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TECHNICAL AND ECONOMIC ASPECTS OF HYDROGEN STORAGE IN METAL HYDRIDES

R. Schmitt

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16. Abstract The recovery of hydrogen from such metal hydrides as LiH, MgH2, TiH2,CaH2 and FeTiH compounds is studied, with the aim of evaluating the viability of the technique for the storage of hydrogen fuel. The pressure-temperature dependence of the reactions, enthalpies of formation, the kinetics of the hydrogen absorption and desorption, and the mechanical and chemical stability of the metal hydrides are taken into account in the evaluation. Economic aspects are considered. Development of portable metal hydride hydrogen storage resevoirs is also mentioned.

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TECNISCHE UND WIRTSCHAFTLICHE ASPEKTE DER WASSERSTOFF SPEICHERUNG IN METALLHYDRIDEN

[Technical and economic aspects of hydrogen storage in metal hydrides]

by

R. Schmitt

Batelle-Geneva, Switzerland

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SUMMARY

/1* Due to the limited resources of fossil fuels, a gradual change of the energy economy to non-fossile fuel primary energy will occur within a reasonable amount of time. In this evolving energy situation, hydrogen will play an important role as an energy carrier in addition to electricity. Problems still to be solved in this context concern in particular its storage. Among the different possibilities, the storage of hydrogen in metal hydrides is considered especially favorable. Some technical and economical aspects of this storage technique are discussed in the light of the present state of the art and future developments.

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1. INTRODUCTION

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The limited occurrence of fossil fuels and the worldwide constant increase in fuel consumption will necessarily lead, in the foreseeable future, to a conversion to non-fossil fuel in the economy of primary energy sources. Following the last energy crisis, this conversion will proceed at an accelerated pace in those industrialized countries that do not dispose of sufficient fossil fuel reserves of their own. The increased resort to nuclear energy to satisfy future energy needs poses the question of an energy carrier. Of the purely synthetic fuels possible, hydrogen and electricity have the best chance of playing the role of today's fossil energy carriers - coal, oil and natural gas - in a future energy economy, be it totally or partially.

In fact, hydrogen represents an ideal fuel. It can be obtained from practically unlimited water resources, largely independently of location, by means of nuclear power. For its transportation and distribution, extensive use can be made of already existing piping networks. Its use as heating fuel can be implemented today without any fundamental difficulties, to replace the natural gas being used. The use of nuclear power-produced hydrogen instead of hydrogen obtained from fossil fuels will allow the stretching of fossil fuel reserves.

However, before a large scale use of nuclear hydrogen as energy carrier can be contemplated, a series of problems, related also to its storage, among other things, must be resolved.

For hydrogen storage, the following possibilities can essentially be considered:

- compressed into pressure tanks; /6
- liquified, in cryogenic storage containers;
- condensed in metal hydrides.

The decision in favor of one or the other of these storage technologies depends mainly on the envisoned use. For a broader aplication, however, in the context of a post-fossil fuel hydrogen economy, this decision must be made under previous consideration of scientific and technological aspects.

Hence, below we shall refer briefly to the advantages and disadvantages of the storage technologies mentioned, followed by a technological-economic analysis of the perspectives for the future of the reversible hydrogen storage in metal hydrides. Other storage technologies, such as cavern storage and underwater storage, shall not be considered here.

2. SURVEY OF HYDROGEN STORAGE TECHNOLOGIES /7

2.1. Storage under pressure

The storage of gaseous hydrogen under high pressures requires relatively heavy pressure containers and considerable energy expenditures for its compression. Customary commercial high pressure cylinders permit the storage of approximately 10 Nm^3, at 200 bar, in a volume of approximately 50 l. Hence the storage capacity of these steel cylinders lies at approximately 1.6 weight %. Pressure cylinders made of light metals, already commercially used in some countries, permit storage capacities of over 2 weight %. Special construction devices made of titanium alloys as used in space travel, have led to a storage capacity as high as 5% by weight[1]. The development of pressure resistant and cost efficient fiber compound materials should make possible the manufacture of recipients with a storage capacity of 3% and above.

While the pressurized storage of hydrogen is state of the art, the use of high pressure containers remains questionable for large quantities, especially for economical and safety-technology reasons.

2.2. Storage as a liquid

The liquid storage of hydrogen is obtained at its boiling temperature of -253°C, in vacuum-insulated containers. This technology /8 was considerably improved especially during these last years, in connection with space travel development. However, the use of liquid storage for earthside applications remains limited to a few exceptions. Reasons against this storage technology for large scale application include high initial capital investment and the high cost of liquidification itself. Hydrogen's energy content of approximately 34 kWh/kg is faced by an energy expenditure for liquidification of approximately

14 kWh/kg H_2, today. A further disadvantage of criogenic storage are the unavoidable evaporation losses caused by heat leaks, which amount to 0.5-1.0% in the most favorable cases, per day; for certain applications this creates problems from a safety technology point of view, besides the losses. Such a problem would be particularly disadvantageous in the case of a passenger car, which is in use only approximately 10% of the time. For continuous operation as in the case of trucks, buses and airplanes, heat leaks would be negligible or play, at the most, a very subordinate role.

2.3. Storage in metal hydrides

The storage of hydrogen in metal hydrides is based on the reversible reaction between a metal or alloy (Me) and gaseous hydrogen, according to the reaction equation

$$x\,Me + y\,H_2 \rightleftarrows Me_xH_{2y} + |\Delta H|,$$

where ΔH is the reaction enthalpy.

Hydride formation is an exothermal reaction and the quantity of heat released is the larger, the more stable the hydride is. Hydrogen desorption is an endothermal process and hence requires a heat supply.

The relationship between hydrogen equilibrium pressure (p_{H_2}) and temperature is given, for each metal hydride-hydrogen system, by the van't Hoff isochore /9

$$\log p_{H_2} = -\,(A/T) + B \qquad [1]$$

The constants A and B have characteristic values for each hydride and serve to define the hydride thermodynamically

$$A = \frac{\Delta H^\circ_T}{4.57} \qquad B = \frac{\Delta S^\circ_T}{4.57} \qquad [2,\ 3]$$

Figure 1 (2) shows the family of curves $\log p_{H_2} = f\,(1/T)$ for a series of known hydrides.

In comparison to pressurized and criogenic storage, hydride storage has a significant advantage from the point of view of safety technology. For most metal hydrides, the hydrogen equilibrium pressure is low at normal temperatures. If a storage container were to become damaged, the hydrogen under low pressure, would evaporate through the leak. This would upset the equilibrium conditions of the system, with the consequent desorption of hydrogen from the hydride. Since, however, desorption occurs only if heat is supplied, in the absence of a heat source the hydride would cool down, thus checking the desorption process.

The storage of hydrogen in metals and alloys has received particular interest, in the last years, for both portable and stationary applications.

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The portable storage, for use as truck fuel with slightly modified combustion engines, eliminates the disadvantages of pressurized and cryogenic storage and offers an alternative to electrically powered vehicles with lead accumulators.

In connection with nuclear power plants, the storage in metal hydrides of the electrolytically generate hydrogen during peak load periods is being considered[3,4] for short-term, peak-load storage. The hydrogen stored would be used, during periods of high power consumption, to generate electricity in fuel cells or gas turbines.

3. REVERSIBLE HYDROGEN STORAGE IN METAL HYDRIDES /11

The technical applicability and the economy of hydrogen storage in metal hydrides is usually given by the interplay of several factors. These focus on

- the metal hydride (its thermodynamic and physico-chemical properties, availability, cost of starting metal, etc.);
- the hydrogen (required purity, pressure);
- the storage function (portable or stationary application, quantity of hydrogen needed per unit time, acceptable reservoir filling time, available waste heat for hydride dissociation, etc.).

While the purely technical evaluation of hydride storage in connection with a specific application is usually readily possible, the economic part of this process is often not as satisfactorily solved.. The reason for this is the complexity of the factors affecting the cost and, often, a lack of sufficiently proven data as a basis for any calculations.

Thus, the construction and operation of portable[5-7] and stationary[8,9] FeTi hydride storers, most recently finally brought a practical demonstration of the technical applicability of this storage method. In contrast, some of the data necessary for economic analysis - such as hydride lifetime (number of absorption-desorption cycles that can be reached) or purity of the hydrogen - are still available only spottily.

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The most important technical and economic aspects that are significant in the selection of a metal hydride for hydrogen storage shall be discussed in subsequent chapters, considering the current state of knowledge.

