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Hydrogen Storage for Aircraft Applications Overview

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September 2002

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Introduction

Hydrogen is a very high energy density element that holds much promise as a potential fuel for aircraft. The energy density of hydrogen, which is around 120 MJ/kg, is more than double that of most conventional fuels (for example natural gas: 43 MJ/kg and gasoline 44.4 MJ/kg). The main issue with using hydrogen in aircraft is its very low density. At ambient conditions 1 liter of hydrogen contains only 10.7 KJ of energy. Even in its liquid state the volumetric energy density of hydrogen (8.4 MJ/liter) is less then half that of other fuels (natural gas 17.8 MJ/liter, gasoline 31.1 MJ/liter). Storing a sufficient amount of it for use in most applications requires a large volume. Therefore, in order to make it practical for aircraft applications, the storage method utilized must increase the density of hydrogen.

Conventional methods of storage are as a compressed gas or as a cryogenic liquid. Work is being done in these areas that would make them more applicable to an aircraft by reducing storage tank weight (carbon composite tanks) [1,15] or increasing the density of cryogenic hydrogen (gelled or slush hydrogen) [12,13]. In addition new storage methods are being devised that may be capable of storing hydrogen without the need for high pressure tanks or the need to manage a cryogenic liquid (carbon nanotubes, carbon fullerenes, and hydrides) [1,9].

Aside from storing hydrogen directly, it can also be stored as a component of a hydrocarbon fuel. Since most conventional fuels contain hydrogen, this method of storage can be utilized as long as there is a method of removing the hydrogen from the fuel that does not require more energy than that provided by the hydrogen itself in this case. A reformer would be used to break apart the hydrocarbon fuel and liberate the hydrogen.

Regardless of the storage mechanism the first thing that must be known when determining which type of storage is most applicable is the amount of hydrogen that is required. For a polymer electrolyte membrane (PEM) fuel cell application, an estimate of the hydrogen requirement can be determined by the following basic analysis.

The voltage of an individual cell in a PEM fuel cell stack is given by:

$$V = 1.2\,\eta_{fc} \qquad [1]$$

Where V is the cell voltage and η_{fc} is the electrical conversion efficiency of the cell. The power produced per plate (P_p) is given by equation 2 where I is the current density (Amps/ m^2) of the plate and A is the plate area:

$$P_p = VIA \qquad [2]$$

For a given desired output power (P_o) the number of plates (N_p) can be calculated.

$$N_p = P_o / (VIA) \quad [3]$$

The flow rate of hydrogen (F_H) in moles of H_2 per second needed to produce the given output power is

$$F_H = N_p I A / (2)(96{,}500) \quad [4]$$

Combining equations 1,3 and 4 and changing the units from moles to kilograms (500 moles H_2 per kg) yields the following.

$$F_H = P_o /(1.2\, \eta_{fc}\, (2)(96{,}500)\, (500)) = P_o / (1.158E8\, \eta_{fc}) \quad [5]$$

The total mass of hydrogen (M_H) needed is based on the operation time (t) of the fuel cell (in hours).

$$M_H = F_H\ t = P_o\, t / (32{,}167\, \eta_{fc}) \quad [6]$$

Based on this quick method of calculating the mass of hydrogen needed for a given application, an estimate of the size of the storage system can be determined.

Gaseous Hydrogen Storage

Pressure Tank

High-pressure hydrogen storage is the most conventional type of hydrogen storage. As the storage pressure increases, the density of the hydrogen gas will also increase. This relationship is shown in figure 1. This figure represents the change in density (ρ) of hydrogen gas at various temperatures and pressures. This figure is based on the ideal gas law with a compressibility factor (Z) for the hydrogen gas [5]. Where P and T are the gas pressure and temperature respectively and R is the gas constant for hydrogen (4157 N m / kg K)

$$\rho = P / ZRT \quad [7]$$

$$Z = 0.99704 + 6.4149E\text{-}9\ P \quad [8]$$

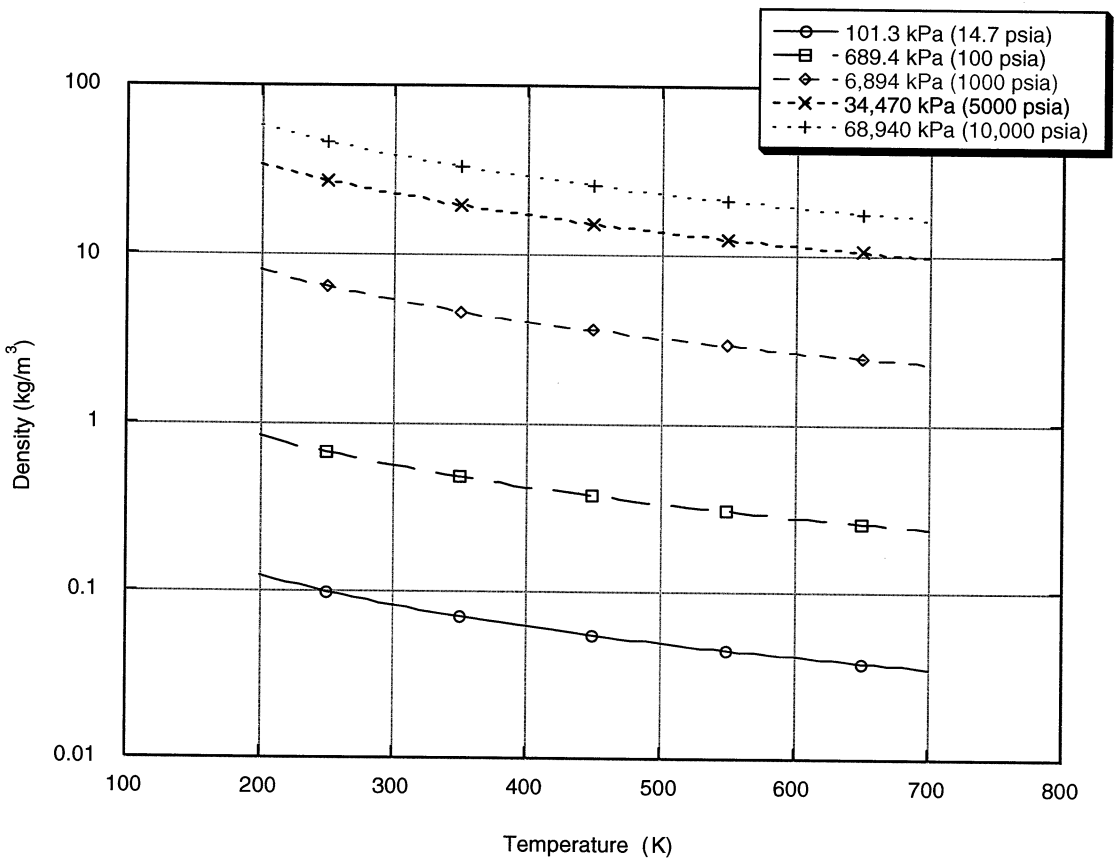

Figure 1.—Hydrogen Density at Various Pressures and Temperatures

The tradeoff with utilizing high density / high pressure storage is the increase in tank mass necessary to withstand the higher pressures. The wall thickness of the tank will increase with the increasing hoop stress due to the higher gas pressure. The calculation of the tank mass for hydrogen gas stored under pressure is a fairly straightforward analysis. This analysis is outlined below.

For this analysis it is assumed that hydrogen will follow the behavior of an ideal gas represented by the equation of state, where m_H is the mass of hydrogen;

$$P\,V_H = m_H\,RT \qquad [9]$$

Where R is the gas constant for hydrogen and has a value of 4157.2 (N m/K kg), P (Pa) is the pressure of the gas, V_H (m^3) is the volume and T (K) is its temperature.

