um 4076

Hydrides

Application

(NASA-TM-4076) RECHARGEABLE METAL HYDRIDES FOR SPACECRAFT APPLICATION (NASA) 37 p CSCL 21I

N89-10184

Unclas

H1/31 0166940

NASA Technical Memorandum 4076

Rechargeable Metal Hydrides for Spacecraft Application

J. L. Perry
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

National Aeronautics
and Space Administration

Scientific and Technical
Information Division

1988

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

TECHNICAL MEMORANDUM

RECHARGEABLE METAL HYDRIDES FOR SPACECRAFT APPLICATION

INTRODUCTION

A metal hydride is a chemical compound formed from the reaction of hydrogen with a metal or metal alloy. Many hydrides absorb and release hydrogen like a solid sponge at temperatures and pressures which are useful for storing hydrogen on board the space Station U.S. Laboratory module. Metal hydrides may also be used to pump, compress, or expand hydrogen gas. These uses may provide safer ways for handling hydrogen onboard spacecraft such as the Space Station.

Metal hydrides undergo a reversible reaction of a solid metal or metal alloy with gaseous hydrogen to form a solid metal hydride according to the reaction,

$$M + \tfrac{1}{2}xH_2 \leftrightarrows MHx + \text{heat} .$$

Several metals react directly and reversibly with hydrogen at room temperature and at or near atmospheric pressure. These metals include elements, solid-solution alloys, and intermetallic compounds. Hydrides formed from these materials are known as rechargeable metal hydrides. In these hydrides, the metal behaves like a solid sponge that can be charged and discharged at will.

Metal hydrides possess advantages for storing and transporting hydrogen in spacecraft over other methods such as compressed gas and cryogenic liquid storage. First, metal hydrides have a high volumetric packing density. Table 1 compares the packing density for some typical metal hydrides, compressed gas, and liquid. The volumetric density for hydrides is many times that of the conventional storage methods. Second, storage using metal hydrides requires low pressures. This has significant safety implications. Third, hydride storage is very energy efficient [1].

TABLE 1. HYDROGEN CONTENT OF VARIOUS MEDIA

Medium	wt% H	Volumetric Density (atoms H/ml, x 10^{-22})
H_2, liquid	100.0	4.2
H_2, gas at 10.1 MPa	100.0	0.5
MgH_2	7.6	6.7
UH_3	1.3	8.3
$FeTiH_{1.74}$	1.5	5.5
$LaNi_5H_{6.7}$	1.5	7.6

Although metal hydrides have some significant advantages over high pressure and cryogenic hydrogen storage, they do have some disadvantages. The metals and metal alloys used for rechargeable metal hydrides are extremely rare. This results in high costs for the alloys and a high cost for each kilogram of hydrogen stored. Also, the alloy weight is higher than conventional storage methods. However, this disadvantage has been shown to be insignificant for spacecraft applications when compared to high pressure storage.

The flexibility and advantages of metal hydrides make them very attractive for use on board the Space Station where significant quantities of hydrogen must be handled. These applications include the process fluid supply subsystem of the Process Material Management System on board the U.S. Laboratory Module, the life support system which may produce hydrogen as a by-product, and the propulsion system. However, significant development efforts will have to be made to apply metal hydrides to these areas of the Space Station and other spacecraft and hydriding phenomena must be fully understood.

METAL HYDRIDE THEORY

Rechargeable metal hydrides exist in several families of intermetallic compounds which consist of at least one element A that has a high affinity for hydrogen and a second element B that has a low affinity for hydrogen. Among the families of compounds which are practical for hydrogen storage are the AB and AB_5 compounds. These compounds exhibit good hydrogen storage properties at room temperature and atmospheric pressure.

AB Compounds

One of the most-used room temperature AB compounds is FeTi. It is relatively inexpensive but has some definite disadvantages. The first is high hysteresis. The alloy has a large hysteresis ratio resulting in a hydriding process which is not completely reversible. Second, FeTi has a low resistance to poisoning by oxygen. Finally, the alloy has a heating requirement for activation. FeTi can be combined with other elements such as Mn, Cr, Co, Ni, and V to produce an alloy which is more useful [1].

AB_5 Compounds

The most popular AB_5 compound is $LaNi_5$. This alloy has very attractive properties for use in storing hydrogen. These properties include convenient plateau pressures, low hysteresis, excellent kinetics, easy activation, and good resistance to poisoning. Because of its overall good performance properties as a rechargeable metal hydride, this alloy was selected as the candidate for use on the Space Station during the Phase B study [1].

Other Compounds

Several other compositions for metal hydrides exist. An example is the A_2B compounds of which Mg_2Ni is a member. This alloy is extremely lightweight and has a small hysteresis. Unfortunately, it requires a temperature of 573°K (300°C) for hydrogen desorption. Also the energy of reaction is high. These problems make it impractical for Space Station application. Other compounds are based on Mg, Zr, and Ti. These compounds show promise but their kinetics are very slow or they are unstable at room temperature and are not cost competitive with other compounds.

Hydride Phenomena

At normal temperatures and pressures, hydrogen cannot be condensed regardless of the amount of pressure applied. However, in the presence of AB or AB_5 compounds, a vapor pressure relationship is established between hydrogen gas and a solid form of hydrogen which is bound in the crystal structure of the metal alloy. The hydride equilibrium conditions are expressed in terms of pressure, temperature, and composition [2]. Figure 1 shows a sample equilibrium isotherm.

At point 1 in Figure 1, the metal phase and hydrogen are separate. A constant temperature is maintained between points 1 and 2 while the hydrogen pressure increases. As the hydrogen pressure increases, a small amount of hydrogen goes into solution in the metal phase. At point 2, the hydriding reaction begins and large quantities of hydrogen are absorbed at constant pressure. This pressure is known as the plateau pressure, P_p. The plateau is characterized by a two phase mixture of metal and metal hydride. At point 3, the alloy has been completely converted to the hydride phase and any increase in pressure results in only a small addition of hydrogen to the

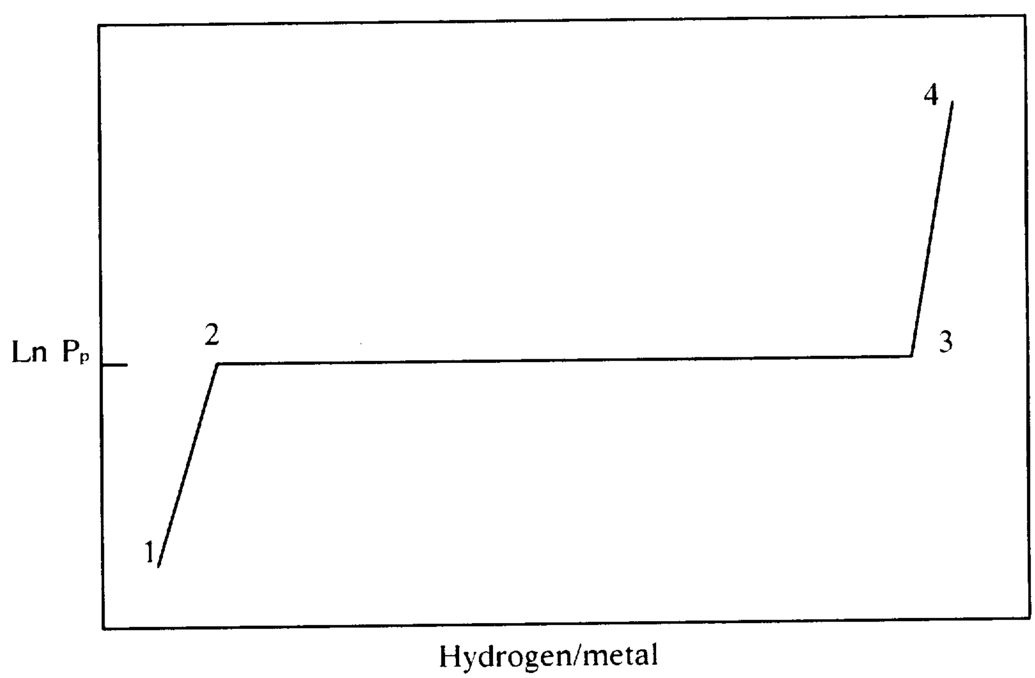

Figure 1. Ideal equilibrium isotherm.

hydride phase. This is the ideal behavior of metal hydrides. Ideal behavior is seen occasionally but in most practical hydriding reactions the plateau may be sloped slightly and some pressure hysteresis between absorption and desorption is observed. Hysteresis for $LaNi_5$ is small, making the alloy suitable for many applications.