3.1. Technical aspects

A metal hydride is characterized by a series of physicochemical properties that are primarily responsible for its technical adequacy as hydrogen storing material; secondarily, in addition they also help to determine the economy of the storage process. The most important are:

- Hydrogen storage density
- Equilibrium pressure/Temperature dependence
- Enthalpy of formation
- Hydrogen reaction kinetics
- Chemical stability
- Mechanical stability.

Naturally, there are other properties, besides these that can affect the possible applications of a hydride for certain hydrogen storage tasks. Among them are the hydride's volume storage density (kg H_2/100 1 hydride) which is, however, in general larger than that of liquid hydrogen (approximately 7 kg/100 1 H_2 at -253°). Furthermore, in this connection should be mentioned the heat capacity and thermal conductivity of the hydride, the possibilities for its regeneration or recycling, as well as safety technology aspects.

3.1.1. Hydrogen storage density /13

The hydrogen storage density (kg H_2/100 kg hydride) of different metal and alloy hydrides is given in Table 1, below. Besides the total hydrogen content, this Table shows, whenever available, also the reversible hydrogen content, i.e., the hydrogen usable in a practical application. This corresponds to the quantity of hydrogen that can be desorbed at a given temperature and at constant pressure. Its value can be derived from the corresponding pressure-concentration isotherms

If the solubility of hydrogen is small in the metal and the hydride, then total and useful storage density will be practically

TABLE 1. Characteristic physico-chemical data for different metal hydrides[2].

REACTION	STORAGE DENSITY ($kg\ H_2/100\ kg$ Hydrid)		EQUILIBRIUM TEMP. AT 1 atm. (°C)	DISSOSIATION ENTHALPY	
	TOTAL	REVERSIBLE		Kcal/mol H_2	kWh/kg H_2
$Li + 1/2\ H_2 \Leftrightarrow LiH$	12,6	12,6	800	43,4	25,2
$Mg + H_2 \Leftrightarrow MgH_2$	7,65	7,5	280	17,8	10,3
$Ca + H_2 \Leftrightarrow CaH_2$	4,8	4,8	920	41,7	24,2
$Ti + H_2 \Leftrightarrow TiH_2$	4,0	-	-	29,6	17,2
$TiH_{0,92} + 0,26\ H_2 \Leftrightarrow TiH_{1,44}$	2,92	1,1	640	40,4	23,5
$Mg_2NiH_{0,3} + 1,95\ H_2 \Leftrightarrow Mg_2NiH_{4,2}$	3,77	3,5	250	15,4	8,9
$FeTiH_{0,1} + 0,47\ H_2 \Leftrightarrow FeTiH_{1,04}$	1,0	0,9	-9	6,7	3,9
$FeTiH_{1,04} + 0,45\ H_2 \Leftrightarrow FeTiH_{1,95}$	1,84	0,8	-19	7,5	4,4
$LaNi_5 + 3,35\ H_2 \Leftrightarrow LaNi_5H_{6,7}$	1,5	1,3	+10	7,2	4,2
$MMNi_5 + 3\ H_2 \Leftrightarrow MMNi_5H_6$	1,36	1,1	-45	2,8	1,6

(Commas in the above Table denote decimal points) identical. This is the case, for instance, for the salt-like hydrides such as LiH or CaH_2 and to a certain extent also for MgH_2 and Mg-alloy hydrides. In the pressure-concentration isotherms represented for the system Mg_2Ni-H_2 in Figure 2[10], the horizontal portion (two phase range) corresponds almost to the entire available hydrogen.

For most metal hydrides, however, the hydrogen solubility is high in the metal and in the hydride phase and the quantity of hydrogen absorbed or desorbed at a given temperature and under constant pressure is often only a fraction of the total hydrogen content. This becomes particularly clear following the course of the Pressure-concentration isotherms for the system Ti-H_2, in Figure 3[11]. Thus, for instance at 640°C and a hydrogen pressure of around 1 atm, only approximately one fourth of the hydrogen present is desorbed. Hence, in such metal-hydrogen systems the useful storage density can be influenced to some extent controling the storer's operating conditions. Of course, in that case desorption does no longer take place at constant pressure but within a certain pressure range.

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The same is true, in this sense also for systems the pressure-concentration isotherms of which show two or more plateaus, as in the case of the known FeTi-H_2 system, for instance. According to the pressure-concentration isotherms diagram reproduced for this system in Figure 4[12], the first plateau corresponds to a hydrogen conversion of 0.9% and the second to 0.8%. Thus, to make the total reversible amount of 1.7% available, two different pressure levels are going to have to be accepted.

It is readily understandable that for a hydride to become interesting for storage purposes, it must show the highest possible reversible hydrogen content, but certainly at least 3% by weight. Unfortunately, especially hydrides with such high storage densities often must be at first discarded for other reasons, such as insufficient reversibility (MgH_2) or a thermal stability that is too high (LiH), so far as hydrogen storage is concerned. The currently most promising hydrides are predominantly within the realm of Mg and Ti alloys, the best known representatives being $Mg_2NiH_{4.3}$ and $FeTiH_{1.9}$.

3.1.2. Pressure/Temperature dependence

If in a metal-hydrogen system a hydride phase occurs, it will be in equilibrium with a certain hydrogen pressure at a given temperature. The dependence of this equilibrium pressure on the temperature, in the two-phase domain metal-hydride (plateau = horizontal portion of the pressure-concentration isotherm), is described by the van't Hoff isochore

$$\log p_{H_2} = -\frac{A}{T} + B \qquad [4]$$

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This equation determines the thermal stability of the hydride, i.e., how readily it can be dissociated by either temperature increase or pressure decrease. This pressure/temperature function is represented for a number of known hydrides in Figure 1[2].

It follows from equation [1] that the dissociation enthalpy (ΔH°_d) of a hydride and its thermal stability - or dissociation temperature (T_d) are related by the equation

$$-RT\ln pH_2 = \Delta H^\circ_d - T_d \Delta S^\circ_d \qquad [5]$$

$$\text{for } pH_2 = 1 \text{ atm}, \; \Delta H^\circ_d = T_d \Delta S^\circ_d \qquad [6]$$

The entropy change (ΔS°_d) associated with hydride dissociation corresponds essentially to the entropy of gaseous hydrogen (∿31 cal/mol $h_2 \cdot {}^\circ K$ at 300°K) and is thus practically the same for all hydrides. This means that the enthalpy of dissociation of a hydride can be calculated approximately from its dissociation temperature at atmospheric pressure. This dependence on dissociation temperature and enthalpy of dissociation is shown in Figure 5[13] for some hydrides.

What the pressure temperature dependence of an ideal hydride should be can be ascertained only in connection with a given application problem. A thermally stable hydride such as LiH (left side of the diagram in Figure 1) only dissociates at very high temperatures (approximately 800°C at $pH_2 = 1$ atm.), and if supplied heat in large quantities (43.3 kcal/mol H_2), as can be expected with the $\Delta H°_d/T_d$ relationship indicated above. For thermally less stable hydrides, such as $MnNi_5H_6$ (on the diagram's right side) the equilibrium pressure achieves fairly high values already at relatively low temperatures (50° - 100°C): 30 - 100 atm; this limits the advantage of hydrogen storage as compared to compressed hydrogen, in terms of safety considerations.

3.1.3. Enthalpy of formation /17

As is the case in all chemical reactions, in the metal-hydrogen reaction also there is a change in enthalpy:

$$x\ Me + y\ H_2 \underset{\text{dissociation}}{\overset{\text{formation}}{\rightleftarrows}} Me_xH_{2y} \pm \Delta H$$

Depending on the type of the metal, the hydride formation can take an exothermal (for salt-like and metallic hydrides) or an endothermal course (for most covalent hydrides). The reaction between hydrogen and intermetallic compounds is determined extensively by the kind and concentration of the alloy components. Here, often the combination between a metal that forms stable hydrides exothermally with a metal that forms endothermal or no hydrides, leads to interesting alloy hydrides (such as TiFe, $LaNi_5$, Mg_2Ni).

The formation of all hydrides to be considered for hydrogen storage occurs exothermally, however (cf. Table 1). Hence it becomes necessary to supply heat for hydrogen desorption. As a first approximation, the absolute value of the enthalpies of dissociation and of formation are practically equal. Table 1 shows the enthalpy of dissociation values for a few known hydrides.

