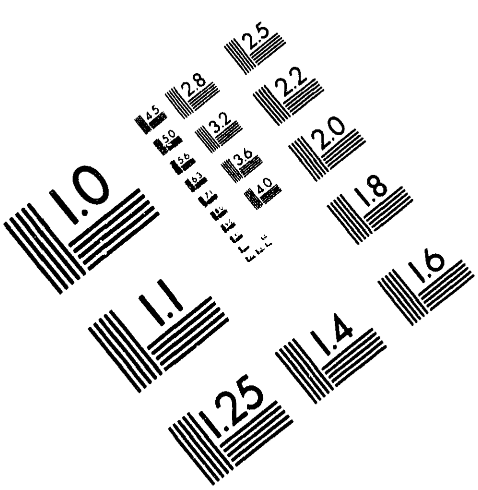

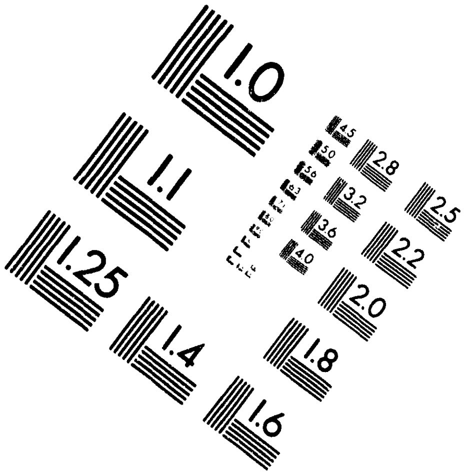

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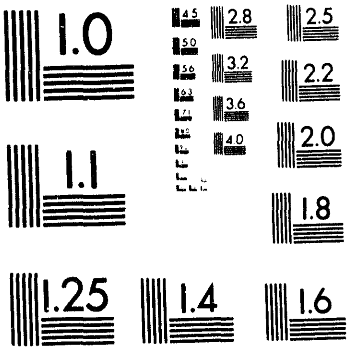

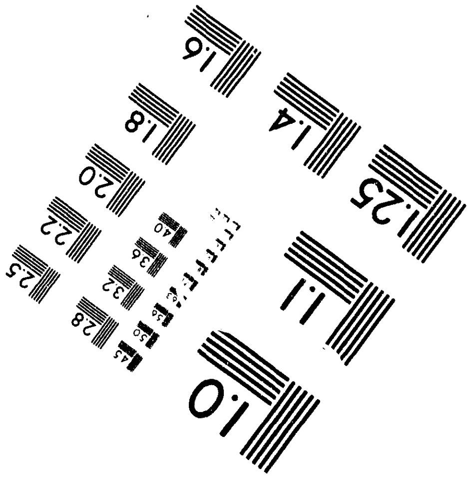

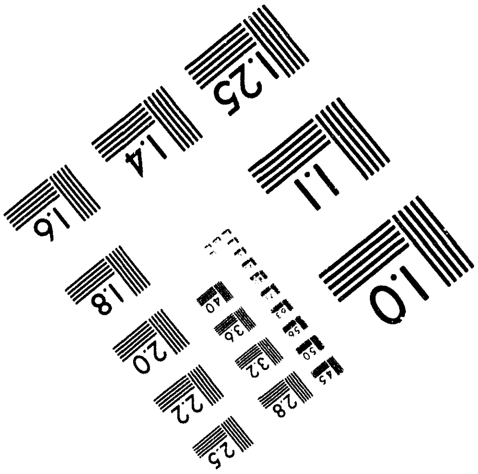

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MULTI-FUEL REFORMERS FOR FUEL CELLS USED IN TRANSPORTATION

ASSESSMENT OF HYDROGEN STORAGE TECHNOLOGIES

PHASE I. FINAL REPORT

March 1994

Prepared for

U.S. Department of Energy
Office of Transportation Technologies

Contract No. DE-AC02-92-CE50343

Arthur D Little

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FOREWORD

This report documents a portion of the work performed by Arthur D. Little, Inc. under contract DE-AC02-92-CE50343, Multi-fuel Reformers for Fuel Cells Used in Transportation. One objective of this program is to develop advanced fuel processing systems to reform methanol, ethanol, natural gas, and other hydrocarbons into hydrogen for use in transportation fuel cell systems, while a second objective is to develop better systems for on-board hydrogen storage.

Specifically, this report examines the techniques and technology available for storage of pure hydrogen on board a vechicle. The report focuses separately on near- and far-term technologies, with particular emphasis on the former. Development of lighter, more compact near-term storage systems is recommended to enhance competitiveness and simplify fuel cell design. The far-term storage technologies require substantial applied research in order to become serioius contenders.

Significant contributions were also made by Brian James and Ira Kuhn of Directed Technologies, Inc., whose work is also reflected in an interim report on this subject entitled "Feasibility Study of Onboard Hydrogen Storage for Fuel Cell Vehicles," issued by the Department of Energy (DOE), Office of Propulsion Systems in March 1993.

This work was funded by the U.S. DOE, Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Office of Propulsion Systems, Electric/Hybrid Propulsion Division. Project and technical management was provided by DOE's Electric/Hybrid Propulsion Division with technical oversight and advice provided by Argonne National Laboratory under the direction of Mr. Clinton C. Christianson, Manager Power Source Technology, Chemical Technology Division. Mr. Jeffery Bentley was the project manager for this project.

Lucito Cataquiz
Office of Transportation Technologies
U.S. Department of Energy

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ABBREVIATIONS

CNG	compressed natural gas
DOE	Department of Energy
DOT	Department of Transportation
FC	fuel cell
FCV	fuel cell vehicle
FUDS	Federal Urban Driving Schedule
HHV	higher heating value
HTH	high temperature hydride
H_2	hydrogen
ICE	internal combustion engine
ICEV	internal combustion engine vehicle
kpsia	thousands of pounds per square inch absolute
LH_2	liquefied hydrogen
MLI	multilayer insulation
NGV	natural gas vehicle
NTP	normal temperature and pressure
PAFC	phosphoric acid fuel cell
PEM	proton exchange membrane
psia	pounds per square inch absolute
SF	safety factor
STP	standard temperature and pressure
ZEV	zero emission vehicle

1.0 INTRODUCTION

Fuel cells are being developed for application in the transportation sector because the expected energy security, environmental, and economic benefits to the nation are truly significant. Fuel cells combine hydrogen (H_2) with oxygen from the air to produce electricity without using moving parts. Unlike ICEs, there is no combustion process which generates airborne pollutants. An FCV operating on pure hydrogen and air produces only water at the tailpipe and thus qualifies as a zero emission vehicle (ZEV).

The Department of Energy (DOE) has in place a fuel cell propulsion system development program with a goal of providing an alternative to internal combustion engines (ICEs) for the U.S. transportation sector. Fuel cell vehicles (FCVs) fueled by hydrogen stored on-board or using domestically-produced alternative fuels such as methanol, ethanol, or natural gas with a reformer could provide superior performance and lower emissions compared to conventional vehicles, while simultaneously reducing the nation's petroleum demand. Fuel cells can provide the power for vehicle propulsion systems with nearly twice the overall fuel efficiency and greatly reduced emissions and noise, compared with ICEs.

In the DOE Fuel Cells in Transportation Program, two basic strategies are being considered for providing the fuel cell with a supply of hydrogen at the required purity: (1) onboard fuel processing whereby methanol, ethanol, natural gas, or other alternative fuels stored on the vehicle undergo reformation and subsequent processing to produce hydrogen, and (2) onboard storage of pure hydrogen provided by stationary fuel processing facilities. Onboard fuel reformation adds significant complexity to the system; however, it has the advantage of using an alternative fuel for which the distribution infrastructure is already being developed. Onboard hydrogen storage greatly simplifies the vehicle design; however, storage technology meeting stringent weight, volume, and safety constraints must be identified. Based on preliminary analyses, summarized in this report, several hydrogen storage technologies can be developed in this decade, assuming sufficient research and development is undertaken to establish the technical and cost characteristics needed for large transportation markets. Several hydrogen storage technologies are likely to be utilized to address the unique requirements of both light-duty and heavy-duty vehicles.

Because the existing hydrogen market is very small today, a production and distribution infrastructure must be developed to support any significant use of hydrogen for transportation. This is a major thrust of DOE's Hydrogen Program Plan (Reference 1) for enabling the wide-scale use of hydrogen in the transportation sector. Near-term options for hydrogen production include fixed-site natural gas reformers that are located at vehicle refueling stations and take advantage of the pervasive natural gas distribution network. Longer-term options include electrolysis of water using electricity generated from renewable energy sources.

This interim report examines the leading methods for hydrogen storage on-board a fuel cell vehicle, focusing on current or near-term technologies. The following sections discuss (1) the candidate storage technologies, including their strengths and weaknesses; (2) the selection criteria for the most promising storage technologies; (3) system characterization of various storage technologies; (4) hydrogen fuel safety-related issues; and (5) further research needs in hydrogen storage for transportation applications.

2.0 OVERVIEW OF HYDROGEN STORAGE OPTIONS

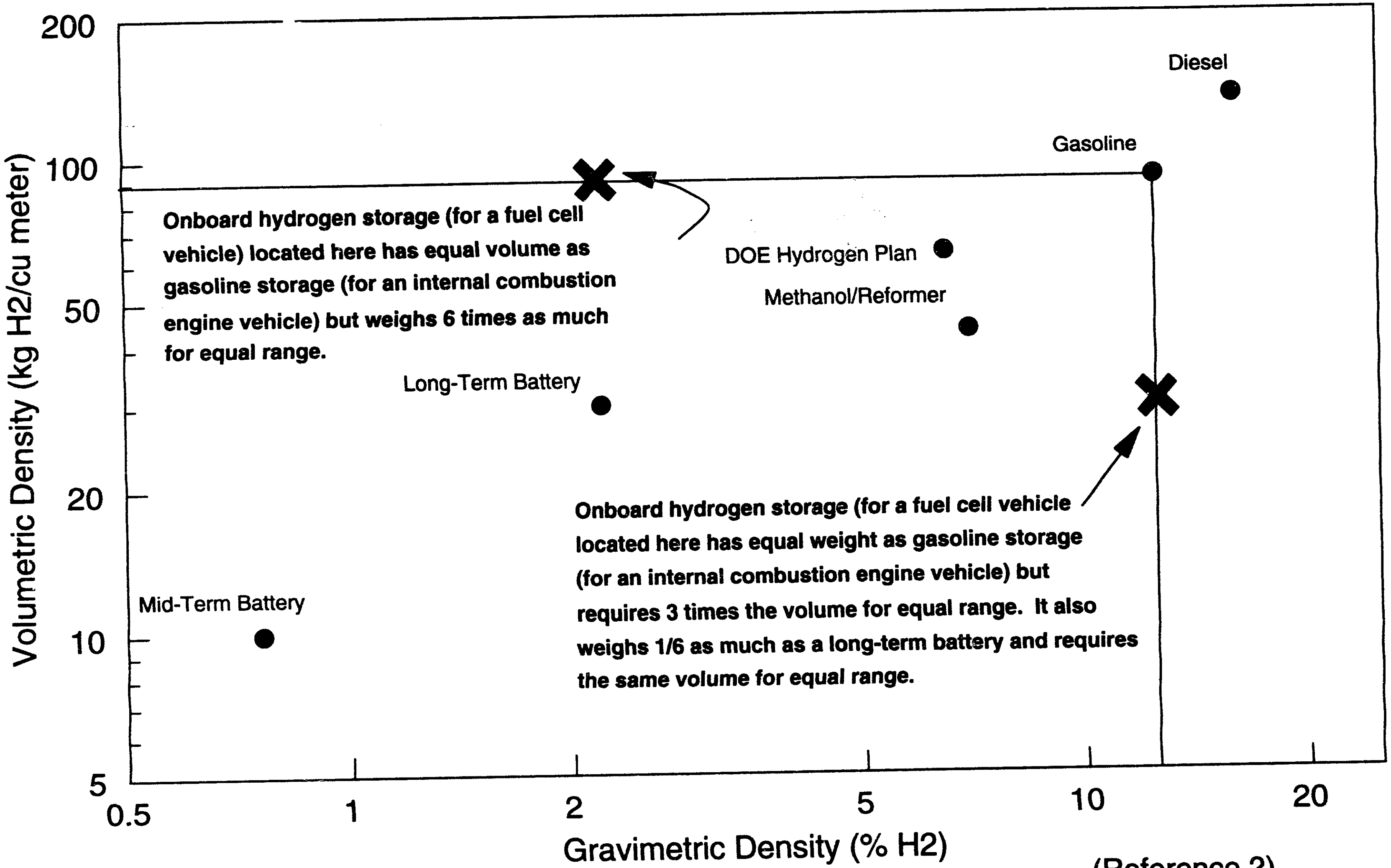
Like all other alternative vehicular fuels, hydrogen and its associated storage system occupy a greater volume and weigh more than an equivalent amount of energy in gasoline or diesel fuel. Although the much greater efficiency of the fuel cell vehicle means that less energy is required per mile, the hydrogen storage system onboard a vehicle will still exceed the weight or volume of gasoline. Therefore, storage system weight and volume characteristics are some of the most important aspects for matching fuel cell vehicular applications to the appropriate hydrogen storage technology.

Figure 1 is a graph of fuel system weight density on the horizontal axis and volumetric density on the vertical and provides a useful tool for comparing hydrogen storage alternatives to other energy sources:

- *System gravimetric density* is defined as the weight of stored hydrogen divided by the weight of the fully loaded storage and regeneration systems ($kg_{HYDROGEN}/kg_{SYSTEM}$).
- *System volumetric density* is defined as the weight of stored hydrogen divided by the external volume of the hydrogen storage and regeneration systems ($kg_{HYDROGEN}/m^3_{SYSTEM}$).