Temperature Dependence

The hydriding reaction is very dependent on temperature. As the temperature increases so does the plateau pressure. The heat of reaction is also a factor since the absorption reaction is exothermic and the desorption reaction is endothermic. The plateau pressure is related to the absolute temperature by the van't Hoff equation

$$\ln(P/P_0) = \Delta H/RT + C$$

In this equation, T is the absolute temperature, ΔH is the enthalpy change per mole of H_2, R is the universal gas constant, and C is a constant related to the entropy change of the reaction. A family of isotherms can be plotted as $\ln(P_p/P_0)$ versus 1/T to obtain the van't Hoff plot for a particular material. The slope of the plot gives the value of ΔH. The van't Hoff plot for $LaNi_5$ is given in Figure 2. Data for this plot are tabulated in Appendix A. The enthalpy of reaction for $LaNi_5$ is -30861.57 J/mole H_2. This is for the absorption reaction. The same amount of energy must be supplied to the hydride during the desorption reaction.

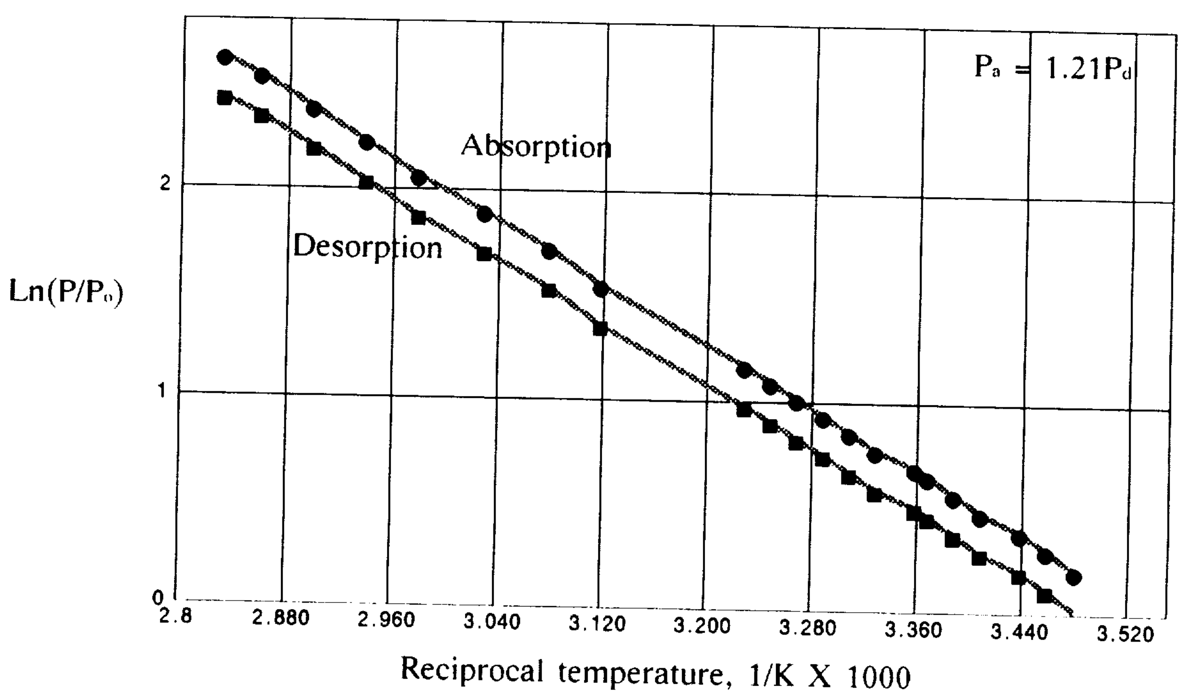

Figure 2. Van't Hoff relationship for $LaNi_5$.

Different hydrogen pressures may be provided simply by heating or cooling the hydride to a temperature corresponding to the pressure desired. By cycling the temperature of a metal hydride, hydrogen may be absorbed and desorbed under various conditions. This flexibility makes a metal hydride an excellent medium for handling various hydrogen operations ranging from storage to compression.

ENGINEERING PROPERTIES OF METAL HYDRIDES

Several engineering properties are important to the application of metal hydrides to storage and other problems. These include the plateau pressure, hysteresis, enthalpy of reaction, hydrogen capacity, chemical stability, reaction kinetics, and tolerance to poisoning. These properties aid in selecting a particular metal hydride for a specific use. Engineering properties for $LaNi_5$ are summarized in Appendix B.

Plateau Pressure

The plateau pressure and associated operating pressure of the metal hydride depend on the application. Plateau pressure is directly related to the metal composition. By altering the composition, a metal hydride can be tailored specifically to meet the pressure and temperature requirements of a particular application [1].

Hysteresis

Practical application of metal hydrides to hydrogen storage and other uses requires a small difference between the absorption and desorption pressures. Hysteresis varies according to the alloy used in a manner which is not clearly understood. However, empirical knowledge can show which systems exhibit small hysteresis and thus can be used practically [1]. The degree of hysteresis is expressed as the ratio between the absorption pressure and the desorption pressure, P_a/P_d [3].

Enthalpy of Reaction

The enthalpy of reaction is very important from a container design viewpoint. Energy is generated during the exothermic absorption reaction while energy must be provided to sustain the endothermic desorption reaction. As a result of the energy requirements to support the hydride cycling, the hydride container must be an effective energy exchanger [1]. Most applications require rapid cycling to be effective and the more efficiently the container can exchange energy during each cycle, the more use can be obtained from the hydride.

Hydrogen Capacity

The hydrogen capacity is a function of the crystal structure and base composition of the hydride-forming alloy. Metallurgical factors which result from alloy preparation may also be involved. The hydrogen capacity may also drive the size and cost of a particular hydride system since it varies according to the desired pressure range required for the application [3]. Large volume changes are also associated with the absorption and desorption reactions. For example, $LaNi_5$ may expand by as much as 25 percent during absorption and contract by a similar amount during desorption. This expansion and contraction must be considered in container design [1].

Chemical Stability

The chemical stability of the compound must be considered for high temperature applications. Under certain conditions some undesireable reactions can occur resulting in reduced performance of the compound. An example is disproportionation. $CaNi_5$ undergoes the reversible reaction,

$$CaNi_5 + 3H_2 \leftrightarrows CaNi_5H_6 \ ,$$

near room temperature. However, the disproportionation reaction is thermodynamically preferred.

$$CaNi_5 + H_2 \leftrightarrows CaH_2 + 5Ni$$

At high temperatures, diffusion of the metal atoms can be significant and result in the disproportionation reaction being favored over the reversible reaction. The result is a loss of reversible capacity. Most compounds used for reversible metal hydrides are unstable with respect to disproportionation and their tendency to disproportionate varies from compound to compound. Most compounds which are useful at room temperature exhibit more resistance to disproportionation than those used in high temperature applications [1].

A second form of chemical instability lies in degradation resulting from temperature induced cycling. Most applications for reversible metal hydrides involve repeated absorption-desorption cycles. Studies of this phenomenon have concluded that $LaNi_5$ at 2.17 MPa (315 psia) cycled between room temperature and 573°K (300°C) retains only 26 percent of its original hydrogen-absorbing capacity after 1550 cycles at a rate of three cycles per hour. An extrapolation of the data of these studies indicates that the alloy would lose 50 percent of its absorbing capacity at room temperature after 4×10^5 cycles at a rate of one cycle every ten minutes for eight years. The degradation rate also depends on the pressure and rates of absorption and desorption [4]. A reasonable limit for replacing a metal hydride to maintain its efficiency would be after 50 percent of its original absorbing capacity had been lost. This maintenance would occur after a relatively long service life and shows that metal hydrides would require little or no maintenance during its useful life.

Reaction Kinetics

The reaction kinetics of metal hydrides are very important to the selection of operating temperatures, pressures, and cycle times for hydrogen storage and other applications. Kinetics are a function of the alloy composition and its crystal structure. Investigations of the reaction kinetics of $LaNi_5$ at room temperature show that the absorption and desorption reaction rates are extremely fast and are limited by energy transfer in practical applications. A properly designed container with good energy transfer characteristics would provide an excellent means for rapidly storing and providing hydrogen [5,8].