For most applications - with the possible exception of thermal energy storage - an absolute value of the enthalpy of formation that is as small as possible, would be of advantage. This quantity is the one to determine the quantity of heat that will have to be made available, from an external energy source (for instance, engine waste heat), to the storer, for hydrogen desorption. A corresponding quantity of heat will have to be removed by cooling, later, during the recharging of the hydride storer. If the quantities of heat in play are large, than the kinetics of hydrogen absorption or desorption, respectively, may be limited by heat /18 transfer problems. The absolute value of the enthalpy of formation should, however, also not be too small, since the thermal stability of the hydride decreases in the same proportion (cf. Chapter 3.1.2.), so that its usage as a storage material could entail safety technology problems. Because it is precisely the endothermal character of hydride dissociation that is responsible for the operational safety of the hydride storer. Every more significant hydrogen loss leads to hydride cooling and hence to a decrease of its equilibrium pressure and a consequent decrease in the rate of desorption.

3.1.4. Kinetics of the hydrogen reaction

The kinetics of the hydrogen absorption or desorption process determines - in the absence of heat transfer limitations - the quantity of hydrogen available per unit time or, respectively, the time required for replentishing the hydrogen storage. For most hydrides, the formation reaction is slower than that of its dissociation. On occasion, this hysteresis effect can be so large - as is the case with MgH_2 - that reversible hydrogen storage becomes impossible, in practice.

Hydrogen reaction can occur only under pressure and temperature conditions that deviate from the equilibrium conditions. The larger this difference is, the faster it will generally be possible to absorb or desorb hydrogen.

The following dependence relationships between the sorption rate (kg H_2/h.l), the temperature T and the difference between equilibrium desorption pressure P_D and the effective pressure P_B in the filling, were found[1] for $FeTiH_2$ and Mg_2NiH_4, respectively Mg_8CuH_3:

$$\mathrm{FeTiH_2} \qquad : 2{,}57 \cdot 10^{6} \left(\frac{P_D - P_B}{P_D}\right) \cdot e^{-\frac{3\,720}{T}}$$

$$\begin{array}{l} \mathrm{Mg_2NiH_4}, \\ \mathrm{Mg_2CuH_3} \end{array} \quad : 8{,}23 \cdot 10^{15} \left(\frac{P_D - P_B}{P_D}\right) \cdot e^{-\frac{18\,100}{T}}$$

The rate of hydride formation and dissociation depends very strongly on the quantity of metal surface available. This explains why during the course of the first absorption/desorption cycles (activation phase), usually combined with considerable grain refinement, the reaction rate gradually increases until a certain limiting value is attained. Other factors - determined by the nature of the metallic element - that can affect the kinetics, are the chemical sorption of molecular hydrogen onto the metal surface and its subsequent dissociation into atomic hydrogen, as well as the diffusion of hydrogen into the alloy and the hydride. These processes are often affected adversely by the presence of impurities, be it on the metal surface or within the metal itself, thus making any estimation of kinetic data impossible, in practice. Thus the kinetics of hydrogen reaction under different operating conditions, typical for a given storer, can be determined only experimentally.

Characteristic kinetic data are known for only a few metal hydrides. The only systematic investigations in this respect refer to $LaNi_5$ (Figure 6[14-16]) and FeTi (Figure 7[17,18]). The rate of dissociation of Mg_2NiH_4 at different temperatures is shown in Figure 8[17].

3.1.5. Chemical stability /20

By chemical stability we mean here the influence of impurities on the hydrogen absorption characteristics of a hydride. The impurities can be mainly of the following origin:

- constituents of the starting metals;
- consequences of the manufacturing process;
- adsorption of gaseous materials on the metallic surface prior to the first hydration;
- impurities in the hydrogen.

Most of the published work on metal hydrides was performed using the purest starting metals with ultra-high purity (>99.99%) H_2. The effects of impurities on the characteristics of hydride formation and dissociation have so far barely been investigated systematically. Nevertheless it is known, for instance, that the thermal stability of VH_2[19,20] depends decisively on the purity of the metallic Vanadium used. Some information also exists on the negative influence of impurities on the absorption of hydrogen onto palladium[21] as well as on the relatively good resistance of AB_5 hydrides[22,23] to O_2, CO, CO_2 and hydrogen containing water vapor. The hydride of TiFe seems to require a hydrogen purity of 99.99%[24,25] to achieve a satisfactory lifetime of absorption/desorption cycles. Traces of oxygen in FeTi unfavorably affect the storage capacity and the reaction kinetics[8,9].

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While so far there is little known about the influence of impurities in indivual cases, it may generally be assumed that it is going to be negative, especially in regard to hydrogen reactions, hydrogen storage density and the lifetime of the hydride itself. The adsorption of gaseous impurities on the metal/hydride surface may impede the chemical sorption of hydrogen and its dissociation into atomic hydrogen. The formation of surface films (for instance, oxide or nitride layers), through which hydrogen diffuses only very slowly, can severely reduce the metal-hydrogen reaction rate and thus determine the lifetime of the hydride.

The sensitivity of a hydride towards impurities will thus have a very decisive influence on the purity requirements for the starting metals, the fabrication technology, the quality of the hydrogen, the lifetime of the hydride and, hence, the economy of the storage technology.

3.1.6. Mechanical stability

The grain size of a hydride normally decreases with the number of absorption/desorption cycles performed. How fast, or to what extent this process proceeds is what we mean here by the concept of mechanical stability.

The mechanical stability of a hydride may depend on various factors; for instance, on the dimension of the lattice expansion due to hydrogen absorption or whether the hydride formation is accompanied by a structural change. The volume change determined by the lattice expansion can often be considerable; for instance, it is approximately 17% for Ti_2Ni[25] or even 25% for $LaNi_5$[26].

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If grain refining goes so far that it comes to dust formation, some technological problems can come up, other than a decrease in the hydride's lifetime. This may make the inclusion and frequent cleaning of special filters necessary and, additionally, lead to an inadmissibly high pressure drop in the hydride bed. Since the pyroforicity and danger of explosions is usually fairly high for very fine metal powders[28], it is also for reasons of safety technology that high mechanical stability be considered of great value.

There are only few experimental values for hydrides. For $LaNi_5$[25] a very fast grain size reduction to 1-4 µm can be observed already in the activation phase. In this regard, FeTi seems to be more stable. Thus, for instance, after 840 absorption/desorption cycles, only some 6% of the hydride powder had a grain size below 50 µm, for an initial grain size of 400-600 µm[24].

3.2. Economic aspects

The economy of hydrogen storage in metal hydrides is influenced primarily by the following factors:

- cost of the storage material (availability and cost of starting metals, cost of alloy fabrication and material preparation);
- hydrogen costs (required quality, necessary filling pressure);
- hydride lifetime; /23
- possibilities for regeneration or reuse of the spent hydride and costs associated with such recovery;
- reservoir costs (construction type, operating conditions, safety requirements);
- Operating and maintenance costs.

The most important of the cost-determining factors, which often directly or indirectly depend on each other, are briefly analyzed below. What makes a cost analysis even more difficult is the facts that these factors can usually be judged only in connection with the technological characteristics of a given hydride and for a certain, specific storage application. Because of the lack of the corresponding operating experience values, a cost estimate for hydride storage can at this point in time be only very gross.

3.2.1. Cost of the storage material

The costs of the storage material are determined, in the first place, by the cost of the metals that make up the alloy. Depending on the purity requirements placed on the starting material, these costs can fluctuate considerably. In this connection the availability of the individual metals - especially for long range cost developing - plays a significant role. Alloys on a sodium, calcium, potassium, magnesium, aluminum, silicon, titanium and iron base thus appear economically particularly advantageous.

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The alloys are usually manufactured using vacuum or protective atmosphere melting procedures. In special cases manufacture can also be based on powder technology methods. The metal type will determine the melting or respectively sintering temperature and hence the energy costs - the main cost factor in metallurgical processes.

A further cost factor results from the breaking up and crushing of the ingot, which in the case of ductile alloys can prove difficult, as well as the taking of the granules to a grain fraction of approximately 1 mm. There are two advantages to this size reduction prior to hydration: in the first place, due to the increase in metallic surface area the activation phase (the required absorption/desorption cycles until the reversible hydrogen storage density is reached) is significantly shortened. In the second place activation, which usually requires higher hydrogen pressures, can be performed in the storage itself, thus obviating pretreatment in a hydration autoclave.

Since the costs for the manufacture and preparation of an alloy should be essentially independent of its nature and composition, the metal costs themselves are practically the only ones responsible for any differences in cost between different storage materials. Since, however, as we have shown before, the hydrogen storage density of the individual hydrides can be very different, an economic comparison is possible only on the basis of specific storage costs (i.e., cost of storage material per unit hydrogen stored). /25

Based on the prices of metals in early 1976, Table 2, below, shows a comparison of costs for the storage-hydrides that looked most promising at the time: $TiFeH_{1.9}$, $Mg_2NiH_{4.3}$, $LaNi_5H_{6.7}$ and $MMNi_5H_6$. Based on a cost estimate for the melting of iron in a 25 ton induction furnace[30], a cost of alloy manufacture (double melting) of $20/t was assumed. Costs for crushing and sizing were estimated at $50/t of alloy. These values are comparatively small in comparison to the metal costs and so is, correspondingly, their influence on the specific storage costs.

