NBSIR 75-803

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U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

ABSTRACT

The National Bureau of Standards played a vital role in developing hydrogen technology for the space age and is now engaged in efforts to adapt and improve this technology for the commercial use of hydrogen fuel. This document is a summary report on selected hydrogen-fuel topics and was prepared to identify cost and technical barriers to the commercial use of hydrogen fuel and to generate reference data for policy-planning, decision-making and design. Cryogenic hydrogen fuel technology is emphasized in the economic and systems analyses reported herein. Using the best available technical and economic data, hydrogen fuel is not currently cost competitive with alternate fuels; however, we must not reject hydrogen on the basis of current economic comparisons. Increased efficiencies of production, liquefaction, and energy conversion may drastically change these comparisons-of-today as will increased fossil fuel prices and more stringent environmental and pollution constraints. Hydrogen appears currently marketable in certain integrated utility systems, in transoceanic transport of energy produced far at sea, and is a necessary element in a wide variety of growing industrial processes and in the liquefaction of coal. This publication identifies research and development needs within selected areas of NBS competence and future research plans are outlined.

Key words: Conservation; conversion; cost; cryogenics, economics; embrittlement; energy; hydrogen; industrial, instrumentation, liquefaction; literature; materials; production; solar; storage; transmission; transportation; utilities.

PREFACE

BACKGROUND. The National Bureau of Standards (NBS) has been actively engaged in hydrogen research for over twenty years and in mid-1972 our interests were rekindled by the obvious need for an abundant, clean-burning fuel. Convenient energy storage and distribution, portable power and reduced air pollution are some of the advantages of recyclable hydrogen fuel. In the fall of 1972 the NAS-NAE-NRC* evaluation panel for the Cryogenics Division (CD) of the NBS recommended renewal of a modest effort on hydrogen fuel technology. The scientific staff of the NBS-CD responded enthusiastically and a state-of-the-art survey paper [1] was released in the summer of 1973. An economic analysis [2] of hydrogen-fueled electrical utility systems was published in March 1974, and a benchmark literature bibliography [3] was completed in June 1974. The work reported herein was initiated in July 1973.

The rapid momentum achieved in this program was made possible by the cognizant support of management at all levels of the NBS, e. g., Institute Director's Reserve funds were made available to initiate this study.

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* National Academy of Science (NAS), National Academy of Engineering (NAE) and National Research Council (NRC).

1. Hord, J., Cryogenic H_2 and National Energy Needs, Book, Advances in Cryogenic Engineering 19, (Ed.) K. D. Timmerhaus, p. 1-11 (Plenum Press, Inc., New York, N. Y., 1974).

2. Parrish, W. R., An Economic Study of Electrical Peaking Alternatives, Proceedings of THEME Conference, University of Miami, Coral Gables, Fla. (March 1974).

3. HYDROGEN FUEL - SUMMARY BIBLIOGRAPHY, Cryogenic Data Center, NBS, Boulder, Colo. (June 1974).

Because the Cryogenics Division of the NBS is primarily concerned with low temperature research, this study emphasizes the cryogenic aspects of hydrogen fuel. In the market place the application dictates the most suitable physical form of the fuel and cryogenic hydrogen is a contender in many potential fuel systems.

MOTIVATION. Hydrogen is a prime candidate to satisfy many long-term national (and international) fuel requirements. It is no longer necessary to justify hydrogen fuel research because hydrogen is a clear contender for the synthetic fuel market of the future--only the time scale for implementation of this fuel is uncertain. Economical production of hydrogen,from coal or water, could easily occur within the next decade and initiate major transitions in current modes of distributing marketable energy. Thus, it is apparent that hydrogen fuel research will have a major impact on future dispensation of energy in this country and offers great potential benefit to the public.

The need to accelerate hydrogen fuel research is accentuated by the fuel shortages that we have experienced over the past few years and by a nationally acclaimed goal--energy-fuel self-sufficiency by 1985. The NBS has a history of assisting industry in major national programs. The NBS mission stresses conservation of our natural resources, equity in the marketplace, transfer of existing technology to industry and research applied to industrial needs.

OBJECTIVE. Our goal is to provide the cryogenics industry with innovative cryogenic technology so that hydrogen may be liquefied, stored and distributed efficiently and with safety and fairness to the consumer.

APPROACH. Economic and systems analyses are performed to identify cost and technical barriers to the use of hydrogen fuel and to aid in program planning and definition. We endeavor to provide rational analyses based on the best available technical/economic information and to generate valid data for decision-making and design.

The work reported herein was selected to 1) coincide with the NBS-CD mission, 2) avoid repetitious efforts and augment studies of others, 3) serve national interests by supplying unbiased technical assessments of hydrogen's potential as a fuel and, 4) provide authoritative reference data in areas where the NBS is uniquely qualified.

This report was prepared for an interdisciplinary audience and is intended to afford maximum usefulness to the reader. Therefore, conventional units and terminology, common to the particular topic, are used in each chapter without regard for consistency from chapter-to-chapter. Metric units are used where appropriate. Each chapter is self-standing for ready reference; therefore, there is necessarily some overlap in individual chapter narratives. Authors of these chapters are senior staff scientists and engineers of the Cryogenics Division of the NBS.

PROGRESS. Analyses and summary reports are presented herein--the topics covered are: (1) cost and availability of hydrogen, (2) hydrogen in the electrical utility industry, (3) hydrogen-fueled automobiles, (4) survey of materials for hydrogen service, (5) instrumentation for cryogenic hydrogen fuel, (6) transmission and distribution of hydrogen, (7) solar energy--liquid hydrogen, (8) industrial applications of hydrogen and (9) hydrogen fuel literature.

SUMMARY. Based on current economic data, hydrogen fuel appears economically marginal in auto transportation and in electrical utility systems; however, we must be continuously aware that these conclusions are influenced by cost parameters that are changing daily. Consequently, cost parameters are provided in this study so that cost comparisons can be readily upgraded to reflect future cost factors, by-product credits and technological advances. Also, cost factors are not currently known well enough to justify elimination of hydrogen fuel on economic grounds.

At this writing hydrogen appears attractive as an aircraft and aerospace fuel, in certain integrated gas-electric utility systems (e. g. , use of hydrogen to store solar or off-peak electrical energy), for transport of energy from solar sea power plants and is an essential ingredient in a wide variety of prolific industrial processes.

Widespread use of hydrogen fuel will generate a significant need for construction and insulation materials research--this need for materials with suitable characteristics is defined herein.

Cryogenic instrumentation has not noticeably advanced in the past ten years. Large scale commercial use of cryogenic hydrogen will require major research and development efforts in this area.

When liquid fuel is required, our cost study shows that it is usually economically prudent to produce liquid hydrogen at the use-site. It is advantageous to liquefy hydrogen at the source when energy must be transported from power plants far at sea.

The NBS-CD provides hydrogen fuel literature services for the general public and these services are described herein.

PLANS. Priority research elements that have been identified and selected for future study are: (1) improve hydrogen liquefaction efficiency, (2) evaluate methods of recovering liquefaction energy and, (3) evaluate hydrogen compatible materials of construction. Long-term plans include the development of insulation transfer standards, the development of improved insulation systems and the standardization of measurement techniques for commercial exchange of liquid hydrogen.

J. Hord
December, 1974.

CONTENTS

CHAPTER 1

COST AND AVAILABILITY OF HYDROGEN

W. R. Parrish and R. O. Voth

1.0 SUMMARY

The feasibility of using hydrogen as a fuel will be determined by the availability and cost of hydrogen. This chapter considers techniques and costs of producing gaseous hydrogen along with costs of producing liquid, slush and solid hydrogen. It also examines the potential by-products that could lower the overall cost of using hydrogen.

Fossil fuels and water are the two sources of hydrogen. Today most industrial hydrogen is derived from hydrocarbons (mainly natural gas) and costs 10 to 15¢/kg to produce. When natural gas costs more than approximately 80¢/MBTU, coal becomes a competitive source with production costs of 20 to 25¢/kg. MBTU = BTU x 10^6 throughout this chapter.

As the fossil fuels are depleted, water will become the principal source of hydrogen. The two most promising means of producing hydrogen from water are electrolysis and thermochemical decomposition. Although electrolysis is an existing technology, it is not cost competitive with other existing processes unless electrical power costs less than 5 mills/kW-h--exceptions occur in those cases where ultra-high purity and/or small quantities of hydrogen are required. Thermochemical decomposition uses a combination of heat and chemicals to decompose water; the process requires several intermediate steps involving chemical reactions and separations. Thermochemical decomposition offers the possibility of producing hydrogen from water at lower cost and more efficiently than electrolysis; however, this hydrogen will still be more expensive than hydrogen produced from fossil fuels (even when fossil fuels cost double their current price).

Using current technology, it costs 15 to 20¢/kg to liquefy, slush or solidify hydrogen in a high capacity plant. In terms of energy required, it takes 20 to 30 percent of the lower heating value of hydrogen to convert it into the condensed phases. Although the economic and energy penalties are significant, the end-use of the fuel prescribes the optimum physical state of hydrogen.

At least three by-products of hydrogen production and liquefaction could increase the economic attractiveness of hydrogen as a fuel: oxygen, deuterium, and recovery of liquefaction energy. If hydrogen is produced from water, selling the by-product oxygen could reduce the selling price of hydrogen by as much as 10¢/kg, provided the oxygen demand met the supply. Distillation of liquid hydrogen offers an attractive means of obtaining deuterium which is a fuel for fusion reactors. Current estimates indicate that sale of deuterium could lower the cost of liquid hydrogen by 2 to 3¢/kg. Although the maximum amount of energy recoverable from liquefaction is only 10 percent of the heat of combustion, it represents a significant amount of energy in large vaporizing facilities. A preliminary analysis indicates that 25 percent of the ideal liquefaction energy of a kilogram of hydrogen is comparable to the actual separation energy required to extract eight kilograms of oxygen from air. This observation implies an overall energy recovery system efficiency of about ten percent. Thus, the refrigeration energy recovered by warming a liquid hydrogen stream could theoretically

power an air separation plant sized to provide enough oxygen for stoichiometric combustion with the hydrogen stream. This availability of both oxygen and hydrogen at the use-point may prove both economically and environmentally attractive.

1.1 INTRODUCTION

This chapter discusses methods of producing and liquefying hydrogen. The first section covers methods of hydrogen production. Whenever possible, production costs are included.

The second section covers the cost of producing liquid, slush and solid hydrogen. These costs include the cost of purifying the hydrogen. The effect of cycle efficiency on production costs is also demonstrated.

The last section looks at possible by-products of hydrogen which could reduce the net cost of hydrogen. It also discusses the feasibility of recovering liquefaction energy.

1.2 GASEOUS HYDROGEN SOURCES AND PRODUCTION TECHNIQUES

The two primary sources of hydrogen are fossil fuels and water. This section briefly describes some of the more important hydrogen producing processes. It also considers some innovations which could become important in the future.