Surface Poisoning

Impurities in the hydrogen used in the absorption or desorption reaction results in a loss of hydrogen absorption or desorption kinetics. Gaseous impurities such as O_2, H_2O, and CO may form a surface film or structure which poisons the surface catalytic properties of the alloy. The poisoning may result from surface film formation, surface physisorption, or surface chemisorption. Little information is available about the actual mechanisms of hydride surface poisoning. Cyclic poisoning tests of several alloys show that these impurities do reduce the ability of hydride alloys to absorb and desorb hydrogen. $LaNi_5$ shows the most resistance to surface poisoning when compared to alloys of FeTi and Mn-substituted FeTi. Hydrogen containing 300 ppm of oxygen and water cause $LaNi_5$ to lose some absorption-desorption ability after approximately four 0.5-hr cycles. However, the alloy recovers and returns to an absorption-desorption ability which is very close to its original ability. Hydrogen containing 300 ppm of CO causes the alloy to lose its hydriding ability after approximately 16 of these cycles. Fortunately, it can be reactivated by using suitable procedures such as continued cycling or heating [6].

HYDROGEN STORAGE SAFETY

Conventional Storage

The main safety threats encountered when handling hydrogen are fire and explosion. These threats are present any time hydrogen is transported since the container can be damaged or ruptured releasing its contents into the laboratory module. For gaseous and liquid hydrogen storage, such a rupture would release all the contents of the container. Several minutes would be required for the spill to dissipate. On Earth this type of spill would be diluted by air and present a fire risk for several minutes. The time depends, of course, on the size of the spill. On board the Space Station and other spacecraft, the diluting atmosphere has a much smaller volume, causing an increased risk for explosion or fire. This risk causes the design of hydrogen storage containers, which cannot leak or rupture, to be extremely important. The high pressures and cryogenic temperatures involved in conventional storage techniques contribute to the risks of handling hydrogen. High pressures cause any leak or rupture to release hydrogen rapidly and cause the rupture itself to be dangerous since the storage container could be launched like a rocket. The cryogenic temperatures cause a risk of injury to personnel who may experience direct contact to their skin causing burns. Liquid hydrogen could also adhere to surfaces which are not easily accessed, causing a spill to be even more difficult to contain.

Hydride Storage

Storage using rechargeable metal hydrides requires low temperatures and pressures. This results in very little free hydrogen present at any time. If the container is damaged or ruptured the hydride would only liberate free hydrogen at a rate dependent on the hydride bed temperature, the ambient temperature, and the rate of energy transfer to and from the hydride bed [7]. Hydrogen may be released at a significant rate if the hydride reactor is operating at a high temperature, however, the rate can be reduced quickly by cooling the hydride bed as quickly as possible. Overall, the rechargeable metal hydride is safer since an explosive rupture is highly unlikely and any flame would be for only a brief time. An example is a test which involved firing incendiary shells into a hydride tank. This test resulted in only a brief flame [7].

SPACE STATION APPLICATIONS

Application of rechargeable metal hydrides to hydrogen handling problems on board the Space Station may be possible in several areas. Among these are as an accumulator between the electrolyzer and the CO_2 reduction process, an accumulator for excess hydrogen generated by the ECLSS, and hydrogen supply for U.S. Laboratory experiments and operations.

ECLSS Application

A hydrogen accumulator can be useful to reduce transient flow problems between the electrolyzer and the CO_2 reduction process. This application can also prove useful for collecting any residual hydrogen generated by the ECLSS. A container having a 10.2 kg mass and 1.25 percent useable hydrogen by weight may be used. The reference hydride is an AB_5 type. Assuming the electrolyzer produces 1.13 kg/day of hydrogen, the hydride accumulator would require a 200 W load to be removed. This load may be removed by water flowing at 0.6 liters/min with a 5°K temperature differential between the inlet and exit temperatures. The 293°K (20°C) equipment loop may be used for the shell side fluid [2].

U.S. Laboratory Application

Rechargeable metal hydrides can be used on board the U.S. Laboratory Module for storing hydrogen for experiment use or for collecting waste hydrogen from experiments. A suggested system would collect hydrogen from the ECLSS which is not used by the CO_2 reduction system. This application is summarized in Figures 3 and 4. Hydrogen is generated by the electrolyzer at 298°K (25°C) and 1.79 kPa (26 psia). When the Bosch process is used for CO_2 reduction, approximately 0.206 kg H_2/day is left over. A survey of experiment requirements shows that 0.006 kg H_2/day is required to maintain a 14 experiment set. This leaves 0.200 kg H_2/day which must be stored or used as a fuel source. Once the hydride has been charged, it is replaced by another hydride container. The charged container is then taken to the laboratory module where it is discharged to support experiment operations.

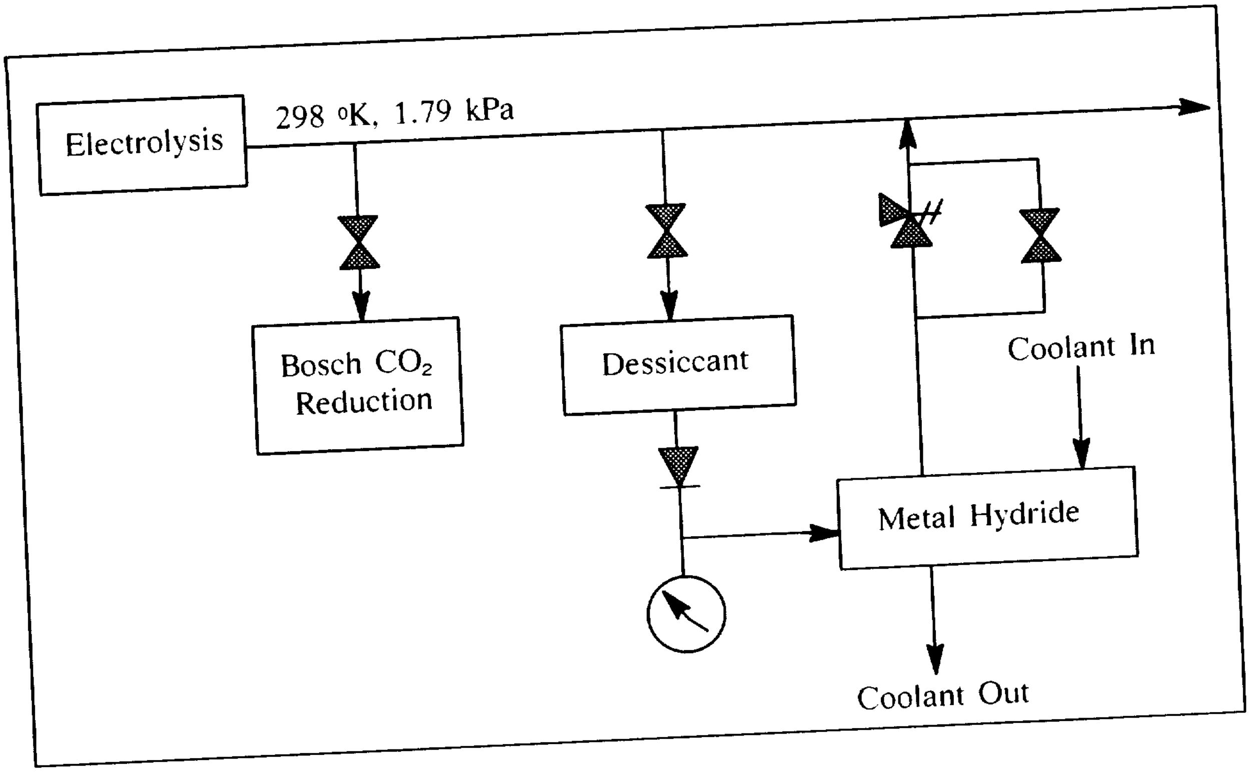

Figure 3. Charging a metal hydride.