TABLE 2. Storage material costs and specific storage costs for various metal hydrides

	FE	TI	MG_2	NI	LA	NI_5	MM	NI_5
STORAGE MATERIAL								
Metal price*($/kg)	0.2	5.9***	2.0	4,9	30	4.9	6	4.9
Composition (kg/t)	540	460	450	550	320	680	300	700
Metal costs ($)	110	2710	900	2700	9600	3330	1800	3430
Fabrication costs** ($/t)	70		70		70		70	
STORAGE MATERIAL COSTS ($/t)	2890		3670		13000		5300	
HYDRIDE	$FE\ TI\ H_{1,95}$		$MG_2NI\ H_{4,3}$		$LA\ NI_5\ H_{6,7}$		$MM\ NI_5\ H_6$	
Useful storage density (kg H_2/100 kg hydride)	1.7		3.4		1.3		1.1	
Quantity of storer material (kg/t hydride)	983		966		987		989	
SPECIFIC STORAGE COSTS ($/kg H_2)	167		104		990		477	

* Metallwirtschaft u. Metallmarkt, Metall 4, 385 (1976); manufacturers information

** Melting $20/t, preparation $50/t; estimated

*** Titanium sponge 99.3%; free New York, March 1976.

On the basis of ferrotitanium the corresponding costs would be $1500/t, respectively $90/kg H_2. The costs for FeTi could possibly be reduced using direct reduction of ilmenite[18].

Strictly speaking, the costs of the storage material should be related to the quantity of hydrogen storable over the entire hydride lifetime. In addition, there should also be considered any possibility for regeneration and its related costs and/or a credit for the storage material used up. The latter aspect could lead to a larger cost deferment in the case of expensive metals such as lanthanum. In addition, consideration should also be given to the hydrogen quality required for individual storage materials. Thus, for instance, the storage of cheaper hydrogen on a more expensive hydride could be more economical than the reverse combination.

In addition to the specific storage costs of a hydride, its reversible mass (kg H_2/100 kg) and volume (kg H_2/100 l) storage densities are also significant. These will of course determine the quantity of hydride necessary to store the required quantity of hydrogen., its volume and hence also weight and the size of the reservoir, as well as its cost. However, we shall not deal here with this aspect in any more detail.

3.2.2. Hydrogen purity requred

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Since the hydrogen costs increase with increasing purity, the hydrogen quality required for the technological usability of a certain hydride also determines the economy of its use. In each case it is of course only the quality-determined cost difference that is significant, i.e., the additional costs that result when purer hydrogen is required for the storage in a given hydride, than is required by the envisoned end use. The same applies in the sense of the hydrogen filling pressure for the hydride storer.

Current prices for compressed hydrogen* (200-250 atm), for delivery of 25-50,000 Nm^3/a, are, depending on its quality:

- \$0.75/Nm^3 for technical hydrogen (99.5% H_2)

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* Manufacturer's information

- \$0.90/Nm³ for pure hydrogen (99.99% H_2)
- \$1.25/Nm³ for highest purity hydrogen (99.995% H_2)

Based on these cost relationships, the following theoretical considerations can be made:

1 ton of a hydride with a reversible storage capacity of 3% by weight H_2 will store - assuming a lifetime of 1000 absorption/desorption cycles - in the course of that lifetime approximately 30 t or $3.3 \cdot 10^5$ Nm³ of hydrogen. If for a certain end use technical purity hydrogen is sufficient, but for the storage in hydrides, however pure or highest purity hydrogen becomes necessary, the additional cost of hydride storage would be \$50,000 or respectively \$165,000.

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Since hydrogen costs depend very crucially on the total quantity delivered[31], the values given above should be more favorable, in reality. For instance, if the quantity delivered increased to 10^6 Nm³/a, the cost for commercial hydrogen is reduced to approximately \$0.25/Nm³ H_2 (cf. Figure 9[31]). Assuming that the quality-related cost differences mentioned above remain constant on a percentage bases, then for the delivered quantity here assumed we will have costs of approximately \$0.30/Nm³ H_2 of pure grade and approximately \$0.42/Nm³ H_2 of highest purity grade. The additional costs shown in the numerical example above, over the entire lifetime of the hydride, would then become reduced to \$16,500 and \$56,000 respectively.

To what extent, however, such a hypothesis is admissable and how the costs of hydrogen of different degrees of purity would evolve in dependence of actual demand, is uncertain. Nevertheless these considerations should clarify how big the influence is of hydrogen purity on the economy of hydride storage. In more detail, the following conclusions are possible:

- in general, hydride storage will be economical only in cases in which the end use has the same or higher quality requirements of the hydrogen than does the storage hydride;
- even expensive storage materials such as $LaNi_5$ need not be

uneconomical in principle, if they show good chemical stability and can be loaded with less pure and hence cheaper hydrogen;

- a shorter lifetime of the storage material using technical grade hydrogen could be more favorable, in some cases, than a longer one, purchased at the price of hydrogen quality. In this case, any additional regeneration costs or labor costs for the exchange of hydride or storer, etc., must also be taken into consideration; /29
- Because of its high degree of purity, electrolytic hydrogen should be sufficient for most hydride storage systems. The hydrogen costs should then lie between .1 and 0.2 dollars per Nm^3 of H_2 (cf. Figure 10[31]);
- the cycle water electrolysis-hydride storage-fuel cell, or gas turbine, respectively, for peak load storage, as well as the electrolytic hydrogen generation on board of a hydride storage-hydrogen engine vehicle during the standstill period, could continue to gain in economic interest.

From practical experience we know, however, that for most metal hydrides a reasonable lifetime is assured, without too frequent intermediate regeneration of partially spent storage material, using pure (99.99% H_2) hydrogen. Thus, the use of ultra-high purity hydrogen does not seem necessary, in this context.

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4. POSSIBLE APPLICATION AREAS

A series of metal hydride properties can be called upon to solve certain technical problems. Thus, hydrides can be considered for the following applications:

- hydrogen purification through selective absorption of the hydrogen in gas mixtures;
- reduction agents in metallurgical processes;
- hydrogenation catalyst in organic Chemistry;
- reversible heat storage for the storage of solar or respectively nuclear heat, etc.

The biggest interest in metal hydrides, however, is for the reversible of hydrogen, for stationary or portable applications, or for its transport in locations where transportation through pipelines is not feasible or practical, as for instance where hydrogen is produced far from the user location. Below, we shall deal in further detail with

- stationary hydrogen storage for electrical peak load storage;
- portable hydrogen storage for use in motor vehicles.

In the second case, we shall deal exclusively with the use of the stored hydrogen in a combustion engine. On a short-term basis this solution poses fewer technical problems as its use in an electrical vehicle equipped with a fuel cell (cf. also Reference 2).

4.1. Stationary Storage

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The reversible storage of electrical energy by means of the electrolytic generation of hydrogen, its storage in metal hydrides and reconversion into electrical energy is currently being considered especially in the US as an alternative to pumped storage[9]. For the stationary storage of hydrogen in hydrides, the stringent weight and volume limitations applicable to portable storage do not apply. Here, the selection of the hydride will be based more on economical (material and investment costs) and technological criteria (temperature and heat requirements).

Magnesium, with its approximate price of $2/kg is very advantageous and its hydride MgH_2 has a high storage capacity (approximately 7.6% by weight H_2); however, hydrogen desorption, even for the magnesium alloy hydrides known today, requires temperatures of 250-300°C, with a simultaneous high desorption enthalpy of 15-17 kcal/mol H_2[10,32].

From the technological point of view, the situation is more favorable for fe-Ti, the hydride $FeTiH_{1.95}$ of which, while having a smaller storage capacity, dissociates already at temperatures between 50 and 100°C with a sufficient velocity. Furthermore, its heat of formation of approximately 7 kcal/mole H_2 is relatively low. The heat energy necessary for its dissociation could that be obtained without any fundamental difficulty using water as heat carrier, from the waste heat of the energy transformer to be used (turbine or fuel cell). Figure 11[9] shows such a hydrogen-energy storage system in schematic form.