Using the gas constant given above, equation 9 can be restated as follows.

$$V_H = Z\,4157.2\,m_H\,T / P \qquad [10]$$

The tank radius (r) can be calculated from the volume determined in equation 10. The tank is assumed to be either a sphere or a cylinder. The sphere is actually a special case of the cylinder in which the length (L) is zero. Equation 11 can be solved for r through an iterative process.

$$V_H = 4 \pi r^3 / 3 + \pi r^2 L \qquad [11]$$

With the radius and tank pressure known the required wall thickness (t_w) can be determined based on the maximum allowable stress (σ_y) and a factor of safety (FoS). The following two equations represent the wall thickness for a spherical tank and a cylindrical tank with hemispherical end caps, respectively.

$$t_w = P\, r\, FoS / \sigma_y \qquad [12]$$

$$t_w = P\, r\, FoS / (2\, \sigma_y) \qquad [13]$$

From the wall thickness and the density of material used to construct the tank (ρ_t), the mass of the tank (m_t) can be calculated.

$$m_t = \rho_t\, (4/3)\, \pi\, (r + t_w)^3 + \pi\, (r + tw)^2\, L - V_H \qquad [14]$$

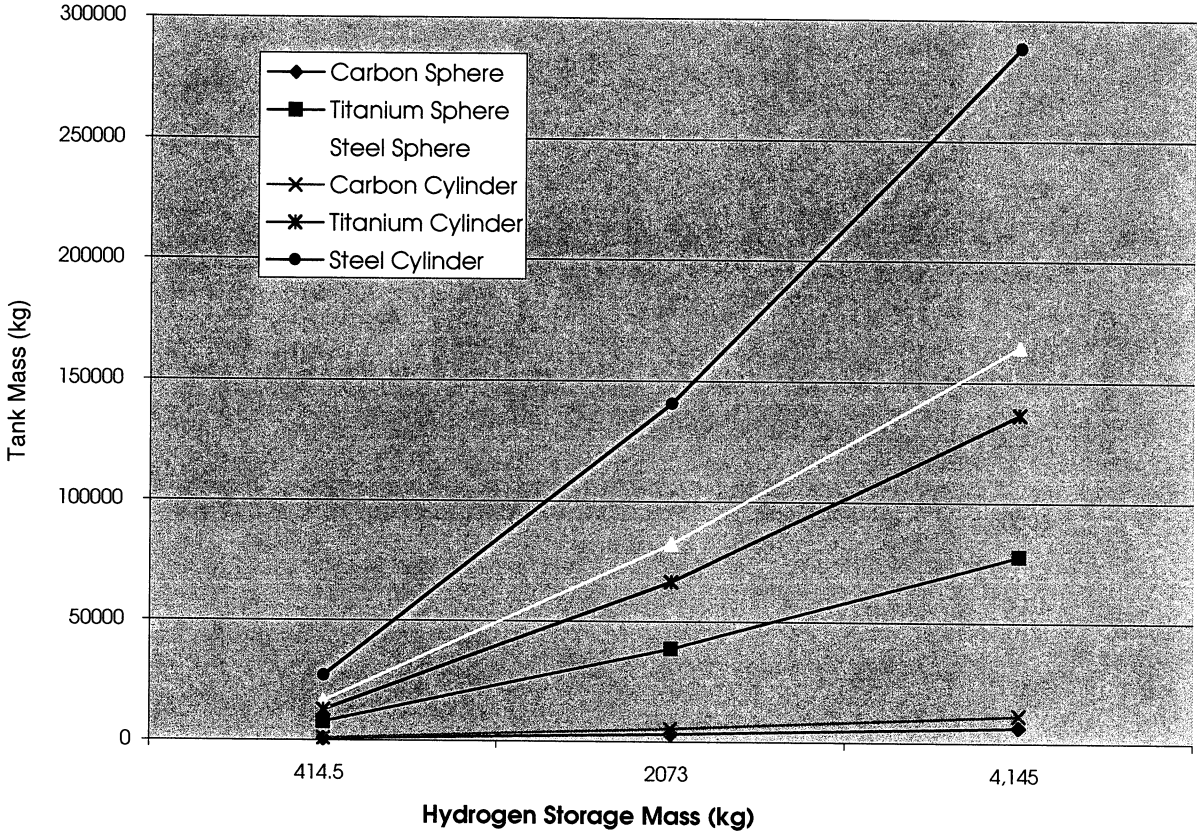

Figure 2.—Pressure Tank Mass for Various Materials, Configurations and Storage Volumes

Figure 2 shows how the mass of the tank will vary with different construction materials. The curves were generated for steel, titanium and carbon. The volumes of hydrogen used were calculated from the amount of hydrogen consumed by a fuel cell to produce 1 MW, 5 MW and 10 MW of power for 8 hours. For comparison purposes the length of the cylindrical tank was assumed to be 3 m. Due to the compressibility effects of hydrogen, the change in storage pressure does have an effect on the mass of the tank. This is because the reduction in gas volume is not linear with the increase in pressure, as it would be if compressibility were not considered. The pressure tank mass and volume as a function of storage pressure for various amounts of stored hydrogen are shown in figures 3 through 5. These figures are for the same hydrogen storage volumes that were given in figure 2. From these figures it can be seen that at low pressures the tank mass is fairly constant. However at higher pressures the tank mass rises. This is due to the compressibility effects of hydrogen gas. The Titanium tanks have a much greater mass then the carbon tanks. This is due to the low density and high strength of carbon composites. The carbon tanks however require a liner to prevent the hydrogen gas from leaking through the tank wall.

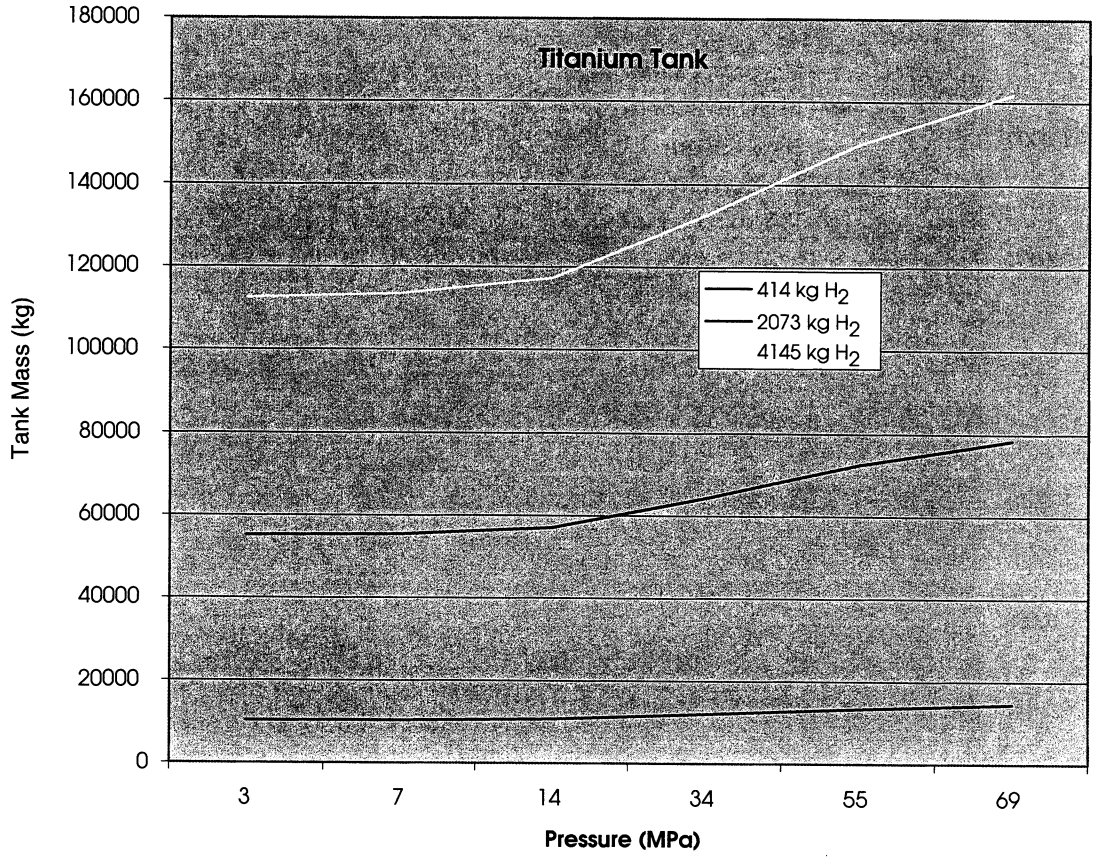

Figure 3.—Effect of Pressure on Mass of a Titanium Tank for Various Amounts of Hydrogen Stored

TABLE 1.—PRESSURE TANK MATERIAL PROPERTIES [19, 20]

Material	Density	Yield Strength
Steel (quenched and tempered alloy ASTM–A514	7860 kg/m^3	690 MPa
Aluminum (4.4% Cu) 2014–T6	2800 kg/m^3	410 MPa
Titanium Alloy (6% AL, 4% V)	4460 kg/m^3	825 MPa
Carbon Composite	1530 kg/m^3	1900 MPa