Note that a logarithmic plot is required in order to display the large differences between different technologies. On this graph, bigger is better so that diesel, in the upper right hand corner represents the energy storage system which provides the lowest weight and volume to travel a given distance. The goal of the DOE Hydrogen Plan (Reference 1) under the Matsunaga Hydrogen Act (P.L. 101-556), shown in Figure 1, is to develop hydrogen storage technologies that compare favorably with gasoline. Also shown in Figure 1 are technologies which are candidates to replace diesel including the methanol reformer (coupled with a fuel cell) and batteries (installed in an electric vehicle). The relative propulsion efficiencies of each system have been incorporated so that each plotted value is proportional to the vehicle range that can be provided for a given weight or volume. Two examples are provided in Figure 1 to assist in interpretation. The large X in the upper portion represents a hypothetical hydrogen storage technology which would provide an FCV with range equal to a gasoline vehicle if the gasoline and hydrogen storage system were the same volume. However, that storage system would weigh six times as much as the gasoline system. Similarly, the X on the right hand side indicates a technology which will provide equal range for equal weight but requires about 3 times more storage volume than the gasoline system.

Figure 1: Hydrogen Storage System Comparison, How to Interpret This Chart



Onboard hydrogen storage (for a fuel cell vehicle) located here has equal volume as gasoline storage (for an internal combustion engine vehicle) but weighs 6 times as much for equal range.

Onboard hydrogen storage (for a fuel cell vehicle located here has equal weight as gasoline storage (for an internal combustion engine vehicle) but requires 3 times the volume for equal range. It also weighs 1/6 as much as a long-term battery and requires the same volume for equal range.

(Reference 2)

As shown in Table 1, a variety of techniques (mechanisms) can be employed to store hydrogen reversibly.

Table 1: Characteristics of Reversible Hydrogen Storage Technologies

Storage Mechanism	Implementation	Key Characteristics
Gaseous	Pressure Vessels	3,000-5,000 psia, 150-300°K
Liquid	Cryogenic Tanks	15-100 psia, 20°K
Solid	Metal Hydrides	45-280 psia, 300-650°K
Hybrid	Carbon Adsorption 77-150°K Ambient Temperature	600-5,000 psia, 150-300°K

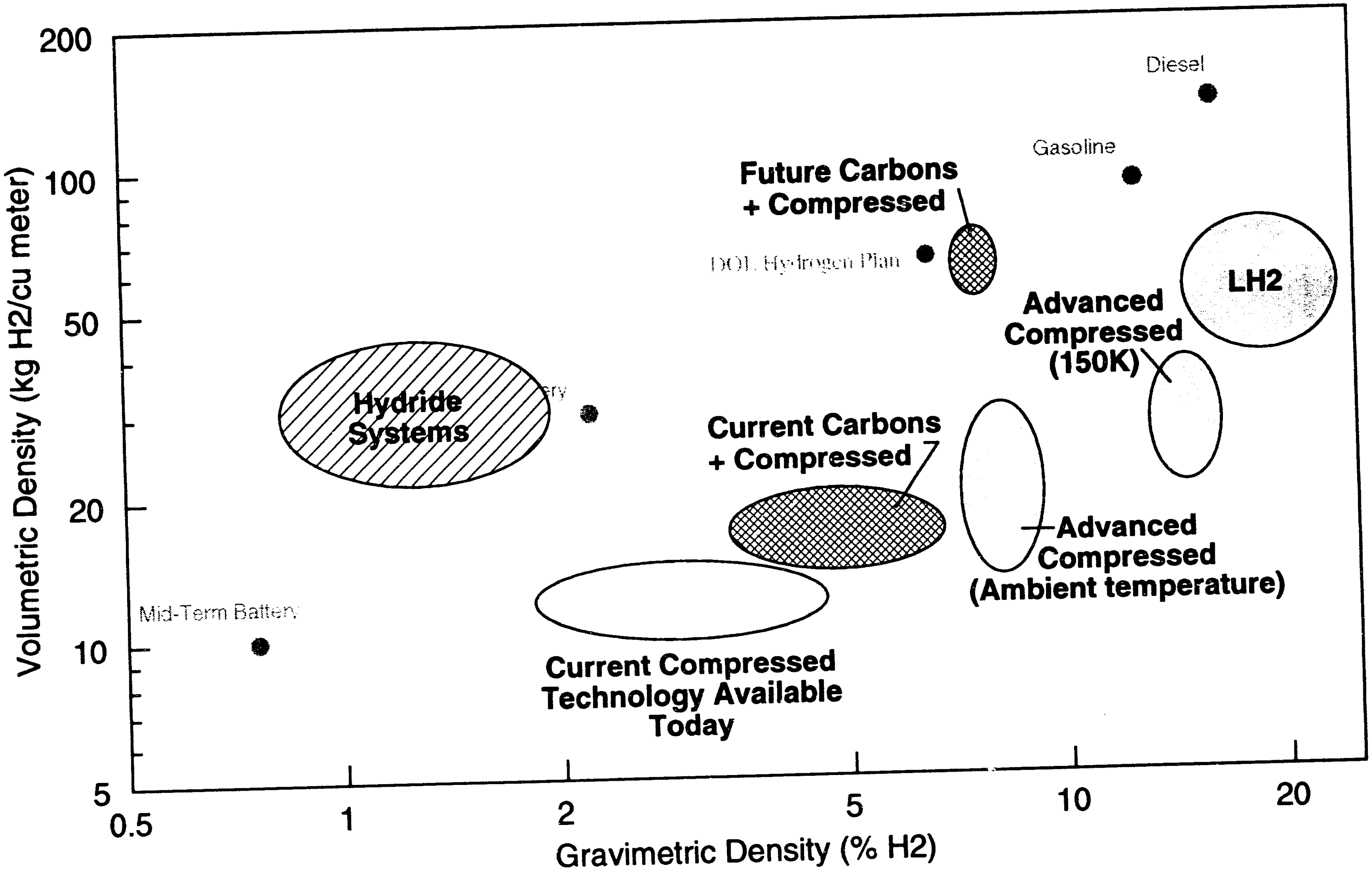
Other systems that are currently insufficiently characterized for evaluation at the system level may have merit in the longer term. These are:

- Iron and Water: The combination of iron and steam to form hydrogen and iron oxide.
- Liquid Hydrides (cyclohexane, methylcyclohexane): Liquid hydrocarbons that evolve hydrogen upon heating and pressurization. All carbon molecules remain trapped in hydrocarbon form (ex.: cyclohexane ⇔ benzene + $3H_2$). Also called recyclable liquid chemical carrier.
- Dihydrides (iridium-phosphorus complex): The reversible attachment of hydrogen molecules to metal complexes (metal atoms plus ligands).

Figure 2 shows how the characteristics of hydrogen storage technologies compare to diesel/gasoline with respect to gravimetric and volumetric densities. Several observations can be made from this figure:

- Compressed hydrogen using current technology falls short of the Hydrogen Plan goal and is well short of petroleum fuels storage systems. However, potential exists for significant advances in the near-term; namely, advanced tank technology, chilling the contents of the tank, reducing the pressure vessel safety factor within acceptable limits, or any combination of the three.

Figure 2: Hydrogen Storage System Comparison, Summary of Current and Future Systems



- A liquefied hydrogen (LH_2) storage system has a higher gravimetric energy density that a diesel system, but takes up almost three times the volume for a given range. The potential for further advances is not as great as with compressed and carbon adsorption storage systems. Moreover, the energy required to liquefy the hydrogen is a significant fraction of the available energy.

- Rechargeable metal hydride storage has numerous advantages (safety and volumetric density) but suffers from very low gravimetric energy density (i.e., high system weight).

- Carbon adsorbents when included in compressed storage systems have potential for increasing hydrogen storage density. However, advances in carbon manufacturing technology will be required to achieve the DOE goals for hydrogen storage.

The criteria for hydrogen storage on FCVs differ from those for ICEs. Fuel cells are much more efficient than ICEs--roughly 2.5 times on the Federal Urban Driving Schedule (FUDS). Thus the amount of stored fuel energy required for an equivalent driving range is much less than that required for ICEs.

From the perspective of fuel cell vehicles, criteria for evaluating hydrogen storage systems are:

- *System gravimetric density* is defined as the weight of stored hydrogen divided by the weight of the fully loaded storage and regeneration systems ($kg_{HYDROGEN}/kg_{SYSTEM}$).

- *System volumetric density* is defined as the weight of stored hydrogen divided by the external volume of the hydrogen storage and regeneration systems ($kg_{HYDROGEN}/m^3{}_{SYSTEM}$).

- *Storage system cost*

- *Energy cost of delivering fuel to the fuel cell*

- *Dormancy* - the ability of storage system to remain idle for long periods with no loss of hydrogen.

- *Safety*

The primary criteria for near-term vehicle application relate to packaging and efficiency. Since fuel cells are being considered for such diverse applications as passenger cars, buses, and railroad locomotives and since the various transportation sectors rank the importance of these criteria differently, a single hydrogen storage technique may not be appropriate for all future FCVs. Instead, a mix of storage techniques may be employed to fulfill the spectrum of future needs. The aspect of differing fuel storage system requirements is qualitatively demonstrated in Figure 3 (Reference 2). Different transportation applications which could eventually be candidates for fuel cell propulsion were subjectively rated for weight and volume criticality. Many important candidate applications were determined to be or very sensitive to additional intrusions of the fuel storage system into the vehicle passenger or cargo space. These are termed "volume-limited" or "cube-limited" and are shown in the upper-left quandrant. Other important applications were judged to be significantly constrained by weight (lower right). Some candidates were judged to be approximately equal in sensitivity applications to weight and volume (center band). When annual fuel consumption of each sector is considered, each of these three broad categories represents substantial national energy demand. In order to support widespread fuel cell penetration, both weight-efficient and volume-efficient hydrogen storage technologies will be required.

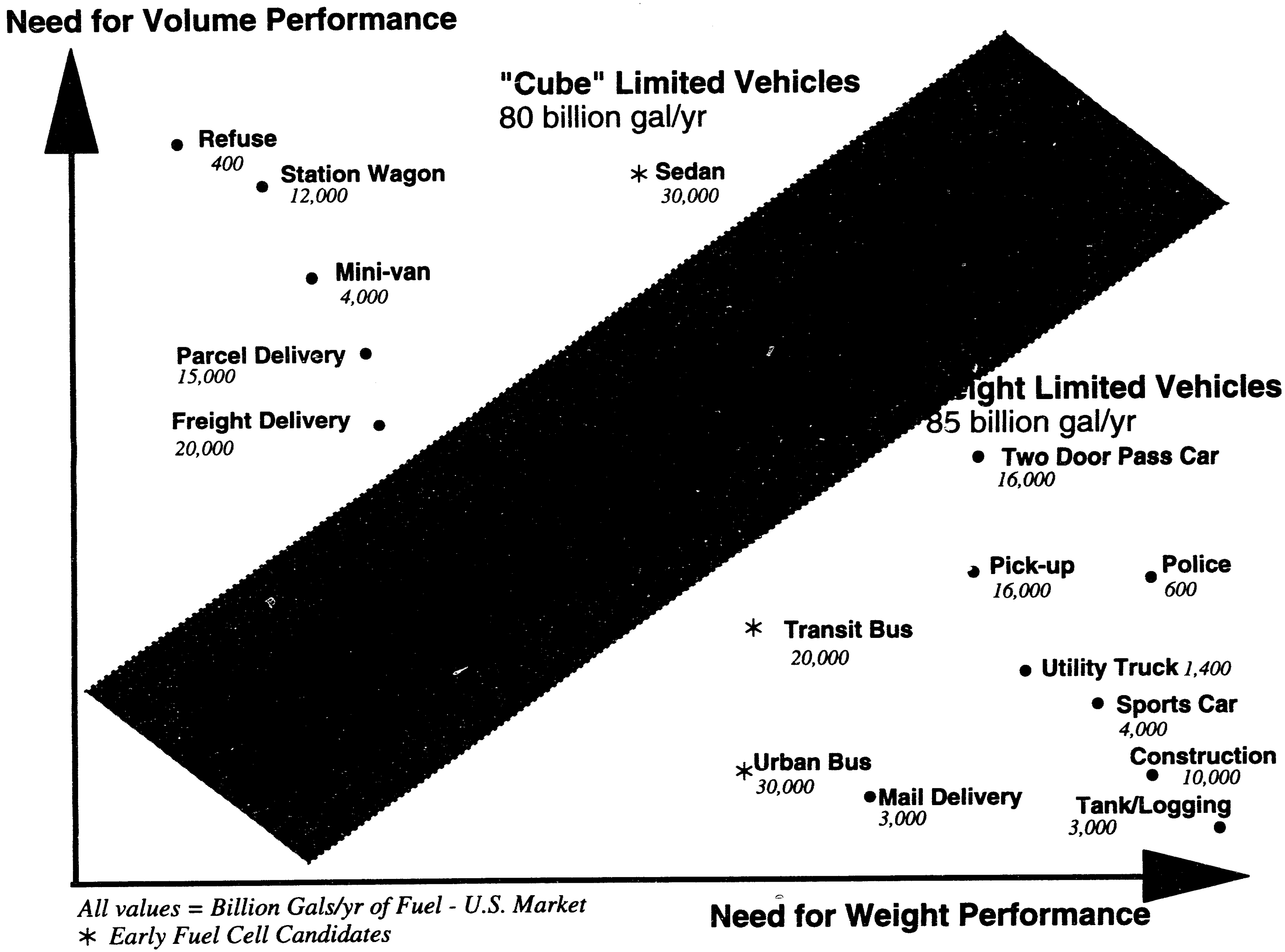
3.0 HYDROGEN-ONLY STORAGE SYSTEMS

There are fundamentally two categories of hydrogen storage systems: (1) those that contain hydrogen, and only hydrogen, within a vessel, and (2) those that contain hydrogen associated with some other substance within a vessel. The first category will be examined in this section of the report and the second category will be examined in Section 4.