1.2.1 Hydrogen from Fossil Fuels

There are at least five processes for producing hydrogen from fossil fuels. Today most of the hydrogen in the U.S. comes either from steam reforming or partial oxidation of hydrocarbons.[1] As hydrocarbon stocks become more expensive, coal gasification will become an important hydrogen-producing process. This subsection briefly describes these three processes. For more details about all of the processes, excluding coal gasification, one can refer to reference books such as Faith, Keyes, and Clark [1].[2]

Steam Reforming: Steam reforming of hydrocarbons is the major source of industrial hydrogen today; it produces relatively high purity (97%) hydrogen in a two or three stage process. The first stage is the reforming stage where steam and hydrocarbons react over a nickel catalyst in a furnace operating at 1000 to 1200 K and 30 atm. The basic reactions are:

$$C_mH_n + m\ H_2O \rightleftarrows mCO + (m + n/2)H_2$$

$$C_mH_n + 2m\ H_2O \rightleftarrows mCO + (2\ m + n/2)H_2.$$

The product gas containing H_2, CO, and CO_2 goes to a shift converter where it is mixed with more steam and undergoes the following reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

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[1] Hydrogen is a major by-product in the catalytic reforming of petroleum. Since the hydrogen is consumed within the refinery, this process will not be discussed here.

[2] Numbers in brackets indicate references at the end of this paper.

The shift converter requires an iron catalyst and operates at a lower temperature (900 K). Whereas the reforming is endothermic, the converter reaction is exothermic; this heat is used to generate some of the process steam.

After cooling the converter gas to around 350 K, the gas is scrubbed with a caustic or an ethanolamine to remove the carbon dioxide. To obtain 97% H_2, the gas goes through another shift conversion and scrubbing.

Many times part of the feedstock is the fuel for the reforming furnace; waste heat in the flue gas generates roughly half of the steam required in reforming. Quade [2] suggests using a nuclear high temperature gas reactor (HTGR) to supply the process heat. Nuclear heat has the attraction of reserving hydrocarbons for chemical purposes instead of using them as fuels.

Partial Oxidation: The partial oxidation process produces hydrogen by partial burning of the hydrocarbon; the overall reaction is

$$C_mH_n + 1/2(m + n + x - y)O_2 \rightarrow xCO_2 + (m-x)CO + yH_2 + (n-y)H_2O,$$

where x and y are respectively, the number of moles of carbon dioxide and hydrogen produced per mole of feedstock. The reaction apparently goes to completion because only a trace of oxygen is found in the synthesis-gas stream. The process is attractive because the reaction requires no catalyst and has a high thermal efficiency (60%)[3]. However, the process requires an oxygen plant which is roughly 25% of the total capital cost. The operating conditions are comparable to those in steam reforming but in this process the reactants are preheated before entering the reactor. As in the case of steam reforming, to obtain a high purity product, the syn-gas must go through one or two stages of shift conversion and scrubbing.

Coal Gasification: Coal gasification is a relatively new technology and not yet fully developed in this country. Although most of the gasifier research today relates to low or high BTU gas and liquefaction processes, the same gasifier technology can be used to produce hydrogen from coal. In fact, most liquefaction processes require large amounts of hydrogen (~7000 SCF/bbl of synthetic liquid [4]) and coal may be the most economical source of hydrogen gas in the future.

The coal gasification process is quite similar to the partial oxidation process except that instead of preheating the reactants, they are heated in the gasifiers by the partial oxidation of coal.[3] Steam is required to supply an additional source of hydrogen according to the reaction

$$C + H_2O \rightleftarrows CO + H_2.$$

To produce hydrogen from coal requires 1.7 kg of steam per kg of coal consumed (0.3 kg in the gasifier) and 0.75 kg of oxygen per kg coal. This all produces 0.16 kg of hydrogen at 97% purity [3]. (This particular process used only one shift converter.)

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[3] In theory, this same process could be used to produce hydrogen from garbage or other organic wastes.

1.2.2 Economics

Figure 1.1 gives the production cost of hydrogen from various fossil fuels and by electrolysis. This figure assumes that all of the different hydrogen production plants have a capacity of 180 million SCFD (17750 kg/h). The solid portions of the curves represent current or near-term raw materials cost (or electricity in the case of electrolysis). Figure 1.2 shows our estimated selling price of hydrogen for the various processes. The selling price is based on a discount cash flow of 18%, it includes a 50% state and federal tax rate and straight-line depreciation over 20 years. It excludes transmission costs and local taxes.

Based on these curves, the cheapest source of hydrogen is natural gas--providing it costs less than roughly 80¢/MBTU. Higher costs make coal competitive. The current cost of fuel oil makes it a much less attractive source of hydrogen.

1.2.3 Hydrogen from Water

The most abundant source of hydrogen is water. Electrolysis is the only commercial process existing today for obtaining hydrogen directly from water. However, several new techniques are under development, the most promising alternate approach is thermochemical decomposition. Electrolysis and thermochemical decomposition are considered first, while the more exotic methods are discussed at the end of this section.

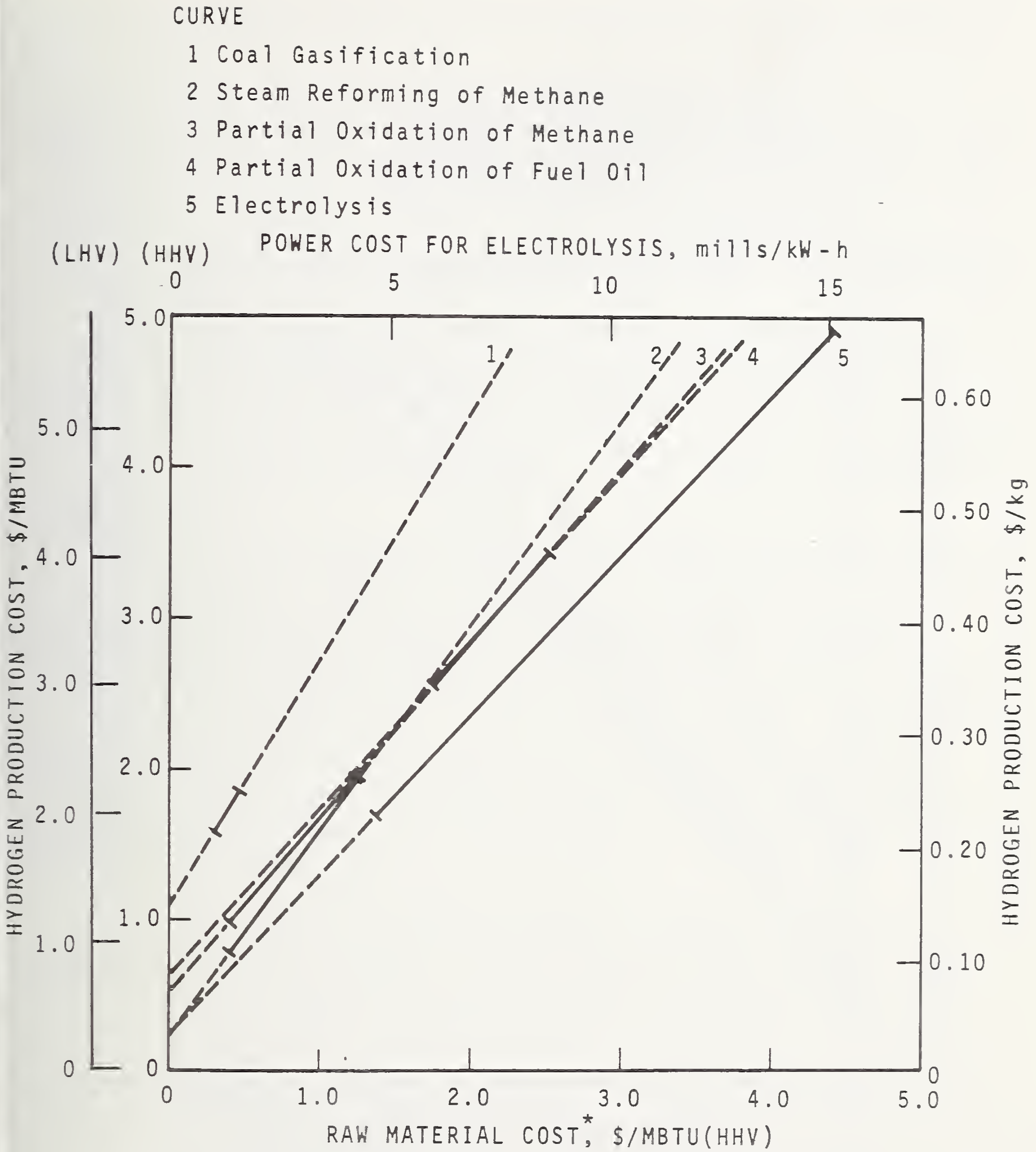
Water Electrolysis: Electrolysis produces a high purity hydrogen, which today is more expensive than hydrogen from hydrocarbons. Some reasons for this include:

1. It takes more energy to remove hydrogen from water than from hydrocarbons.
2. Electrolysis requires a high-grade energy (electricity), whereas hydrocarbon reduction requires a low-grade energy (heat).
3. Hydrocarbons are usually relatively cheap compared with electrical power.

However, electrolysis becomes attractive if power is inexpensive or where hydrogen demand is too small to justify a hydrogen-from-fossil fuels plant. Also, as nuclear power becomes more important, the third reason may vanish.