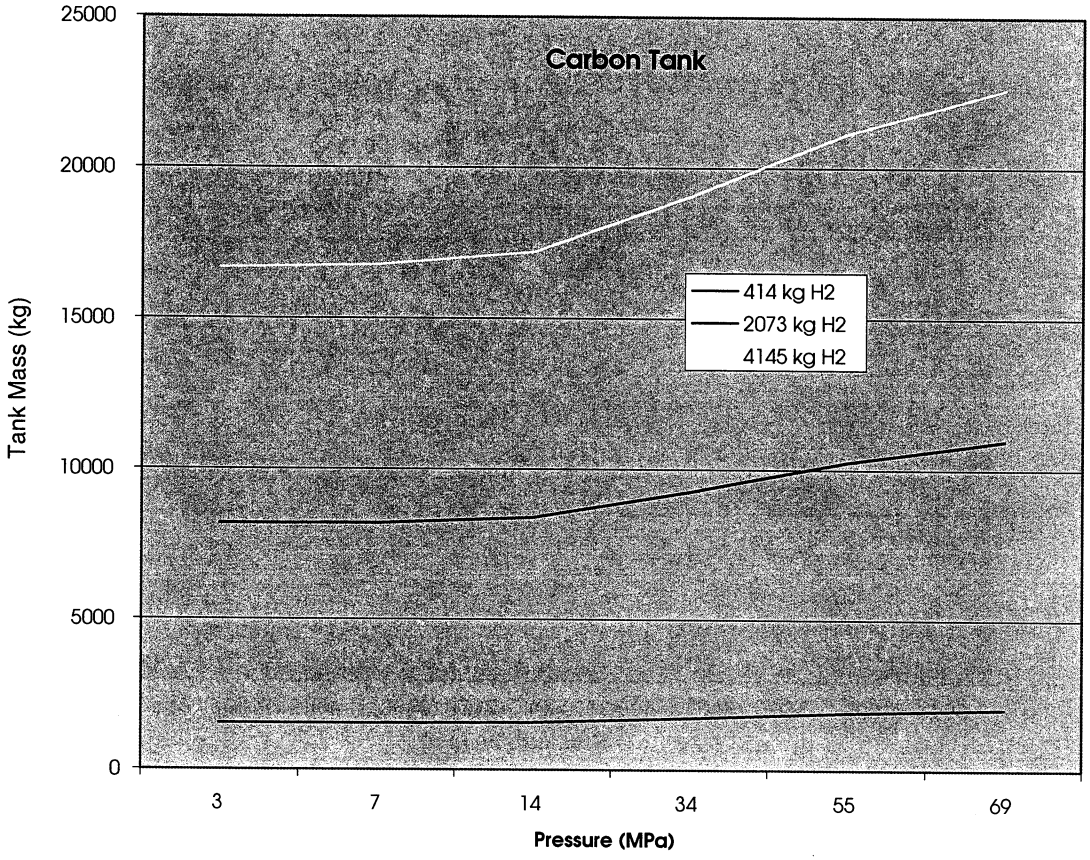

Figure 4.—Effect of Pressure on Mass of a Carbon Tank for Various Amounts of Hydrogen Stored

The material utilized in constructing the tank can be either a metal such as steel, titanium or aluminum, or a composite. Properties of these materials are given in table 1. Since most composites are porous to hydrogen, a composite tank will require a liner to prevent the hydrogen from migrating through the tank wall. Liner materials are usually a type of polymer or a metal such as aluminum. Also coatings are being investigated as a lightweight means of preventing hydrogen penetration through the tank. Composite tanks offer the best weight density of hydrogen. Tanks under development at Quantum Technologies have achieved up to 11.3% hydrogen by weight [4]. However a more realistic number for composite storage tanks under practical use is between 7.5 % and 8.5% weight of hydrogen [4,15].

In addition to the stress placed on the tank due to the pressure loading, additional issues will arise when utilizing a high pressure tank over a period of time and cycle loadings. These issues include aging, creep, fatigue and hydrogen embrittlement. Depending on the tank material chosen, the effect of design life and the operating pressure on each of these factors would need to be investigated to determine their effect on a particular tank design.

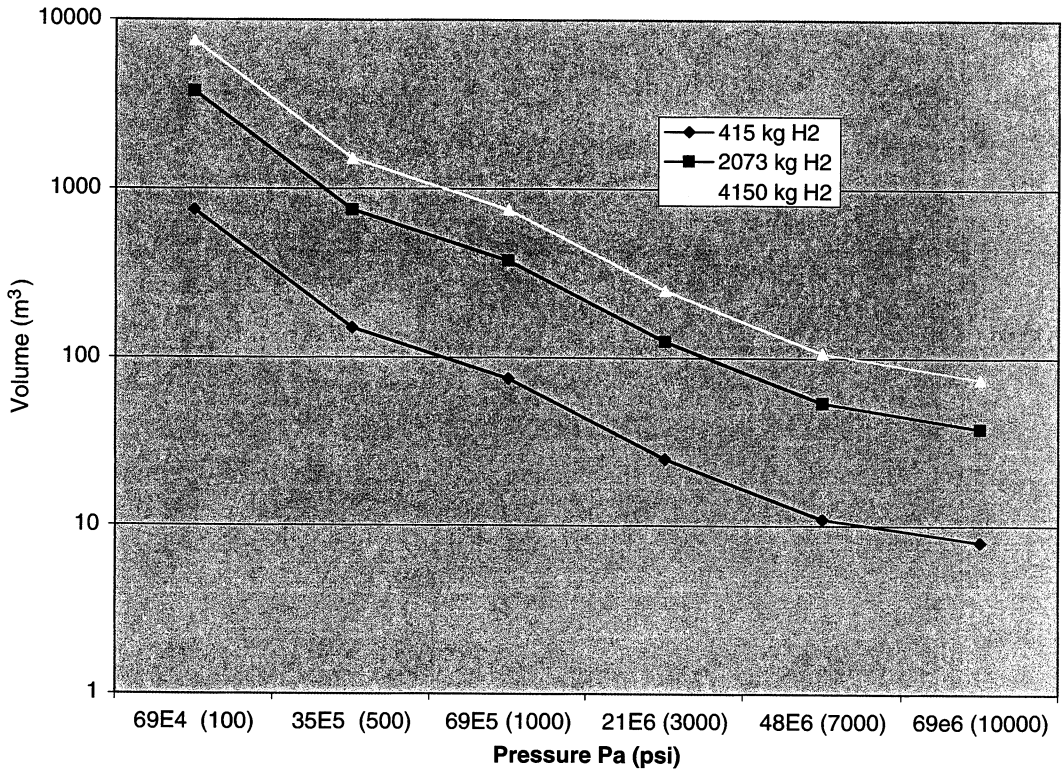

Figure 5.—Tank volume as a function of storage pressure for various masses of H_2

To maximize the storage volume for a given tank placement, the ideal configuration would be to construct a conformal tank. A conformal tank can hold up to 20% more hydrogen in a given envelope and pressure then a cylindrical or spherical tank. This is based on the presumption that a conformal tank can utilize over 80% of its envelope volume. This increase in useable storage compared to a conventional cylindrical tank is shown in figure 6. The ability to construct a lightweight high pressure conformal tank is presently being investigated by Thiokol Propulsion under a Department of Energy contract [4].

