HY-STOR Alloy	Nominal Composition	ΔH (kcal/mole H_2)	A deg K	C	P_d^{**} (atm)	P_a^{**} (atm)	P_a/P_d	$\ln(P_a/P_d)$	Reference
- 101	FeTi	-6.7	-3383	12.76	5.3 ⁽¹⁾	10.0	1.89	.64	Reilly, 1977
- 102	Fe ₉ Mn ₁ Ti	-7.0	-3545	12.87	4.7 ⁽²⁾	8.7	1.85	.62	Reilly and Johnson, 1977
103	Fe ₈ Ni ₂ Ti	-9.8	-4952	14.29	0.87 ⁽³⁾	0.91	1.05	0.05	---
201	CaNi ₅	-7.6	-3838	12.17	0.47	0.55	1.17	0.16	Sandrock, 1977
202	Ca ₇ M ₃ Ni ₅ [*]	-6.4	-3204	12.08	3.8	4.2	1.11	0.10	Sandrock, 1977
- 203	Ca ₂ M ₈ Ni ₅ [*]	-5.8	-2923	13.08	25	37	1.48	0.39	---
- 204	MNi ₅ [*]	-5.0	-2539	11.64	23	120	5.2	1.65	Reilly, 1977
- 205	LaNi ₅	-7.4	-3712	12.96	1.65	2.0	1.21	0.19	Van Mal et al, 1974
207	LaNi _{4.7} Al _{1.3}	-8.1	-4090	12.84	0.42	0.44	1.05	0.05	---
- 208	MNi _{4.5} Al _{0.5} [*]	-6.7	-3366	12.61	3.8	4.25	1.12	0.11	Sandrock, 1978
- 209	MNi _{4.15} Fe _{0.85} [*]	-6.0	-3041	12.60	11	13	1.18	0.17	---
301 ⁽⁴⁾	Mg ₂ Ni	-15.4	-7736	14.71	-	-	-	-	Reilly, 1977
302	Mg ₂ Cu	-17.4	-8771	17.12	-	-	-	-	Reilly, 1977
-	Mg	-18.5	-9314	16.63	-	-	-	-	Reilly, 1977

From Huston and Sandrock (1980)

* M = Mischmetal, ** 25 deg C, H/Me = 0.5, (1) 30 deg C, (2) 40 deg C, (3) 70 deg C, H/Me = 0.3
 (4) HY-STOR 301 is a 2 phase mixture of Mg₂Ni and Mg. Actual composition is Mg_{2.4}Ni.

Table A2. ADDITIONAL PROPERTIES OF HY-STOR ALLOYS

Trade Name	Alloy Composition	Plateau Slope* $\frac{d(\ln P_d)}{d(H/M)}$	Useable Capacity** ($\Delta H/M$)	Heat Capacity (cal/g deg C)	Current Price (\$/kg)
HY-STOR 100 Series					
101	(Fe-Base) FeTi	0.00 ⁽¹⁾	0.90 ⁽¹⁾	0.13	28.20
102	Fe ₉ Mn ₁ Ti	0.65 ⁽²⁾	0.92 ⁽²⁾	0.13	28.50
103	Fe ₈ Ni ₂ Ti	0.36 ⁽³⁾	0.62 ⁽³⁾	0.12	30.00
HY-STOR 200 Series					
201	(Ni-Base) CaNi ₅	0.19	0.71	0.13	22.20
202 [#]	Ca ₇ M ₃ Ni ₅	3.27	0.96	0.12	28.20
203 [#]	Ca ₇ M ₆ Ni ₅	0.98	0.74	0.105	31.20
204 [#]	MNi ₂ M ₆ Ni ₅	0.54	1.01	0.10	32.10
205 [#]	LaNi ₅	0.09	1.02	0.10	57.30
206 [#]	(CFM)Ni ₅	0.32	0.91	0.095	50.40
207 [#]	LaNi _{4.5} Al _{0.3}	0.48	0.95	0.10	58.50
208 [#]	MNi _{4.5} Al _{1.5}	0.36	0.83	0.10	28.20
209 [#]	MNi _{4.15} Fe _{0.85}	0.43	0.82	0.00 ⁺	22.50
HY-STOR 300 Series					
301	(Mg-Base) Mg _{2.4} Ni ⁽⁴⁾	0.02 ⁽⁴⁾	1.31 ⁽⁴⁾	0.18	24.60
302	Mg ₂ Cu	0.17 ⁽⁵⁾	0.75	0.18	23.70