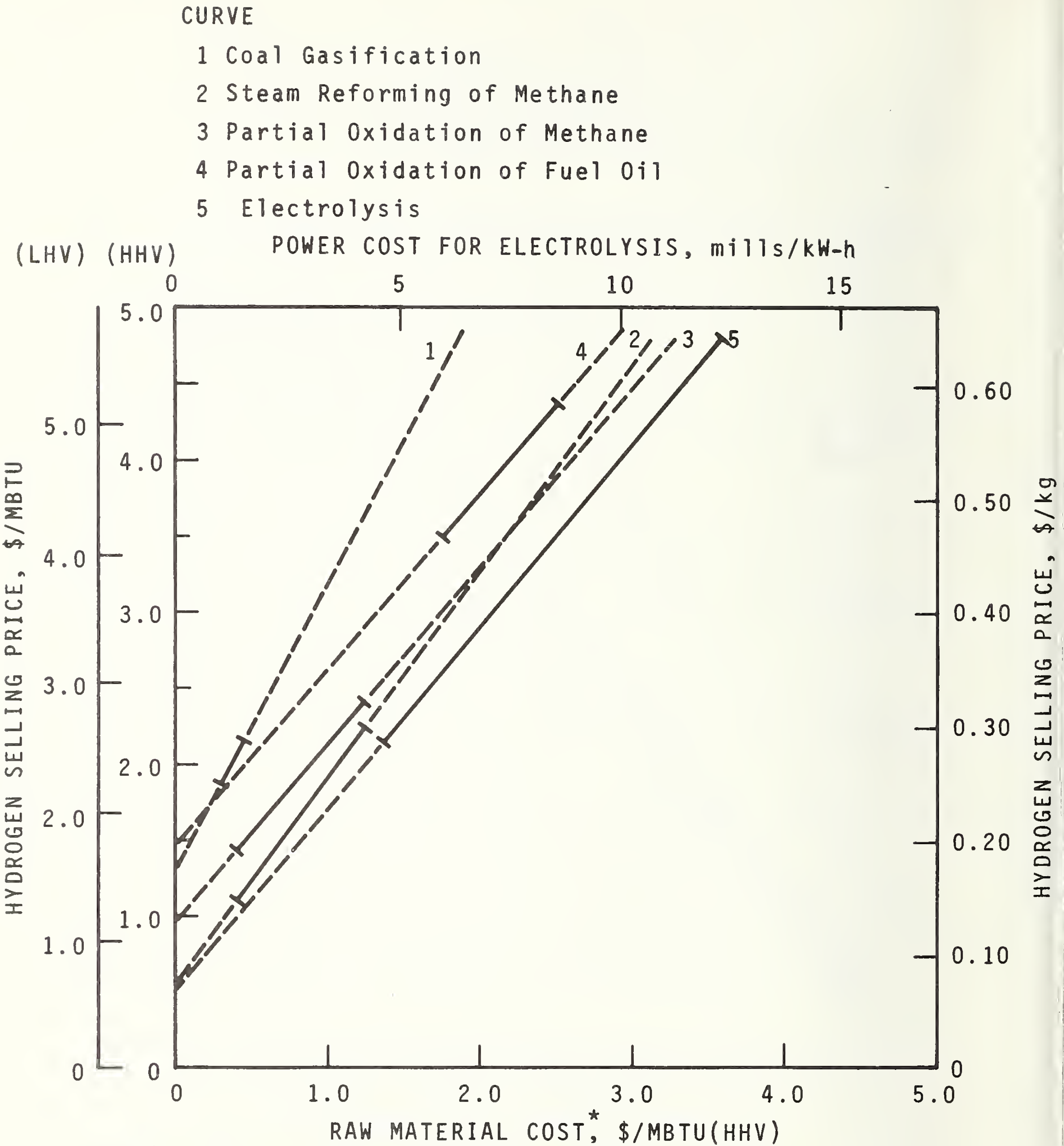
The basic electrolysis unit consists of two electrodes, which are separated by a membrane and immersed in water. Since pure water conducts electricity poorly, a strong electrolyte, such as potassium hydroxide, is added to the water to reduce ohmic losses. As current passes through the electrodes, hydrogen evolves from the cathode and oxygen from the anode. The hydrogen production rate is directly proportional to the current; from Faraday's law, each kilogram of hydrogen produced requires 26,532 ampere-hours.

In theory, only the free energy (237.3 kJ/g-mol at 25°C and 1 atm) of dissociation needs to be supplied by electricity. The remaining portion of the heat reaction (286.0 kJ/g-mol at 25°C and 1 atm) can be supplied by heat from the surroundings or from ohmic losses within the cell. However, commercial cells operate at such a low efficiency that heat must be removed from the cell. For a given cell design, the cell efficiency is inversely proportional to the current density. However, the lower the current density, the greater the number and/or size of cells (and capital cost) required to provide a given hydrogen production rate. Thus, the optimum current density depends upon the relative contributions of fixed costs (i.e., costs related to capital investment) and operating costs (i.e., power, labor and maintenance costs). Based on an advanced cell design [5], the optimum current



*Raw material costs are commonly based on HHV.

FIGURE 1.1 Hydrogen Production Cost vs. Raw Material Cost for Various Processes, 180×10^6 SCFD Plant. HHV=High Heat Value and LHV=Low Heat Value.



*Raw material costs are commonly based on HHV.

FIGURE 1.2 Selling Price of Hydrogen vs. Raw Material Cost for Various Processes, 180×10^6 SCFD Plant. HHV=High Heat Value and LHV=Low Heat Value.

density decreases roughly 25 - 30% if the cost of power doubles. However, as figures 1.1 and 1.2 point out, for any reasonable power cost, the cost of power is the major component of the total cost.

Several ways are being pursued to lower the cost of hydrogen via electrolysis. One obvious way is to improve electrode efficiency at high current densities while keeping the capital costs down. Assuming constant capital costs and a power cost of 10 mills/kW-h, the selling price of hydrogen would vary from 4 \$/MBTU to 3 \$/MBTU if the cell efficiency increased from 77 to 100% (i.e., low-grade heat, taken at no charge would have to be added); this gives a rough lower bounds on hydrogen costs that could never be obtained in commercial units.

If high pressure hydrogen is the end product, electrolysis has an advantage in that the free energy change is a weak function of pressure at temperatures below 400 K [6]. Therefore, the unit has very little penalty in power consumption at high pressures. However, more heat must be added because the heat of reaction is increased. Also, the economics of using high pressure vessels must be included. Even so, Kincaide [7] believes that high pressure electrolysis could be attractive at pressures of 6 MN/m^2 with conventionally designed electrodes.

Conventional electrode designs use membranes made of materials such as asbestos to separate the electrodes. The membrane prevents mixing of the evolved gases but permits the flow of ions, electrons, and water between compartments. These membranes can be a source of problems if the cell is operated at elevated pressures. One solution to this problem is to use a solid polymer electrolyte (SPE) [6]. This system replaces the membrane with a polymer that, when saturated with water, becomes a good conductor. The SPE is strong enough to withstand high differential and operating pressures. It has the additional advantage of eliminating the strong electrolyte, which can cause corrosion problems in the gas collecting system. Nutall et al. [6] claim that future developments will make the SPE concept competitive with conventional electrolysis systems, both in higher efficiency and lower capital and operating costs.

1.2.4 Thermochemical Decomposition of Water

There has been a recent surge of interest in producing hydrogen from water via thermochemical processes. The primary attraction is that heat, probably nuclear or solar, instead of electricity is used, which could reduce production costs and increase the overall efficiency. (The overall efficiency of electrolysis is limited by the conversion of heat to electricity.) The processes fall into two categories--open and closed cycle. Open-cycle systems consume the reactants; examples of open-cycle processes include coal gasification and shift conversion, which were discussed previously in this section.

Today the main interest is in closed-cycle systems. A hypothetical two-step, closed-cycle process is

$$X + H_2O \rightarrow XO + H_2$$

$$XO + \text{heat} \rightarrow X + 1/2\ O_2$$

so that the net reaction is

$$H_2O \rightarrow H_2 + 1/2\ O_2.$$

However, the processes being considered contain three to six steps and reaction temperatures ranging from 273 to 1200 K. From a capital and operating cost standpoint six steps is the maximum if the process is to compete with electrolysis. On the other hand, Funk and Reinstrom [8] found that no material X exists which could make the two-step cycle above as efficient as electrolysis. The same is probably true for three step processes; therefore, the optimum processes will probably contain four to six steps.

Many organizations are investigating possible closed cycles [9]. Possible cycles must first be evaluated using thermodynamics. As Funk et al. [10] points out, the work of separation and degree of completion of each reaction must be considered. Incomplete reactions result in larger recycle streams and increased separation work; both of these problems decrease the economic feasibility of the cycle. If the process looks thermodynamically attractive and offers minimal corrosion problems (many of the most promising reactants are corrosive), then the reaction kinetics must be studied. Usually this takes a substantial effort, especially if gas phase reactions and/or catalysts are involved. Several processes have passed the thermodynamics stage and are in the kinetics stage.

At this time, any economic analysis of closed-cycle thermochemical processes must be considered preliminary; however, Wentorf and Hanneman [11] estimate production costs to be at least 2.60 $/MBTU. Comparing these costs with data shown on figure 1.1 indicates that this process could be competitive with electrolysis; but even if the anticipated price range of coal were doubled, hydrogen from coal would still be cheaper.

1.2.5 Other Methods of Producing Hydrogen from Water

This section includes some of the more speculative methods suggested for producing hydrogen. The technical feasibility of some of the methods is questionable, and an economic analysis of the process at this time would be meaningless.

High Temperature Decomposition: The free energy of decomposition of water vapor decreases and the concentrations of free oxygen and hydrogen increase with increasing temperatures. Thus, water can be decomposed at high temperature using only heat. This concept seems promising, but no one has found a way of separating hydrogen from the gas mixture at 3000 K. The separation cannot be made at lower temperatures because the hydrogen and oxygen will recombine. (The equilibrium mole fraction of hydrogen at 3000 and 1000 K are 0.65 and 10^{-6} respectively [12].) Just the material problems make thermal cracking look unattractive, even if the heat source were available.

High Temperature Electrolysis: Operating an electrolysis unit at higher temperatures lowers the electrical energy input because the free energy is lower; e.g., operating at 1000 K instead of 300 K reduces the electrical energy demand by roughly 10%. However, solid electrolytes, similar to the solid polymer electrolyte, that can operate at high temperatures need to be found (SPE cannot operate long at temperatures above 380 K); also, gasket materials are a problem at higher temperatures [6].

Ultra-Violet Photolysis of Water: Eastlund and Gough [13] suggest using ultraviolet photons to photodissociate water. The photon source would be leakage plasma from a fusion reactor. It is possible that this process will have a higher overall efficiency than the conventional electrolysis system. However, the process must wait for the development of fusion reactors, which may not occur before the year 2000 or later.

Biophotolysis of Water: Mitsui [14] is investigating the use of microorganisms and sunlight to produce hydrogen. This concept is attractive because it offers the potential of a relatively high conversion efficiency of sunlight to chemical energy, at least when compared to conventional solar heat-to-hydrogen systems. However, many problems must be solved before the process can be considered commercially viable.

1.3 COST TO MAKE LIQUID, SLUSH, AND SOLID HYDROGEN FROM GASEOUS HYDROGEN

Producing liquid, slush, and solid hydrogen from gaseous hydrogen requires capital investment, energy expense, and operating expense for the liquefier and/or refrigerator. An estimate of these costs can be obtained using information from a survey and correlation of current refrigerator/liquefier capital costs and energy requirements by Strobridge [15]. Liquefaction costs presented herein include the cost of gas purification; however, we are unable to supply a breakdown of purifying costs, as these are proprietary industrial data. Figures 1.3 and 1.4 are reproduced from Strobridge's report to show the efficiencies and capital costs of existing refrigerators and liquefiers. The numerous points on the curves show the performance for refrigerators and liquefiers at various low temperatures using various cryogenic fluids. The basis of comparison is the ratio of ideal work to actual work of producing refrigeration or liquid.

Figure 1.3 shows the efficiency of refrigerators versus the refrigerator capacity. To convert the refrigeration capacity to an equivalent liquefier capacity, the refrigeration capacity from the graph is multiplied by the ideal work of compression per unit of refrigeration at the liquefaction temperature of interest and divided by the ideal work of liquefaction per unit of liquid.