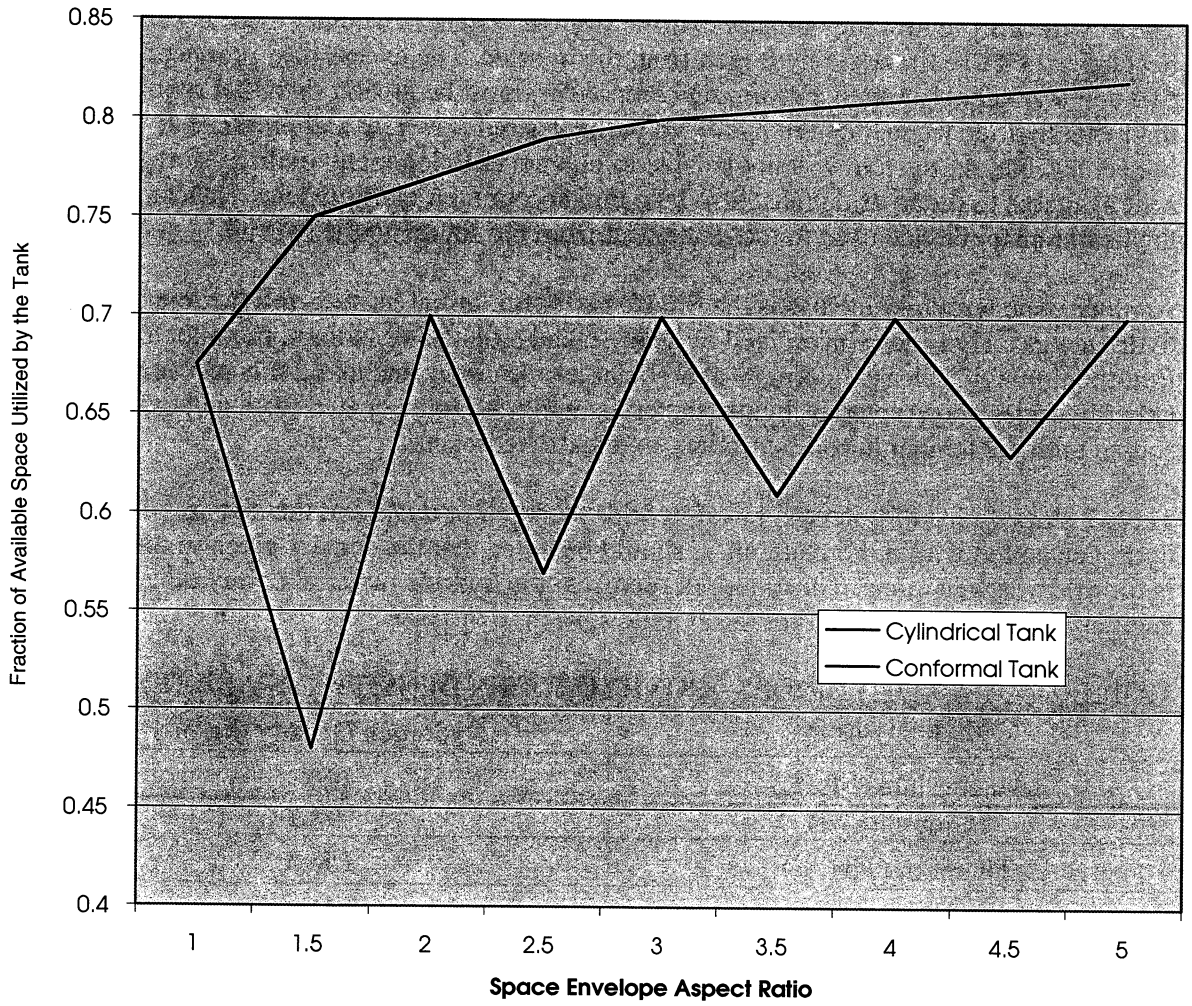

Figure 6.—Effect of Conformal Tanks on Available Space Utilization [4]

Metal Hydride

Metal hydrides are metallic alloys that absorb hydrogen. These alloys can be used as a storage mechanism because of their ability to not only absorb hydrogen but also release it. The release of hydrogen is directly related to the temperature of the hydride. Typically metal hydrides can hold hydrogen equal to approximately 1% to 2% of their weight. If active heating is supplied to remove the hydrogen this can increase to 5% to7% of the hydride weight. If the temperature is held constant the hydrogen is released at a constant pressure. The metal hydride tank can be used repeatedly to store and release hydrogen. The limiting factor on its ability to store hydrogen is the accumulation of impurities within the tank. These impurities fill the spaces that would normally store the hydrogen and thereby reduce the tanks capacity.

The key tradeoff to utilizing a metal hydride storage system is whether there is sufficient heat generated to extract the hydrogen from the hydride. The excess heat produced by the fuel cell (or other hydrogen consuming component) must be greater than that required by the metal hydride to liberate the hydrogen at the desired flow rate and pressure. If this is not achievable, the system will not be able to operate utilizing metal hydride storage. The heat available to the hydride must also take into account the inefficiencies associated with the heat transfer device used to move the heat from the source to the hydride.

Another issue with hydride use is the time lag between initial heating and the release of hydrogen gas. Hydrides constructed of heavy metals such as vanadium, niobium and iron-titanium will release hydrogen at ambient temperatures and avoid this problem [6]. Other hydrides constructed of lighter materials will need to be heated from an auxiliary source until the temperature is sufficient to release hydrogen.

Table 2 shows a list of potential metal hydride storage materials and the density of the hydrogen stored within the material. It should be noted that the density given in the table is for the hydrogen alone. This does not represent the hydride material or any other ancillary components needed for the storage system to operate.

TABLE 2.—METAL HYDRIDES AND HYDROGEN DENSITY CAPABILITY [6]

Metal Hydride	Hydrogen Density (kg/m^3)
Magnesium (MgH_2)	109
Lithium (LiH)	98.5
Titanium ($TiH_{1.97}$)	150.5
Aluminum (AlH_3)	151.2
Zirconium (ZrH_2)	122.2
Lanthanum ($LaNi_5H_6$)	89

Even though the storage density of hydrogen in a metal hydride is high the total mass of the system is large. The following table lists the specifications for commercially available state of the art metal hydride storage tanks.

TABLE 3.—COMMERCIALLY AVAILABLE METAL HYDRIDE HYDROGEN STORAGE SPECIFICATIONS [7]

Volume H_2 (m^2)	Mass H_2 (kg)	Metal Hydride Tank Mass (kg)	Percent Mass of H_2 of Total Tank Mass
0.042	0.0036	1	0.36%
0.068	0.0058	0.86	0.68%
0.327	0.0273	6.1	0.45%
0.906	0.0767	16.78	0.46%
1.274	0.1078	24	0.45%
2.547	0.214	36	0.59%

Other systems are under development that can offer higher mass fractions of hydrogen. These systems promise mass fractions up to 5% (6 kg hydrogen storage for a 120 kg system mass) [8].

Carbon Nanotubes

Carbon nanotubes are tubular carbon structures on the order of 2 nanometers in size. These structures are theoretically capable of storing hydrogen within the tube structure. The storage mechanism is similar to that of metal hydrides except the amount of hydrogen capable of being stored is much greater. It is theorized that carbon nanotubes can store anywhere from 4% to 65% of their weight in hydrogen [1,4]. This technology is very new and still within the development stage. However if it can live up to its projected potential, this would by far be the lightest, most efficient way to store hydrogen.

Glass Microspheres

Glass microspheres store hydrogen in tiny hollow spheres of glass. If heated the spheres permeability to hydrogen will increase. This provides the ability to fill the spheres by placing the warmed spheres in a high-pressure hydrogen environment. The hoop stresses achievable for glass microspheres can range from 345 Mpa (50,000 psi) to 1,034 Mpa (150,000 psi) [9]. The corresponding maximum pressure sustainable by the microsphere is calculated in the same manner as that for any other sphere. This is given by equation 12, which would be solved for P for a given will thickness (on the order of 0.68 μm). On the high end this is comparable to the stress achievable with carbon fiber tanks. Once cooled the spheres lock the hydrogen inside. The hydrogen is released by subsequently increasing the temperature of the spheres. This method of storage provides a safe, contamination resistant method for storing hydrogen.

The fill rates of microspheres are related to the properties of the glass used to construct the spheres, the temperature at which the gas is absorbed (usually between 150 °C and 40 °C) and the pressure of the gas during absorption. Fill and purge rates are directly proportional to the permeability of the glass spheres to hydrogen which increases with increasing temperature. At room temperature the fill / purge rate is on the order of 5000 hours, at 225 °C it is approximately 1 hour and at 300 °C it is approximately 15 minutes [9]. This dramatic increase in hydrogen permeability with temperature allows the microspheres to maintain low hydrogen losses at storage conditions while providing sufficient hydrogen flow when needed.

Engineered microspheres provide the greatest advantage for high density storage of hydrogen. The engineered microspheres can achieve the high hoop stress values suggested above. It is estimated that a bed of 50 μm diameter engineered microspheres can store hydrogen at 62 Mpa (9000 psi) with a safety factor of 1.5 and a hydrogen mass fraction of 10% [9]. This produces a hydrogen density of 20 kg / m^3. There is a trade off between storage pressure and mass fraction of hydrogen stored. At lower storage

pressures the mass fraction of hydrogen stored increases but the overall hydrogen volumetric density decreases. This is caused by the increase in the glass sphere wall thickness needed to withstand the increase in storage pressure and maintain the same factor of safety. Figure 7 shows how the hydrogen mass fraction and volumetric density change for various storage pressures [9].

Although the storage capabilities of glass microspheres looks impressive there are a number of drawbacks to their use from a system standpoint. The main issue is that to get the hydrogen into and out of the spheres, they must be heated. This heating takes considerable energy and time to accomplish. The higher the heating, the quicker the hydrogen will purge from the spheres. But from a system standpoint this heating must be accounted for. For a fuel cell system it is conceivable that the waste heat from the fuel cell operation can be used to liberate the hydrogen from the microspheres. This scheme, although promising, requires a heat exchange loop between the fuel cell and storage tanks which can add significant weight to the system.