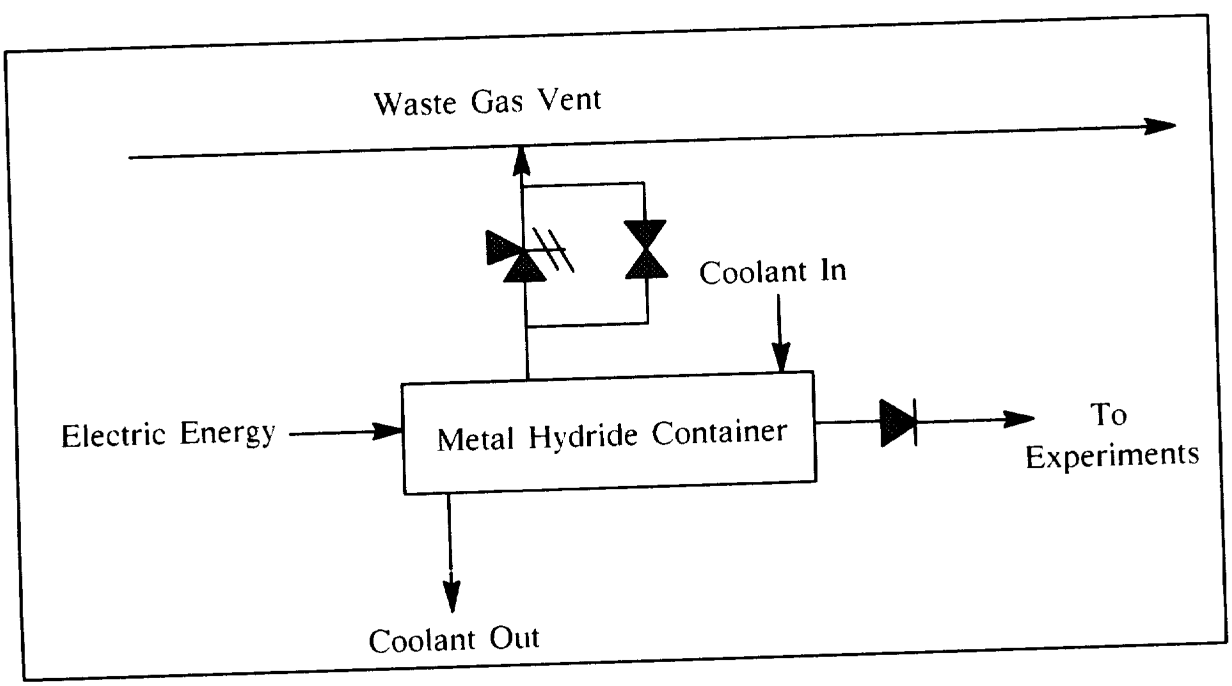

Figure 4. Discharging a metal hydride.

A REFERENCE HYDRIDE CONTAINER

Container Features and Geometry

The design of a container for rechargeable metal hydrides must perform several functions. It has to be a pressure vessel, a heat exchanger, a gas distribution system, and a filter, in addition to containing the hydride powder. The container cannot provide these functions at optimal levels since some conflict exists between them, therefore, the overall design is a compromise among the tasks it performs.

The container provides a closed volume for the powdered alloy which absorbs and desorbs hydrogen. The powdered alloy is contained in tubes like those found in a shell and tube heat exchanger. Each tube also contains a filter and a copper brush which enhances heat transfer. Seven tubes are included in each container. The shell is large enough to reduce pumping power requirements of fluids flowing axially along the tubes. The tubes have an outside diameter of 1.270 cm and an inside diameter of 1.2192 cm. Similarly, the shell has an outside and inside diameter of 4.445 cm and 4.343 cm, respectively. The tubes are capable of holding 5 g H_2/meter of tube. The maximum tube length is 40 cm and the overall container length is 44.44 cm. This design has a 0.000690 m^3 volume and a total dry mass of 1.45 kg. Sizing calculations are summarized in Appendix C. Fourteen grams of hydrogen can be stored in a single container. This is a 2.5 day supply of hydrogen for a 14 experiment payload complement. Figure 5 shows a metal hydride container [2].

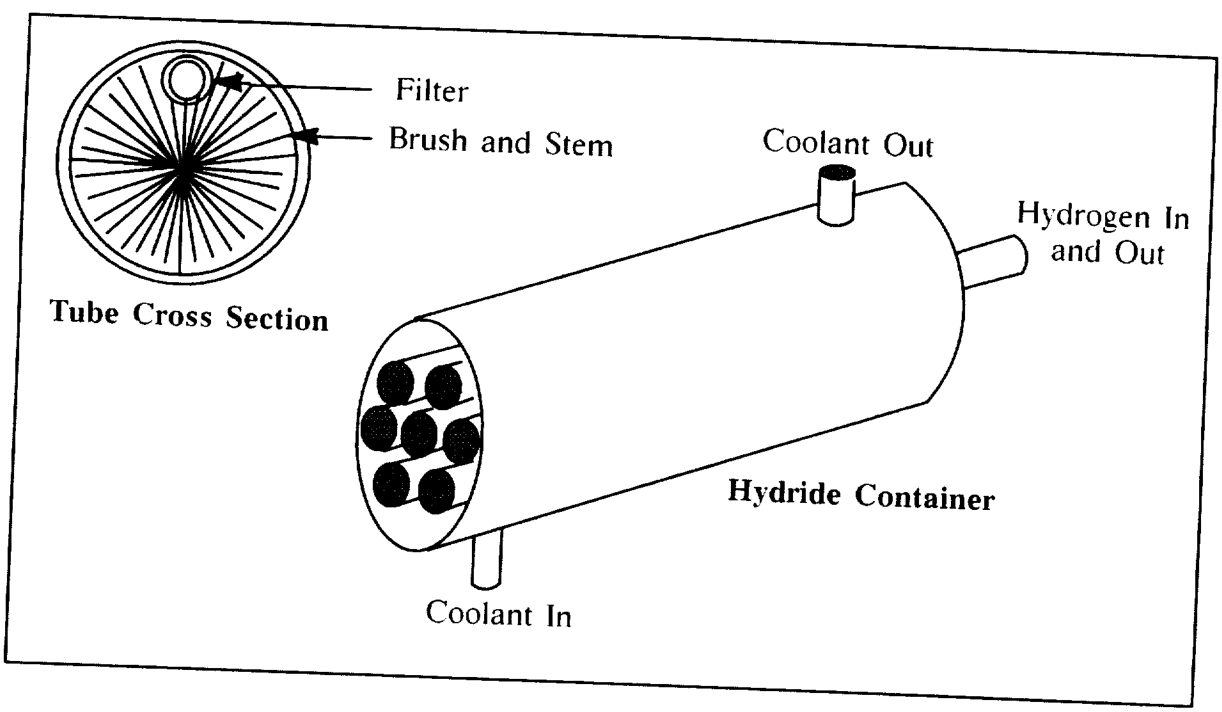

Figure 5. A rapid-cycling hydride container.

Materials of Construction

For Space Station use, the container used must also be lightweight. This requirement can be met by selecting a material with low density and high yield stress. Many of the low density metals which may be used structurally, such as magnesium and titanium, are attacked by hydrogen and may become brittle. However, aluminum shows excellent resistance to hydrogen in addition to its good structural properties. It should be noted that high temperature applications would require using stainless steels and other more corrosion resistant alloys.

Energy Requirements

Energy requirements for a typical hydride container are based on the geometry of the container and the hydrogen absorption and desorption rates required. In order to provide the 5.54 g H_2/day required by the 14 experiment set, energy must be removed during the absorption reaction and supplied during the desorption reaction. The reference container has 1117.2 cm^2 of total surface area available for energy transfer. An energy balance on each tube yields an energy flux of 0.00667 W/cm^2 or 52.2 W during the entire hydride charging process. This equals a total flux of 0.0467 W/cm^2 for the entire exchanger. During the desorption reaction, energy must be supplied at the same rate it is removed during the absorption reaction. Coolant, assumed to be water at 277°K (4°C) inlet temperature and 282°K (9°C) outlet temperature, must be supplied at 0.0025 kg/s to provide the absorption rate necessary to support the experiments. The energy input for desorption requires a heater which will provide 102.9 W. This heater will be able to raise the hydride temperature from room temperature, 298°K, to its upper operating limit, 353°K, in five minutes. This will provide a plateau pressure of 1.17 MPa (169.3 psia). The energy required to sustain the desorption reaction is small compared to the heating requirement. It is 0.981 W. The same amount of energy, 102.9 W, must be removed by the coolant when the hydride is being cooled to room temperature from its maximum operating temperature. This requires 0.00294 kg/s of water at 277°K inlet temperature and a 282°K outlet temperature. For an entire cycle which includes absorption, hydride heating to its maximum operating temperature, sustained desorption, and cooling to the original temperature, the total net energy requirement is 51.22 W removed. Appendix D summarizes the energy requirement calculations.

COMPARISON TO BOTTLED STORAGE

Rechargeable metal hydrides offer an alternative to bottled storage, but to actually compare the two storage techniques requires comparison of weight and volume for both the hydride container and bottled storage. This comparison has been made for several hydrogen storage amounts to show the mass and volume characteristics for varying requirements.