Two classes of hydrogen-only storage systems are generally considered: liquefied and compressed. However, a continuum of such systems, as indicated in Figure 4 (Reference 2), can be imagined where hydrogen storage density is increased (either by a temperature decrease, pressure increase, or both) at the expense of increased system "filling" or preparation energy.

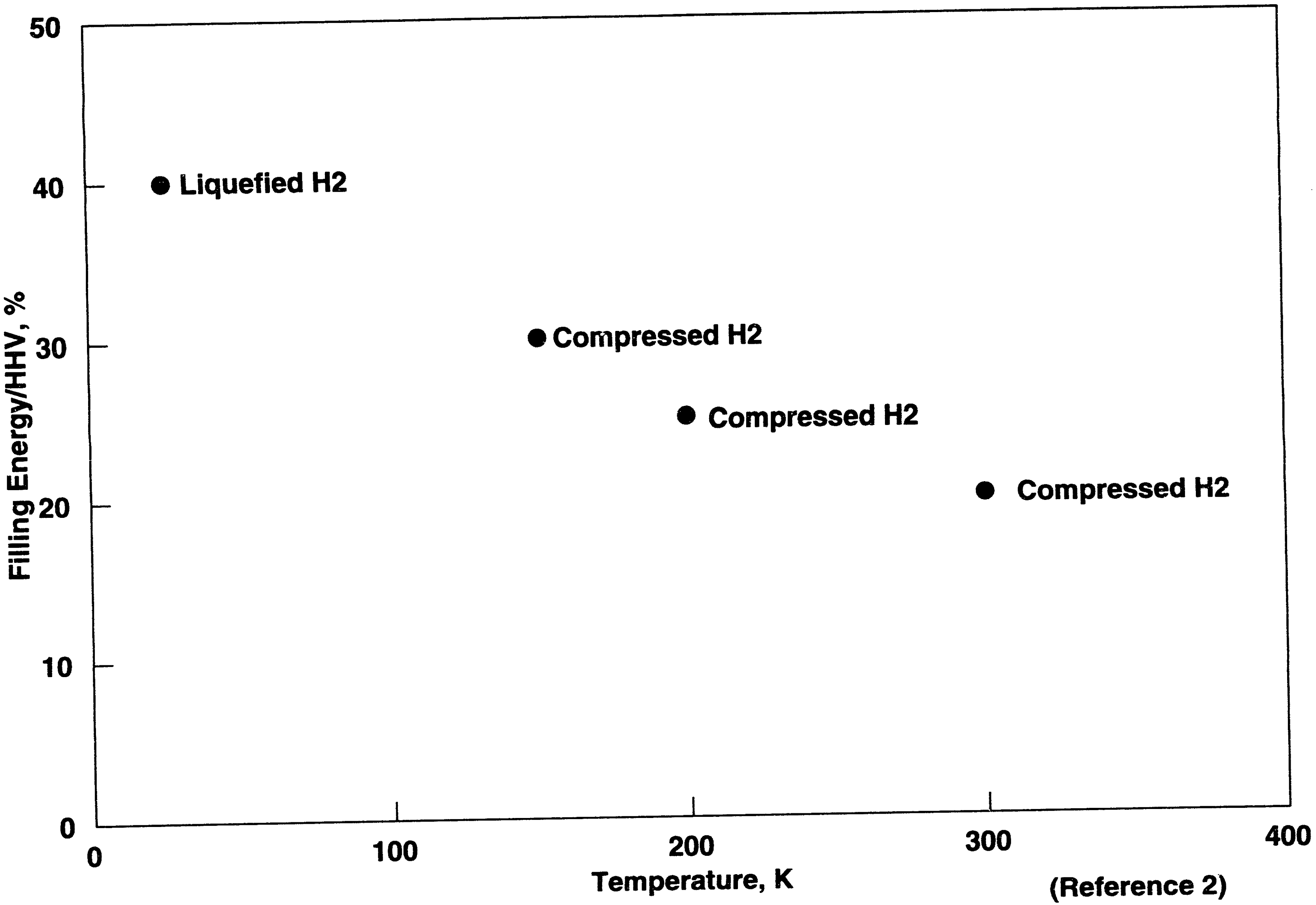
The distinguishing characteristic of all hydrogen-only storage systems is that energy must be provided to the system before the tank is filled (for compression, liquefaction, or chilling) rather than when the tank is discharged, as is the case for bonded-hydrogen systems. This filling energy comes from the infrastructure, and need not be carried onboard the vehicle; this is a major advantage since it eliminates the added weight, volume, cost, and complexity of onboard fuel preparation apparatus. However, the total energy required to prepare and deliver a quantity of hydrogen to the fuel cell is still a key measure of attractiveness.

Figure 3: Application Segmentation According to Weight and Volume Sensitivity (Ref 2.)



All values = Billion Gals/yr of Fuel - U.S. Market
∗ *Early Fuel Cell Candidates*

Figure 4: Continuum of Hydrogen-Only Storage



(Reference 2)

3.1 Liquid Hydrogen

Liquefied hydrogen (LH_2 at 20 K), favored by NASA for multi-ton bulk storage in support of Space Shuttle Operations and by industry for bulk over-the-road transport, is attractive because of its high gravimetric energy density. It becomes less attractive, however, as tanks get smaller (the storage vessel surface-to-volume ratio becomes large allowing greater heat flux into the vessel resulting in LH_2 boiloff) and the energy for liquefaction and maintenance of H_2 in the liquid state are considerable. "Lockup" time, defined as the time it takes a garaged cryogenically-fueled vehicle to reach its maximum design pressure due to boiloff and as a consequence vent hydrogen, is short for LH_2 systems: a tank designed to hold liquefied natural gas for ten days will hold liquefied hydrogen for less than two.

Magnetic liquefaction could help reduce the high energy demand of liquefaction by removing energy from hydrogen more efficiently. Refueling and handling difficulties associated with the extreme temperature can be made more tractable through better component and system design. Studies to investigate low cost, high efficiency liquefaction techniques and to determine the shortest lockup time acceptable to the driving public are needed.

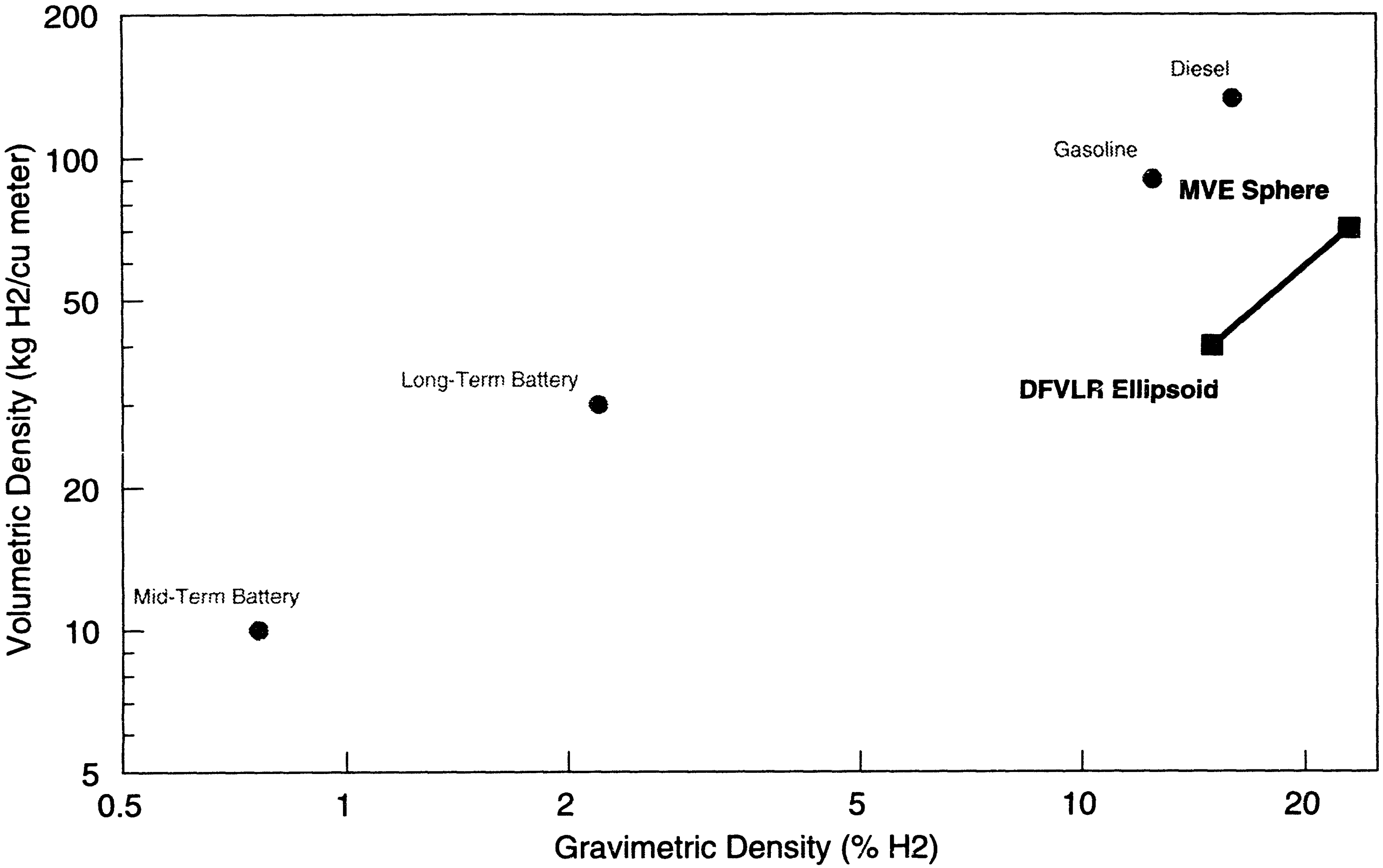
Figure 5 shows how two prototype LH_2 storage systems compare on the same weight/volume axis shown in Figure 1. MVE and DFVLR are the acronymns of the responsible research agencies. When the greater efficiency of the fuel cell is considered, a liquid hydrogen storage system for a tuel cell vehicle is likely to be lighter but about twice as bulky as an equivalent gasoline tank in a current ICEV with the same range.

3.2 Compressed Hydrogen

There is a substantial rationale for considering compressed hydrogen as a storage technology:

- It is conceptually the simplest on-board storage system;
- Nearly 100% of the contents are available on demand without dynamic, kinetic, or energy addition considerations;
- There is a well-documented design/materials/certification basis from commercial, vehicular and aerospace applications;

Figure 5: Prototype Hardware Performance Data for Liquefied Hydrogen Systems



- Considerable R&D and commercialization leverage can be gained from current natural gas vehicle activity including plastic liners and advanced composite tank development; and

- A high potential exists for aerospace technology transfer and greater utilization of the defense production base.

Compressed cylinder efficiency can be measured by the performance factor (P.F.):

P.F. = p_bV/W where

p_b = Burst Pressure
V = Internal Volume
W = Total Weight

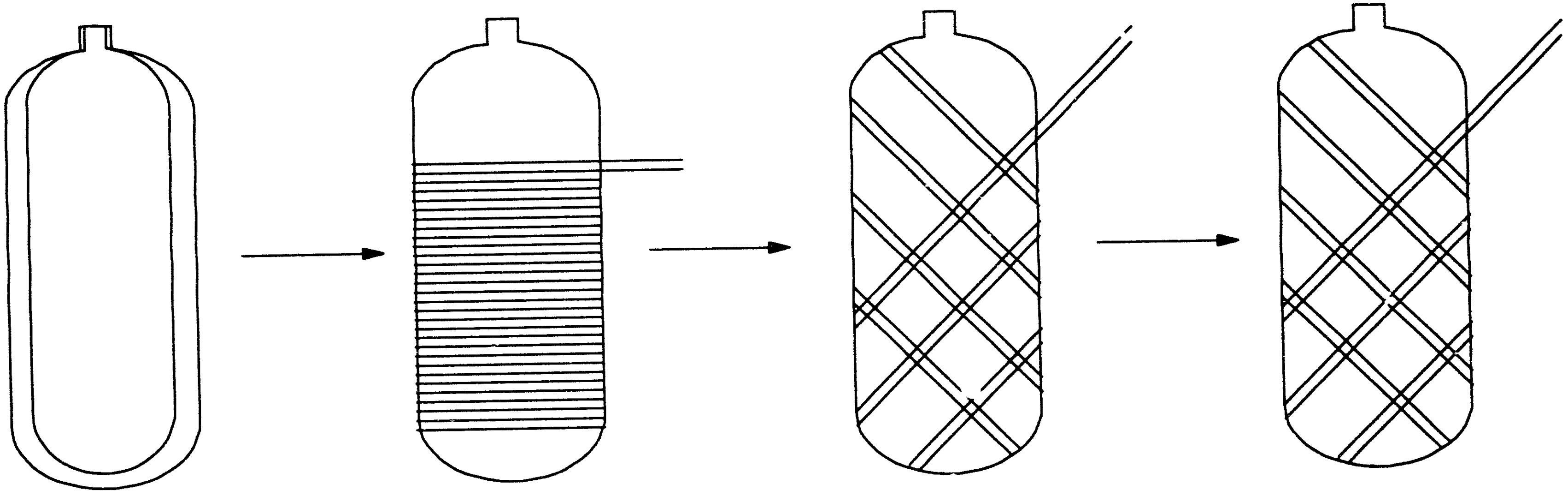
For a given burst pressure and safety factor, the volume of 1 kg H_2 is fixed by the thermodynamic properties. Also for a given volume and material/technology, weight is proportional to pressure (this assumes a thin-walled container). This means that the weight of a compressed cylinder can only be optimized by selection of material/technology. Figure 6 shows schematically the progression of tank materials and technology or construction. Figure 7 shows the steps in fabrication of aluminum liners, and Figure 8 shows how plastic liners are formed.