Properties from Huston and Sandrock (1980). Prices From ERGENICS

*Principal Plateau, $\frac{dP}{dH}$ deg C. **Capacity between 0.1P_d and 10P_d. ***Cost as of 1-31-84, (51-250 kg purchase) -
[#]M = Mischmetal ^{CFM} = Cerium-free mischmetal ⁺Data not available
 (1) 30 deg C, (2) 40 deg C, (3) 70 deg C, (4) 298 deg C, 2 phase mixture of Mg₂Ni and Mg (5) 324 deg C

APPENDIX B. DETAILS OF TEST FACILITY

FIGURE B1. Test System Schematic

FIGURE B2. Test System Photograph

FIGURE B3. Hydrogen Control System

FIGURE B4. Hydride Hydrogen Compressor

FIGURE B5. Water Control System

AUTO CYCLER

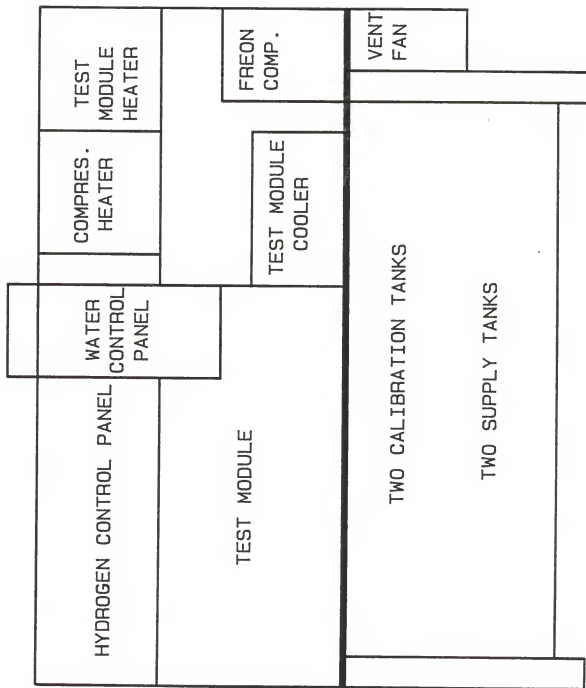


FIGURE B1. TEST SYSTEM SCHEMATIC

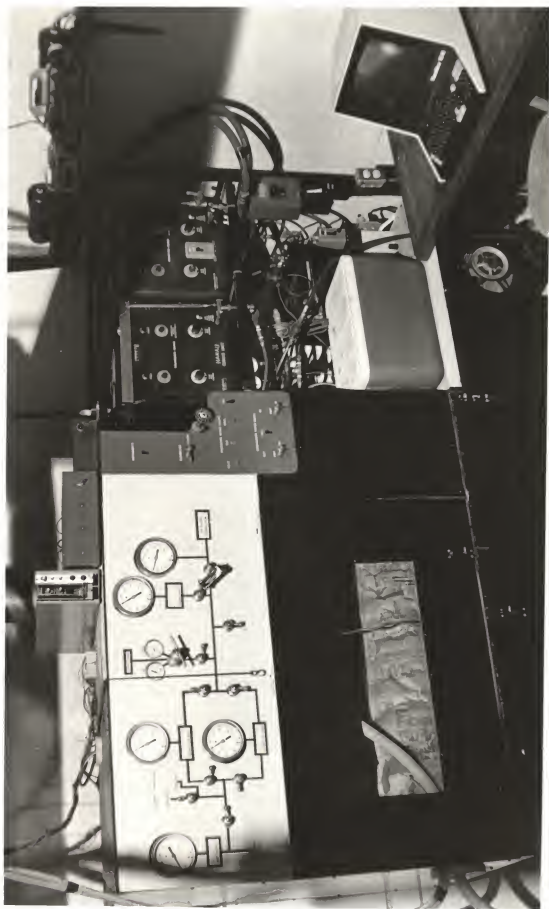


Figure B2. Testing Facilities

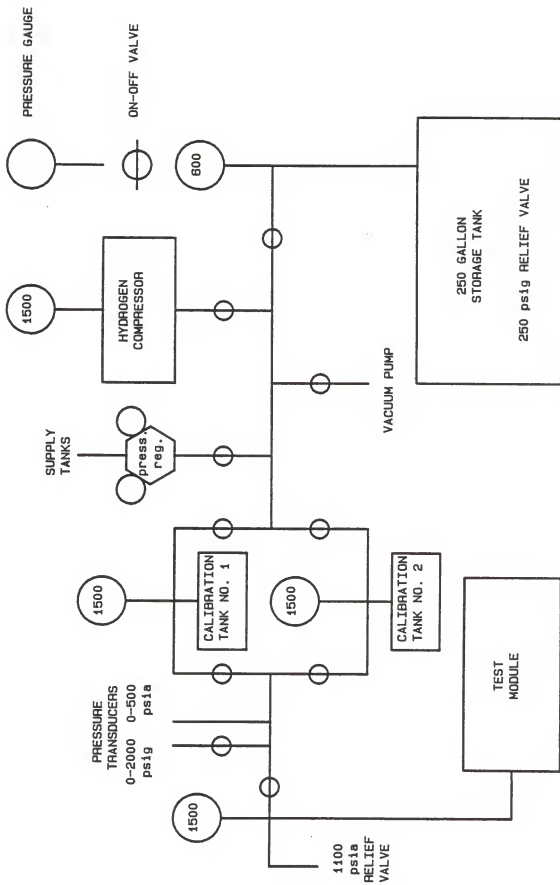


FIGURE B3. HYDROGEN CONTROL SYSTEM

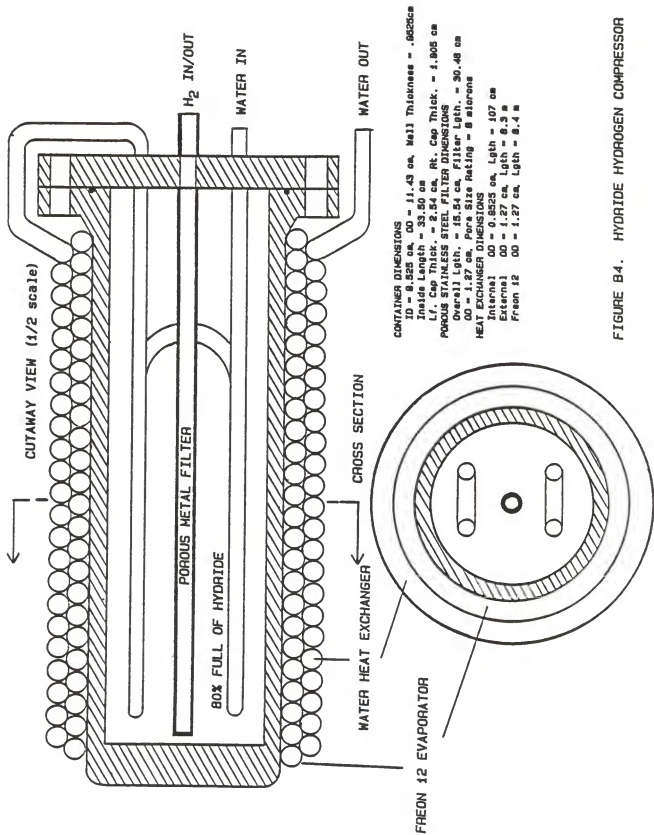


FIGURE B4. HYDRIDE HYDROGEN COMPRESSOR

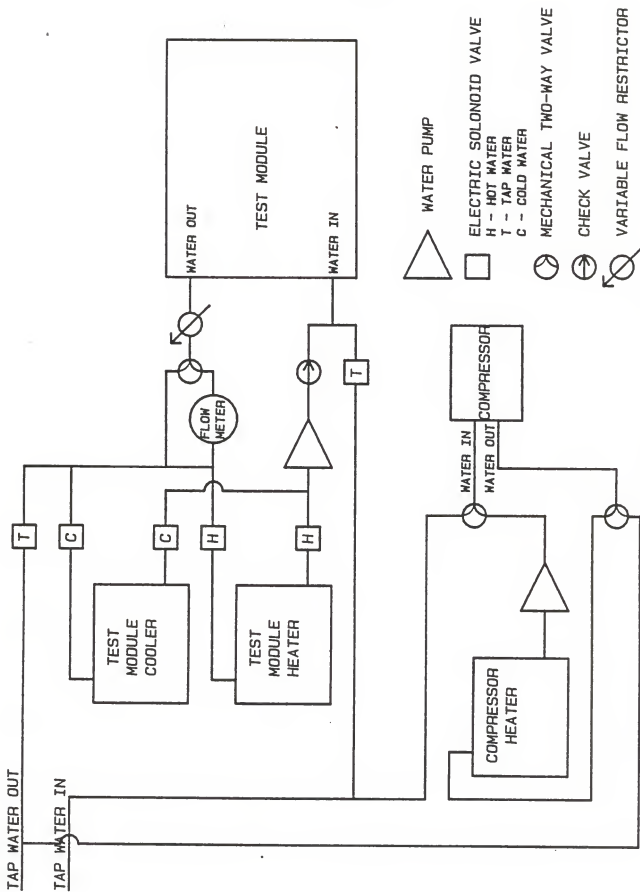


FIGURE B5. WATER CONTROL SYSTEM

DESIGN AND TESTING OF A MODULAR HYDRIDE HYDROGEN
STORAGE SYSTEM FOR MOBILE VEHICLES

by

DENNIS PATRICK SCHMIDT

B. S., Kansas State University, 1984

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

Department of Agricultural Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1985