Volume Comparison

The total volume for a reference hydride container 4.445 cm in diameter and 44.44 cm long is 0.000690 m^3. Each container can hold 14.0 grams H_2. This is equivalent to a 2.5 day supply of hydrogen for the U.S. Laboratory. Bottled storage for laboratory use would be approximately 0.00230 m^3 and the same amount of hydrogen would be stored in this container at 7.85 MPa (1138 psia). An external storage concept proposed during the Phase B study provides 0.0116 m^3 of storage from two storage tanks. As the amount of hydrogen storage is increased, the volume for the two internal storage techniques also increases. Two days of storage requires a hydride container which occupies 0.000560 m^3 while a single 0.00230 m^3 bottle will store the hydrogen at 5.92 MPa (858.2 psia). Up to 15 days of storage has been investigated. This storage amount requires six hydride containers with a total volume of 0.00414 m^3 while bottled storage requires six bottles with a total volume of 0.0138 m^3. Figure 6 illustrates this comparison.

Mass Comparison

The total mass of the storage techniques is also important to spacecraft application. The reference hydride container has a mass of 1.45 kg while the bottle's mass is 7.0 kg. The Phase B external storage option has a total mass of 68.8 kg. For up to 15 days of storage, the hydride container mass climbs to 8.70 kg while the bottled storage mass reaches 42.0 kg. This comparison is shown by Figure 7.

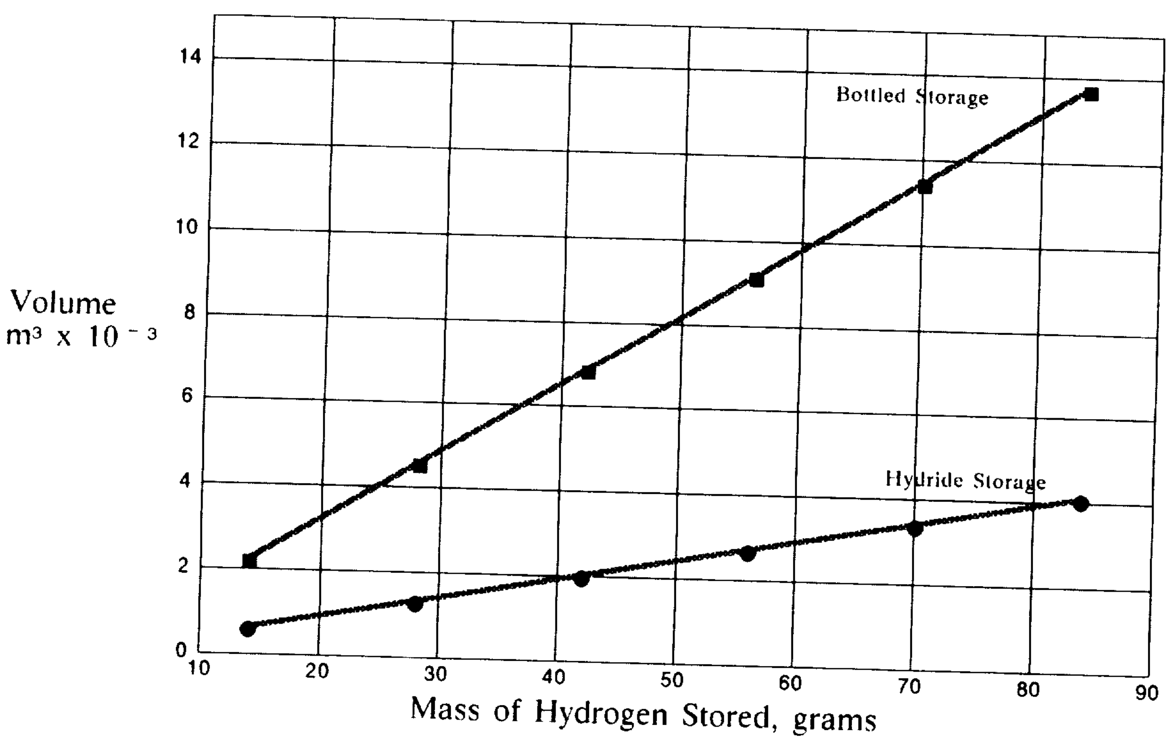

Figure 6. Storage volume comparison.

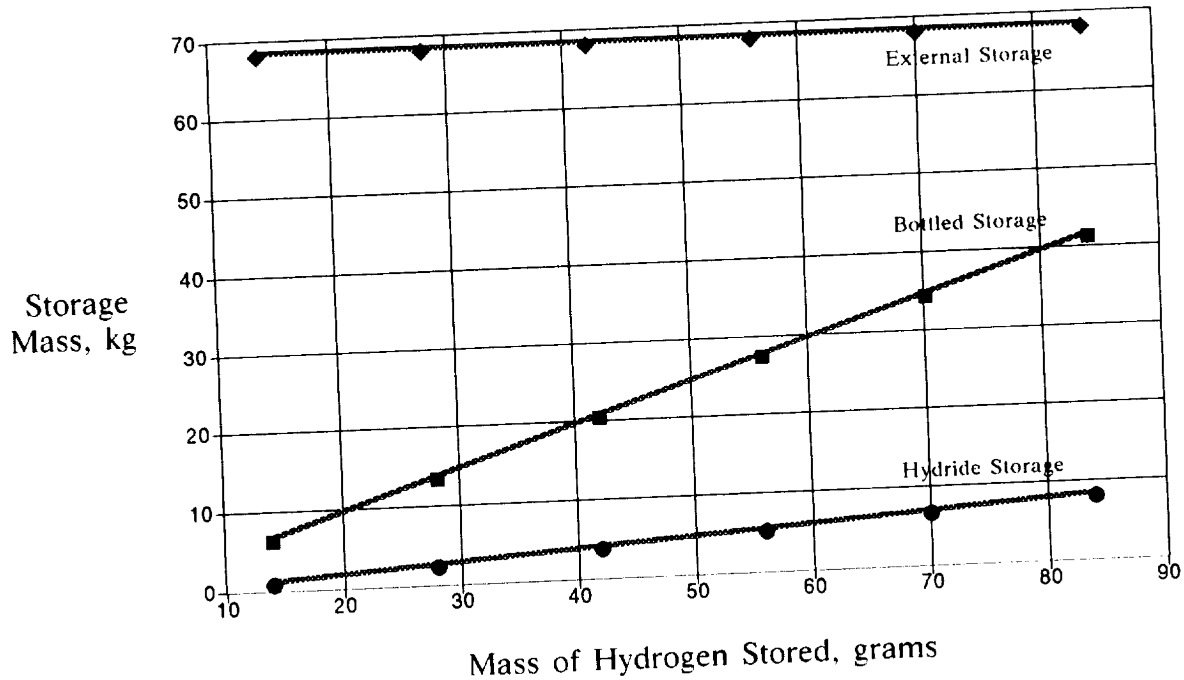

Figure 7. Storage mass comparison.

Pressure Comparison

A third area of comparison for the storage techniques is pressure. At room temperature, the hydride container stores hydrogen at 2.00 kPa (29 psia) while bottled storage requires 7.85 MPa (1138 psia). The external storage pressure depends on the amount of hydrogen stored since the volume does not vary in this comparison. For 2.5 days of storage, the pressure is 1.49 kPa (21.60 psia) while 15 days of storage results in a pressure of 8.97 kPa (130.06 psia). Figure 8 shows the pressure differences beteeen the three storage techniques as the mass of hydrogen stored increases.

Storage Technique Safety

The overall safety of a storage technique is a combination of several factors. Among these are the storage pressure and volume. Bottled storage requires higher pressures for storing an equal amount of gas as a rechargeable metal hydride at the same temperature. In the event of a storage container failure such as a rupture or valve failure, a large amount of hydrogen may be released into the laboratory if the container is a pressurized bottle. The bottle contains free hydrogen and the higher the pressure, the more rapid the leak. This implies that any bottled storage should be low pressure, small volume. Unfortunately, this approach results in a large number of bottles to meet the hydrogen supply requirements. Metal hydride storage is a low pressure technique and very little hydrogen is present in its free form. Therefore, a container failure would not release all the hydrogen into the laboratory. The major safety risk with metal hydrides is the high temperatures which may be necessary to provide higher pressure hydrogen. These temperatures may not be necessary if a compressor is used but this introduces a mechanical system which may leak or be more prone to failure. These factors indicate rechargeable metal hydrides may be safer with respect to leaks and container failure.