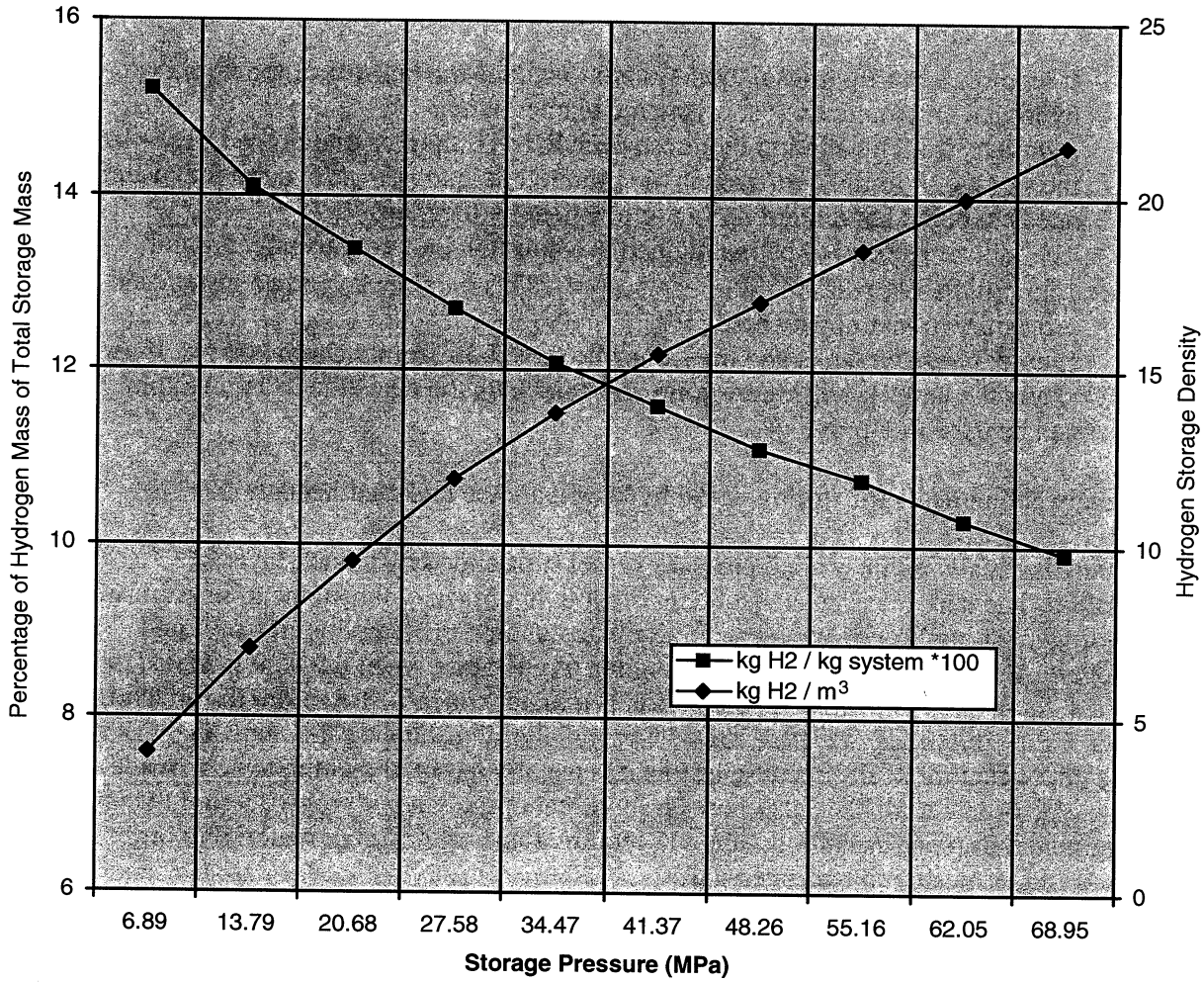

Figure 7.—Glass Microsphere Hydrogen Storage Mass Fraction and Density for Various Storage Pressures

Cryogenic Hydrogen Storage

To reduce tank mass and volume over high-pressure gas storage, cryogenic storage of hydrogen can be used. The properties of liquid hydrogen enable significant increases in density over high-pressure gas storage as well as reduced tank mass due to lower pressure operation. Liquid hydrogen is at a temperature of around –260 °C (–425 °F) and has a density (ρ_{LH}) of 71 kg/m^3 (4.43 lb/ft^3). To get a further increase in density above that of liquid hydrogen, a mixture of solid and liquid hydrogen can be produced. This mixture is called slush hydrogen. For a 50% solid / 50% liquid mixture the hydrogen density is 80.9 kg/m^3 [12].

Cryogenic storage maximizes the density of hydrogen but does impose some significant operational constraints on the fuel system.

1. It requires an airtight insulation system to reduce the boil-off of the liquid hydrogen and maintain it at cryogenic temperatures.
2. Liquid hydrogen handling requires specialized equipment and procedures. Also the storage of liquid hydrogen is time limited (due to boil-off) so the fuel usually needs to be manufactured on site or at a near by location.
3. The fuel tanks need to be maintained at a constant pressure, usually around 1.45×10^5 Pa (21 psia) to minimize boil-off. This requires a venting system and procedure to be implemented [10].
4. Liquid hydrogen tanks and lines must be sealed off from the atmosphere. If air enters the tanks it will freeze solid and can block the flow lines. Only helium can be used as a purge gas.

The main components for storing liquid hydrogen are the tank and insulation.

The tank is usually a thin-walled pressure vessel surrounded by a thick layer of insulation. The tank materials must be resistant to hydrogen embrittlement, impermeable to hydrogen gas and capable of structurally withstanding the temperatures of liquid hydrogen. Also, because of the great change in temperature when the tank is fueled or emptied, thermal expansion and contraction is a major concern. Therefore the attachment points of the tank to any structure must be capable of withstanding this movement as well as the tank structure itself. Because of this it is usually required that the tank be made out of one type of material. This also poses a significant problem with regard to lightweight strong materials, such as carbon, that will require a liner of different material in order to be made impermeable to hydrogen gas.

The storage tank for holding the liquid hydrogen can be sized by the following analysis.

The tank volume (V_t) required to hold the hydrogen is given by the following equation.

$$V_t = M_H \ (1+V_i)/ \rho_{LH} \qquad [15]$$

The mass of hydrogen to be held in the tank is given by equation 6. There must be space left in the tank in order to maintain a constant pressure as well as provide space for boil-off. This excess volume is estimated to be around 7.2% ($V_i = 0.072$) of the total tank volume.

From this the tank radius (r) can be calculated by solving the following equation for r. If the tank is a cylinder then this will have to be done iteratively.

$$V_t = 4 \pi r^3 / 3 + \pi r^2 L \qquad [16]$$

The wall thickness for the tank is given by equations 12 and 13 for a cylindrical and spherical tank respectively. Utilizing the wall thickness and tank radius, the mass of the tank (m_t) can be calculated.

$$m_t = \rho_t (4/3) \pi (r + t_w)^3 + \pi (r + tw)^2 L - V_t \qquad [17]$$

The next main component of a liquid hydrogen storage system is the insulation that is needed surrounding the tank as well as any fuel lines or handling devices. The insulation serves a few purposes. It is necessary to reduce the amount of boil-off from the storage tanks. Without the insulation the boil-off rate would make the use of liquid hydrogen completely impracticable. Also the insulation prevents or reduces the frost buildup on the outer surface of the aircraft. Without proper insulation, the frost build up can pose a serious hazard to the aircraft's ability to fly. The insulation must be impervious to air to eliminate the possibility of frozen air particles forming and it must be capable of withstanding the extreme thermal cycling to which it will be subjected.

There are two main categories or types of insulation that can be used. The first is a vacuum-jacketed system consisting of a layers of Mylar (or a similar type of low emissivity, high reflectivity material) separated by thin fiberglass sheets, to maintain spacing, surrounded by an outer container capable of maintaining a low pressure within the insulation layers. The low-pressure environment minimizes the conductivity between the insulation layers and the layers act as a radiation barrier keeping heat out of the tank. The pressure within the vacuum-jacketed insulation is typically kept around 0.1 torr. The main drawback to the vacuum-jacketed insulation is that if the vacuum is lost the insulation will fail, causing a large and rapid boil-off of propellant [10].

The second type of insulation is a rigid closed-cell foam. This type of insulation can be applied to the outside of the tank. If needed, a thin metal-walled enclosure can be placed on the outside of the foam to maintain its integrity and protect it from damage. The foam type of insulation is much more resistant to catastrophic failure than the vacuum-jacketed type of insulation. However, the density and thermal conductivity of the foam insulation is greater.

The following table lists a number of different insulation types and the effective conductivity and density [10,11]. The amount of insulation that is needed on the tank will vary depending on the insulation properties, tank size, allowable boil-off rate and overall allowable weight. In order to get an estimate of the insulation requirements, a brief analysis on the heat flow into the tank needs to be performed. The analysis is a one dimensional heat flow from the surrounding to the liquid hydrogen. The heat transfer mechanisms are shown in figure 8.