The weight of compressed gas systems can be reduced greatly by using advanced materials, such as carbon-graphite composite, for the storage cylinders. The benefits of composites include:

- Greatly improved strength,
- Uniformity of properties in the finished article, and
- Tailoring of windings to provide greater strength in required directions (i.e., hoop).

Figure 9 shows that the performance factor for advanced designs can reach nine times that of steel tanks and almost six times that of aluminum tanks. Furthermore, cold compressed vapor at 150°K will have twice the density of ambient temperature compressed vapor. It does so, however, at the cost of additional equipment at the refueling station: a multi-stage, intercooled compressor, a cascaded refrigeration system, and multiple high-pressure heat exchangers. Also, the vehicle tank must be both vacuum-insulated and capable of containing high-pressure. Whenever hydrogen is stored at reduced temperatures, "lockup" and dormancy of the system become an issue.

Figure 6: Progression of Tank Material/Technology



All Metal

Aluminum Liner Composite Hoop Wrap

Aluminum Liner Composite Overwrap

Plastic Liner Composite Overwrap

Figure 7: Aluminum Liner Fabrication Process

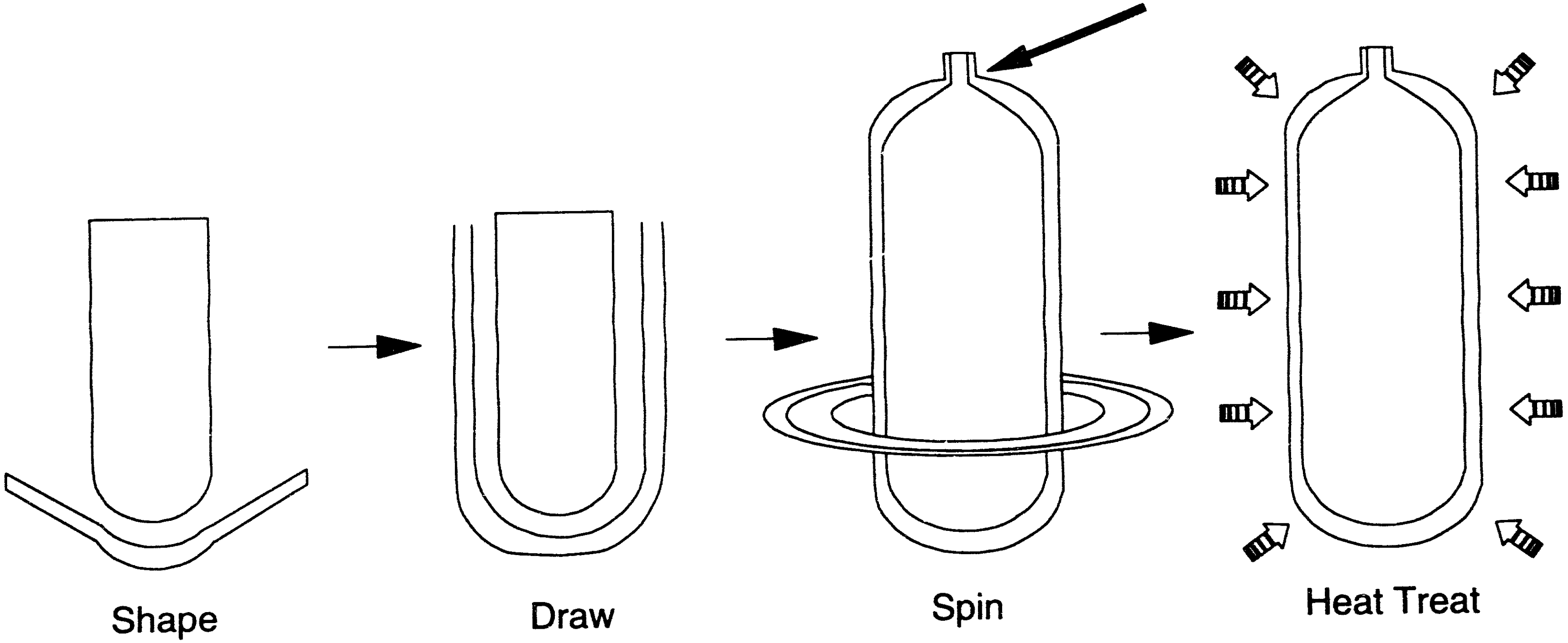
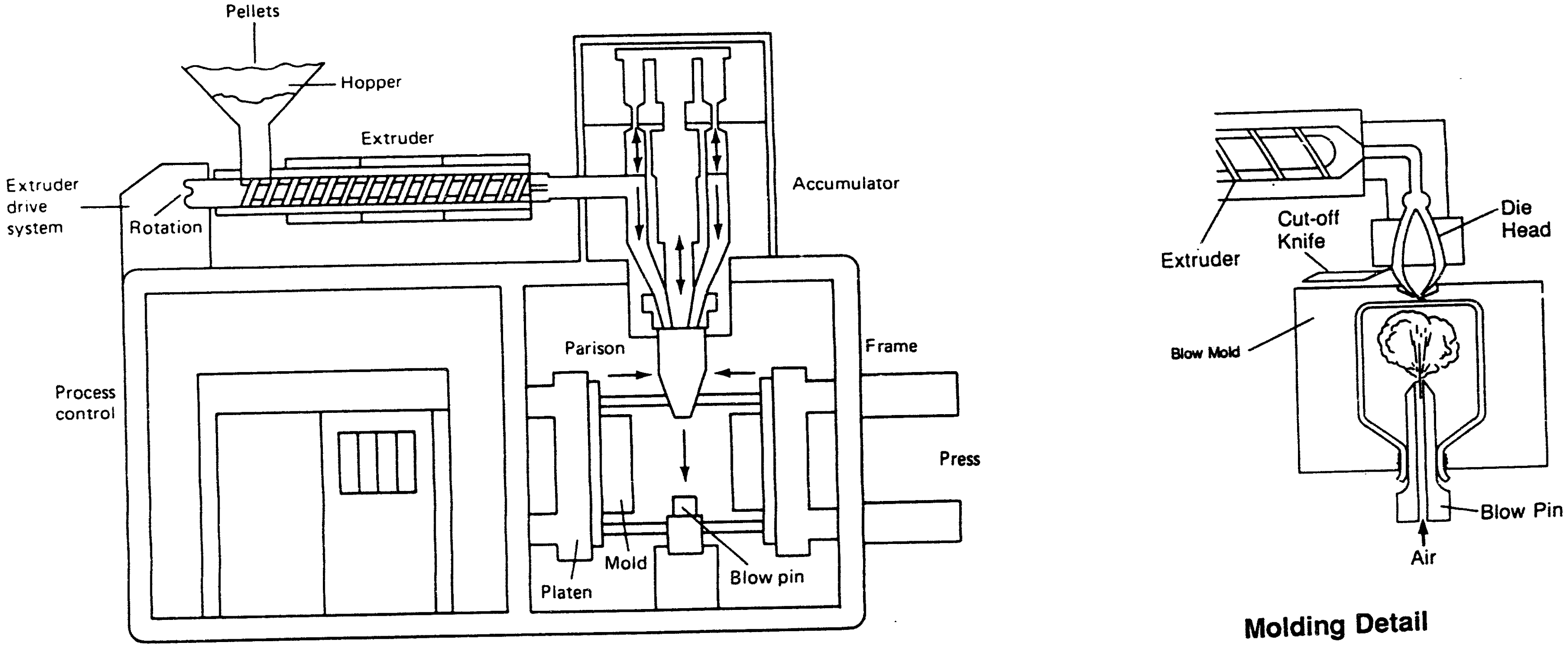
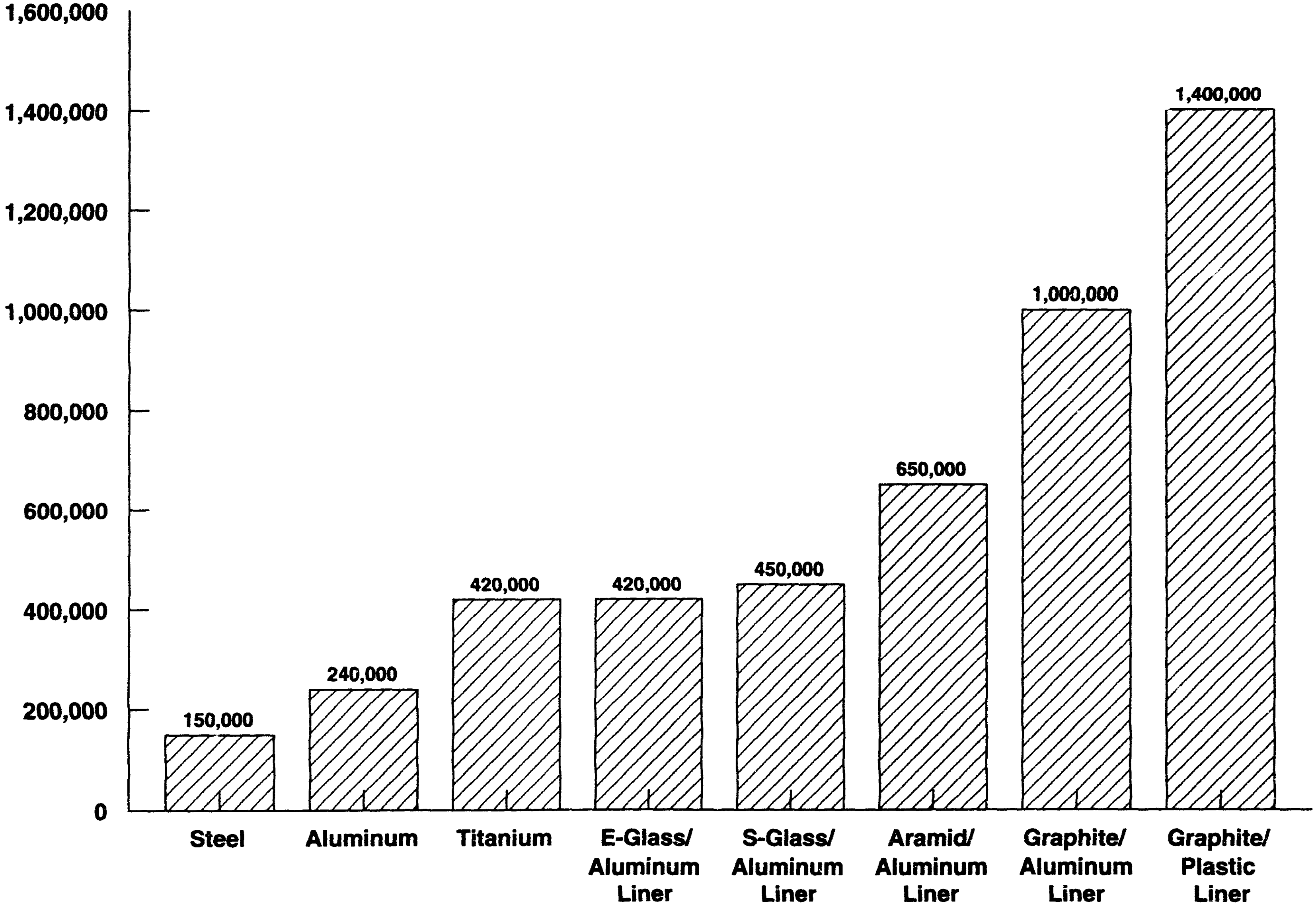


Figure 8: Plastic Liner Fabrication Process



Molding Detail

Figure 9: Comparison of Tank Performance Factors for Various Materials/ Technologies



Performance Factor defined as: $\left(\frac{\text{Burst Pressure x Volume}}{\text{Tank Weight}},\ \frac{\text{psi x cu in}}{\text{lbs}} = \text{Inches}\right)$ (Reference 2)