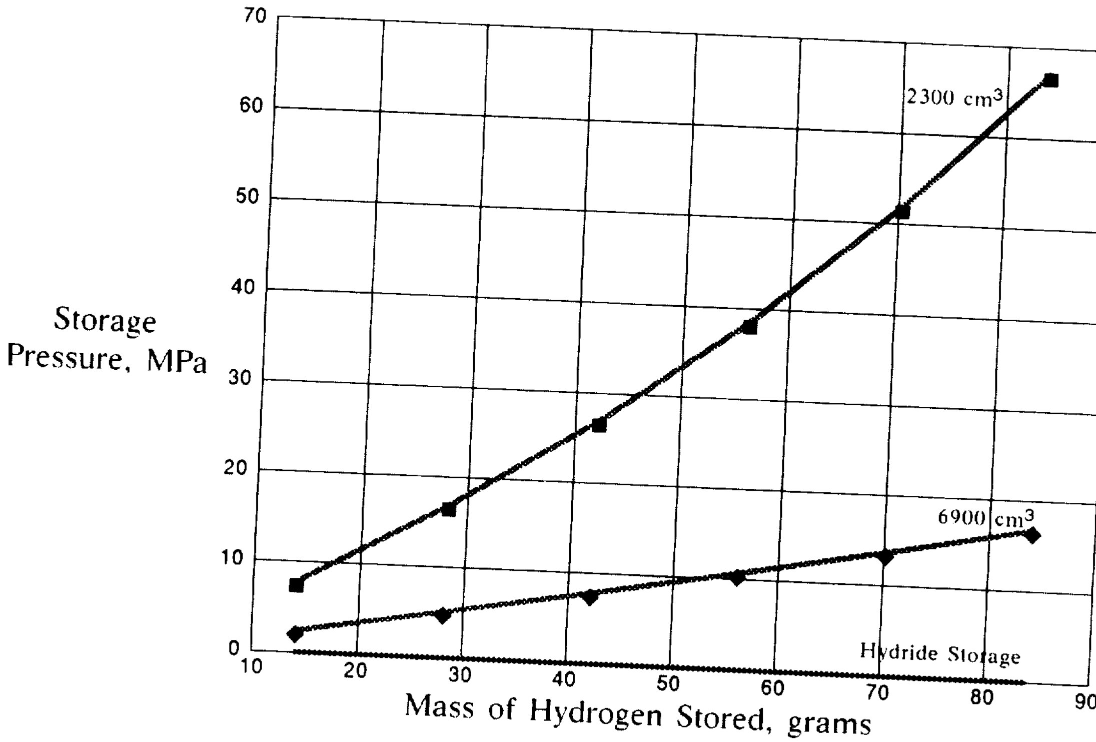

Figure 8. Storage pressures at 298°K.

CONCLUSIONS

Analysis of the techniques available for storing hydrogen on board the Space Station indicates that rechargeable metal hydrides may be competitive with conventional storage techniques such as bottled and liquid storage. However, a substantial amount of development work and further analysis of specific applications is required to determine the actual usefulness of rechargeable metal hydrides in spacecraft. Preliminary analysis shows the volume required by the hydride container is less than storage bottles. The hydride container mass is also less. In addition, lower pressures are needed by metal hydrides to store hydrogen at room temperature. The lower pressure and small amount of free hydrogen present in a hydride container may increase the safety of the storage technique over bottled storage. Energy exchange is required for cycling the hydride between absorption and desorption but the net energy requirement is relatively small. The apparent advantages rechargeable metal hydrides have over conventional storage techniques in volume, mass, and safety make them very attractive for spacecraft use.

APPPENDIX A

TABULATED ABSORPTION AND DESORPTION DATA

Absorption and Desorption Data for $LaNi_5$

Desorption Pressure MPa	ln(P_d/P)	Absorption Pressure, MPa	ln(P_a/P)	Temperature K	1/T x 10^{-3} K^{-1}
0.0866	-0.157	0.105	0.0344	283	3.53
0.0949	-0.065	0.115	0.126	285	3.51
0.104	0.0266	0.126	0.218	287	3.48
0.114	0.116	0.138	0.307	289	3.46
0.124	0.204	0.150	0.394	291	3.44
0.136	0.291	0.164	0.482	293	3.41
0.148	0.377	0.179	0.568	295	3.39
0.161	0.462	0.194	0.652	297	3.37
0.168	0.504	0.203	0.694	298	3.36
0.182	0.587	0.220	0.777	300	3.33
0.198	0.669	0.239	0.860	302	3.31
0.214	0.750	0.259	0.940	304	3.29
0.232	0.829	0.281	1.020	306	3.27
0.251	0.908	0.304	1.098	308	3.25
0.272	0.986	0.329	1.176	310	3.23
0.395	1.360	0.478	1.551	320	3.12
0.472	1.538	0.571	1.729	325	3.08
0.561	1.711	0.679	1.902	330	3.03
0.664	1.879	0.803	2.070	335	2.98
0.781	2.042	0.945	2.233	340	2.94
0.915	2.201	1.107	2.391	345	2.90
1.067	2.354	1.291	2.545	350	2.86
1.168	2.444	1.413	2.635	353	2.83

APPENDIX B

ENGINEERING PROPERTIES

Metal Hydride Calculations and Notes

Reaction: $LaNi_5 + 3H_2 \leftrightarrows LaNi_5H_6$

Plateau Pressure-Temperature Relationship:

$$M + \tfrac{1}{2}xH_2 \leftrightarrows MH_x$$

van't Hoff relation: $\ln(P/P_o) = \tfrac{2}{x}\Delta H/RT + C = A/T + C$

$$A = -3712\ K \text{ and } C = 12.96$$

Absorption-desorption Enthalpy:

$$\Delta H/R = -3712\ K \Rightarrow (-3712\ K)(8.314\ J/mole{\cdot}K) = \Delta H$$
$$\Delta H = -30861.57\ J/mole$$

Solution for Plateau Pressure:

Desorption: $\ln(P_d/P_o) = -3712/T + 12.96$

$P_d = P_o Exp[(-3712/T) + 12.96]$

where $P_o = 1.01$ kPa (14.696 psia)

Absorption: $P_a/P_d = 1.21 \Rightarrow P_a = 1.21P_d$

or $P_a = 1.21P_o Exp[(-3712/T) + 12.96]$

Solution for Plateau Temperature for Absorption and Desorption:

$$\ln(P/P_o) = -3712/T + 12.96$$
$$T\ln(P/P_o) = -3712 + 12.96T$$
$$T = -3712/[\ln(P/P_o) - 12.96]$$

Engineering Properties of $LaNi_5$:

$\Delta H_a = -30861.57$ J/mole H_2 $\quad$ $\Delta H_d = 30861.57$ J/mole H_2

$LaNi_5$: $\rho = 8.3\ g/cm^3$ (ref 1) $\quad$ $C_p = 0.364$ J/g·K (ref 2)

$LaNi_5H_6$: $\rho = 6.59\ g/cm^3$ (ref 1) $\quad$ $C_p = 0.435$ J/g·K (ref 2)

Hydrogen mass percent = 1.38; 80%-90% exchanged in a cycle

Hysteresis pressure ratio = 1.21 = P_a/P_d (ref 3)

Powder thermal conductivity = 1.32 W/m·K (ref 2)

Hydrogen requirements:

Excess hydrogen: 18.57 kg/90 days or 0.206 kg/day

Hydrogen required by experiments: 0.44 kg/90 days + 10%

= 0.499 kg/90 days

$\Rightarrow$ 0.00554 kg/day

APPENDIX C

HYDRIDE CONTAINER SIZING CALCULATIONS AND BOTTLED STORAGE CALCULATIONS

Laboratory Hydride Exchanger Sizing (for maximum exchanger size):

Maximum tube length = 40 cm
Reference exchanger holds 5 g H_2/meter of tube
Seven tubes are in a single exchanger
Total tube length = (40 cm)(7) = 280 cm = 2.80 m

Amount of hydrogen stored in a single exchanger:

$$(5 \text{ g } H_2/\text{m})(2.80 \text{ m}) = 14.0 \text{ g } H_2$$

Provides ~ (14.0 g)/(5.54 g/day) = 2.5 days of hydrogen storage

Exchanger dimensions:

Shell I.D. = 4.343 cm
Shell O.D.= 4.445 cm

Tube I.D. = 1.2192 cm
Tube O.D.= 1.270 cm

Exchanger length:

$$L = \text{tube length} + 4.44 \text{ cm} = 40 \text{ cm} + 4.44 \text{ cm} = 44.44 \text{ cm}$$

Exchanger volume:

$$V = \tfrac{1}{4}\pi D^2 L = \tfrac{1}{4}\pi(4.445 \text{ cm})^2(44.44 \text{ cm})$$
$$V = 689.6 \text{ cm}^3$$

