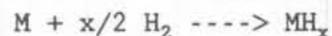


2.2 Metal Hydride Storage

2.2.1 Thermodynamics. Associated with absorption or desorption of hydrogen by a metal hydride is a substantial heat which must be rejected or supplied, respectively. The amount of energy is about 30 kJ per gram mole of hydrogen. Different metal hydrides exhibit heats of hydriding above or below this number, but still in the same order of magnitude. As hydrogen initially diffuses into the pure metal interstices, the equilibrium pressure rises sharply, analogous to physical adsorption. After the physical sites are saturated, a second phase, the metal hydride, begins to form. The hydrogen-metal reaction follows a constant pressure isotherm as if a liquid-vapor phase change were occurring. Thus, a plateau is observed on the pressure versus hydrogen/metal ratio for fixed temperature. When the reaction is complete, another sharp pressure rise is seen if more hydrogen is added. At a given temperature, the plateau pressure represents one point on a pressure-temperature (van't Hoff) plot. The log of pressure versus reciprocal temperature is linear with a negative slope, which is related to the heat of reaction, i.e., heat of hydriding. If hydrogen is removed from the saturated hydride, a lower pressure versus concentration profile is observed, representing a hysteresis effect.

The equilibrium pressure exhibited by a metal hydride at a given temperature and given hydrogen saturation is purely dependent upon the alloy forming the hydride. Hydrides would be greatly advanced in utility if they could be formulated such that the pressure could be raised or lowered at will by doping the alloy with different metals or other materials. A recent report gives evidence of this phenomenon. One system is comprised of lanthanum-rich mischmetal (Mm) in the form $MmNi_5$ and another of cesium-rich mischmetal (4). The pressure plateaus can be altered at will by partially replacing the nickel with manganese, iron or both simultaneously. Also, the desorption pressure increases as the concentration of cesium in mischmetal increases. The plateau is decreased by partially substituting manganese for nickel, or increased by substituting iron. When both manganese and iron are used together, the pressure dependence on temperature is decreased.

Thermodynamic relationships for the metal hydrides are discussed widely in the literature. Because the alloy or metal phase is essentially a pure solid, its chemical activity is very nearly unity (5). The same is true for the metal hydride which is also a pure metal phase. The chemical equilibrium is expressed by



A result of these unit activities is that the chemical equilibrium constant for the reaction is very simply related to the pressure (or fugacity) of hydrogen gas above the solid phases:

$$K = (P_{H_2})^{-x/2}$$

It then follows that the free energy change in the reaction is:

$$G = (x/2) RT \ln (P_{H_2})$$

The heat of reaction, i.e., hydriding, gives an opportunity to exploit metal hydrides for heat pump and thermal storage uses. In contrast, this heat is problematic when considering hydrogen storage and use in vehicles. Compounds which have high reaction heats are more desirable. Nevertheless, the higher the heat of reactions, the lower is the equilibrium pressure at a given temperature. If the pressure is too low, the material cannot be used in practical devices. Higher heats of reaction are also indicative of more stable compounds, which means the metal-hydrogen bond is difficult to break. As for storage of hydrogen, metal hydrides have peculiar properties which render their utilization difficult. Light-weight metals and alloys form strong, energetic, and more easily poisoned bonds with hydrogen, whereas heavier and more expensive materials, have lower bond energies, are thermally more labile, have conveniently high equilibrium pressures, and are more stable in the presence of contaminants (5).