TABLE 4.—TANK INSULATION PROPERTIES

Insulation Type	Density (kg/m^3)	Thermal Conductivity (W/m K)
Rigid closed cell polymethacrylimide	35.3	0.0096
Rigid open cell polyurethane	32.1	0.0112
Rigid closed cell polyvinalchloride	49.8	0.0046
Rigid closed cell polyurethane and chopped glass fiber	64.2	0.0064
Evacuated aluminum foil separated with fluffy glass mats	40	0.00016
Evacuated aluminum foil and glass paper laminate	120	0.000017
Evacuated silica powder	160	0.00017

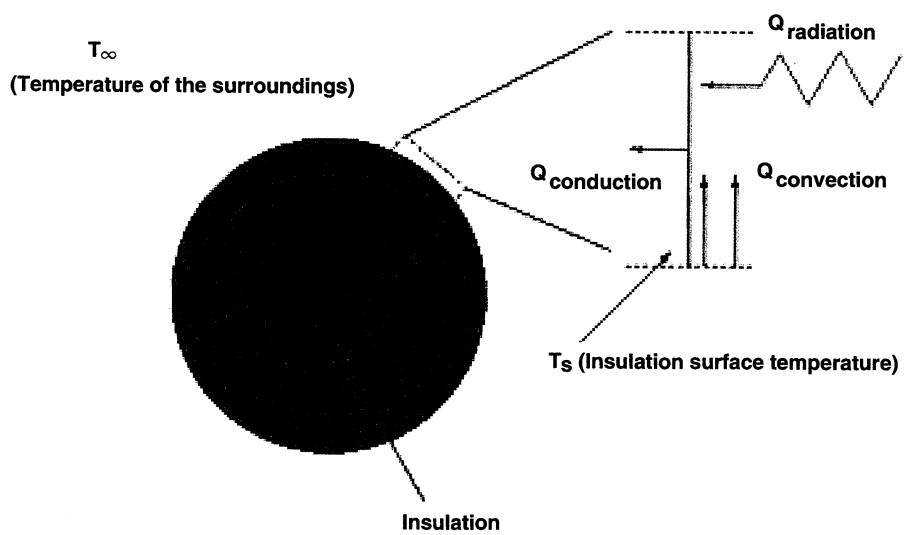

Figure 8.—One Dimensional Heat Transfer for Liquid Hydrogen Tank

Initially the outside surface temperature of the insulation (T_s) needs to be determined. This wall temperature is based on the heat flow into the insulation from convection and radiation and heat flow to the liquid hydrogen by conduction through the insulation.

$$Q_{in} = Q_{convection} + Q_{radiation} = h(T_\infty - T_s) + \varepsilon\sigma(T_\infty^{\ 4} - T_s^{\ 4}) \qquad [18]$$

$$Q_{out} = Q_{conduction} = K\,(T_s - T_{LH2})\,/L \qquad [19]$$

Where ε is the emissivity of the insulation surface, σ is the Stefan-Boltzmann constant (5.67×10^{-8} W/m^2 K^4), h is the convection coefficient for the air surrounding the tank and K is the thermal conductivity of the insulation. It is assumed that the tank is in an isolated environment in which there is no active blowing of air surrounding it. Therefore the convection coefficient is based on natural convection of the air surrounding the tank. This coefficient can be represented by the following equation.

$$h = N_{UD}\,K_g\,/\,D \qquad [20]$$

The thermal conductivity of the air (K_g) is a property of the fluid at a given temperature and pressure and D is the tank diameter. The Nusselt number (N_{UD}) is dependent on the geometry of the tank. Expressions for this are listed for spherical and cylindrical tank shapes [11].

For a sphere:

$$N_{UD} = 2 + 0.589\,R_{ad}^{\ 1/4}\,/\,[1 + (0.469\,/PR)^{9/16}]^{4/9} \qquad [21]$$

For a cylinder:

$$N_{UD} = [0.60 + 0.387\,R_{ad}^{\ 1/6}\,/\,[1 + (0.559\,/PR)^{9/16}]^{8/27}\,]^{2} \qquad [22]$$

Where the Rayleigh number (R_{ad}) is given by the following equation in which g is the gravitational constant.

$$R_{ad} = g\,\beta\,(T_\infty - T_s)\,D^3\,/\,(\nu\,\alpha) \qquad [23]$$

By assuming an ideal gas, the volumetric thermal expansion coefficient (β) is equal to the inverse of the gas temperature in degrees K. ($\beta = 1/\,T_\infty$)

The gas diffusivity and viscosity can be represented by the following data curve fits for air.

$$\alpha = -3.119\times10^{-6} + 3.541\times10^{-8}\,T_\infty + 1.679\times10^{-10}\,T_\infty^{\ 2} \qquad [24]$$

$$\nu = -2.079\times10^{-6} + 2.777\times10^{-8}\,T_\infty + 1.077\times10^{-10}\,T_\infty^{\ 2} \qquad [25]$$

Once the insulation outer surface temperature is known, the boil-off rate (M) in kg/s of the liquid hydrogen can be calculated. This is done through an energy balance between the heat flow through the insulation and the energy taken to boil the liquid hydrogen. The energy to boil the liquid is based on the latent heat of vaporization of liquid hydrogen (h_{fg} = 446592 J/kg)

$$K\,A\,(T_s - T_{LH2})\,/L \;=\; M\,h_{fg} \qquad [26]$$

Using the above analysis, an estimate of how the total tank system mass is affected by the amount of insulation can be determined. For a storage duration of 8 hours, figure 9 shows how the total mass of the tank, including boil-off, is affected by the insulation thickness. Figure 10 shows the tank and boil-off mass as a percent of the liquid hydrogen used during an 8 hour period.