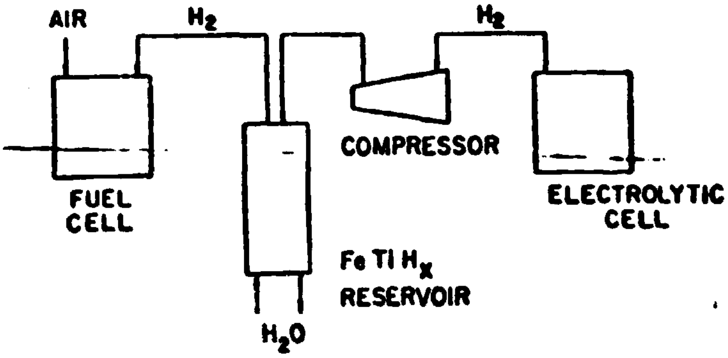

Figure 11. Hydrogen-energy storage system with hydride storer for peak-load storage[9]

Model tests for peak load storage for the cycle water electrolysis-hydride storage-fuel cell are currently being conducted at BNL by contract for PSE&G[9]. The hydride storer used contains 400 kg of $FeTiH_x$ in a stainless steel container.. A heat exchange system consisting of U-shaped tubes permit the supply of the quantities of heat needed for desorption, or, respectively, removes the heat during Absorption. Table 3 below provides some of the numerical values related to the test storer:

TABLE 3. Characteristic data for the PSE&G reservoir

	Required	Obtained
Quantity of hydrogen available	4.5 kg	6.4 kg
Rate of loading (average)	4.5 kg/10h	5.3 kg/6 h
Rate of removal	0.45 kg/h	1.3 kg/h

/33

The energy density of the titanium-iron-hydride was close to 590 Wh/kg. To store 1 MWh, nearly 1.7 t $TiFeH_x$ would be required, and approximately 10^5 kcal would be required for the desorption of the hydrogen.

Cost estimates for such a storage system oscillate between 120 and 190 dollars per stored normal cubic meter of hydrogen[31]. Figure 12[33] provides a comparative survey of total facility costs for different peak load storers, including hydride storage, with reconversion by means of a gas turbine or fuel cell, respectively, corresponding to the current state of knowledge.

Optimistic estimates[4], assuming an overall efficiency of 40-50% make a total facility cost of approximately \$350/kW appear feasible, for the cycle electrolysis-hydride storage-fuel cell, for an 8 hour storage.

4.2. Portable storage

Under the increasing pressure of oil scarcity, the use of hydrogen as an alternate fuel for motor vehicles is receiving increasing interest. The conversion of a combustion engine for use with hydrogen or partial hydrogen use requires only minimal technical changes and has already been performed for prototype models[6,7].

In the search for technologically and economically acceptable storage possibilities, the storage in metal hydrides can be judged the most useful one for use in motor vehicles. However, of the hydrides known to date that are suitable for use in motor vehicles, not one permits achieving the energy densities given by a gasoline tank. In the selection of an appropriate hydride for storage on board a motor vehicle, the following are of primary importance: /34

- high storage capacity;
- low desorption temperature and enthalpy;
- good reversibility and sufficient lifetime;
- high reaction kinetics;
- low material costs.

To date, no hydride meets all of these requirements. Magnesium alloy hydrides have high storage capacities, but in turn have relatively high desorption temperatures and enthalpies. In spite of these disadvantages, magnesium alloy hydrides can be considered for portable storage, if it becomes possible to optimally use the heat available in the exhaust gases for the desorption reaction. It is particularly necessary, to this end, to solve heat exchange problems between the hot exhaust gas and the hydride bed, as well as material problems.

Based on its favorable thermodynamic and kinetic characteristics, the technial design of a $TiFeH_x$ storer appears essentially simpler and has already been tested in a number of prototype vehicles in the GFR and the US. Recently, the first results obtained with a pure hydride vehicle were published[7]. The hydrogen storer used in this application consisted of a cylindrical 65 1 tank with approximately 200 kg of TiFe filling. Total storer weight was given as 300 kg. The quantity of hydrogen stored at 25-30 bar amounted to 50,000 1 which is equivalent to an autonomy of 100-120 km under inner city traffic conditions. The heat required for desorption is obtained from the cooling water. Loading with hydrogen requires a time investment of 5 to 15 minutes.

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Figure 13 shows schematically the construction of the hydrogen power train. So far there have not been any published data on the technical details of the hydride storers in testing in the US, for portable applications.

1 Emergency valve
2 Dust filter
3 Hydrogen admittance valve to fill up
4 Pressure regulator
5 Hydrogen emergency valve
6 Emergency valve
7 Converter
8 Gas mixer
9 Engine
10 Overflow safety valve
11 Back pressure valve

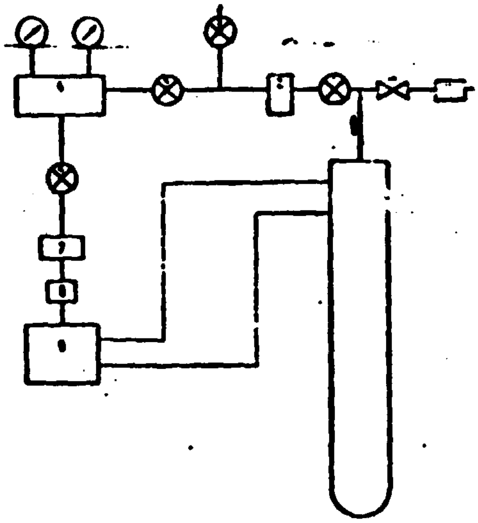

Figure 13. Schematic of a hydrogen power train in the Mercedes Benz test facility; the heat exchange piping are used to warm the storer by means of cooling water[7] .

The technical use of $FeTiH_x$ storers in motor vehicles presents no fundamental difficulties even today. As can be derived from the pressure temperature relations for he Ti-Fe hydride, no fundamental difficulties should be expected during pure hydrogen operation, not even during engine starting at low temperatures. At -10°C the hydrogen equilibrium pressure is still 2 atm.

Due to its unfavorable storage density, however, the $TiFeH_x$ storer is not optimally suited for every type of vehicle, as the following considerations show.

1. Medium-size car /36

Weight empty	1200 kg
Useful load	400 kg
Total weight	1600 kg
Average fuel consumption (intra-city operation)	15 l/100 km (gasoline)

If for gasoline we assume an energy density of 13 kWh/kg and for hydrogen 34 kWh/kg, then, assuming for the sake of simplicity that the same efficiency can be used for hydrogen operation, approximately 4.0 kg H_2/100 km would be required. For a range of 100 km, this corresponds to a quantity of $TiFeH_2$ (1.7% H_2) of approximately 235 kg, without including the tank weight.

2. Bus

Weight empty	10,000 kg
Useful load	7,000 kg
Total weight	17,000 kg
Average fuel consumption (intra-city operation)	70 l diesel/100 km

The energy density of diesel fuel, at approximately 12 kWh/kg, is a little lower than that of gasoline. Performing calculations analogous to those performed above, we arrive at a hydrogen consumption of 24.7 kg/100 km, corresponding to nearly 1450 kg.

For the ratio between total weight and hydride storer weight we obtain the following values:

Medium-size car: 6.8 /37
Bus 11.7

which would argue in favor of a preferred usage in the bus

One interesting possibility is offered by the use of hydride storers in a mixed gasoline/hydrogen operation[7,9]. In particular, two possibilities may be considered:

a) Intermittent operation: intra-city: hydrogen; open road: gasoline.

b) Continuous, mixed operation, gasoline/hydrogen

In both cases a combined hydride-gasoline tank system is required and would lead to noticeable savings in fossil fuels. The intermittent operation would furthermore contribute to the solution of air pollution problems within residential zones. During continuous mixed operation, the addition of hydrogen causes an increase in the efficiency and further, a decrease in the noxious products emitted in the escape gases.

While the use of hydride storers in motor vehicles is technically feasible, before a broader use can be contemplated it will be necessary to solve a series of problems that to a certain point also relate to stationary storage, and that are connected especially with the lifetime of the hydride and the purity of the hydrogen to be used. As already mentioned, the useful life of the hydride depends on its mechanical and chemical stability during the absorption/desorption cycles. Tests recently performed with with Ti-Fe hydride in hydrogen (99.99%) led to lifetimes of nearly 1000 cycles[21], without any special problems occurring in terms of grain refinement.

Nevertheless, hydrogen purity remains a problem. Fe-Ti is an excellent getter material for practically all impurities possible in hydrogen (CO, CO_2, H_2O, H_2S, O_2, N_2, etc.), and they become enriched on the powder particle surface during the absorption/desorption cycles, leading to irreversible poisoning of the hydride mass (cf. also reference 24).