3.3 Compressed Hydrogen Tank Safety Factor

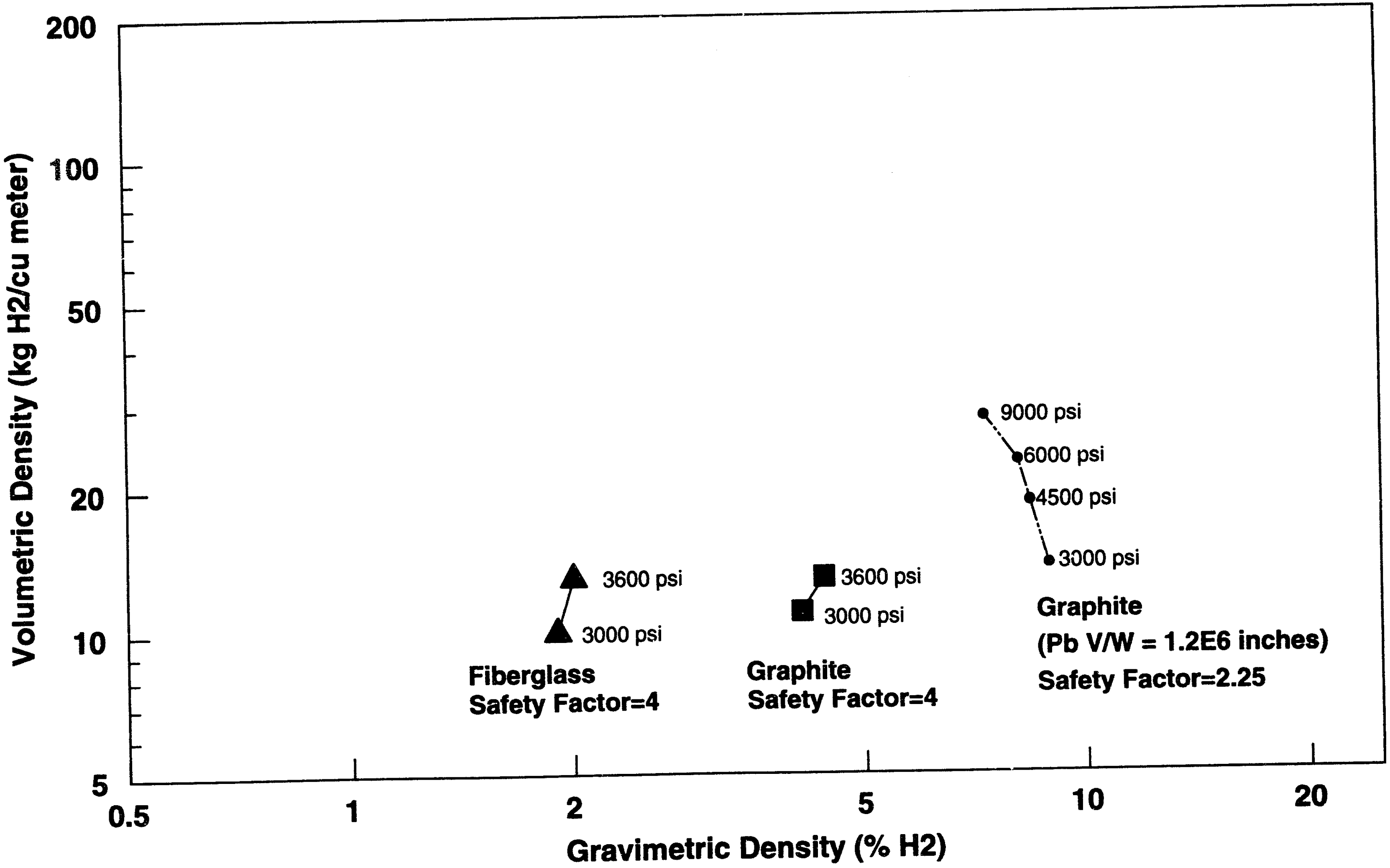
Tank safety factors define the relationship between the tank design burst pressure and the maximum allowable operating pressure. Thus, a 3000 psi operating pressure tank with a safety factor of 3 is actually designed not to fail (i.e., rupture or leak) below a pressure of 9000 psi. Tanks can be designed to leak before they burst; indeed SCI designs all its tanks to do so. Three main factors influence the level of safety factor: (a) manufacturing tolerances, (b) uniformity of material properties, and (c) degree of post-fabrication non-destructive testing. Currently, the Department of Transportation (DOT) requires a safety factor of around 3 for all vehicular pressure vessels. However, as pressure tanks move into mass production, increased quality control through the use of more automated production techniques and non-destructive diagnostics should greatly reduce the tank performance uncertainty which determines the required level of safety factor. Consequently, the future required structural safety factor may be reduced, thereby significantly decreasing tank weight.

Figure 10 depicts the weight and volume for a wide range of pressurized systems and safety factors. Four levels of safety factor are of importance:

SF = 3.0-4.0:	Current design requirements for non-composite pressure vessel transport.
SF = 2.25:	The natural gas industry lobbying goal for automotive compressed natural gas (CNG) cylinders.
SF = 2.0:	Typical military ground equipment requirement.
SF = 1.5:	Military aircraft and submarine requirement for critical load bearing structures.

Storage at 150 K is examined to represent the effects of moderate cooling and to allow direct comparison with the pressurized 150 K carbon adsorption system (discussed in a later section). Operation of the pressurized system at 150 K results in lower weight and volume than the room temperature pressurized system but only with the penalties of reduced dormancy, a more complicated and costly onboard storage system, and a more complex refueling apparatus.

Figure 10: Hydrogen Storage System Comparison for Compressed Cylinders



4.0 BONDED-HYDROGEN STORAGE SYSTEMS

The primary advantages of bonded-hydrogen storage systems are the potential for high H_2 volumetric density and the increased safety due to the less volatile, more stable storage medium. Each benefit will be further discussed in relation to the individual storage system.

Hydrogen atoms, or even hydrogen molecules, will bond to almost any element under appropriate conditions. Several hydrogen-containing compounds considered potential sources of hydrogen aboard vehicles are represented in Figure 11 (Reference 2), which demonstrates that one disadvantage of high hydrogen weight percentage in a bonded-hydrogen storage system is high dissociation temperature. Methane or ammonia onboard reforming systems have the added disadvantages of irreversibility and process complexity.

4.1 Metal Hydrides

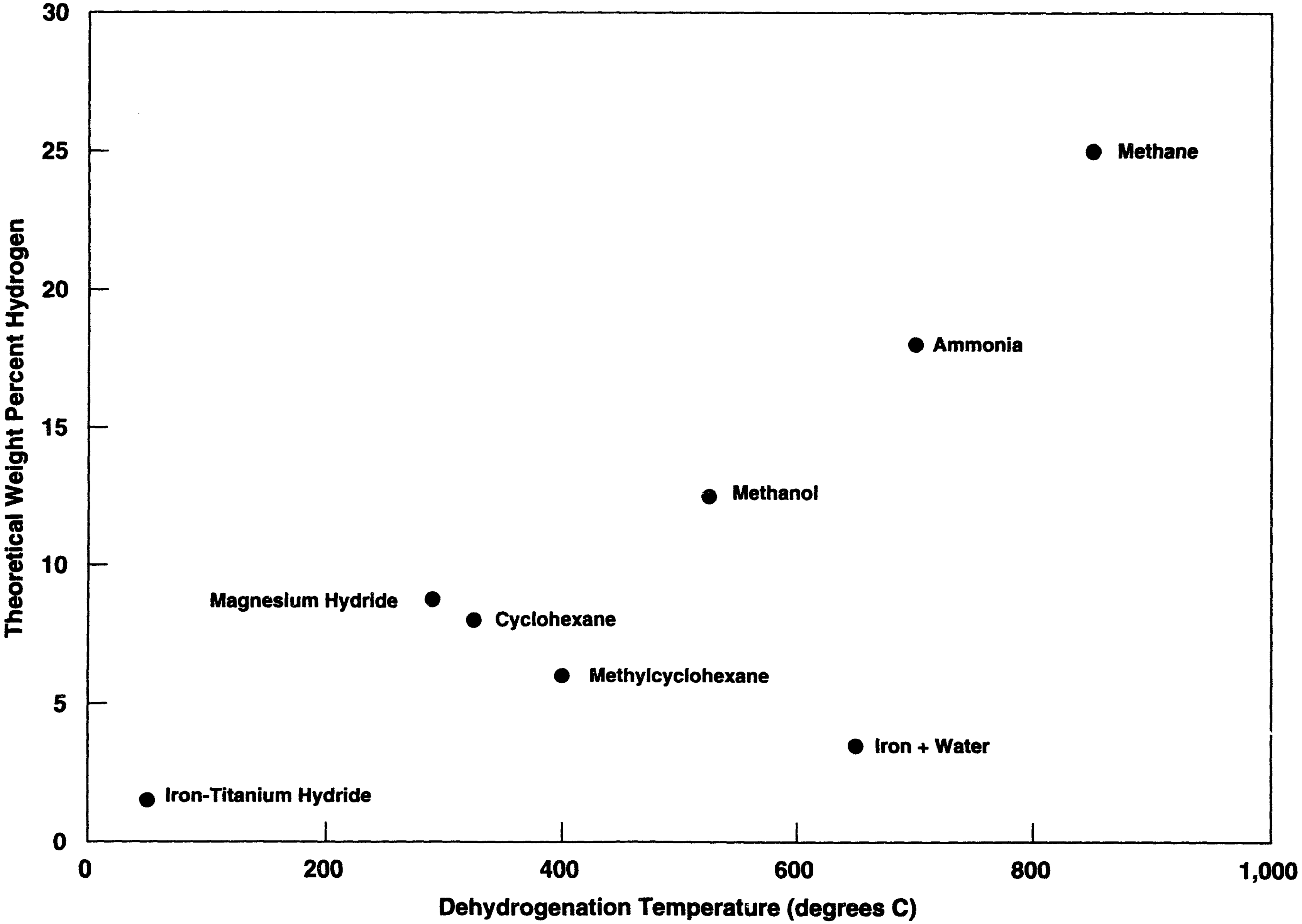
In theory, metal hydrides can store hydrogen at volumetric densities greater than that of liquid hydrogen. The volumetric densities of actual metal hydride storage systems, however, are somewhat lower, as:

- A metal hydride system is burdened by a pressure vessel, by an internal heat transfer system, and perhaps by thermal insulation; and
- Not all of the hydrogen bound up in such a system is readily recoverable.

Figure 12 (Reference 3) lists many candidate hydrides. Figure 13 shows Van't Hoff plots for several of these commonly studied metal hydrides. These show the combinations of temperature and pressure at which the metal hydride is in equilibrium with hydrogen and the associated pure metal. These plots illustrate the conditions for which:

- Increasing the hydrogen pressure, or decreasing the metal/alloy temperature, favors the hydriding reaction (absorption of hydrogen); and
- Decreasing the hydrogen pressure, or increasing the metal/alloy temperature, favors the de-hydriding reaction (release of hydrogen).

Figure 11: The Penalty of High H_2 Weight Percentage is High Dissociation Temperature

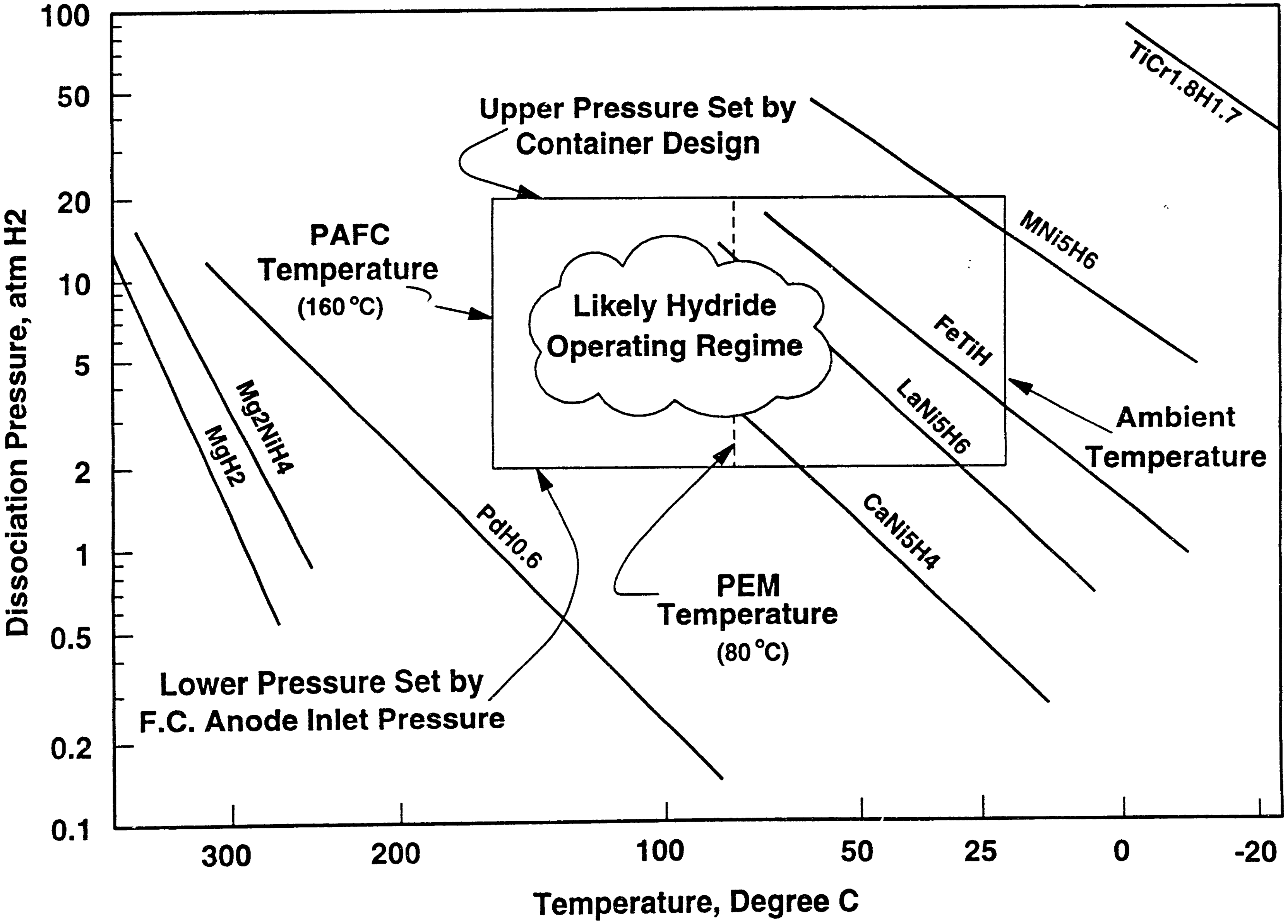


(Reference 2)

Figure 12: Typical Hydrogen Storage Alloys and Their Principal Characteristics

Hydrogen Storage Alloy	% H_2 by Weight (no containment)	Typical Dissociation Pressure (ATM)	Heat of Formation (kcal/mol)
MgH_2	7.6	1 (290°C)	-17.8
$Mg_2NiH_{4.0}$	3.6	1 (250°C)	-15.4
$LaNi_5H_{6.7}$	1.4	4 (50°C)	-7.2
$MmNi_5H_{6.3}$	1.4	34 (50°C)	-6.3
$MmNi_{4.5}Mn_{0.5}H_{6.6}$	1.5	4 (50°C)	-4.2
$LaNi_{4.6}Al_{0.4}H_{5.5}$	1.3	2 (80°C)	-9.1
$TiFeH_{1.9}$	1.8	10 (50°C)	-5.5
$TiFe_{0.85}Mn_{0.15}H_{1.9}$	1.8	5 (40°C)	
$TiCoH_{1.4}$	1.3	1 (130°C)	-1.38
$TiMn_{1.5}H_{2.47}$	1.8	7 (20°C)	-6.8
$Ti_{0.8}Zr_{0.2}Mn_{1.8}Mo_{0.2}H_{3.0}$	1.7	4 (20°C)	-7.0
$Ti_{0.9}Zr_{0.1}Mn_{1.4}V_{0.2}Cr_{0.4}H_{3.2}$	2.1	9 (20°C)	-7.0
$Ti_{0.8}Zr_{0.2}Cr_{0.8}Mn_{1.2}H_{3.0}$	1.8	5 (20°C)	-6.9
$Fe_{0.8}Ni_{0.2}TiH_6$	5.5	1 (80°C)	
$Ti_{0.98}Zr_{0.02}V_{0.45}Fe_{0.10}Cr_{0.05}Mn_{1.5}H_{3.4}$	2.1	10 (24°C)	
H_2	100	1 (0°C)	68.32

Figure 13: Van't Hoff Plots (Desorption) for Various Hydrides



These lines (called isochores) are gathered into two groupings:

- High-temperature hydrides, characterized by ionic bonds and by low atomic weights of the metals (which necessarily correspond to high hydrogen weight percentages); and

- Low-temperature hydrides, characterized by covalent bonds and by high atomic weights of the metals (which necessarily correspond to low hydrogen weight percentages).