2.2.2 Rate Processes: Kinetics And Heat Transfer. In order to keep the weight and volume of hydride small, it is critical to maintain short cycle times for loading and unloading hydrogen. Heat transfer has been shown to be the rate limiting process controlling hydrogen uptake or removal. This is due to the low-conductivity of the finely divided powder and poor heat transfer between the particles and the container wall. Hydrogen flow is not rapid enough to lower these heat transfer resistances. Supper and coworkers (6) showed that it is equally important to improve both the heat transfer and the hydrogen flow to achieve high gas transfer. They studied reaction kinetics utilizing a "fast reactor" for $LaNi_{4.7}Al_{0.3}$ and $CaNi_5$. In thin cylindrical beds, i.e., 1 mm thick by 60 mm diameter, true kinetics were obtained without the limitation of heat or mass transfer, indicated by an increase in reaction rate with increasing temperature. The opposite effect was seen for beds of 4 and 6 mm. To increase heat transfer rate, the hydride powder was distributed into a 2-mm thick porous aluminum disk with 94% porosity. This gave two to three times faster reactions as a comparable hydride bed without aluminum. The effect of flow was studied by inserting stainless steel screen arteries in a hydride bed along with porous aluminum. A pair of axial arteries on the wall of a 14 mm diameter by 180 mm long tube gave 2.5 to 2.9 times faster absorption, and 4.8 to 5 times faster

dissociation rates than without arteries. It is imperative in future practical applications of metal hydrides that enhancements such as aluminum foam and high-porosity arteries be included for optimum hydride performance.

Recently, a series of papers have addressed the use of metal hydride liquid slurries. The work was aimed at improving bed-to-wall heat transfer, and eliminating the problems of gas-solid separation and vessel distortion due to expansion and contraction of solids. Reilly and Johnson (7) developed the fundamental concepts and showed that the hydrogen-metal reaction rate was controlled by the dissolution of hydrogen by the liquid, in this case n-undecane. Further studies by Johnson, Reilly, and Gamo (8 through 10) on n-octane, methane-contaminated hydrogen gas with n-undecane, and aqueous solutions developed the technology further and pointed to some opportunities which could be exploited in related hydride endeavors. For example, activation of metal hydride in water increased the particle surface area from 0.2 to 1.0 m²/g (10). The practical applications cited were: heat transfer no longer need be the controlling rate process, the slurry is potentially pumpable (6 to 20 g solid per 100 ml liquid), gas-solid separation problems are reduced, problems stemming from bed expansion and contraction are eliminated, and much greater flexibility in the design of engineering-scale systems is possible (7). One serious disadvantage was the corrosion of LaNi₅ by aqueous solutions with the subsequent loss of hydrogen capacity (10). In practical terms, the kinetics of hydrogen release from hydride storage tanks in vehicles appears to be at least sufficiently rapid, even without special enhancement devices, to proceed with road tests. Russian workers have modeled a metal hydride storage tank for automobiles and successfully road tested a vehicle with LaNi₅ alloy (11). Satisfactory results were obtained with a combined fuel of gasoline and hydrogen. An Australian hydrogen car gave good road tests with FeTiMn (0.83, 1.0, 0.15) but required up to 20 kW of heat to maintain the tank pressure above two atmospheres (12). This heat was extracted from the engine exhaust by a gas-to-water heat exchanger mounted as a replacement for the rear muffler. Careful design of the hydride tank insured that heat conduction distance through the alloy was kept below 10 mm.

Small quantities of material added to the metal matrix can greatly affect the hydride properties. Magnesium hydride was specially prepared in an organic solvent and in the presence of an organotransition metal catalyst (13). It has outstanding kinetics, high surface area, and high storage capacity (7 wt%), but it suffers from being pyrophoric. But, if doped with small quantities of transition metal complexes or organotransition metal compounds this material can be handled safely in air. Furthermore, the new product has low material and

production costs, high hydrogen and heat capacity (17.9 kcal/mole hydrogen), fast kinetics, relative insensitivity to hydrogen impurities, and stability towards air.