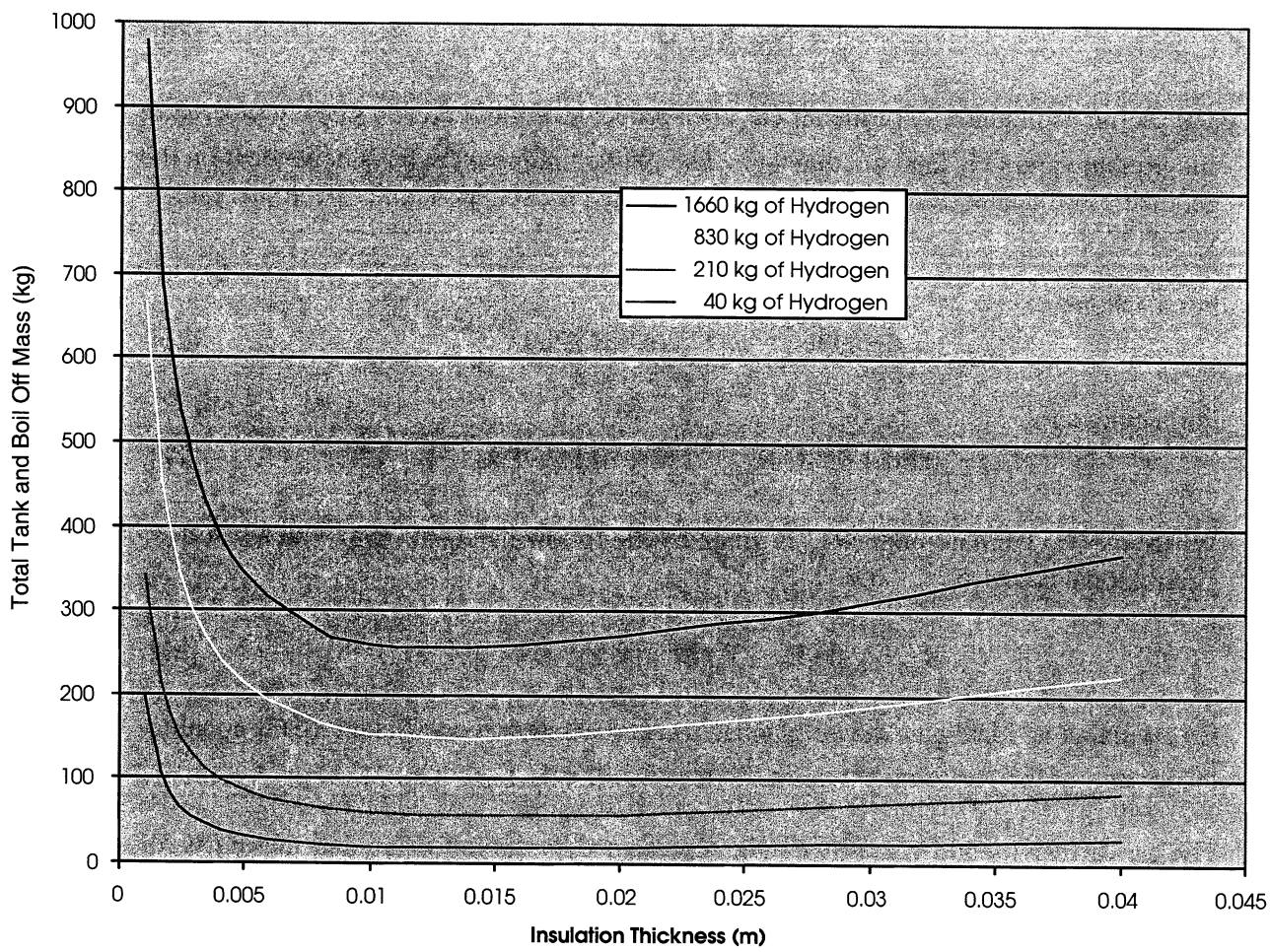

Figure 9.—Effect of Insulation Thickness on Overall Tank System Weight

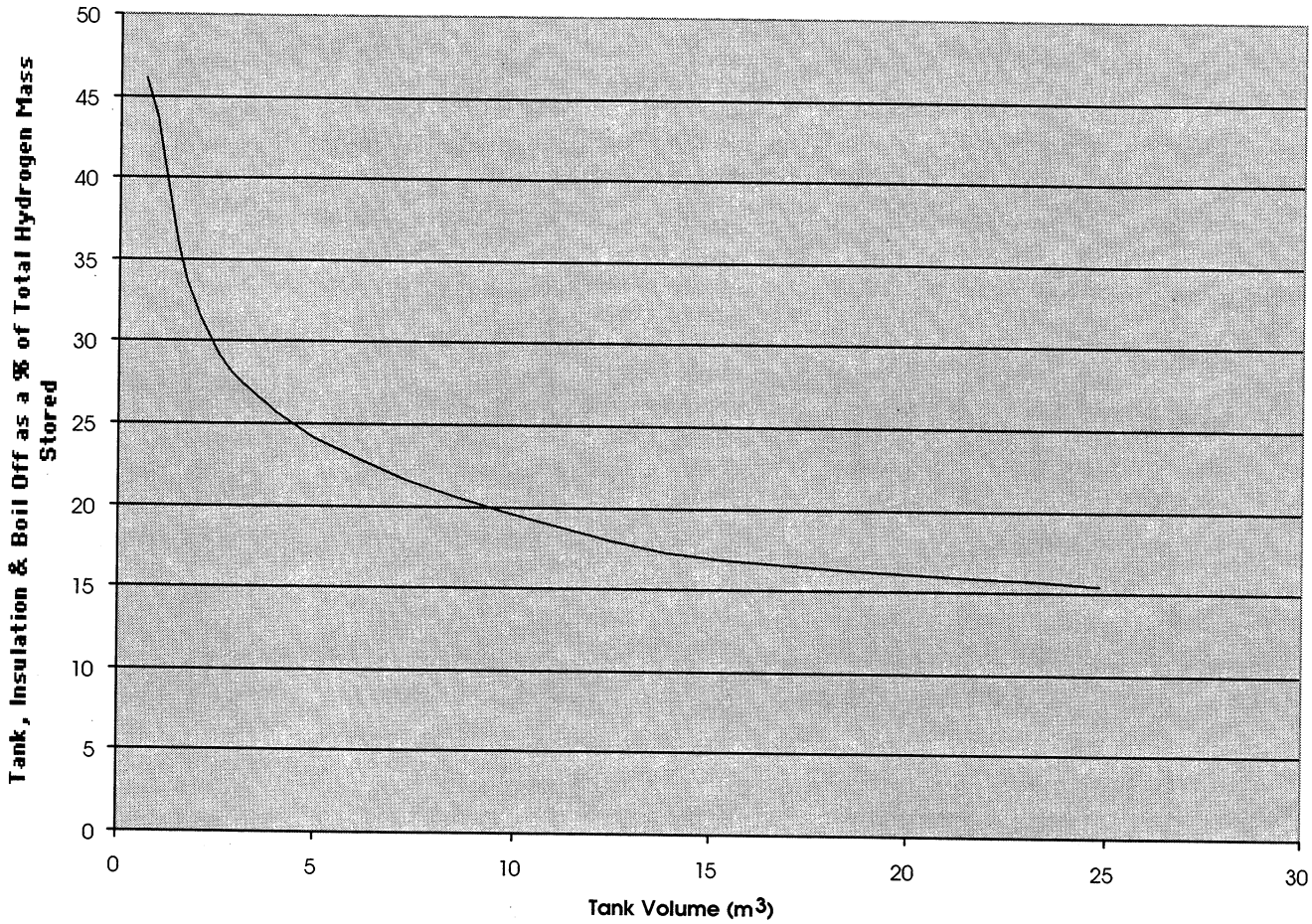

Figure 10.—Tank System Mass as a Percent of Useable Liquid Hydrogen

Gelled Hydrogen

To further increase the density of liquid hydrogen, it is possible to produce a gelled liquid hydrogen which produces an increase in density over conventional liquid hydrogen. It is estimated that gelled hydrogen can produce a 10% increase in the density over standard liquid hydrogen.

Gelled hydrogen is produced by introducing a gellant into the liquid hydrogen. This gellant can be either another cryogenic material, such as solid ethane or methane, or silica particles [4]. Gelling agents constructed from other types of hydrocarbons such as ethyl alkoxides or hexyl alkoxides are also under development [12]. Figure 11 shows how the propellant density can increase with increasing gelling agent concentration. This figure is based on data obtained from reference 4 for methane as the gelling agent.

Gelled hydrogen reduces the boil-off rate by 2 to 3 times compared to standard liquid hydrogen. There is also a significant safety benefit to using gelled hydrogen. It has an inherently smaller spill radius due to its higher viscosity than liquid hydrogen. This minimizes its effect if spilled. The increased viscosity reduces the leak potential by making the hydrogen more resistant to seeping through small openings. The higher viscosity also reduces the amount of hydrogen slosh within the storage tank reducing the chance for instabilities produced by the movement of the hydrogen [11].

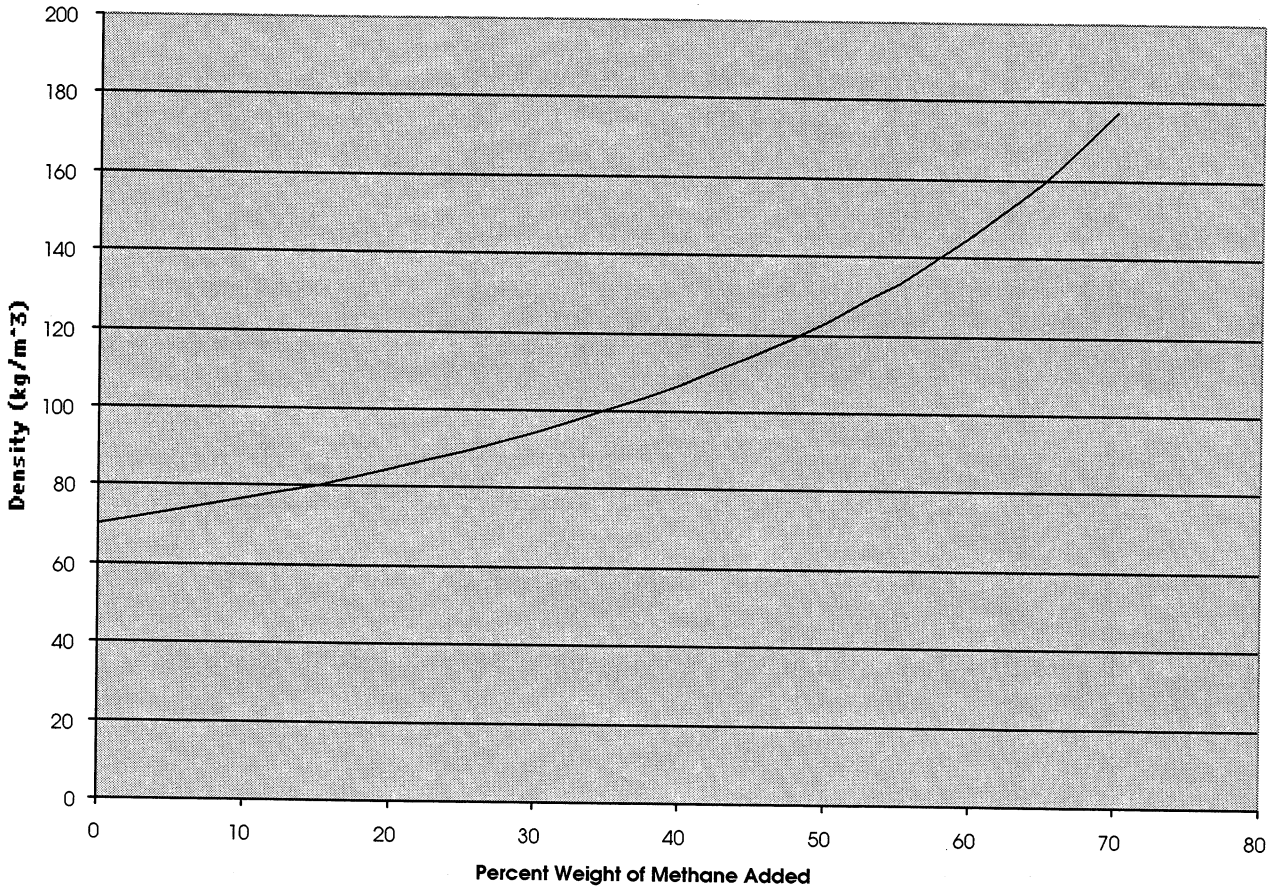

Figure 11.—Theoretical Increase in Density with the Addition of Methane Gelling Agent [13]

Cryo-cooler for Boil-Off Compensation

Depending on the flight time and time on ground between filling and flight, the boil-off rate for the liquid hydrogen may become a significant issue. Therefore it is worth investigating whether a cryo cooler can be utilized as a means of maintaining zero boil-off within the hydrogen tanks. Work has previously been done on the method of eliminating boil-off in cryogenic systems for space applications [14].