Hydride mass:

$$M_H = (\pi/4)\rho_H D^2 L$$

ρ_H = 3.95 g/cm^3 (Ref. 2, p. B-2)
D = 1.2192 cm
L = 280 cm

$$M_H = 1291 \text{ g} = 1.291 \text{ kg}$$

Tube mass:

$$M_t = (\pi/4)\rho_t(D_1^2 - D_2^2)L$$
$$M_t = 75.1 \text{ g} = 0.0751 \text{ kg}$$

ρ_t = 2.70 g/cm^3

Shell mass:

$$M_s = (\pi/4)\rho_s(D_1^2 - D_2^2)L \qquad \rho_s = 2.70\ g/cm^3$$
$$L = 44.44\ cm$$

$$M_s = 84.5\ g = 0.0845\ kg$$

Total dry mass:

$$M_{TOT} = M_H + M_t + M_s$$
$$M_{TOT} = 1.291\ kg + 0.0751\ kg + 0.0845\ kg = 1.451\ kg$$

Exchanger characteristics summary:

Length: 44.44 cm
Volume: 689.6 cm^3
Hydride mass: 1.291 kg
Tube mass: 0.0751 kg
Shell mass: 0.0845 kg
Hydrogen mass stored: 0.0140 kg
Days of storage supply: 2.5

Shell I.D.: 4.343 cm
Shell O.D.: 4.445 cm
Tube I.D.: 1.2192 cm
Tube O.D.: 1.270 cm

Exchanger material: 6016 Al, TIG welded joints, post assembly heat treat to T-6 in vacuum

Note: Austenitic stainless steel or inconel is required for high temperature applications.

Bottled Hydrogen Comparison:

Bottle volume for lab use: 2300 cm^3

14.0 g hydrogen stored = 6.94 moles hydrogen

Redlich-Kwong Equation of State (Properties of Gases and Liquids. Reid, et al.)

$P = RT(V-b) - a/[T^{0.5}V(V + b)]$
$T = 298$ K $\quad\quad T_c = 33.2$ K
$R = 82.06$ cm^3 atm/mol K $\quad\quad P_c = 12.8$ atm

$a = [9(2^{0.333} - 1)]^{-1}R^2T_c^{0.5}P_c = 1428283.133$ cm^6 atm/mol^2 $K^{1.5}$

$b = [(2^{0.333} - 1)/3]RT_c/P_c = 18.44$ cm^3/mol

Solve for the bottled pressure:

$P = (82.06)(298)/\{[(2300)/(6.94)] - 18.44\} - 1428283.133/\{(298)^{0.5}[(2300/6.94) + 18.44]\}$
$P = 77.4$ atm = 7.84 MPa

Boeing End Item Data Book: Hydrogen Storage

2 storage tanks: 34.4 kg, 0.48 m diameter each
Total mass: 68.8 kg

$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(0.48/2)^3 = 0.0579$ m^3

$P = (82.06)(298)/[(115812/n) - 18.44]$
$- 1428283.133/\{(298)^{0.5}[(115812/n)(115812/n + 18.44)]\}$
where n = moles of hydrogen stored

External Storage Summary:

Mass of Hydrogen Stored (grams)	Storage Pressure (MPa)
5.54	0.0588
11.08	0.118
14.00	0.149
28.00	0.298
42.00	0.447
56.00	0.597
70.00	0.746
84.00	0.897

Hydride and Bottled Storage Comparison

Mass of Hydrogen Stored (g)	Exchanger Mass (kg)	Days of Storage	Exchanger Volume (cm^3)	Number of Exchangers	Number of Bottles	Bottle Mass (kg)	Bottle Pressure (MPa)	Bottle Volume (cm^3)
5.54	0.579	1.0	314.6	1	3	6	15.47	1320
11.08	1.150	2.0	560.2	1	1	7	5.92	2300
14.00	1.450	2.5	689.7	1	1	7	7.84	2300
28.00	2.900	5.0	1379.4	2	2	14	7.84	4600
42.00	4.350	7.5	2069.1	3	3	21	7.84	6900
56.00	5.800	10.0	2758.8	4	4	28	7.84	9200
70.00	7.250	12.5	3448.5	5	5	35	7.84	11500
84.00	8.700	15.0	4138.2	6	6	42	7.84	13800

Bottled Gas Storage Pressures at 298 K

Volume (cm^3)	Mass of Hydrogen Stored (g)	Storage Pressure MPa
2300 (7 kg 10 cm x 36 cm)	5.54	3.03
	11.08	6.19
	14.00	7.92
	28.00	16.84
	42.00	26.94
	56.00	38.50
	70.00	51.84
	84.00	67.40
6900 (14 kg 15 cm x 23 cm)	5.54	0.993
	11.08	2.01
	14.00	2.54
	28.00	5.18
	42.00	7.92
	56.00	10.77
	70.00	13.74
	84.00	16.84
126300 (86 kg 38 cm x 137 cm)	5.54	0.0539
	11.08	0.107
	14.00	0.137
	28.00	0.272
	42.00	0.410
	56.00	0.547
	70.00	0.685
	84.00	0.823
438900 (590 kg 57 cm x 305 cm)	5.54	0.0155
	11.08	0.0310
	14.00	0.0392
	28.00	0.0784
	42.00	0.118
	56.00	0.157
	70.00	0.197
	84.00	0.236

APPENDIX D

ENERGY REQUIREMENT CALCULATIONS

Energy Analysis of a $LaNi_5$ Alloy:

Energy Balance in Cylindrical Coordinates

$$\rho C_p(\partial T/\partial t + V_r\partial T/\partial r + V_\theta\partial T/\partial\theta + V_z\partial T/\partial z) = k[(1/4)\partial/\partial r(r\partial T/\partial r) + (1/r^2)\partial^2T/\partial\theta^2 + \partial^2T/\partial z^2]$$
$$+ 2\mu\{(\partial V_r/\partial r)^2 + [(1/r)(\partial V\theta/\partial\theta + V_r)]^2 + (\partial V_z/\partial z)^2\}$$
$$+ \mu\{[\partial V\theta/\partial z) + (1/r)\partial V_z/\partial\theta]^2 + (\partial V_z/\partial r + \partial V_r/\partial z)^2 + [(1/r)\partial V_r/\partial\theta + r(\partial/\partial r)(V\theta/r)]^2\}$$
$$+ S$$

where $S = N\Delta H$

$S > 0$ for an endothermic reaction
$S < 0$ for an exothermic reaction

Simplification gives:

$$\rho C_p(\partial T/\partial t) = k[(1/r)(\partial/\partial r)(r\partial T/\partial r) + S$$

Boundary condition 1: at $r=0$, q_r=finite
Boundary condition 2: at $r=R$, $T=T_o$
Initial condition: at $t=0$, $T=T_o$ for all r

Integrate the right side of the energy balance equation:

$$\rho C_p(\partial T/\partial t)(r^2/2) - Sr^2/2 + C_1 = k(r\partial T/\partial r)$$ at B.C. 1, q_r = finite $\therefore$ $C_1 = 0$

But $q_r = -k(\partial T/\partial r)$

Substitute and solve for q_r:

$$q_r = Sr/2 - \rho C_p(\partial T/\partial t)(r/2)$$ at B.C. 2, $T/\ t = 0$

Energy flux at the hydride container tube surface:

$$q_r = SR/2$$

Energy Requirements for Hydride Cycling:

Calculate energy flux from absorption tube, heater requirements, and coolant flow rates:

1. Energy flux from a single hydride tube:

$q_r = Sr/2$ at $r=R$, $q_R = SR/2$

S = volumetric energy source term = $n\Delta H/V$

ΔH = heat of absorption or desorption
n = molar flow rate of hydrogen
V = hydride volume

Heat of absorption = -30861.57 J/mole hydrogen absorbed

$n = 5.54 \text{ g } H_2\text{/day x mol } H_2\text{/2.016 g } H_2 \text{ x day/24 hrs x hr/3600 s}$
$n = 0.0000318 \text{ mol } H_2\text{/s}$

$V = M_H/\rho_H = (\pi/4)D^2\rho_H L/\rho_H = (\pi/4)D^2L = (\pi/4)(1.219 \text{ cm})^2(40 \text{ cm/tube})$
$V = 46.68 \text{ cm}^3$ for a single tube of the reference exchanger

$S = (0.0000318 \text{ mol/s})(-30861.57 \text{ J/mol})/(46.68 \text{ cm}^3)$
$S = -0.0210 \text{ J/cm}^3\cdot\text{s}$