Low-temperature metal hydrides with high hydrogen weight content would be desirable and may yield to further research, although no clearly promising areas were identified during this work. Innovative methods for low weight containment systems and efficient heat transfer are also needed since these factors account for significant fractions of total storage system weight and volume. Only a few ioschores on Figure 13 pass through the usable range of pressure and temperature, defined by:

- Pressures above atmospheric (to prevent oxidation due to inleakage), and

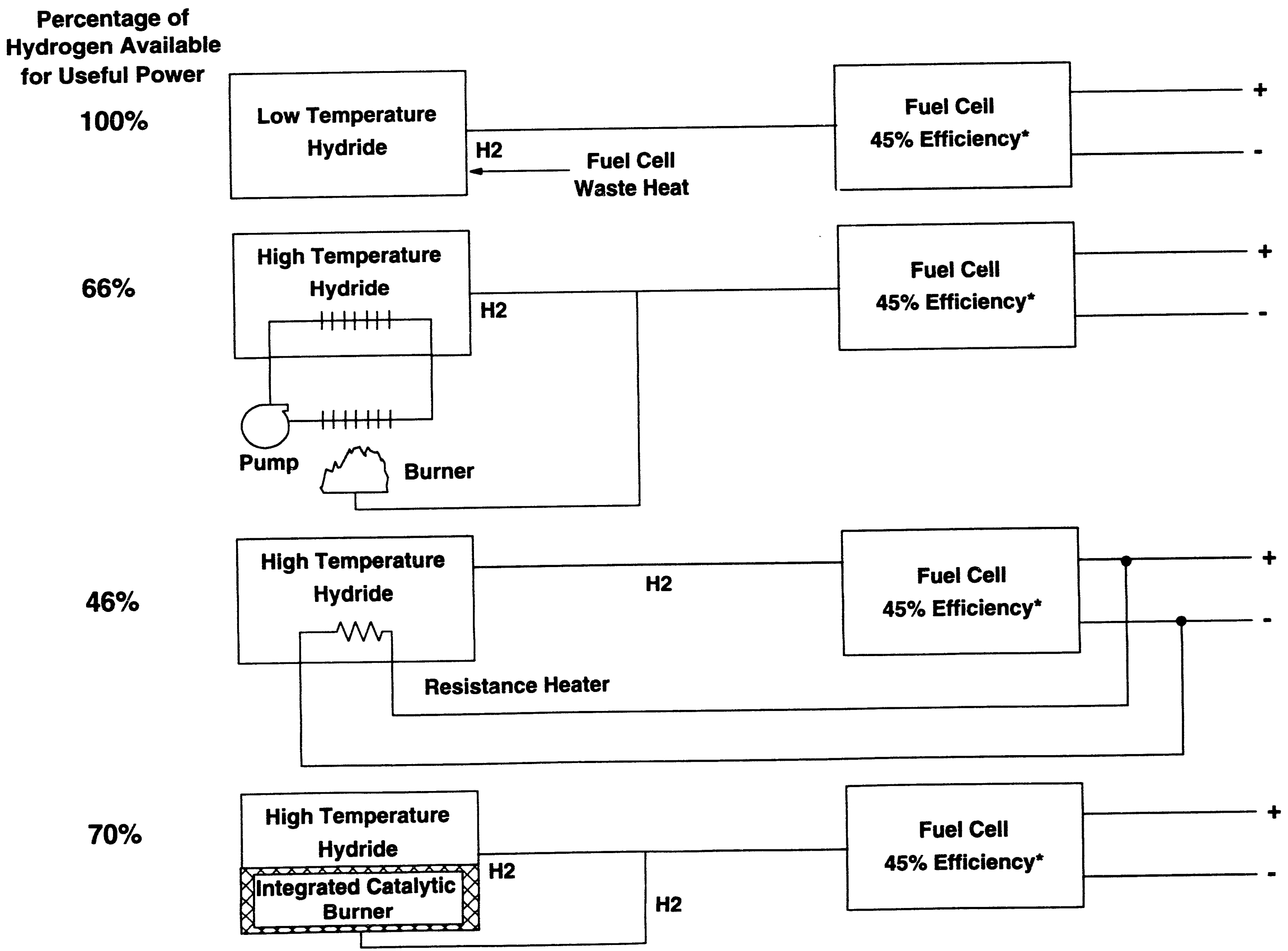
- Temperatures within the range of waste heat available from either phosphoric acid or solid polymer electrolyte fuel cells.

All of these hydrides which are compatible with proton exchange membrane (PEM) and phosphoric acid (PA) fuel cell temperatures are low-temperature hydrides. Figure 14 presents the inefficiencies attendant to using some of the stored hydrogen to provide the dehydriding energy for high-temperature metal hydrides. As shown in Figure 14, the consumption of hydrogen to produce the required dehydriding energy will consume a significant fraction of the stored fuel.

Both low-temperature hydride (LTH) and high-temperature hydride (HTH) storage system weight and volume characteristics are shown in Figure 15. The weight and volume penalty associated with system components greatly reduces the actual system performance of LTHs. HTH systems suffer additionally from parasitic hydrogen consumption to supply the heat of dehydriding.

Internal combustion engines with higher waste heat temperatures than fuel cells could use the high-temperature hydrides without the parasitic hydrogen consumption problem. However, metal hydrides have other problems:

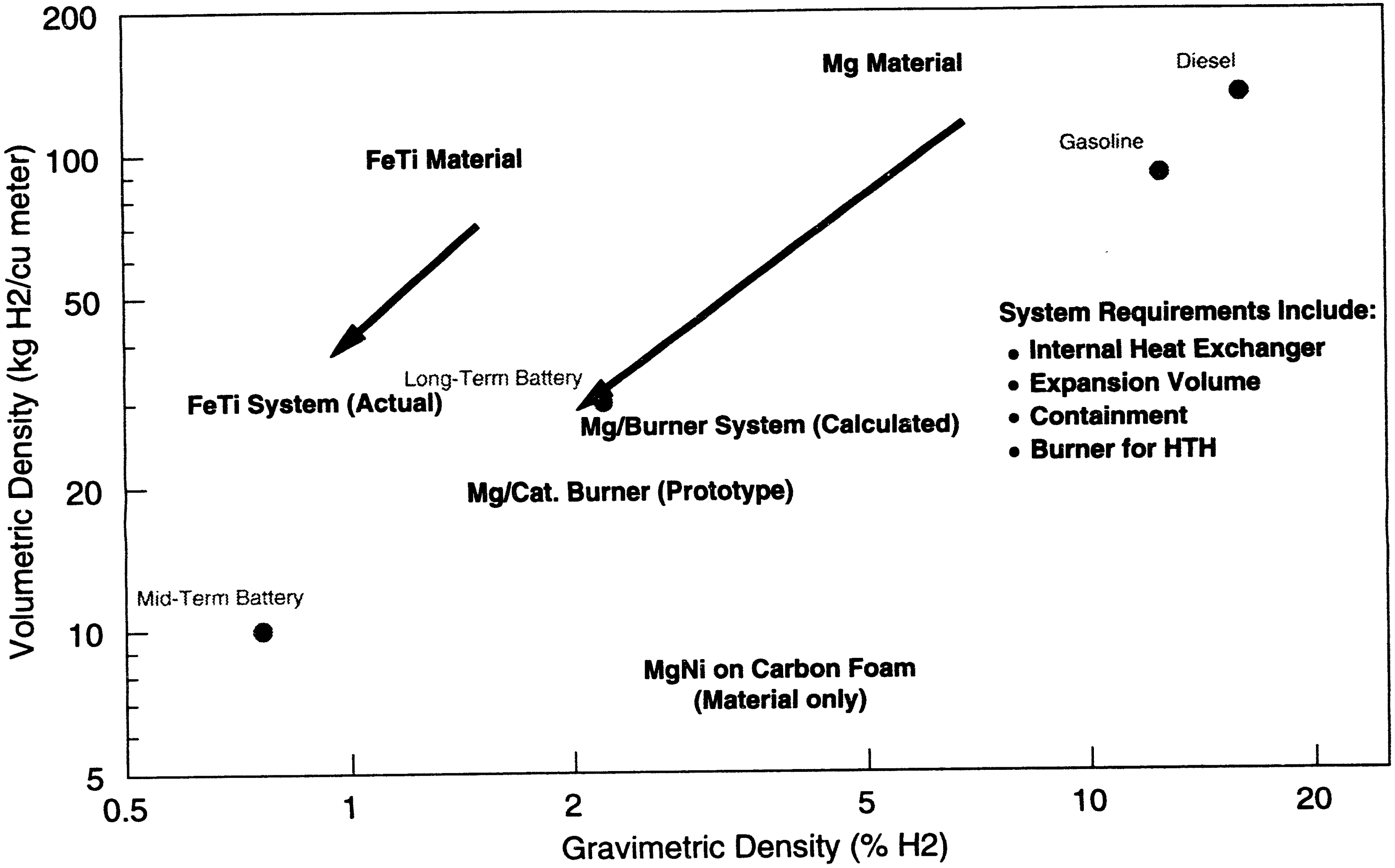
Figure 14: Hydride Storage System Configurations and Energetics



*Based on current DOE/General Motors Program

(Reference 2)

Figure 15: Hydrogen Storage System Comparison for Hydride Materials and Systems



- Some are pyrophoric (especially high-temperature hydrides); others merely oxidize when exposed to air.

- Most are subject to irreversible poisoning by water, oxygen, and other common contaminants, or to segregation of species near the surface.

- Kinetics are often poor especially at the interface, resulting in lengthy charging and discharging cycles.

Some of these secondary problems may be mitigated by creating nanocrystalline (crystal sizes 500 Å) metal hydrides. Still, most metal hydrides under commercial development are low-temperature metal hydrides (see Figure 12). However, the primary problems of high weight (common to all metal hydrides) and high cost (true of most metal hydrides) are inherent and can only be overcome by the discovery/formulation of a greatly improved metal hydride.

For on-board hydrogen storage, major impurities must be controlled in the hydrogen supply coming most likely from a stationary reformer system or electrolyzer. Hydrides can be poisoned by CO, CO_2, H_2O, and O_2, all of which could be present in hydrogen from a stationary reformer. LTHs are less sensitive to impurities than HTHs, are easier to reactivate once contaminated, and reactivated by heat or flushing with pure hydrogen.

Metal hydrides available in the 1990s when compared with those available in the 1970s offer substantial improvements in areas such as:

- Improved cyclability
- Improved ability to tailor equilibrium overpressure
- Improved reversibility
- Lower cost

However, these are all important but secondary benefits to improvements in energy storage density. We found no evidence that hydride systems for the near-term or medium-term will show substantial improvements in energy density.

4.2 Liquid Hydrides

Certain hydrocarbons (napthenes) can be reversibly transformed into other hydrocarbons (aromatics) with the same number of carbon atoms and a smaller number of hydrogen atoms. These napthenes are variously referred to as recyclable liquid chemical carriers or liquid hydrides. For example,

$$\text{cyclohexane} \Leftrightarrow \text{benzene} + 3H_2$$

and

$$\text{methylcyclohexane} \Leftrightarrow \text{toluene} + 3H_2$$

The first reaction has a slightly greater hydrogen weight percentage, but benzene is more carcinogenic than toluene, so the second reaction has received more attention.

The hydrogen weight storage density of methylcyclohexane is 5.9%, far better than those of most metal hydrides currently under development. The hydrogen volume storage density is approximately 46 kgH_2/m^3 (excluding reaction apparatus) which is less than the pure liquid hydrogen density but greater than the liquid hydrogen system density.

Releasing the hydrogen from liquid hydrides is not simply a matter of heating them or reducing the hydrogen overpressure. Cracking methylcyclohexane requires 10 atmospheres, 400°C, a platinum/rhenium catalyst, and 28% of the higher heating value (HHV) of the released hydrogen. Therefore, required onboard equipment includes a catalytic reactor, a catalyst heater, a vaporizer, pumps, an air-cooled condenser, a gas-liquid separator, and a partitioned fuel tank. Since simplicity of storage/retrieval and assured hydrogen purity are key goals of the DOE hydrogen storage program, liquid hydrides were not considered further as candidates.