The cryo-cooler is used to condense the hydrogen vapor that forms in the ullage (excess area in the tank not occupied by liquid hydrogen) of the tank. This vapor is generated by heat leakage into the tank through the insulation. By sizing the cryo-cooler to match the heat leakage, the system can effectively have no boil-off. A typical single stage cryo-cooler for reaching liquid hydrogen temperatures is shown in figure 12.

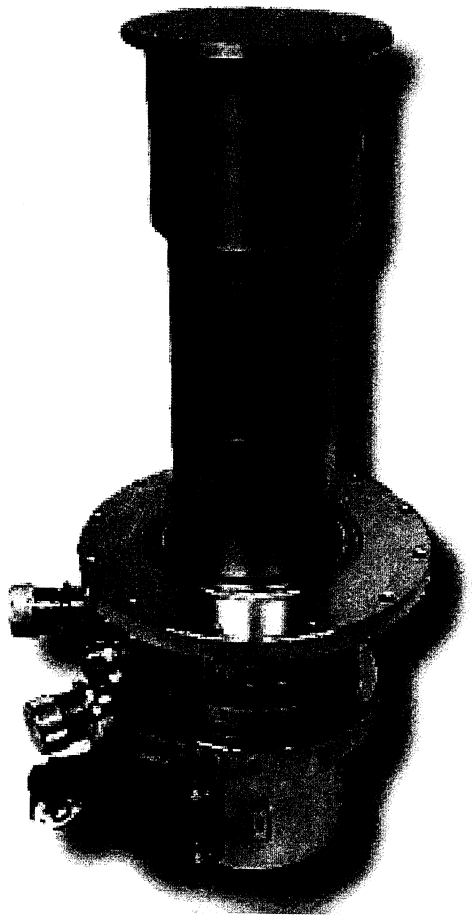

Figure 12.—Single Stage 20 K Cryo-cooler [14]

The cryo-cooler needs to compensate for the leakage of heat into the tank through the insulation. The power consumption is based on the latent heat of vaporization of hydrogen and the rate of heat flow into the tank, previously given in equation 26.

State of the art cryo-coolers require between 2.5 to 7.5 kW of power and provide cooling capacities of between 5 W and 18 W at 20 K. For this analysis the following specifications were used for the cryo-cooler sizing. The ratio of operating power to cooling power at temperature was estimated to be 0.45 kW/W. This was based on an average for the cryo-coolers examined.

A single stage cryo-cooler, like that shown in figure 7, has a mass of 67 kg including the compressor unit (not shown in the picture). This cryo-cooler requires 1.6 kW of continuous power. The mass of the cryo-cooler per cooling capacity was estimated as 0.0419 kg/W.

A mass and power estimate for a zero boiloff system was made. The mass estimate included the tank mass, insulation mass, cryo-cooler mass and additional hydrogen mass needed to operate the cryo-cooler. The results of this analysis showed that the mass of a cryo-cooled zero boil-off system is much greater than that of a conventional cryo tank system that has boil-off. For all the cases examined the hydrogen required to produce the power needed to run the cryo-cooler was much greater then the boil off that would have occurred with out it. Also the mass of the cryo-coolers themselves increased the overall system mass by an order of magnitude. Based on these results it was obvious that a zero boil-off system was not beneficial for a system with an operating time on the order of 8 to 12 hours or less.

Chemically Bound Hydrogen Storage

Another approach to storing hydrogen is to have it chemically combined with other elements to form a stable, easily handled (usually liquid) material that posses a relatively high weight fraction of hydrogen. The simplest method for this type of storage is to use a conventional hydrocarbon (such as gasoline or methane) as the storage compound. This greatly simplifies the transportation and storage of the hydrogen since there is extensive worldwide experience in handling and utilizing these compounds. The main issue with this type of hydrogen storage is that the hydrogen has to be released from the chemical compound in order to be used. This requires the consumption of energy to break the chemical bond as well as the potential for producing by-products that can be pollution causing. Even though energy needs to be added to liberate the hydrogen, the overall conversion efficiency of using the liberated hydrogen can still be higher than burning the compound directly. This is mainly due to the higher conversion efficiency of a fuel cell as compared to a conventional combustion engine. However, because this initial energy consuming step is required for this form of hydrogen storage, the complete system has to be analyzed (hydrogen liberation, consumption and conversion to the desired objective such as motion) to determine if this type of storage is more beneficial than utilizing the storage compound directly.

The volumetric energy density of hydrogen within some common fuels is shown in table 5.

TABLE 5.—HYDROGEN WEIGHT AND ENERGY DENSITY WITHIN COMMON FUELS [1]

Fuel (in liquid state)	Hydrogen Weight Fraction	Hydrogen Volumetric Energy Density (MJ/liter)
Hydrogen	1	8.4
Methane	0.25	10.8
Ethane	0.2	12.0
Propane	0.18	10.6
Gasoline	0.16	13.2
Ethanol	0.13	12.3
Methanol	0.12	11.9

In addition to the fuels listed in table 4 other more non-conventional compounds can be utilized. Examples of these include ammonia and lithium hydride slurry. Ammonia is a non-flammable liquid that contains 1.7 times the hydrogen per unit of volume as liquid hydrogen. Also ammonia can be cracked easily into nitrogen and hydrogen in a single step conversion ($2NH_3 > 3H_2 + N_2$) [2]. Lithium hydride slurry (LHS) provides 15.3% hydrogen by mass or 14.2 MJ/liter of energy storage. The advantage of LHS over other hydrocarbons is that it is storable at ambient pressure and temperature and the hydrogen within the slurry can be easily released by mixing it with water through a process called hydrolysis [3]. The hydrolysis is controlled by the addition of mineral oil to the mixture. This oil prevents runaway hydrolysis by limiting the hydride–water contact. This LHS storage system is presently under development, funded by the Department of Energy, by Thermo Technologies [3]. Operating systems utilizing this hydrogen storage concept have been demonstrated. In addition to lithium hydride, calcium hydride and magnesium hydride can also be used in a similar fashion to store hydrogen [4].

Hydrogen Reforming

Reforming of most hydrocarbon fuels takes place through a reforming catalyst to produce hydrogen and by-product compounds such as carbon dioxide. Some of the more common fuels that have logistical advantages to their use include diesel and jet fuels. However these fuels present a difficulty in reforming due to their relatively high carbon and sulfur content which tend to saturate the reforming catalyst. This poisoning of the catalyst needs to be addressed to enable reformers to be able to utilize these types of fuels.

The most common methods presently used for reforming hydrocarbon fuels is partial oxidation, steam reforming, thermal decomposition and exhaust gas reforming. Some of these methods however, are not applicable to the use of hydrogen as an on-board fuel. Of these partial oxidation and thermal decomposition would not be applicable methods. Partial oxidation requires more energy to produce the hydrogen than is available in the liberated hydrogen itself. Because of this, it would be more beneficial to utilize the stock fuel itself versus converting it to hydrogen through this method. Thermal decomposition requires the gasification of the hydrocarbon fuel and produces carbon solids, both of which are difficult to manage. The other methods, steam and exhaust gas reforming, are both potentially applicable to on-board hydrogen production. This is mainly because they

can utilize the waste heat from the hydrogen consumption to augment the hydrogen production. This greatly enhances the overall efficiency of the system [16].

The most promising would be exhaust gas reforming which uses the waste heat from the hydrogen consumption and a catalyst bed to produce the hydrogen. A converter utilizing this method is being developed at Argonne National Laboratory [17]. This converter can be made very compact and potentially operate at lower temperatures then other hydrogen generating systems. It also has quick start-up and demand-following capabilities. The rate of hydrogen production is dependent on the rate of fuel and water flow into the reaction chamber. The reaction chamber consists of a catalyst filled cylinder. As fuel and water are sprayed in, an ignition source begins the reaction. This type of reformer can convert a wide variety of hydrocarbon based fuels to a hydrogen rich gas on the order of 60% hydrogen at temperatures of between 450 °C and 670 °C, depending on the type of fuel used. A test was run on an experimental version of this reformer using gasoline as the hydrogen source. It was capable of producing 40 L/min of hydrogen gas at standard atmospheric conditions for a 22 mL/min flow rate of gasoline, 24 mL/min flow rate of water and a 45 L/min flow rate of air [18]. This hydrogen production rate is sufficient to operate a 3 kW fuel cell stack.

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Advances in fuel cell technology have brought about their consideration as sources of power for aircraft. This power can be utilized to run aircraft systems or even provide propulsion power. One of the key obstacles to utilizing fuel cells on aircraft is the storage of hydrogen. An overview of the potential methods of hydrogen storage was compiled. This overview identifies various methods of hydrogen storage and points out their advantages and disadvantages relative to aircraft applications. Minimizing weight and volume are the key aspects to storing hydrogen within an aircraft. An analysis was performed to show how changes in certain parameters of a given storage system affect its mass and volume.

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