The ideal work of compression per unit of refrigeration is defined as the work required by an ideal Carnot cycle refrigerator operating between the same temperature limits. For a unit operating at hydrogen temperatures this work is

$$\frac{W_c}{Q} = \frac{T_H - T_C}{T_C} = \frac{300 - 20}{20} = 14 \text{ watts/watt.}$$

The ideal work per unit of product for a liquefier can be derived from the thermodynamic availability of the product. Thermodynamic availability is defined by

$$A = T_o (s_o - s_L) - h_o + h_L$$

where T is the absolute temperature, s is specific entropy, and h is specific enthalpy. The subscript o designates ambient conditions and L designates the low temperature product conditions. Table 1.1 is a list of ideal work requirements for various cryogenic states of hydrogen.

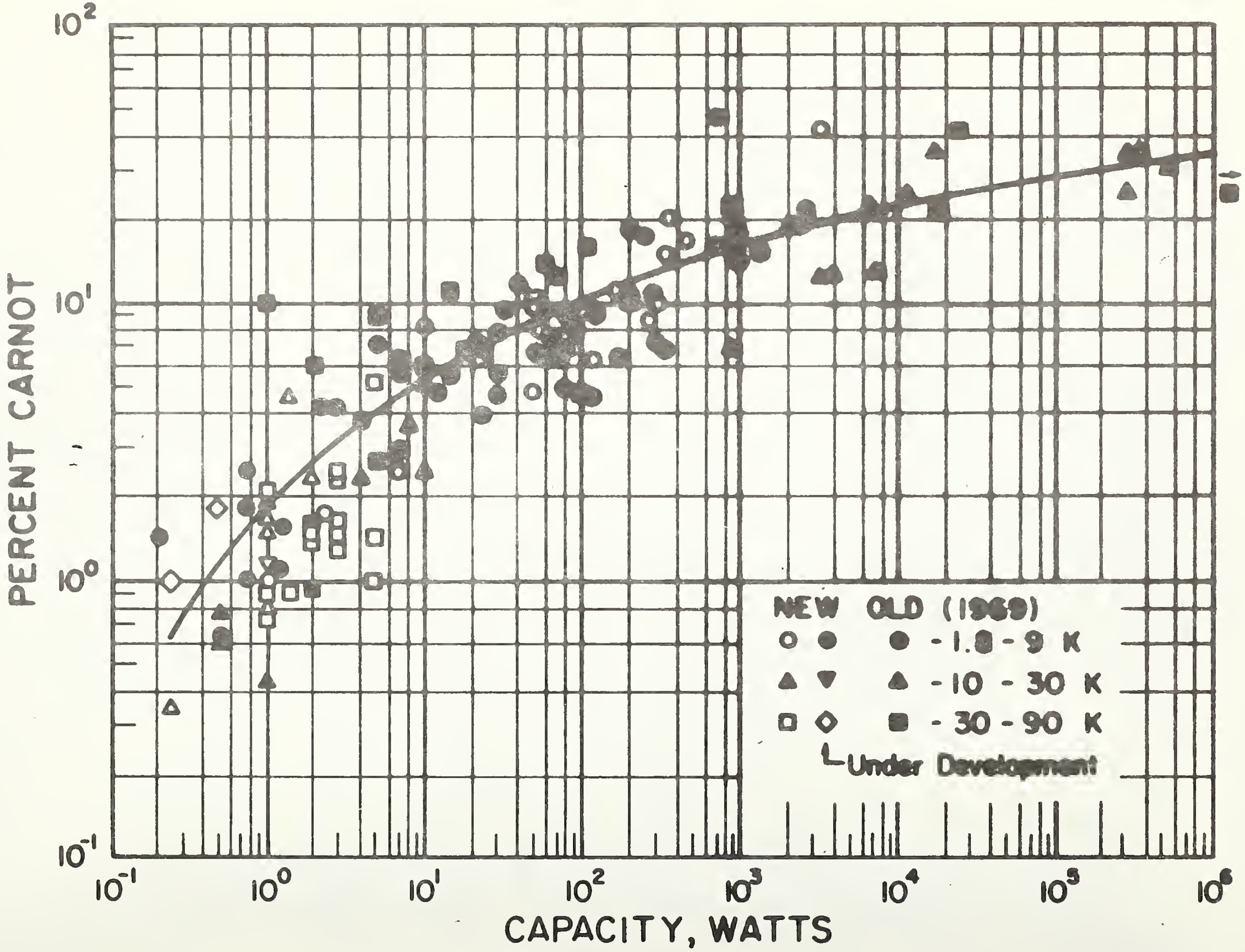


Figure 1.3 Efficiency of low temperature refrigerators and liquefiers as a function of refrigeration capacity.

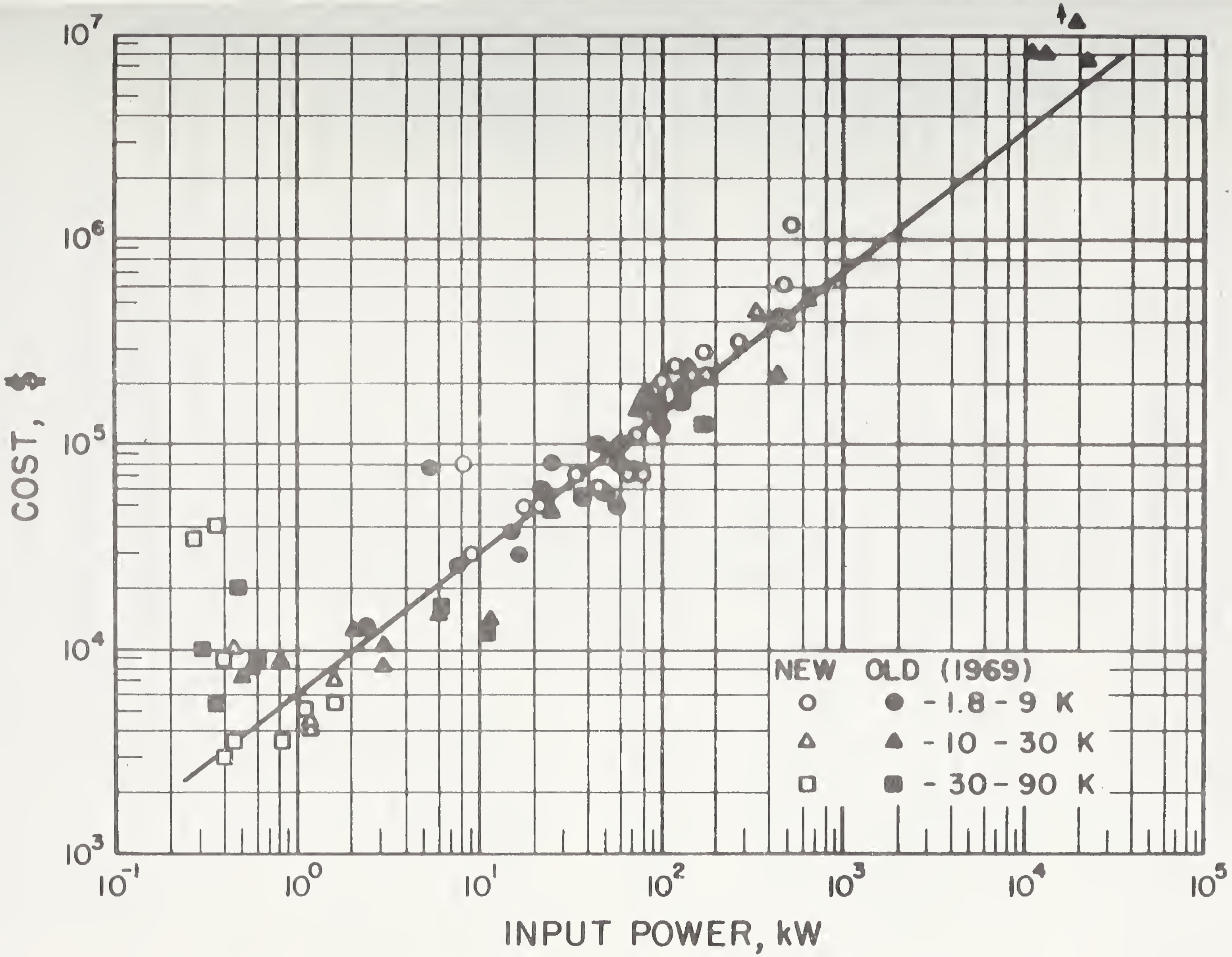


Figure 1.4 Cost of low temperature refrigerators and liquefiers as a function of installed input power.

It is assumed that normal hydrogen at 1 atmosphere pressure and 300 K is used to produce cryogenic parahydrogen in the various states.

Figure 1.4 shows the capital investment required for commercial refrigerators and liquefiers [15]. The cost is plotted against the installed compressor power of the available units. The line on the plot is for the equation

$$C = 6000\ P^{0.7}$$

where P is the kilowatts of installed compressor power, C is cost in dollars (1973). This equation is used to calculate capital investment costs in this section.

In order to determine the cost of producing liquid, slush, or solid hydrogen, the cost of the required power, the operating and maintenance costs (O&M), and the fixed charges on the capital investment must be included. The fixed charges are based on operation of the plant 90 percent of the time. The power costs are simple functions of the ideal power requirements and conversion efficiency. The O&M costs include maintenance, labor and operating costs other than fuel costs. The fixed charges include interest on the capital investment and debt retirement. The cost of land for the liquefier installation is neglected in the costing figures.

Table 1.1 Ideal work required to liquefy, slush or solidify hydrogen. (Initial state of normal hydrogen gas: pressure, 1 atm absolute; temperature, 300 K.)

Final State	Ideal Work Required		
	kW-h/kg	kW-h/lb	Btu/lb
Saturated liquid at 1 atm	3.971	1.801	6147
Slush hydrogen:50-50 mixture of solid-liquid by weight at triple point temperature and pressure	4.375	1.985	6773
Solid hydrogen at triple point temperature	4.543	2.061	7032

Table 1.2 shows the capital costs and energy requirements for various sized units. The 3500 kg/h capacity approaches the capacity of the largest plant currently in service with the larger capacities being an extrapolation of the trends apparent in the existing units. The efficiency figures were based on existing plant operations with a reasonable extrapolation to a 40 percent efficient process for the largest plant.

The production of slush hydrogen (a 50-50 mixture of solid and liquid by mass) is a batch process [16]. Because of the batch process inefficiencies and the lack of definitive data, the efficiency of the overall slush manufacturing process was arbitrarily reduced by one percentage point and costs were based on this assumption. For the large plants considered herein, this assumption is considered reasonable.

Table 1.2 Capital costs and energy requirements for producing cryogenic hydrogen from gaseous hydrogen.