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A further problem that at present impedes a wider use of hydride storers, is the lack of a corresponding hydrogen distribution network. Until the necessary infrastructure becomes available, it would be possible to generate the hydrogen electrolytically during pauses in vehicle utilization and, after appropriate purification, use it to load the hydride. Electrolytic hydrogen already has a high degree of purity and the impurities coming from electrolysis (H_2O, KOH) are relatively easy to remove. In this case, hydrogen loading would be comparable to a battery reloading.

5. CONCLUSIONS

From the hydrides studied in detail to date, that of FeTi has the best chances of coming into technical use, both for portable and stationary storage. In the motor vehicle area, the favorable total weight/hydride storer weight ratio points to the development of pure hydrogen operation for preferential application in buses. The use of TiFe hydride storers in a medium size passenger car seems purposive only in combination with a gasoline tank.

Before first-generation TiFe hydride storers are used for a broader application in the motor vehicle area, several problems of hydrogen generation, distribution and loading must be solved. Individual generation of hydrogen and its tanking during non-operation hours would have the advantage of producing relatively pure hydrogen, a solution that is independent also of a hydrogen distribution network.

The goal for the development of a second-generation hydride storer would be the improvement of storage density. Magnesium alloy hydrides could fulfill this requirement.

The problem areas related to the use of hydrides for peak-load storage in a electrolysis-hydride storage-fuel cell or gas turbine cycle, are in the main not related to the hydride storer itself. Here the problem is rather achieving an overall cycle effectiveness that is economically acceptable.

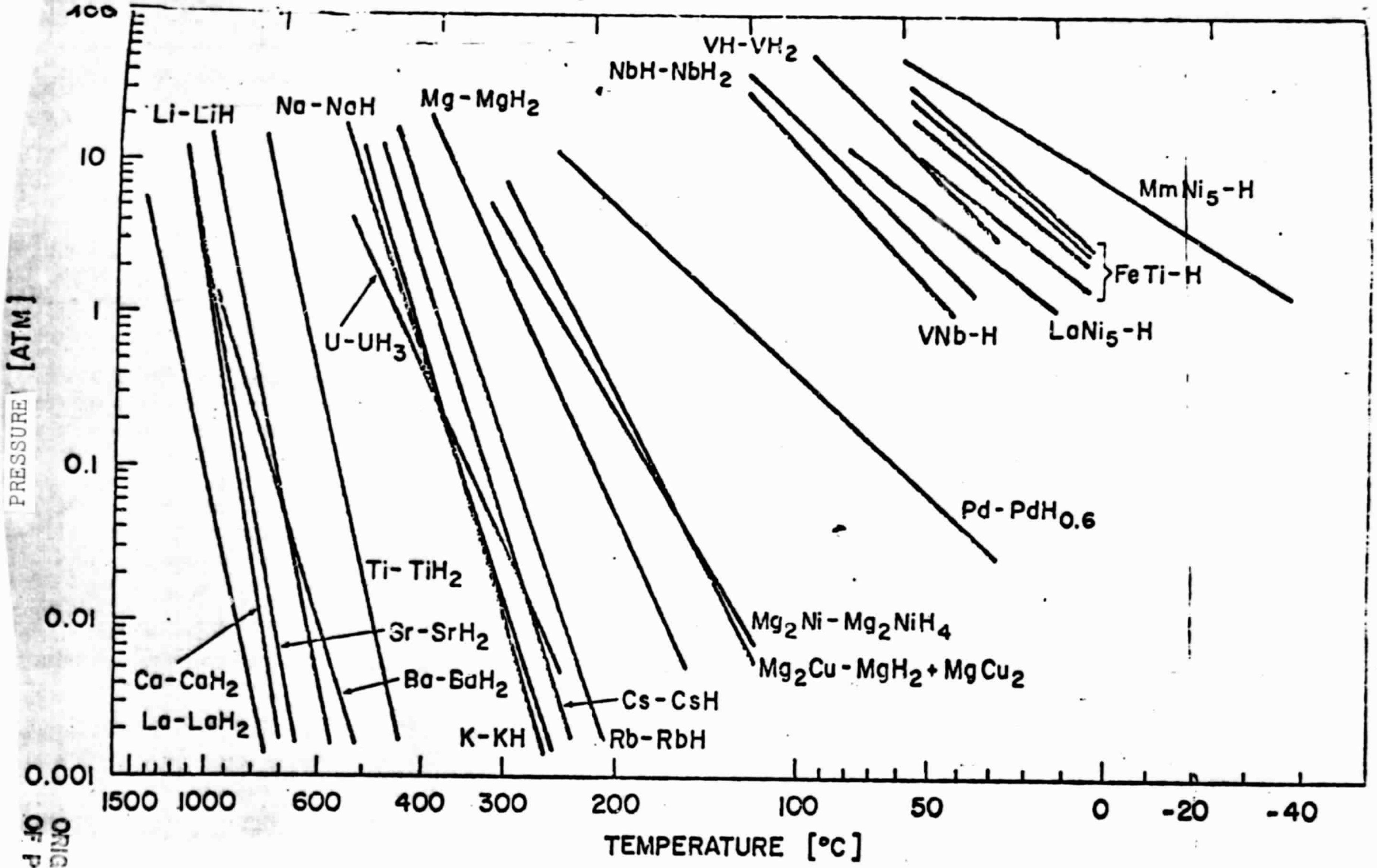

Figure 1. Pressure/Temperature dependence for various metal hydrides[2]

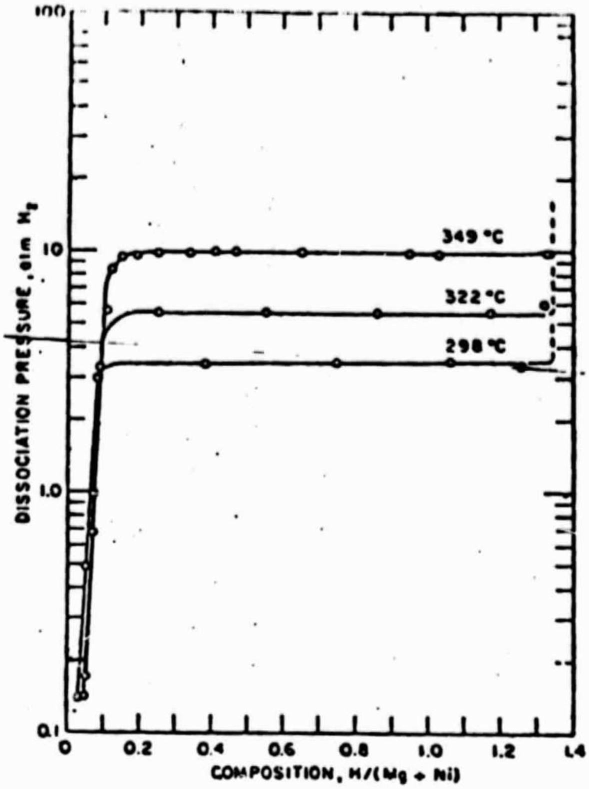

Figure 2. Pressure-Concentration isotherms for the system Mg_2NiH_2[10]

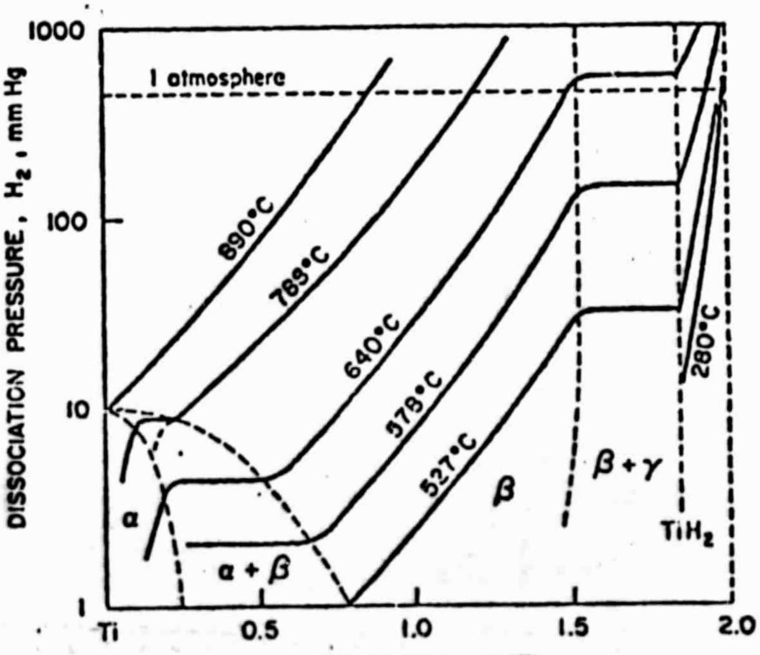

Figure 3. Pressure-Concentration isotherms for the system TiH_2[11]