2.2.3 Candidate Alloys And Costs. The bonding between metals and hydrogen can be divided into three broad types: (1) ionic, (2) covalent and (3) metallic. Of these classes only the metallic type bond offers the necessary behavior for hydrogen storage systems. For a system to be useful, it must be capable of storing large quantities of hydrogen reversibly, have reaction kinetics fast enough to be practical, be insensitive to poisons, and be economically priced. Alloys that can form hydrides that meet these conditions have generally been classed as either AB, ABC, AB₂, AB₅, Mg-based, or other (14). This classification was used to help organize the hydride alloys described in Appendix A. It should be noted that this approach is only approximate, since many alloys have additives to improve their hydriding and dehydriding performance. Some metals that have potential as storage media can form hydrides directly, for example, Mm, Cu, Fe, Mn, Al and Ca.

Due to the large number of alloys that have been studied for potential hydrogen storage systems and the fact that many of these systems are not commercially available, a uniform approach has been applied in the present study to estimate the production costs. This approach is based on the current truck load price of the metal and a tolling charge for the production of the alloy. These calculation factors are compiled in Appendix A. The current costs (\$1987) for the metals and the estimated processing costs are given in Table AI. The results of these calculations are given in Tables AII and AIII. Many of the storage systems are very expensive due to the limited availability of many of the metals. All systems were treated in the same fashion so that relative differences indicate cost trends. There are expensive metals in all types of alloys that are used for hydrogen storage systems. Since the main interest is the storage of hydrogen, then the capital investment per unit of stored hydrogen may be useful. The results from Appendix A are summarized in Table III.

According to Table III, the magnesium systems offer the highest storage capacities and at low costs. Most of the systems in this category can provide hydrogen storage for less than \$100/lb hydrogen. Magnesium and aluminum systems also offer the potential for lower storage costs because of the lower pressures and less potential for fragmentation. It has been shown that aluminum increases the malleability of magnesium metal and thus acts to hold the particles together (15).

Table III
Summary of Alloy Cost Estimates

Alloy Type	Hydrogen Storage, Wt%	Capital Invest., \$/kg Hydrogen
AB	1.0 to 1.9	417-6,354
AB ₂	0.2 to 2.8	3,029-32,300
ABC	1.3 to 1.9	650-13,180
AB ₅	1.0 to 1.9	410-5,190
Mg	2.6 to 8.2	70-2,230

The cost of hydrogen storage in cheap hydrides has a wide range of estimates (2). According to Savage et al. (16), the price would be between \$6 and \$46 (ca. 1980 \$) per 10⁶Btu per year, compared to \$3.50 per 10⁶Btu per year for liquid hydrogen storage. In Fe-Ti-Mn, the cost is around \$4.00 per 10⁶Btu per year. The Brookhaven workers evolved a complex design of cooling and heating devices to move the heat of hydriding (2, 17). The vessel wall was 1/4 in. thick for pressures up to 50 atmospheres. In a typical design, 380 kg of FeTi alloy, containing 4.54 kg of hydrogen, was contained in a tube 6 ft. long and 12 in. in diameter. The cost of such systems has been computed (18). For example, the alloy needed in a medium-sized car would cost about \$2000 or \$14.00/kg (ca. 1976 \$). In comparison, organic-liquid storage (as formate salt) is estimated to be \$1.26/kg hydrogen (19). The latter also is favored by a very low estimate of \$2.32/kg hydrogen for both production and storage (1985 \$).

For purposes of comparison, the relative costs of short-term hydrogen storage hydrogen in various modes are as follows (short term is 30 kWh/kW) (20):

Liquid	1.0
Cryoadsorption	1.0
High pressure gas	1.4
Metal hydride	1.4

New cost estimates for a wide selection of metal hydrides are detailed in Appendix A.

The cost of a hydride system and components depends on the kind of hydride used, the desired operating range, and the cost of other system components, such as packaging and heat exchangers. Given reasonable variations in these parameters, the final cost estimate can vary widely, and it is difficult to make an exact estimate. Data from Lawrence Livermore Laboratory (21), Wallace (22) and Swisher (23), suggest that hydride storage tanks will cost about as much as batteries for

vehicles with roughly similar range. However, the estimates are not current, and in any case they depend greatly on the composition, weight, and storage capacity of the hydride. Blazek et al. (24) and Stewart (25) show a wide range of hydride cost per unit weight. Their data indicate the FeTi hydrides, supplying about a 150-mile range, with tankage, heat exchangers, and other system components, would cost between \$2000 and \$4000 more than a gasoline tank.