Plant Size kg/h	EFF %	Cost[1] 1973 dollars	Energy Requirements kW-h / kg
Liquid Hydrogen			
100,000	40	94.61×10^6	9.93
7,000	35	16.15×10^6	11.35
3,500	34	10.14×10^6	11.68
1,500	33	5.72×10^6	12.03
500	30	2.84×10^6	13.24
Slush, Solid-Liquid (50-50 mixture by mass) Hydrogen			
100,000	39	103.06×10^6	11.22
7,000	34	17.63×10^6	12.87
3,500	33	11.08×10^6	13.26
1,500	32	6.26×10^6	13.67
500	29	3.11×10^6	15.09
Triple-Point Solid Hydrogen			
100,000	40	94.61×10^6	9.93
Aux Ref*	40	33.29×10^6	2.23
7,000	35	16.15×10^6	11.35
Aux Ref	30	6.33×10^6	2.98
3,500	34	9.38×10^6	11.68
Aux Ref	29	3.99×10^6	3.08
1,500	33	5.72×10^6	12.03
Aux. Ref	27	2.32×10^6	3.31
500	30	2.84×10^6	13.23
Aux. Ref	23	1.20×10^6	3.88

---

[1] Cost = 6000 $P^{0.7}$ where P is input power in kilowatts.

* Auxiliary refrigerator of appropriate capacity operating at 10 K.

Table 1.3 Liquefaction/refrigeration costs per unit of product cryogenic hydrogen (from gaseous hydrogen).

Plant Size, kg/h	100,000	7,000	3,500	1,500	500
lb/h	220,462	15,430	7,716	3,307	1,100
		Liquid Hydrogen			
Power Costs[1]	0.119 $/kg	0.136 $/kg	0.140 $/kg	0.144 $/kg	0.159 $/kg
O&M[3]	0.013	0.035	0.045	0.062	0.097
Fixed Charges[4]	0.019	0.045	0.057	0.075	0.111
Total $/kg	0.151	0.216	0.242	0.281	0.367
Total $/lb	0.068	0.098	0.110	0.127	0.166
Total $/10^6 Btu[2]	1.32	1.90	2.13	2.46	3.22
		50-50 Slush Hydrogen			
Power Costs	0.135	0.154	0.159	0.164	0.181
O&M	0.014	0.038	0.049	0.067	0.106
Fixed Charges	0.020	0.049	0.062	0.082	0.122
Total $/kg	0.169	0.241	0.270	0.313	0.409
Total $/lb	0.077	0.109	0.122	0.142	0.186
Total $/10^6 Btu	1.49	2.11	2.36	2.75	3.60
		Solid Hydrogen			
Power Costs	0.146	0.172	0.177	0.184	0.206
O&M	0.018	0.041	0.053	0.072	0.115
Fixed Charges	0.025	0.063	0.075	0.105	0.159
Total $/kg	0.189	0.276	0.305	0.361	0.480
Total $/lb	0.085	0.125	0.138	0.164	0.218
Total $/10^6 Btu	1.65	2.42	2.67	3.18	4.22

---

[1] Electric power costs $.012/kW-h

[2] Based on lower heating value of 33.331 kW-h/kg (51,600 Btu/lb)

[3] $\$/\mathrm{kg} = 301.88\,(P/110372)^{0.65}/\mathrm{liquefaction\ rate}$; P = Input power, kW

[4] $FCR = I\,(1+I)^y/((1+I)^y - 1)$ I = Interest Rate, 15%; y = Plant life, 25 years

The cost of producing solid hydrogen was estimated as follows: First, liquid hydrogen is produced at the N.B.P. and then frozen solid with an auxiliary 10 K refrigerator. The final temperature of the solid is taken at the triple point temperature (13.803 K). Estimates of the time required to freeze hydrogen in various configurations are given in reference [17].

Table 1.3 shows the cost per unit of product for various sized units. Power costs were based on electrical availability at 0.012 \$/kW-h. Operating and maintenance (O & M) costs per unit of product were calculated by

$$C_{O\&M} = \left(\frac{P}{110372}\right)^{0.65} \times \frac{301.88}{\text{Production Rate, kg/h}}$$

where P is the input power in kilowatts and the production rate is for 90 percent plant operating time.

The constant (301.88) includes a correction for kilograms per hour. The equation is a modified version of an equation presented by Hallet [18]. The equation was modified by basing the O&M costs on the installed compressor power instead of the liquefaction rate. This alteration allowed the O&M costs to change with plant size and with changes in efficiency and ideal work of production. The fixed charges on the capital investment (per unit of product) were determined by

$$C_{FC} = \text{FCR}^{*} \times \frac{\text{Capital Investment}}{\text{Production Rate x 0.9 x hours/year}}$$

The costs presented in table 1.3 are based on current technology and extrapolations of trends in efficiency. Improved technology could yield lower costs. The largest reduction in costs would result from improved efficiency in the liquefaction process. Improved efficiency would not only reduce power requirements but would also reduce the capital investment and the related fixed costs and O&M costs. Table 1.4 shows the possible reduction in costs with improved efficiency in the liquefaction process for a plant capacity of 7000 kg/h. Also, since most existing plants are one-of-a-kind, further reduction in plant costs could be expected if many plants of equal size were constructed.

Table 1.4 Effect of efficiency of liquefaction on product costs - (7000 kg/h)

EFF. (%)	35	40	45	50	55	60
Power Costs \$/kg	0.136	0.119	0.106	0.095	0.087	0.079
O&M \$/kg	0.035	0.032	0.030	0.028	0.026	0.025
Fixed Charges \$/kg	0.045	0.041	0.038	0.035	0.033	0.031
Total \$/kg	0.216	0.192	0.174	0.158	0.146	0.135
Total \$/lb	0.098	0.087	0.079	0.072	0.066	0.061
Total \$/10^6 Btu	1.90	1.69	1.53	1.40	1.28	1.18

---

* See footnote 4 in table 1.3.

The liquefaction costs are high and are a deterrent to the adoption of liquid hydrogen as an energy carrier. The energy requirements for liquefaction are shown in a simple block diagram in figure 1.5. The top half of this figure shows an energy balance assuming no recovery of the liquefaction energy. The figure shows that for every kilowatt of chemical energy output in the form of liquid hydrogen, 1.298 kW of energy from chemical and electrical sources must be supplied. The lower diagram in figure 1.5 indicates the energy recoverable from the liquid as an energy output. The recovered energy and the liquefaction energy were estimated by using the ideal work of liquefaction at an efficiency of 40 percent for both processes. Figure 1.5 indicates the energy penalty one must pay for liquefying hydrogen. In addition, liquid storage and handling evaporation losses could impose an additional energy penalty of 10 to 20 percent for reliquefaction; i.e., electrical energy requirements may be as high as 0.358 kW in the diagram shown on figure 1.5.

Thus, the energy and cost penalties incurred in liquefying hydrogen are significant, but we must remember that the fuel application dictates the choice of fuel physical state. Only in a total fuel system can we estimate overall energy conversion efficiencies and fuel economics. Even then, convenience and performance factors favor dense fuels and frequently outweigh cost and efficiency arguments.

1.4 HYDROGEN COST CREDITS

Large scale production and liquefaction of hydrogen offers several by-products that could lower the cost of hydrogen as a fuel. These are oxygen, deuterium, and refrigeration potential, i.e., recovery of liquefaction energy.

1.4.1 Oxygen By-Product Credit

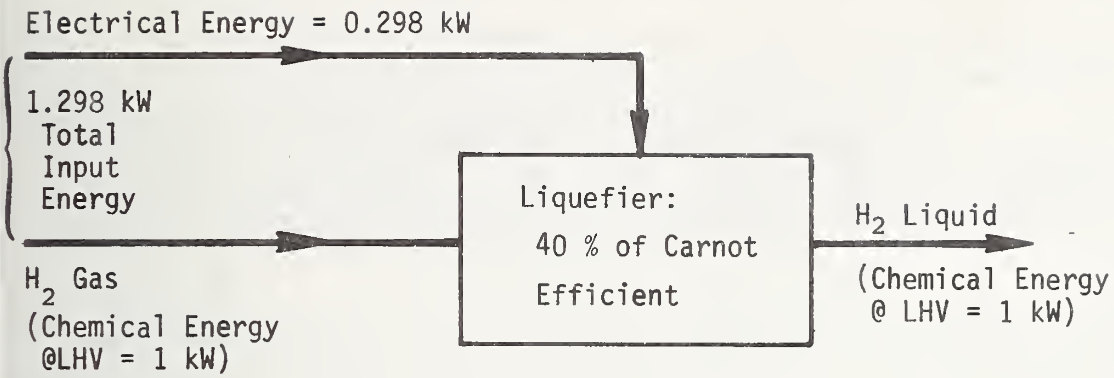
For every kilogram of hydrogen produced from water there are eight kilograms of oxygen produced. Hence, when the hydrogen fuel industry matures, large quantities of oxygen will be available.

The by-product value of oxygen could range anywhere between zero and the cost of oxygen obtained from air separation. In 1972, the average price for large quantities of oxygen from air plants was 0.58¢/lb (1.3¢/kg)[19]. (This cost excludes transmission costs because the air plants are situated near the consumers.)

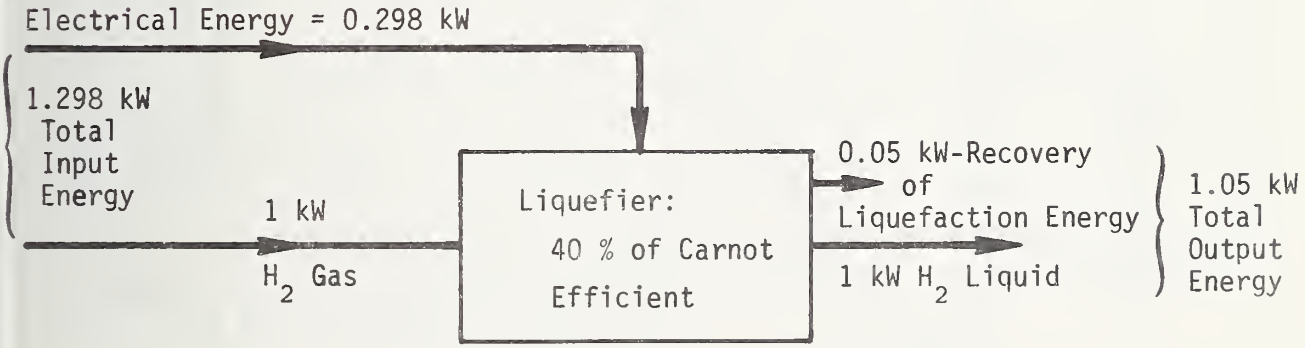
Figure 1.6 shows the effect of oxygen by-product credit on the selling price of hydrogen. Unless large new markets are found, the by-product value will be low because of the large oversupply. Possible large scale future markets for oxygen include sewage treatment [20] and paper processing [21]. To make by-product oxygen more competitive with oxygen from air plants, the source should be close to the consumer to minimize transmission costs. For a given volumetric flow rate, it costs roughly twice as much to pipeline oxygen gas as hydrogen [22].