4.3 Iron and Water

Hydrogen may be stored in the form of water and reduced back to hydrogen by means of the reversible reaction:

$$3Fe + 4H_2O \Leftrightarrow Fe_3O_4 + 4H_2 \qquad \text{(Reference 4)}$$

The forward reaction is simply the formation of rust. The reverse process takes place in blast furnaces between magnetite (Fe_3O_4) and the hydrogen in the water gas (H_2+CO), which in turn comes from the reduction by coke of water vapor in the combustion air.

In a fuel cell vehicle application, the vehicle would begin with a "full charge" consisting of a tank containing iron particles carried on the FCV. When hydrogen was needed by the fuel cell, water and heat would be added to the iron and H_2 drawn off. The tank, therefore, would be insulated, capable of sustaining moderate pressure loads and have passages through it to aid the mixing of steam and iron. These three factors add to system weight and volume.

Neither the forward nor reverse reaction proceeds to completion, but the onboard forward (hydrogen-generating) reaction is favored at temperatures below 1,100°C (which is well beyond red hot). The reverse reaction is less than complete at temperatures below the melting temperature of iron (1,536°C).

The forward reaction is exothermic (heat releasing) at all temperatures of interest aboard a vehicle. However, the heat given off by generating each pound of hydrogen is not enough to boil and superheat the nine pounds of water required for each pound of hydrogen. Thus, the sum of the reactions onboard the vehicle (that convert liquid water to gaseous hydrogen) is endothermic (heat absorbing).

Three percent of the released hydrogen's HHV is needed to heat up the reactant iron to the reaction temperature. If that iron needs to be heated up only once and if heating up other iron that will never react can be avoided, then this is quite tolerable. If it becomes necessary to heat up the bed several times (if, for example, it cooled when the vehicle stopped operating), or if an appreciable fraction of the iron in the reactor will never react, then it may be necessary to supply to the reactor (as heat) an unacceptably large fraction of the HHV of the generated hydrogen. Further research is required to determine how much energy is needed to keep the system functioning during typical driving cycles.

A common approach to creating high surface-to-volume ratio (hence rapid, complete reactions) is to make very fine particles, which would make it possible to react almost all of the iron. The approach currently being taken is grinding "sponge iron" (which already has a high surface-to-volume ratio) into powder. Pelletizing these particles should keep most of them from being swept into the fuel cell by the momentum of the evolved hydrogen. More research in this area is needed.

Technical practicality of this reaction depends on it being made to proceed to completion within a reasonable period of time without compromising the structural integrity of the pelletized sponge iron powder. Economic practicality depends on the iron oxide being reduced to iron or replaced with other pellets of powdered sponge iron inexpensively. These issues can be resolved only be experimentation. No experimental data on the small-scale application of iron/water storage systems is available in the open literature.

4.4 Dihydrides

Dihydrides, which are sometimes referred to as polyhydrides, are metal complexes (metal atoms plus ligands) to which hydrogen molecules rather than hydrogen atoms attach. The ligands are coordination bonded to the metal atom. So far, researchers at the University of Hawaii (Reference 5) have succeeded in storing hydrogen on iridium-phosphorus complexes. They are currently attempting to improve performance with ruthenium and economy by using iron. Hydrogen is more difficult to store on iron because iron has fewer electrons and fewer electron states than iridium. However, unless than can be done with iron or some other low-cost material, this technique is commercially uncompetitive since both iridium and ruthenium are roughly as expensive as platinum.

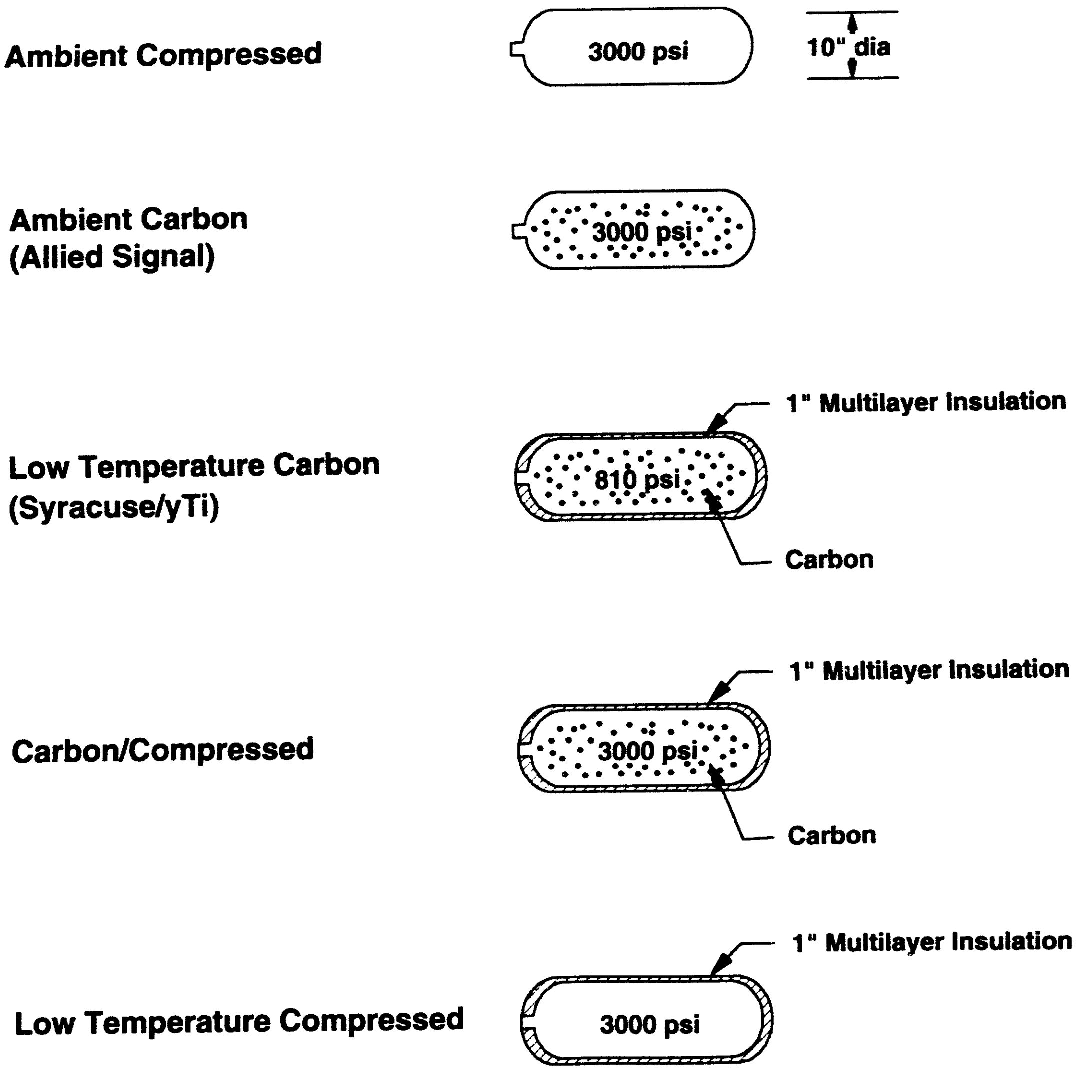
4.5 Carbon Adsorption of Hydrogen

Hydrogen molecules (not hydrogen atoms) can be adsorbed onto carbon. Van der Waals forces account for this association rather than electronic bonds so comparatively little energy is needed to release the hydrogen. Methane can be similarly stored, and many researchers are active in this area in pursuit of improved natural gas vehicle gas (NGV) storage systems.

Carbon systems are actually hybrids that store some hydrogen in adsorbed form and some as pressurized gas. Figure 16 shows the various models that can be used to characterize combinations of compression, carbon adsorption, and temperature variables for carbon storage systems.

Table 2 presents the experimental data and predictions available from two research organizations in the field.

Figure 16: System Models for Carbon, Compressed and Hybrid Storage Systems



- All pressure vessels = 10" dia carbon fiber tank (PV/W = 1.2 x 10^6), 60" long
- 1" thick multilayer insulation for all low temperature tanks adds 40% to total to total volume
- Heat leak = 0.5 - 0.8 watts including insulation and structure

Table 2: Current Performance and Predicted Improvements in Carbon Adsorption

			Current Performance		Goals		
Source	**Temp. (K)**	**Pressure (psia)**	**Carbon Density (g/cc) [skeletal density]**[1]	**Adsorption (g H Adsorbed/ g Carbon)**	**Carbon Density (g/cc) [skeletal density]**[1]	**Adsorption (g H Adsorbed/g Carbon)**	**Ref.**
Syracuse/YTi	150	810	0.32 [16%]	4%	0.80 [40%]	8.0%	6
Allied Signal	298	2000	0.32 [16%]	2%	0.80 [40%]	7.7%	7

[1] Skeletal density corresponds to fraction of internal volume taken up by solid carbon. Balance is assumed to be gaseous H_2.

Figures 17 and 18 show how changes in carbon density and adsorption percentage affect storage system weight and volume. Even at the goal of 40% skeletal density, the majority of the volume within the pressure vessel will be occupied by gaseous hydrogen.
A pressure vessel with carbon-adsorbed hydrogen within it acts much as a pressure vessel without carbon in it; it just contains more hydrogen and weighs more. Very little heat is required to desorb the hydrogen.

Carbons used for hydrogen adsorption differ from one another with respect to surface topology and doping materials. As is apparent from Table 2, some of these carbons work only at borderline cryogenic temperatures.

Carbon storage systems need further development aimed at:

- Increasing the adsorption fraction ($kg_{HYDROGEN}/kg_{CARBON}$);
- Defining best storage system design parameters such as pressure and temperature; and
- Determining cost, longevity, and susceptibility (if any) to poisoning.

If the dramatic performance improvements embodied in the Table 2 goals are achieved, carbon adsorption systems, particularly the room temperature type, have a good chance to surpass the DOE hydrogen storage goals in both volumetric and weight density.