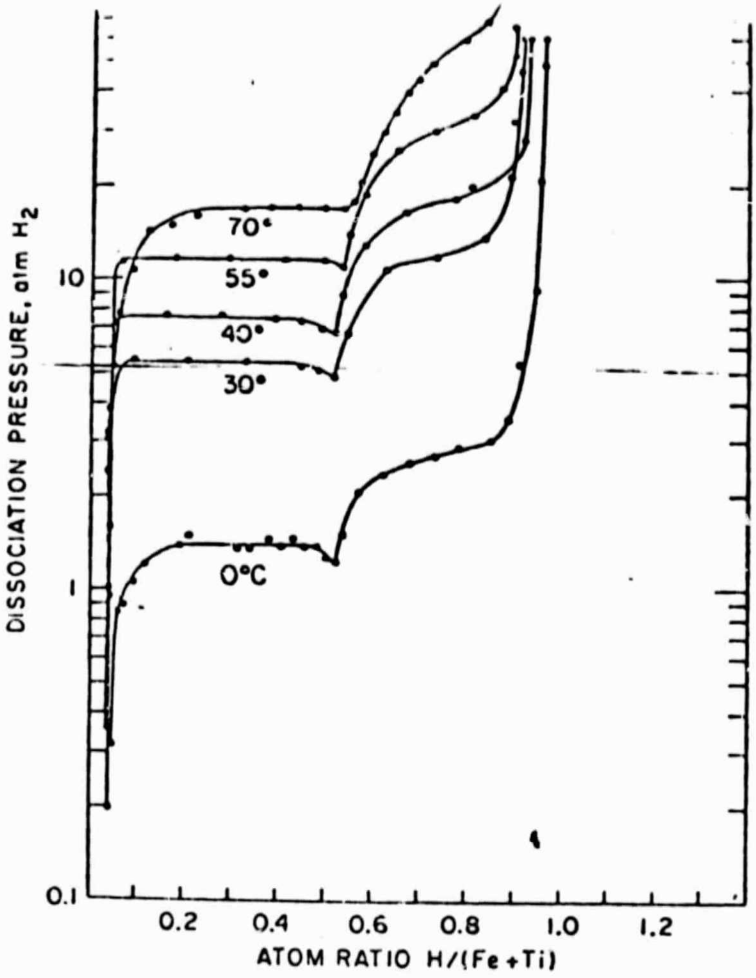

Figure 4. Pressure-Concentration isotherms for the system FeTi-H_2 [12]

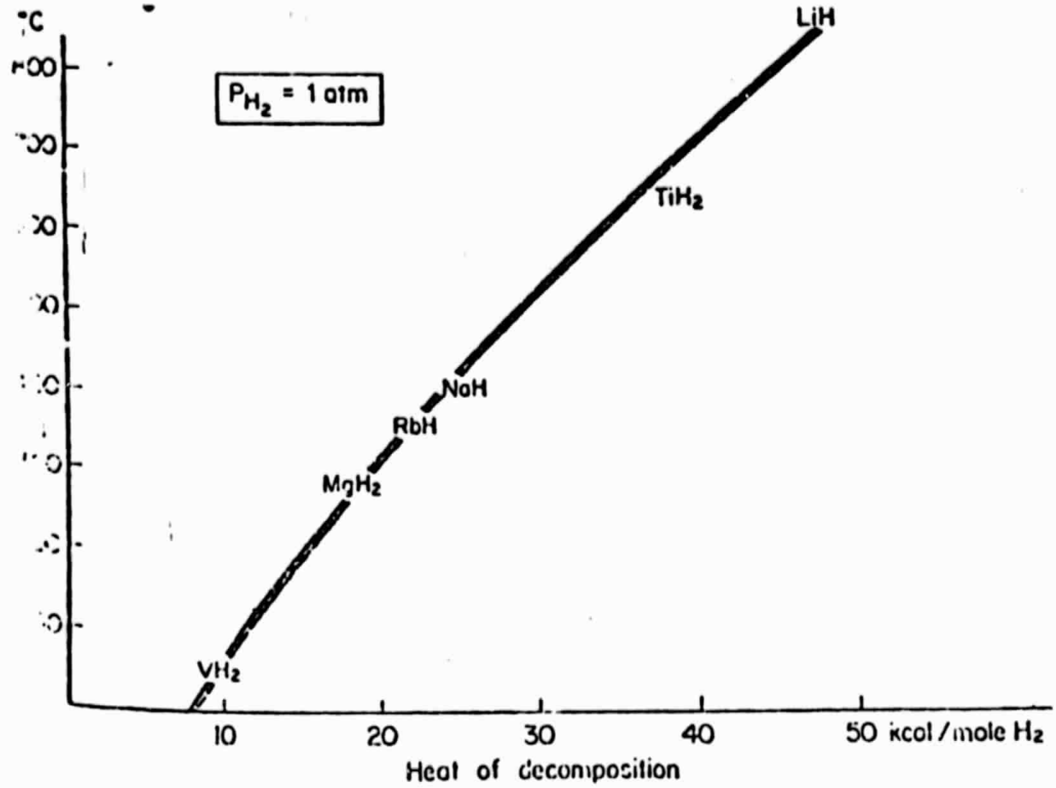

Figure 5. Heat of decomposition as a function of temperature for some hydrides

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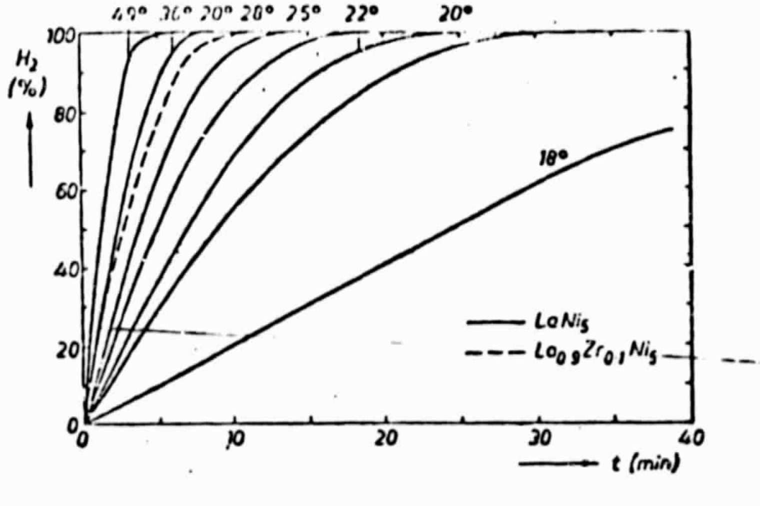

Figure 6. H_2 desorption from $LaNi_5$ hydride at different temperatures (pH_2=1 atm)[19]

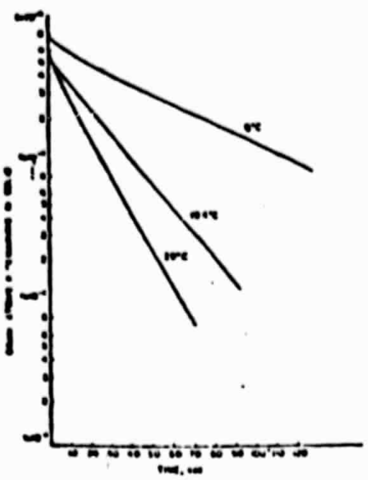

Figure 7. Dissociation rate of FeTi hydride at different temperatures[17]

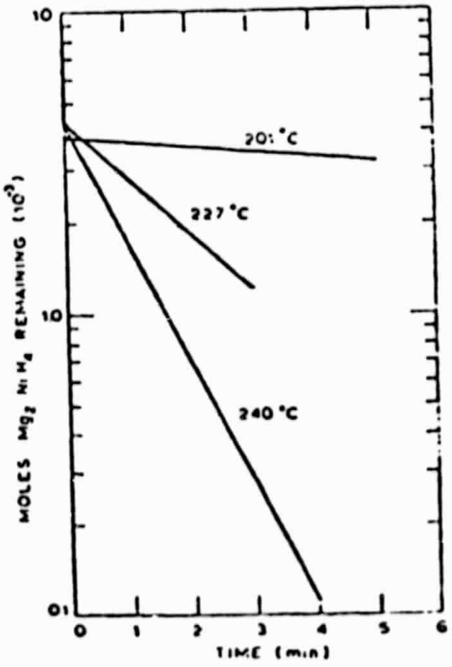

Figure 8. Dissociation rate of Mg_2NiH_4 at different temperatures[17]