$q_r = [(-0.0210 \text{ J/cm}^3\cdot\text{s})(1.270 \text{ cm/2})]/2$
$q_r = -0.00667 \text{ watt/cm}^2$ for each tube of the reference exchanger

For the entire exchanger,

$$q_{r,TOT} = \sum_{i=1,7} q_{R,i} = 7(-0.00667 \text{ watt/cm}^2) = -0.0467 \text{ watt/cm}^2$$

Total surface area available for heat exchange:

$$A = 2\pi rL = \pi DL = \pi(1.270 \text{ cm})(280 \text{ cm}) = 1117.2 \text{ cm}^2$$

Energy release for absorption rate:

$$Q = q_{R,TOT}A = (-\ 0.0467\ \text{watt/cm}^2)(\ 1117.2\ \text{cm}^2) = -52.2\ \text{watts}$$

Water mass flow rate to sustain the absorption rate:

$$-Q = mC_p\Delta T$$
$$m = -Q/C_p\Delta T = -(-52.2\ \text{watts})(0.23901\ \text{cal/s·watt})/(1.0\ \text{cal/g·K})(5\ \text{K})$$
$$m = 2.5\ \text{g/s} = 0.0025\ \text{kg/s}$$

Energy required to heat the hydride from T_1 to T_2:

$$Q = \rho_H V_H C_{p,H}\Delta T$$
$$Q = (6.59\ \text{g/cm}^3)(7)(46.68\ \text{cm}^3)(0.435\ \text{J/g·K})(T_2 - T_1)$$
$$\text{Let } T_1 = 298\ \text{K}$$
$$T_2 = f(P_d) = -3712/[\ln(P_d/P) - 12.96]$$

Tabulated results of the energy calculation:

Temperature, T_2 (K)	Plateau Pressure (MPa)	Energy Required (J)
305	0.223	6556.9
310	0.272	11240.5
315	0.328	15924.0
320	0.395	20607.5
325	0.472	25291.1
330	0.561	29974.6
335	0.663	34658.1
340	0.781	39341.7
345	0.915	44025.2
350	1.067	48708.7
353	1.167	51518.9

Time for heat up and heater requirement for each exchanger:

$$q_H = m_H C_{p,H}(dT/dt) \qquad m_H = 1.29 \text{ kg}$$
$$q_H t = m_H C_{p,H}(T_2 - T_1) \qquad C_{p,H} = 0.435 \text{ J/g·K}$$
$$t = m_H C_{p,H}(T_2 - T_1)/q_H$$

Let T_2 = 353 K, T_1 = 298 K, and t = 300 s for the worst case:

$$q_H = (1290 \text{ g})(0.435 \text{ J/g·K})(353 \text{ K} - 298 \text{ K})/300 \text{ s}$$
$$q_H = 102.9 \text{ watts for each exchanger}$$

$$t = (5.45 \text{ s/K})(T_2 - T_1)$$

Results of heating time calculation:

Temperature, T_2 (K)	Plateau Pressure (MPa)	Heating Time (s)
305	0.223	38.15
310	0.272	65.40
315	0.328	92.65
320	0.395	119.90
325	0.472	147.15
330	0.561	174.40
335	0.663	201.65
340	0.781	228.90
345	0.915	256.15
350	1.067	283.40
353	1.167	299.75

Energy required to sustain the desorption reaction:
(The desorption reaction is endothermic)

$$q_d = n\Delta H = (0.0000318 \text{ mol } H_2/s)(30859.55 \text{ J/mol } H_2) = 0.981 \text{ watts}$$

Energy required to cool the hydride from T_2 to the initial temperature, 298 K:

$$q_c = mC_p(T_2 - T_1)/t$$
$$q_c = (1290 \text{ g})(0.435 \text{ J/g·K})(298 \text{ K} - 353 \text{ K})/300 \text{ s}$$
$$q_c = -102.9 \text{ watts}$$

Coolant flow rate to provide energy removal:
From the energy equation:

$$q_r = Sr/2 + \rho C_p(\ T/\ t)(r/2) \qquad \text{where } S = 0$$
$$q_r = \rho C_p(dT/dt)(r/2) \qquad \text{separate variables and integrate}$$
$$\int_0^t q_r dt = -\rho C_p(r/2)\int_{T_1}^{T_2} dT$$
$$q_r t = \rho C_p(r/2)(T_2 - T_1)$$
$$q_r = \rho C_p(r/2t)(T_2 - T_1)$$

$$q_r = \{|(3.95 \text{ g/cm}^3)(0.3995 \text{ J/g·K})(1.270 \text{ cm}/2)|/2(300 \text{ s})\}(298 \text{ K} - 353 \text{ K})$$
$$q_r = -0.0919 \text{ watt/cm}^2$$

$$Q_c = q_r A_{TOT} = mC_p\Delta T$$
$$Q_c = -(0.0919 \text{ watt/cm}^2)(1117.2 \text{ cm}^2) = -102.6 \text{ watts removed}$$

$$m = Q_c / C_p\Delta T$$
$$m = 102.6 \text{ watts}/(4.184 \text{ J/g·K})(282 \text{ K} - 277 \text{ K})$$
$$m = 4.18 \text{ g/s} = 0.00418 \text{ kg/s}$$

Net energy requirment for an entire cycle:

$$Q_{TOT} = Q_a + Q_{Heat} + Q_d + Q_c$$

Cycle from T = 298 K to T = 353 K and back to T = 298 K

$$Q_{TOT} = -52.2 \text{ watts} + 103 \text{ watts} + 0.981 \text{ watts} - 103 \text{ watts} = -51.22 \text{ watts}$$
51.22 watts must be removed

REFERENCES

1. Sandrock, G. D., and Huston, E. L.: Chemtech, Vol. 11(12), December 1981, pp. 754-762.

2. Egan, G. J.: Investigation of Metal Hydrides for Integration of Spacecraft Hydrogen Resources. NAS8-35270, Hydrogen Consultants, Inc., July 1985.

3. Huston, E. L., and Sandrock, G. D.: Engineering Properties of Metal Hydrides. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 435-443.

4. Cohen, R. L., West, K. W., and Wernick, J. H.: Degradation of $LaNi_5$ by Temperature-Induced Cycling. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 273-279.

5. Goodell, P. D., and Sandrock, G. D.: Kinetic and Dynamic Aspects of Rechargeable Metal Hydrides. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 135-142.

6. Sandrock, G. D., and Goodell, P. D.: Surface Poisoning of $LaNi_5$, FeTi, and (Fe,MN)Ti by O_2, CO_2, and H_2O. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 161-168.

7. Swisher, J. H., and Johnson, E. D.: Hydrides Versus Competing Options for Storing Hydrogen in Enery Systems. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 301-320.

8. Wenzl, H.: FeTi and Lithium Hydrides: Properties and Applications for Hydrogen Generation and Storage. Metal Hydrides 1980, Proceedings of the International Symposium on the Properties and Applications of Metal Hydrides, April 7-11, 1980, Colorado Springs, Colorado. Lausanne, Netherlands, Elsevier Sequoia, Vol. 2, 1980, pp. 351-361.

1. REPORT NO. NASA TM-4076	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE Rechargeable Metal Hydrides for Spacecraft Application		5. REPORT DATE September 1988
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. L. Perry		8. PERFORMING ORGANIZATION REPORT #
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		10. WORK UNIT NO. M-598
		11. CONTRACT OR GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Prepared by Structures and Dynamics Laboratory, Science and Engineering Directorate.

16. ABSTRACT

Storing hydrogen on board the Space Station presents both safety and logistics problems. Conventional storage using pressurized bottles requires large masses, pressures, and volumes to handle the hydrogen which will be used by experiments in the U.S. Laboratory Module and residual hydrogen generated by the ECLSS. Rechargeable metal hydrides may be competitive with conventional storage techniques. The basic theory of hydride behavior is presented and the engineering properties of $LaNi_5$ are discussed to gain a clear understanding of the potential of metal hydrides for handling spacecraft hydrogen resources. Applications to the Space Station and the safety of metal hydrides are presented and compared to conventional pressurized storage. This comparison indicates metal hydrides may be safer and require a lower pressure, less volume, and less mass to store an equivalent mass of hydrogen.

17. KEY WORDS Hydrogen Storage Space Station U.S. Laboratory Module Metal Hydride	18. DISTRIBUTION STATEMENT Unclassified – Unlimited Subject Category 31

19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 40	22. PRICE A03

MSFC - Form 3292 (Rev. December 1972)

For sale by National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1988

National Aeronautics and
Space Administration
Code NTT-4

Washington, D.C.
20546-0001

Official Business
Penalty for Private Use, $300

NASA