Figure 17: Ambient Temperature (2000 psi) Carbon Storage Alternatives

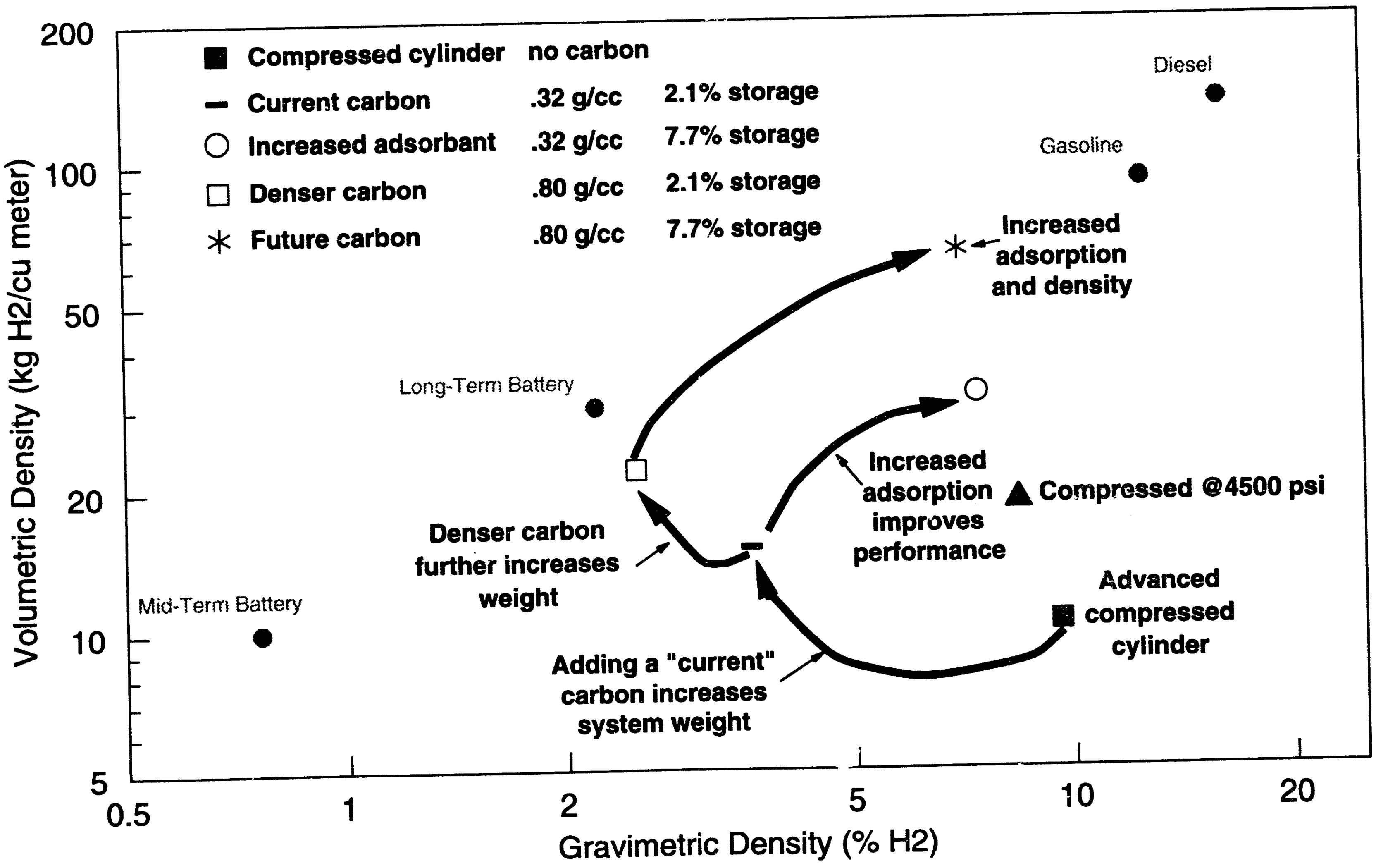
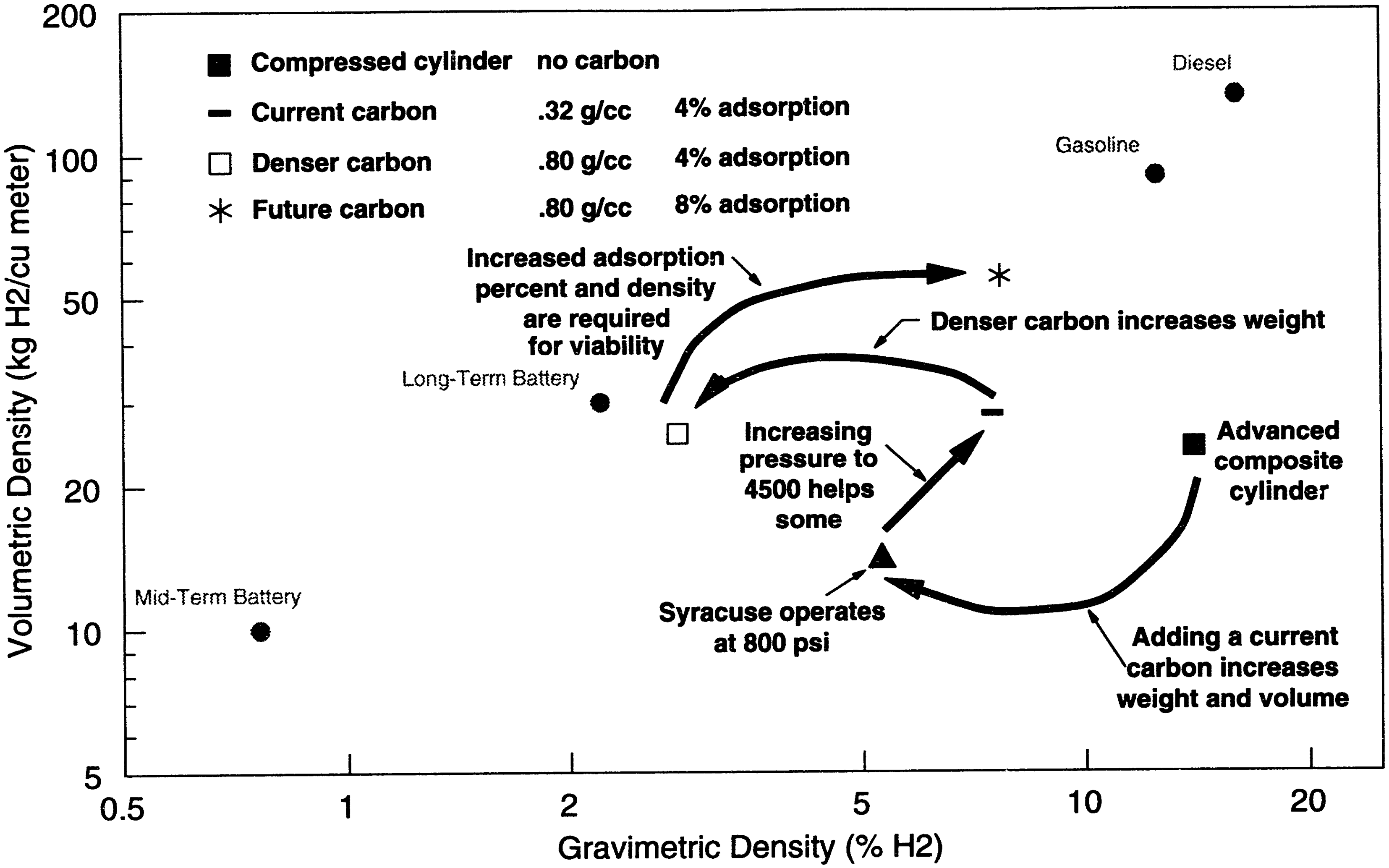


Figure 18: Carbon Storage Alternatives (4500 psi, except as noted)



5.0 HYDROGEN FUEL SAFETY

Assuring safe automobile operation with onboard hydrogen is of prime importance. Hydrogen offers the promise of being safer than gasoline if the vehicle system designs provide for proper venting and elimination of compartments where hydrogen gas may be trapped. The thermo-chemical properties of hydrogen are presented in Table 3.

The three major hazards associated with onboard hydrogen storage are explosion, combustion, and shrapnel-releasing rupture of high-pressure storage cylinders. These hazards and their potential consequences to the automobile are discussed below.

Two types of explosions are possible with hydrogen: detonation and deflagration. Detonation or "high" explosion is the more rapid and stronger of the two and is not possible with hydrogen in an unconfined area. Therefore, by careful design of the fuel cell vehicle to eliminate confined area and provide adequate venting, the possibility of detonation within the vehicle can be virtually eliminated. Deflagration or "low" explosion occurs with peak pressures and reaction rates one to two orders of magnitude less than detonation. It effectively is a very rapid burning of hydrogen. Fortunately, due to hydrogen's low density at atmospheric pressure, the explosive energy of hydrogen by volume is relatively low being only 1/20th that of gasoline and less than 1/3 that of methane. Thus, because less energy (in the form of heat and pressure) is released by a hydrogen explosion, one is actually "safer" in a hydrogen explosion than in a gasoline or natural gas (methane) explosion. The high buoyancy of hydrogen, and the high diffusion velocity of hydrogen, ~2.0 cm/s in STP air, naturally disperse the gas and inhibit poolings of high concentrations as would result in a gasoline spill. Thus, an unintended release of H_2, whether from leak or broken storage vessel, is quickly vented from the vehicle and harmlessly and rapidly disperses upwards into the atmosphere. Should ignition occur, the hydrogen combustion hazard is lower than with gasoline or natural gas due to its low energy content per volume and its rapid upward dispersion. In addition, hydrogen's low flame emissivity and the effect of buoyant velocity on combustion all limit the consequence of a worst case hydrogen fire.

Table 3: Hydrogen Fuel Safety: Property Comparison of Hydrogen, Methane and Gasoline

	Hydrogen	Methane	Gasoline
Molecular Weight	2.016	16.043	~107
Density @ NTP (g/m^3)	83.764	641.19	675,000 (liquid) ~4,400 (vapor)
Heat of Combustion: - Low (kJ/g) - High (kJ/g)	 119.93 141.86	 50.02 55.53	 44.5 48
Flammability Limits (Vol % in air)	4.1% - 94%	5.3% - 14%	1.0%+
Min Detonation (Vol %)	18.3%	6.3%	1.1%
Auto-ignition Temperature (Air @ 1 atm)	1,075°F	999°F	500°F - 800°F
Relative Energy in Equal Volume	1	3.2	19.5 (vapor)
Energy Released From 1 m^3 Volume, 6% Concentration (kJ)*	603	1,954	11,748 (vapor)
Vapor Specific Gravity Relative to STP Air	0.07 @ 32°F	0.554 @ 70°F	3.74
Buoyant Velocity (m/s), NTP Air Diffusion Velocity (cm/s) NTP Air	1.2 - 9 <2.0	-- --	-- --

*Energy release based on hydrogen lower heating value.

STP = Standard, Temperature, and Pressure (0°C, 1 atm)
NTP = Normal, Temperature, and Pressure (20°C, 1 atm)

The heating of adjacent compartments due to a small hydrogen leak and combustion is low. The automobile equipment compartments need to be separated from the passenger compartment and need to be protected by flame retardant insulating material. The elimination of flammable materials inside the equipment compartment will prevent secondary fire hazards.

Hydrogen fuel safety is summarized in Table 4. Liquid hydrogen or high-pressure hydrogen tankage offers the promise of being far superior to current gasoline tankage methods for two reasons:

- Hydrogen is inherently safer than gasoline because hydrogen's volatility carries any release or flame-up and away within seconds, whereas gasoline releases will pool on the ground and burn for prolonged periods.

- DOT-approved pressure tanks are far safer in accidents than are current gasoline tanks because DOT tanks (which are generally designed to a three-fold strength margin) must successfully sustain fire, abrasion, bullet holes, and overpressure without shrapnel failure, instead releasing gas only by delamination failure.

Since trapped gas build-up in garages is the only real safety risk, hydrogen fuel could be odorized by trace additives such as mercaptans in a manner similar to natural gas to alert humans or monitors in the event of a leak in a confined space. In addition, miniature catalytic converters can be placed along the automobile vented pathways and at the high points of enclosed structures (i.e., ceiling of a garage) to harmlessly eliminate hydrogen gas build-up that may occur from LH_2 boiloff or hydrogen leaks.

Hydrogen storage systems will have to be designed, developed, and tested to ensure that their full safety potential is achieved and to demonstrate that these systems can be safe.

Table 4: Hydrogen Fuel Safety

- Hydrogen detonation is not possible in well-vented spaces:
  - only possible in confined volume
  - all compartments passively vented
  - high diffusion and buoyant velocities make it nearly impossible to generate explosive concentrations of hydrogen

- Hydrogen has low energy content by volume due to low density:
  - ignition consequence is much lower than for methane or gasoline

- Hydrogen safer than gasoline because it quickly diffuses upward in air rather than pooling on ground to create secondary fire hazard:
  - small, low-temperature, catalytic devices would be placed along the vent ducts to convert hydrogen gas into an inert compound thereby preventing external gas build-up
  - devices may also be placed in high points of garages to prevent gas accumulation

- Failure mode of high-pressure hydrogen vessels is benign:
  - tanks do not fragment to become shrapnel hazard
  - tank fails by delamination with consequent gas release

- Hydrogen is non-toxic:
  - may be breathed in high concentrations with no systematic effects
  - may lead to asphyxiation if breathed in very high concentrations
  - can be odorized by trace additives to alert humans and monitors of gas leaks

- Liquid hydrogen creates no additional hazards other than frostbite potential if LH_2 or non-insulated piping containing LH_2 contacts the skin

6.0 RECOMMENDATIONS FOR HYDROGEN STORAGE R&D

The storage systems can be placed in one of three groups: (1) relatively mature systems that primarily require developmental effort toward well-defined goals, (2) systems that require basic and applied research to achieve the large gains necessary to make them competitive, and (3) systems that are currently insufficiently characterized at the system level to allow reliable evaluation. Table 5 lists the timeframe and probability of success.

Compressed gas and liquid hydrogen systems can be significantly improved in both areas of materials and testing (i.e., acceptable structural safety factors). Metal hydride systems, however, need major breakthroughs before they can compete on a weight basis. Liquid hydride, iron and water, and dihydride systems are currently not well-characterized at the system level. After such characterization, these last options may become the subject of focused R&D or rejected with low probability for success.

Table 5: Hydrogen Technology Storage Status

Storage Technology	Category of Advancement Needed	Timeframe	Areas of Needed Improvement	Probability for Success
Compressed Gas (cars, buses, rail)	Development	Near-term	Composite fiber strength	Good
			Materials Manufacturing Uniformity	Good
			Non-destructive Testing	Good
Liquefied (fleet use, rail, truck)	Development	Mid-term	Improved Dormancy Characteristics for Light-duty Vehicles	Moderate
		Long-term	Efficient Liquefaction Techniques	
Metal Hydrides	Research and Characterization	Long-term	Adsorption Capacity at Low Temperature	Unknown
Carbon Adsorption	Research and Characterization	Mid-term	Adsorption Fraction and Systems Analysis	Moderate
Iron and Water	Unambiguous Characterization		Systems Analysis	Unknown
Liquid Hydrides	Unambiguous Characterization		Systems Analysis	Unknown
Dihydrides	Unambiguous Characterization		Systems Analysis	Unknown

Specific recommendations for enhanced hydrogen storage system competitiveness and performance include:

1. Current fuel cell vehicle designs favor advanced carbon fiber wrapped 3,000 to 9,000 psi compressed H_2 tanks due to their light weight, simple room temperature operation, and accommodable installation volume. Research improvements are desirable in the areas of fiber strength, material production uniformity, allowable safety factors in a transportation environment, and non-destructive testing techniques.

2. Chilled compressed hydrogen offers lighter weight, lower volume storage of H_2 than room temperature compressed. Research on refrigeration systems and combination compression/refrigeration systems is needed.

3. No near-term R&D activities were identified which would reduce the liquefaction energy penalty and boil-off problems associated with liquefied hydrogen. Liquefied hydrogen could be appropriate for heavy-duty fleet or fixed route fuel cell vehicles with predictable routes, schedules, and terminals where the dormancy issue is of less importance.

4. No near-term R&D activities were identified which would lead to dramatic weight reductions needed for competitive hydride systems. There is a long-term need to identify metal hydrides that function at FCV conditions, i.e., low-discharge temperature, low pressure, lightweight (high H_2 content).

5. Carbon adsorption is a developing technology that may eventually compete with compressed gas for smaller fuel cell powered vehicles. More test data is needed to characterize ambient temperature and low-temperature carbons. A doubling of performance over current carbons is required as shown in Table 2 to be competitive with compressed-only systems. Advanced carbon adsorption systems may still need cryogenic cooling, high pressure, or both. Preferably, an advanced room temperature system can be developed thereby eliminating dormancy concerns and the need for insulation.

6. An iron-water storage system analysis and demonstration is required to objectively determine how the system would be integrated and perform with an FCV.

7. Regardless of storage system choice, the success of direct hydrogen FCVs depends on the establishment of a hydrogen distribution infrastructure. Research into the infrastructure architecture and economics is required.

8. Some of the systems which are not competitive for light vehicular application may find useful roles for stationary storage in the hydrogen infrastructure or other weight insensitive applications. Although outside of the scope of this report, further research into these heavy systems may be warranted.

7.0 References

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