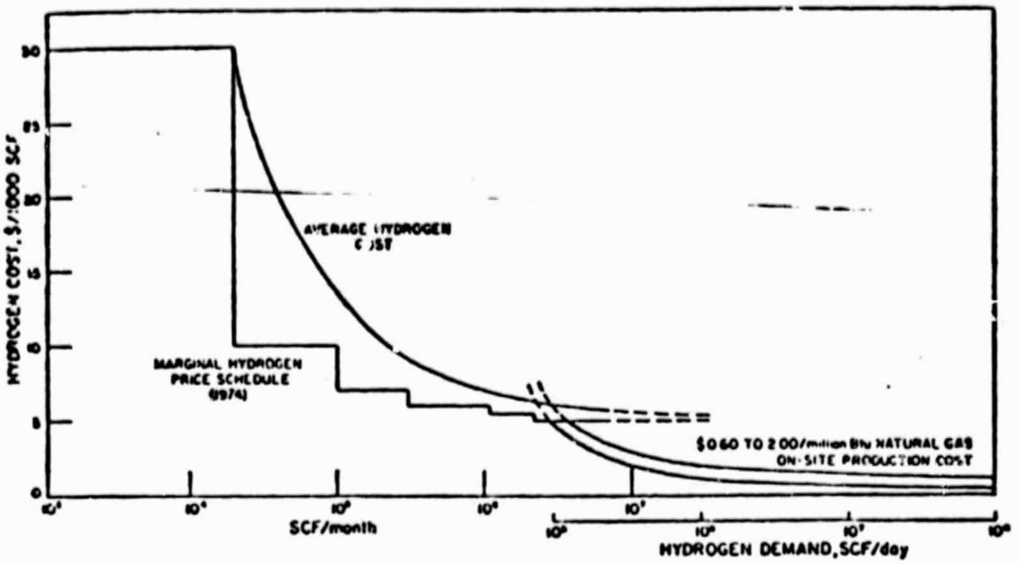

Figure 9. Costs of hydrogen as a function of the quantity ordered[31]

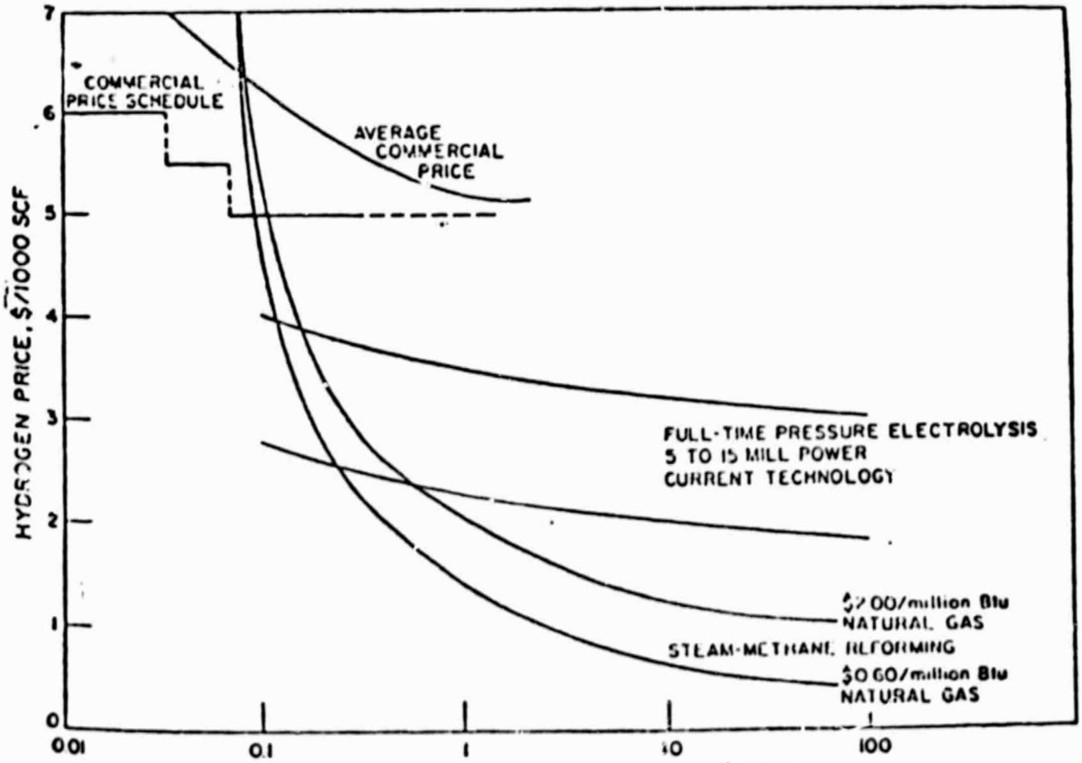

Figure 10. Comparison of different hydrogen costs as a function of the quantity required[31]

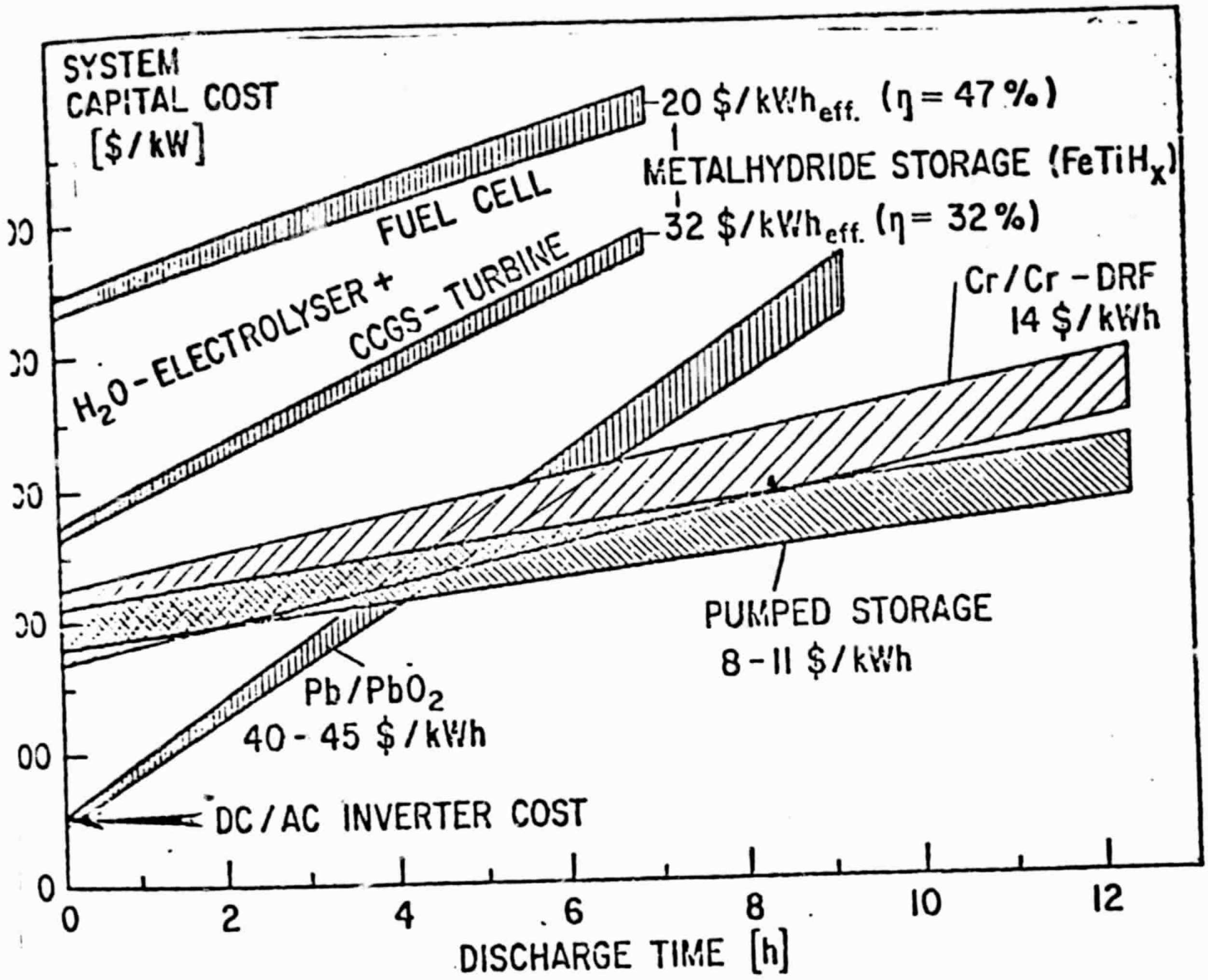

Figure 12. Facility capital costs as a function of storage capacity[33]

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