1.4.2 Deuterium By-Product

The natural abundance of the isotope deuterium is roughly 0.015% that of hydrogen. To obtain deuterium, the U.S. Atomic Energy Commission goes through the costly (in capital and in energy) process of distilling heavy water (D_2O) from water. The heavy water is electrolyzed to produce deuterium. A more direct method, especially if liquid hydrogen is



$$\frac{\text{Input Energy}}{\text{Output Energy}} = 1.298$$



$$\frac{\text{Input Energy}}{\text{Output Energy}} = 1.236$$

FIGURE 1.5 Energy Requirements for Liquefaction of Hydrogen (Based on LHV) With and Without Recovery of Liquefaction Energy.

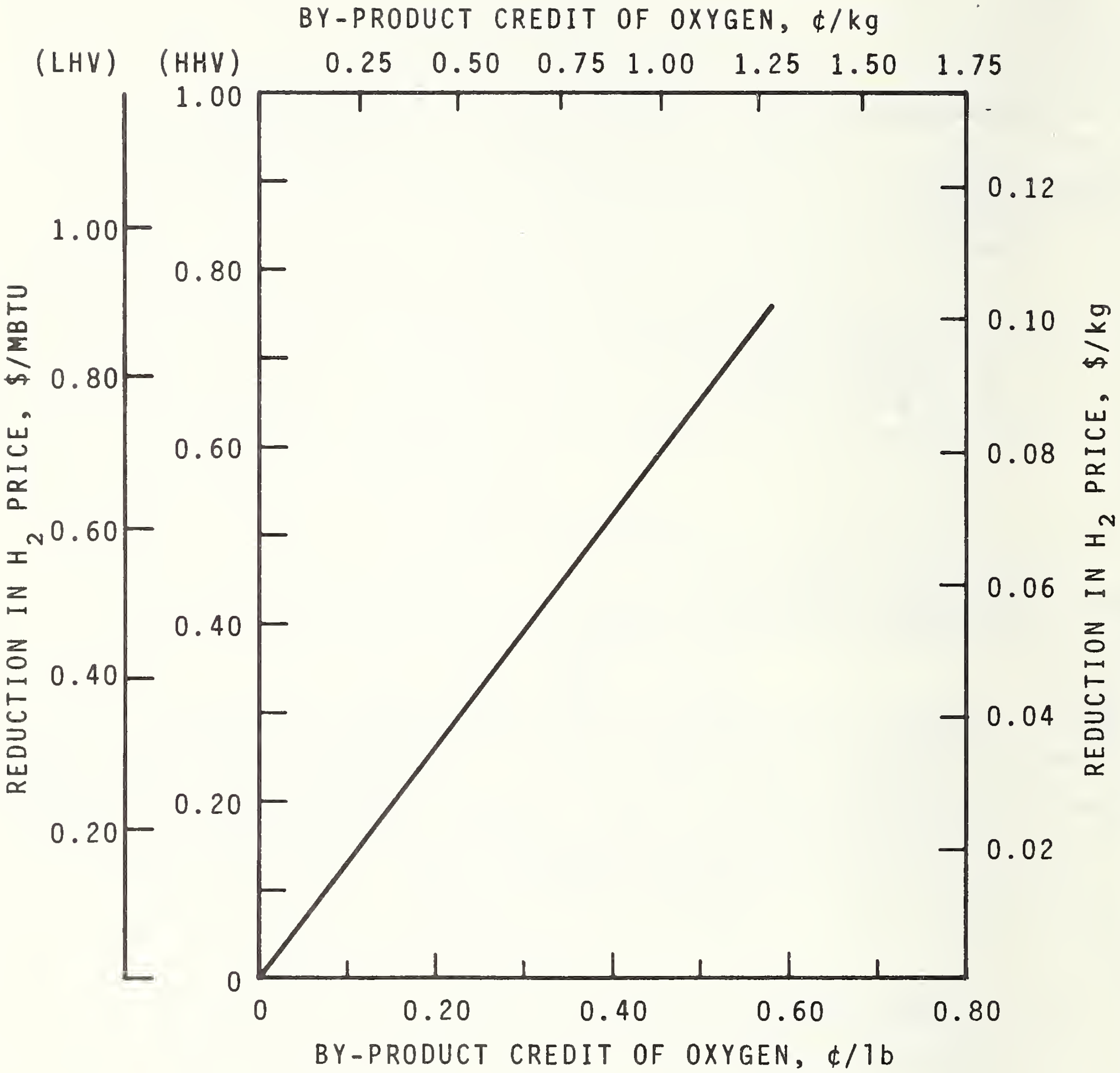


FIGURE 1.6 Effect of Oxygen By-product Credit on the Cost of Hydrogen.

required, is the low temperature distillation of deuterium from hydrogen [23]; this method is used in Europe.

At present, there is little demand for deuterium outside of basic research. However, this could change radically if the fusion reactor becomes a reality since the two most promising fusion reactions use deuterium as a reactant [24].

It is difficult to predict how much credit could be given for deuterium. Two recent estimates [25,26] range between 1.8 and 3.5¢/kg of hydrogen; this amounts to 10% or less of the estimated cost of producing hydrogen gas.

1.4.3 Recovery of Liquefaction Energy

When liquid hydrogen is available but gaseous hydrogen at ambient temperature and pressure is desired, some of the liquefaction energy can be recovered. The amount of energy that can be recovered is no greater than the ideal work of liquefaction ($3.971 \frac{\text{kW-h}}{\text{kg}}$) as shown in table 1.1. Because the ideal liquefaction energy is approximately 10 percent of the chemical energy of the hydrogen, the recovery of the liquefaction energy will probably not be economical in small systems. However, in large vaporizing facilities, the recoverable energy is significant, and several interesting recovery techniques may be employed.

The simplest recovery technique utilizes a system as shown on figure 1.7. The liquid is pumped to a high pressure by a liquid pump, vaporized and heated to ambient temperature by receiving heat from the ambient, and then expanded isothermally back to ambient pressure. The net work from this system is the work output from the isothermal expander minus the shaft work into the liquid pump. Using the conditions of NBP equilibrium liquid hydrogen in the storage container, and 300 K sea level ambient conditions, the net work from the system is shown on figure 1.8 as a function of the pumped liquid pressure. The top curve on the figure shows the recovered work if the pump and expander are 100 percent efficient; the work recovery shown by the lower curve includes an adiabatic efficiency of 80 percent for the pump and 60 percent isothermal efficiency for the expander. Parahydrogen properties from [27] were used to perform the calculations.

A similar work recovery calculation can be made for liquid oxygen. The results of such a calculation are shown in figure 1.9. Oxygen data from [28] were used in the calculation.

A further refinement of the recovery technique would be to use the refrigeration available to precool air in an air separation plant instead of absorbing heat from the ambient. Although large quantities of oxygen are produced by electrolysis and the use of this oxygen will increase the efficiency of a power plant while reducing emissions, the cost of transporting oxygen to a remote site is seldom economical. However, by using the refrigeration energy available from liquid hydrogen, stoichiometric amounts of oxygen can be separated from air on-site with very little additional energy. The capital expense of the on-site air separation plant may be balanced by the reduction in cost of a steam generating plant because of a reduction in boiler complexity. Other by-products from the air separation plant, such as neon and argon in the near future, and perhaps helium in the distant future could be used as cost credits for liquid hydrogen.

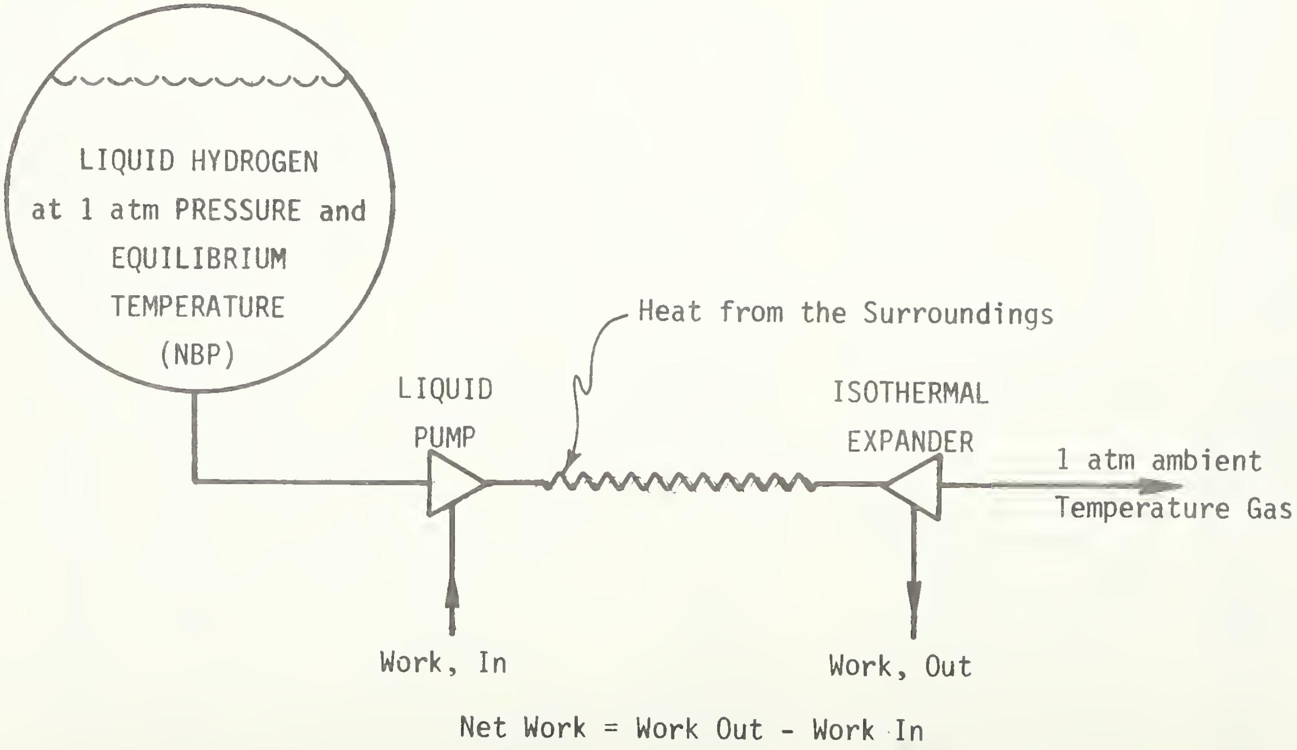


FIGURE 1.7 Schematic of Method to Recover Work from Compressed Liquid Hydrogen:

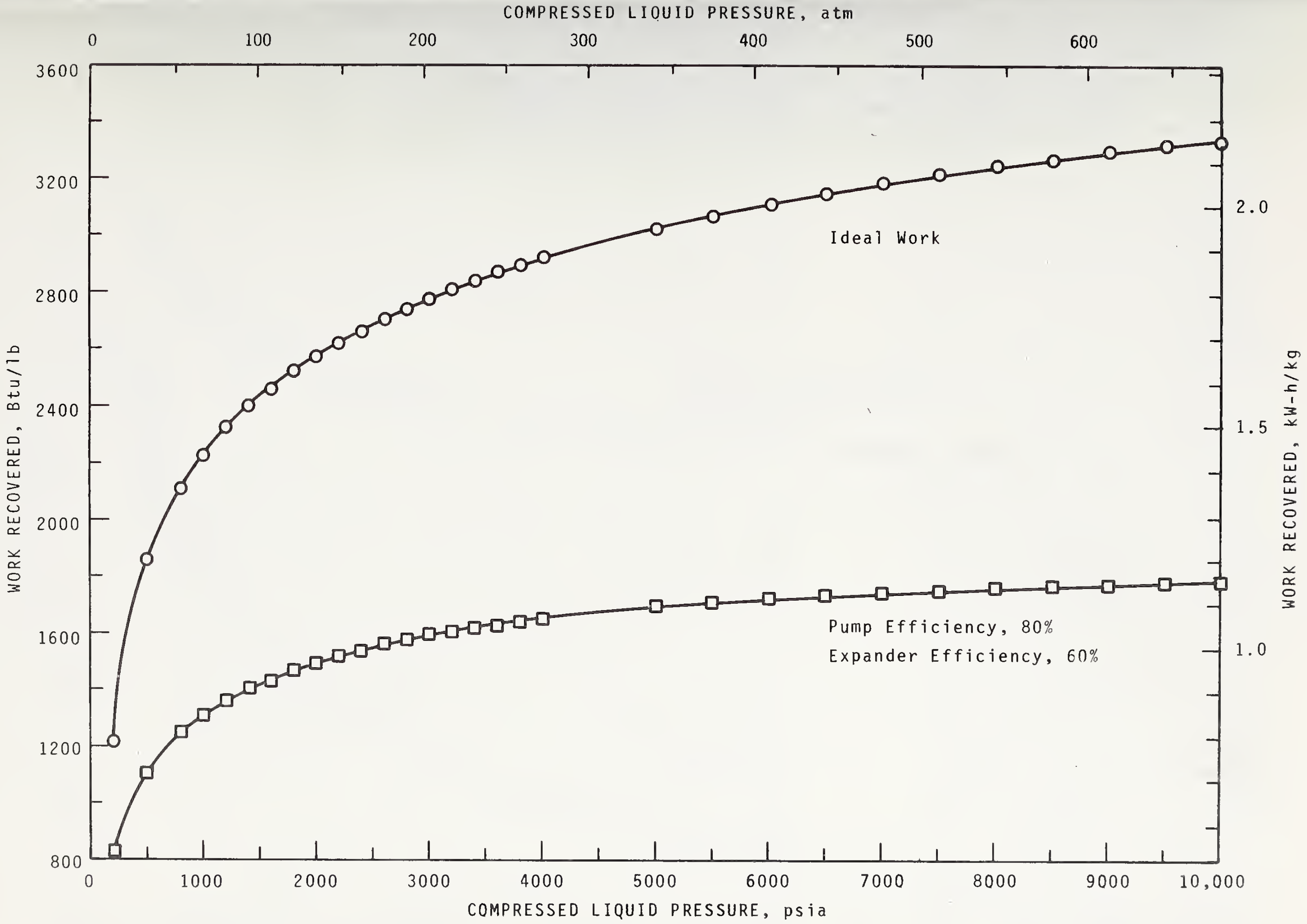


FIGURE 1.8 Work Recovery from Compressed Liquid Hydrogen.

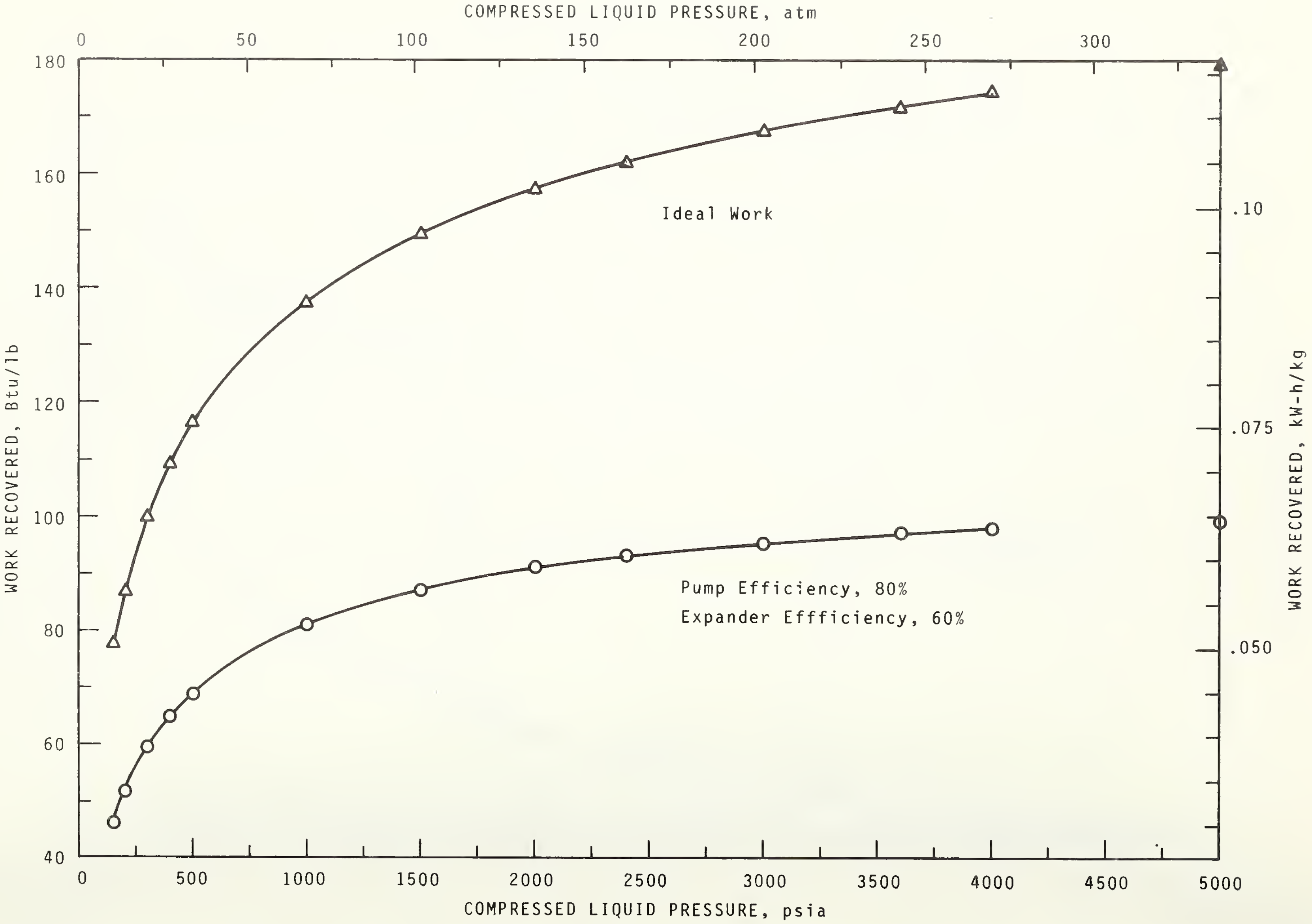


FIGURE 1.9 Work Recovery from Compressed Liquid Oxygen

The feasibility of using an air separation plant to produce gaseous oxygen for combustion with hydrogen can be demonstrated by comparing the work of separation of a stoichiometric amount of oxygen with the energy available from vaporizing the liquid hydrogen. Combustion of hydrogen with oxygen proceeds according to $H_2 + 1/2\ O_2 \rightarrow H_2O$. The ideal work of separation of the oxygen from the air is 52.2 W-h per kilogram of oxygen [29]. Since every kilogram of hydrogen burned requires eight kilograms of oxygen, the required separation energy becomes 417.6 W-h per kilogram of hydrogen. Using the ideal liquefaction energy available from one atmosphere liquid hydrogen (3971 W-h/kg, table 1.1) no additional energy would be required to obtain the gaseous oxygen if the overall efficiency of the recovery system and separation process is (417.6/3971) x 100 = 10.5 percent efficient.

The efficiency data [30] for several nitrogen, air, and separation plants are included on figure 1.10. Percent Carnot refers to the ratio,

$$N_c = \frac{W_i}{W_a} \times 100$$

where W is the work expenditure, subscript i indicates ideal work, and subscript a indicates the actual work requirement of the separator. The solid line was drawn to show average performance demonstrated by existing refrigerators and single fluid liquefiers. Data for refrigeration units operating in the 30 to 90 K temperature range are shown by the open symbols; data for air separation and liquefaction plants are given by the symbols with an enclosed number. Unit 1 is a mobile liquid oxygen-nitrogen generator currently being used by the Navy and Marine Corps; units 2, 3, and 4 are liquid nitrogen generators; unit 5 is a small liquid oxygen generator; and unit 6 produces gaseous nitrogen at room temperature plus a small amount of liquid nitrogen--both products being delivered at about 0.8 MPa (8 atm) absolute pressure. It is apparent that efficiencies of 30 to 40 percent could be expected from large separation plants. Assuming 40 percent efficiency for the air separation cycle, the work required per kilogram of hydrogen to produce a stoichiometric amount of gaseous oxygen would be 417.6 W-h/0.4 = 1.044 kW-h per kilogram of evaporated hydrogen. Recovery of 30 percent of the ideal work of hydrogen liquefaction ($3.971\ \frac{\text{kW-h}}{\text{kg}}$) would provide the energy required to produce this oxygen. Also, we can compare this energy requirement for production of oxygen from air with the energy available in compressed liquid hydrogen. Figure 1.8 indicates that recovery of work from compressed liquid hydrogen could supply enough energy to produce stoichiometric gaseous oxygen from air. A more detailed design analysis is necessary to prove this simple analysis, but the increased efficiency of having both oxygen and hydrogen available at a site remote from a liquid hydrogen generator may prove to be economically and environmentally attractive.