If ultra pure (>99.999%) hydrogen is used, and there is no degradation of storage capacity, hydrides may have extremely long lives. Strickland (26) has remarked that some tests show hydrides lasting 20,000 to 30,000 cycles, with no loss of capacity. Even if a cycle discharges only 50 miles worth of H₂, the total implied life is upwards of 1,000,000 miles. The life on the streets might be lower, but it is clear that hydrides should have a very high salvage value at the end of the life of the vehicle (130,000 to 160,000 miles), perhaps in the range of 25 to 60%, because of their high cost and long useful life.

2.2.4 Practical Problems And Considerations. One of the problems with the use of metal hydrides has been the container. Metal hydrides expand during the hydriding cycle and generate a large stress on the alloy and the container. The alloys tend to fragment into smaller particles as a result of this stress. This causes material movement and segregation in the storage container, which create large internal pressures. Also, as the particles get smaller, there is an increased tendency for entrainment of the hydride fines in the gas streams. Therefore, the container system must provide for these small particles and the resulting expansion. One proposed solution to this problem has been through the use of a lamellae design (27). This system was tested with an alloy that was known for its tendency to degrade to very small particles as a result of the hydriding/dehydriding reactions. The resulting system has been used in commercial designs with good results. Basically, the alloy is placed between radially aligned lamellae (constructed of aluminum). There are spring loaded chambers that can accommodate charging rates of 10 liters of hydrogen per minute. For an 80-kg hydride system, it is possible to charge and discharge about 20,000 cubic meters in one hour.

Strain in the container walls is a major problem when examining the practical use of hydrides for hydrogen storage. Left uncontrolled, these strains can lead to container failure. One study with MmNi₅ has shown that the strain in the container walls can be reduced by mixing the alloy with 6% silicon oil. Pressed pellets of alloy and Al powder at 30% also was effective. Polyurethane and MmNi₅ mixtures were useful up to 120°C, but were not effective above that temperature (28). Suspension of hydrides in liquids is also a means of eliminating tube strain due to expansion (7).

The mechanisms of absorption and desorption are not well understood. It appears that adsorption and desorption are controlled by the precipitation of the hydride phase, heat transfer into the bed, and the prevailing reaction temperatures (29). Heat transfer is known to be the rate-controlling step in hydrogen transfer from the metal hydrides. For this reason, many improvements in container design and other schemes such as liquid suspension to increase powder to wall heat transfer coefficient have been proposed.

2.2.5 Major Development Programs. This year, Daimler-Benz will conclude its \$32-million test program that involves ten hydrogen-powered station wagons and vans in continuous operation in West Berlin. The program has already shown that hydrogen can be handled safely, and that hydride storage is less desirable for mobile applications. Injection of pressurized liquid hydrogen is more efficient, but presents certain technical problems. BMW is working with the German aerospace research agency DFVLR. Two large sedans running on liquid hydrogen are being tested in Munich at BMW headquarters. The company is converting one of its new models for tests next spring, and it plans to have a fleet of hydrogen cars between 1995 and 2000 (30).