ABSTRACT

As hydrogen becomes a more popular fuel candidate for internal combustion engines, a more efficient hydrogen storage system will be necessary. Even though gaseous and liquid hydrogen systems have been used for stationary storage, mobile storage of hydrogen in these phases creates severe problems. Currently, the most feasible form of mobile hydrogen storage is chemical reaction with special metals to form metal hydrides.

The main objective of this study was to design and build a volumetric-efficient modular metal hydride hydrogen storage system. Other objectives included the design and building of the storage system testing facility, and the completion of several preliminary tests exposing possible design problems so that later studies may be more focused.

A modular metal hydride hydrogen storage system has been designed and built. The module consists of a 0.5 micron porous stainless steel sleeve and a bayonet heat exchanger extending through the center of the sleeve. Hydrogen gas freely flows through the porous sleeve to be easily collected from the pressure vessel. The use of small diameter modules provides for expansion of the hydride material and the capability for making larger systems by adding additional modules. Although $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Ti}$ hydride (HY-STOR 102) was used in preliminary testing, other metal hydrides would work equally well in the modular system.

Activation of hydride to 83 percent of full expected activation level was obtained in six absorption-desorption cycles. Full activation of HY-STOR 102 hydride is expected after twelve to fifteen absorption-desorption cycles.

Plateau pressure-temperature relationships of the hydride may be accurately predicted with the use of the Van't Hoff equation. Constants for the Van't Hoff equation were experimentally determined and compared well with reference constants.

Limited heat transfer and temperature profile data was collected. Analysis of this data indicated that the proposed modular system may have problems meeting the dynamic hydrogen demands of an internal combustion engine due to poor hydride heat transfer. Further heat transfer tests need to be performed after the hydride has been fully activated. If the test module has inadequate heat transfer, a possible design modification would be the addition of radial fins extending into the hydride attached to the outer tube of the bayonet heat exchanger.