In Japan, Professor Shoichi Furuhashi at Musashi Institute of Technology has converted more than a half dozen cars to liquid hydrogen. Innovations such as plastic pistons to prevent fuel leaks, and a durable-surface spark plug made of silicon-carbide-based ceramic have been incorporated in a truck with a limited range of 150 miles. Considerable work is in progress on hydrides as stationary devices for hydrogen storage. An agricultural experiment involves a combined \$4.4-million windmill-and-hydride energy system to warm greenhouses at a farm. The windmill provides power to help grow vegetables, and heat stored in a 300-kg hydride tank is released to keep the plants warm when there is no wind. Three companies completed a project last year on a hydride-based 20-ton combined refrigeration and heat-recovery system that produced 120°C steam from waste heat (hot water) at 80°C. Commercially available products include hydride-based heat pumps for water cooling and hot water supply in homes, and a small, fast-start, air-heating system suitable for cars and truck cabs, which can raise the temperature from -30°C to 35°C in five seconds (30). The Australians have successfully built and tested a hydrogen car with an FeTiMn hydride storage tank (12). A program is also underway in the U.S.S.R. as of 1984 involving a mixed gasoline-hydrogen fuel and a mixed hydride tank of FeTi and Mg₂Ni (31).

Hydrogen absorption, transport after repeated metal absorption/desorption cycles, and technically interesting alloys for hydrogen storage are being studied in a project at the Tandem Accelerator Laboratory and the Department of Physics at the

University of Uppsala, Sweden (32). A summary and catalog of DOE hydrogen-related projects is available (33). The topics include production, storage, transportation, and utilization of hydrogen.

2.2.6 Alternative Storage Forms. No single hydrogen storage mode is an obvious choice at present. The leading candidate for transportation seems to be liquid hydrogen. A comprehensive review of this technology is covered in the next chapter. Besides metal hydrides, there are other possibilities to store hydrogen e.g., in a chemical combination. For example, the hydrogen/boron combination, B_2H_6 , is one which has 21 wt% hydrogen (2). The value of such compounds depends on whether they can be easily decomposed into hydrogen and the original storage substance. Other combinations include lithium aluminum hydride, 10.5%, barium borohydride, 10.6%, and lithium borohydride, 18.3% by weight hydrogen. Ammonia can be used as a storage medium for hydrogen (17.6 wt%). It is easily broken down into nitrogen and hydrogen by the use of a catalyst (34). Another system, methylcyclohexane (MCH), is dehydrogenated directly in the vehicle to produce the fuel hydrogen for the engine and toluene (35). A Pt-Sn/ Al_2O_3 catalyst is used in a 15-kg reactor (catalyst plus container) at 450°C. After dehydrogenation, the toluene is recycled and hydrogenated again. In this way, the MCH acts as a hydrogen carrier which contains about 6 wt% hydrogen. Like metal hydride systems, this system will be heat-transfer limited. About 128 lb of MCH is needed for one hour of driving. New chemical systems have been reviewed and compared to metal hydrides and other storage forms (36).

A significant new chemical carrier for hydrogen was recently reported (19). At 20°C and atmospheric pressure, formate salts have been catalytically decomposed to bicarbonate ion and hydrogen gas. The reaction gives good yields with palladium-on charcoal catalyst. Hydrogen can be used to generate the sodium or potassium formate salts, but carbon monoxide or synthesis gas are also feasible, hence a relatively cheap feed stock is possible because pure hydrogen is not required. The volumetric and mass-hydrogen storage densities of formate salts are in the vicinity of 0.05 kg/L and 0.05 kg/kg, respectively. These compare higher than zeolites, glass microspheres, cryoadsorption, high pressure cylinders, and some hydrides, but not as high as some chemical compounds such as methanol, ammonia, cyclohexane, and other metal hydrides (around 0.1-0.2 kg/L and 0.1-0.2 kg/kg). Liquid hydrogen has highest mass density at 1 kg/kg, but has somewhat lower volume density of 0.07 kg/L.

Some forms of hydrogen below the melting point (-253°C) are of interest. Hydrogen slush may be of value, a mixture of solid and liquid hydrogen. Metallic hydrogen is hypothetically formed at several megabars pressure. If it were stable at room

temperature, it would become a superconductor and would have metallic strength with a density of 1 to 1.3 g/ml. It could possibly become a convenient energy storage medium (2).