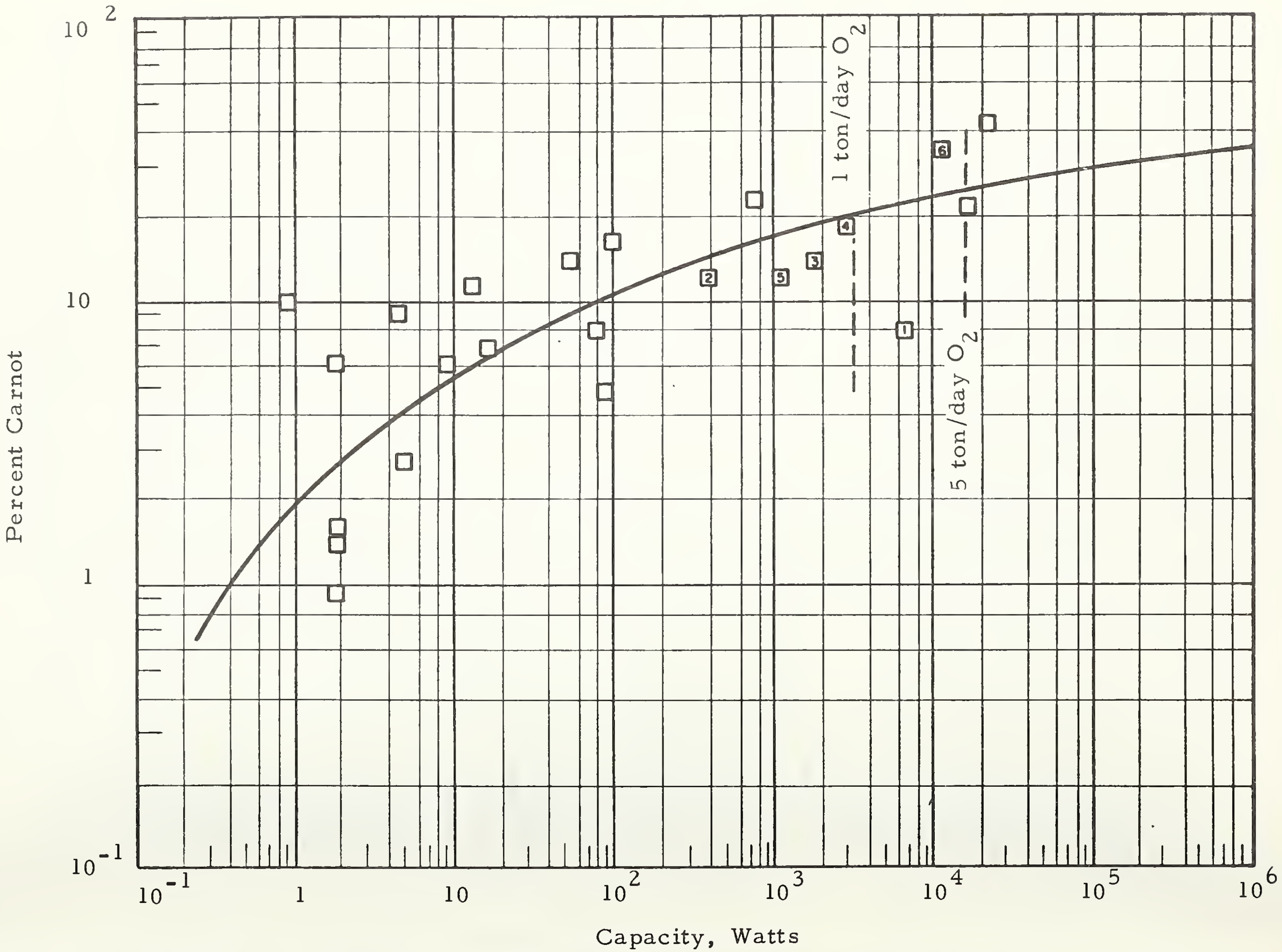


Figure 1.10 Efficiency of Selected Low Temperature Refrigerators and Liquefiers.

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CHAPTER 2

HYDROGEN IN THE ELECTRICAL UTILITY INDUSTRY

W. R. Parrish

2.0 SUMMARY

This chapter considers the economic feasibility of using hydrogen as a fuel in peaking and intermediate power generation. To make the study meaningful, hydrogen was compared with other reasonable alternatives.

The alternatives fall into two categories -- power generation and energy storage. In power generation we consider using gas turbines, fuel cells and combined cycle units. Whereas the first two are considered for both peaking and intermediate duty, the combined cycle is considered for intermediate duty only. The fuels considered were hydrogen, synthetic natural gas (SNG) and methanol. We evaluate the relative merits of two sources of hydrogen: 1) hydrogen produced via electrolysis using off-peak power and 2) hydrogen purchased from an outside source. Methods of storing hydrogen include liquid, compressed gas and metal hydride. Storage methods for SNG include liquid and compressed gas while methanol is readily storable as a liquid.

We evaluate three energy storage concepts: hydro pumped storage, batteries and superconducting magnetic energy storage (SMES).

A simplified approach to the economic analysis is used wherein we assume that sufficient off-peak power is available and that power production costs consist of fuel costs (sometimes off-peak power costs must be considered instead of, or in addition to, fuel costs), operating and maintenance costs, and fixed charges on capital investment. Sample calculations are given in Appendix A. All cost data required for the analysis are based on current costs or currently anticipated costs; for several cases we give estimated cost ranges.

For the economic comparison, we consider a 100 MWe peaking unit and a 400 MWe intermediate unit. In each case we report both total and component power production costs. This allows one to rapidly determine the effect of changing any cost factor used in the base case calculations.

The economic analysis based on the assumptions described below indicates that for peaking operation, pumped storage and methanol-fired gas turbines are currently the most attractive options while batteries and SMES are the least attractive. SNG looks slightly more economical than purchased hydrogen, which, in turn looks slightly more economical than electrolytic hydrogen. The predominant cost in all of the alternatives is the fixed charge on capital. The most attractive physical form of fuel storage appears to be liquid although underground gas storage might be competitive if depleted gas fields are available.

The above conclusions also apply to intermediate operation except that the most attractive means of generating power is the combined cycle unit using methanol.

One must remember that the results presented here are based on present day and anticipated near-future technology. Significant technological advances could radically alter these conclusions. Also other cost-influencing factors such as stricter environmental controls could make hydrogen an attractive fuel for future power generation.

2.1 INTRODUCTION

The electrical utilities must meet daily load variations where the peak demand can be more than twice the minimum demand [1]; figure 2.1 illustrates a typical daily load curve. The exact shape of the curve depends upon the weather and the relative demand of residential and industrial consumers. However, all utilities are faced with the problem of having to meet high demands for relative short periods of time. This is shown more clearly by the annual duration curve in figure 2.2. This curve indicates how many hours per year the utility operates at or above a given power level. Utilities normally divide the curve into three regions. Base load plants have high capital costs and high thermal efficiencies [$\sim$40% for fossil-fired plants based on higher heating value (HHV)] but relatively low operating and fuel costs. To minimize power production costs, these plants must be operated 7000 hours or more per year. Base load plants use either fossil fuels, such as coal and oil, or nuclear fuel (there are base load hydro-electric plants in some areas). Plant sizes range from 200 to 1400 MW.

The intermediate demand is met by pumped hydro-storage and fossil-fired steam plants with variable duty cycles [2]. Combined cycle units which use premium fuels are also used for intermediate loadings. Plant capacities vary between 100 and 500 MW, and they operate between 1000 and 4000 hours per year.

The peaking portion of the curve is supplied predominantly by gas turbines and smaller, old fossil-fired plants with capacities of 200 MW or less [2]. Peaking units are characterized by low capital costs but relatively high operating and fuel costs. Annual operating time is usually less than 1000 hours; while the fossil plants can use a variety of fuels, gas turbines must use expensive premium fuels such as low-sulfur fuel oil and natural gas.

In the next decade, the petroleum shortage will grossly affect the electrical power industry. There will be more nuclear base load plants [3], and fossil-fired plants will return to coal or convert to gas produced from coal [4]. Intermediate plants will also depend more heavily on coal. However, peaking units, especially if they are gas turbines, will continue using premium fuels.

This chapter considers the economics of some alternatives for peak and intermediate power generation. A study of this kind not only points out which alternatives are the most attractive, but it also picks out the major cost items of each alternative; this gives a guide to where technological improvements would be most profitable. Several papers discuss various peaking alternatives, but the report by Kyle, et al. [5] is probably the most comprehensive to date. However, they did not consider fuel cells, superconducting magnetic energy storage or possible synthetic fuels. To our knowledge, there are no comparable studies for intermediate loading.

Table 2.1 lists the alternatives considered here. The options fall into two broad categories--power generation and energy storage.

Power generating alternatives considered include gas turbines and fuel cells for peaking and intermediate operation; combined cycle units are considered for intermediate loading only. We investigate three chemical fuels--hydrogen, synthetic natural gas (SNG) and methanol. It is assumed that hydrogen can be made on site via electrolysis of water or

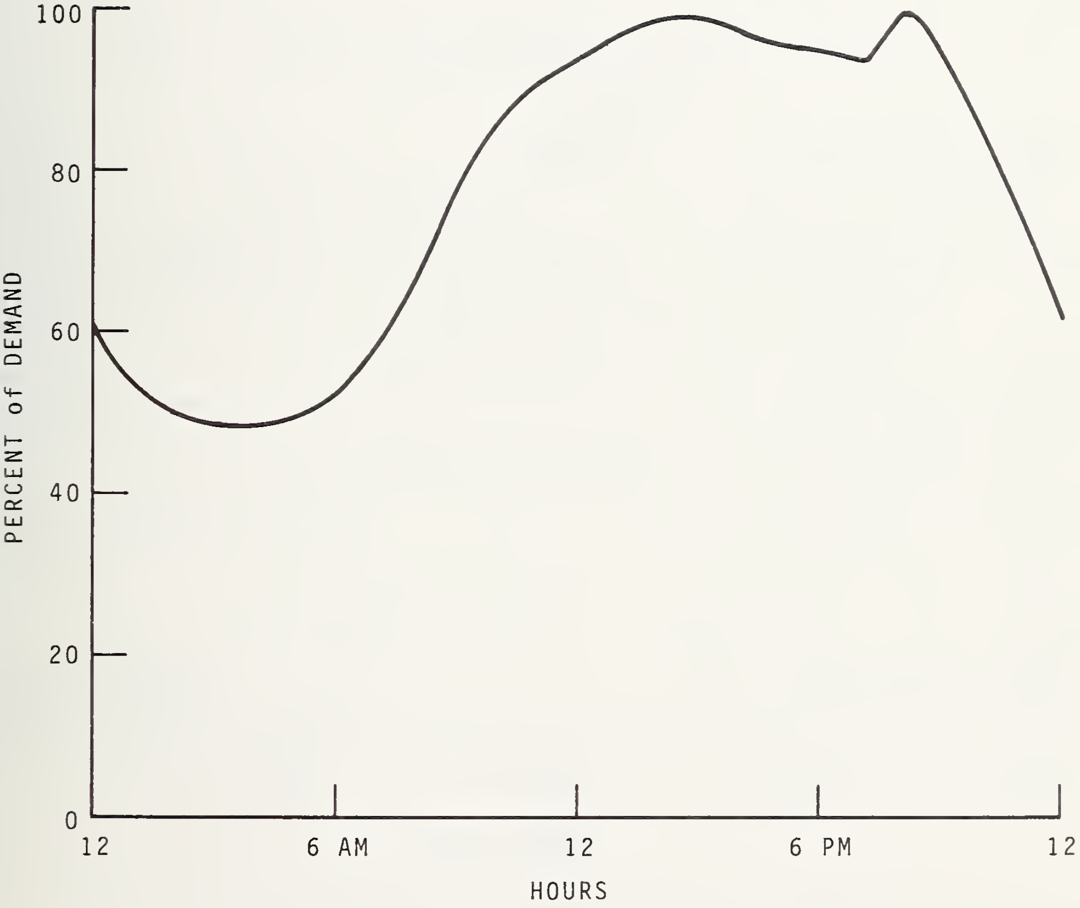

FIGURE 2.1: Typical Daily Load Curve

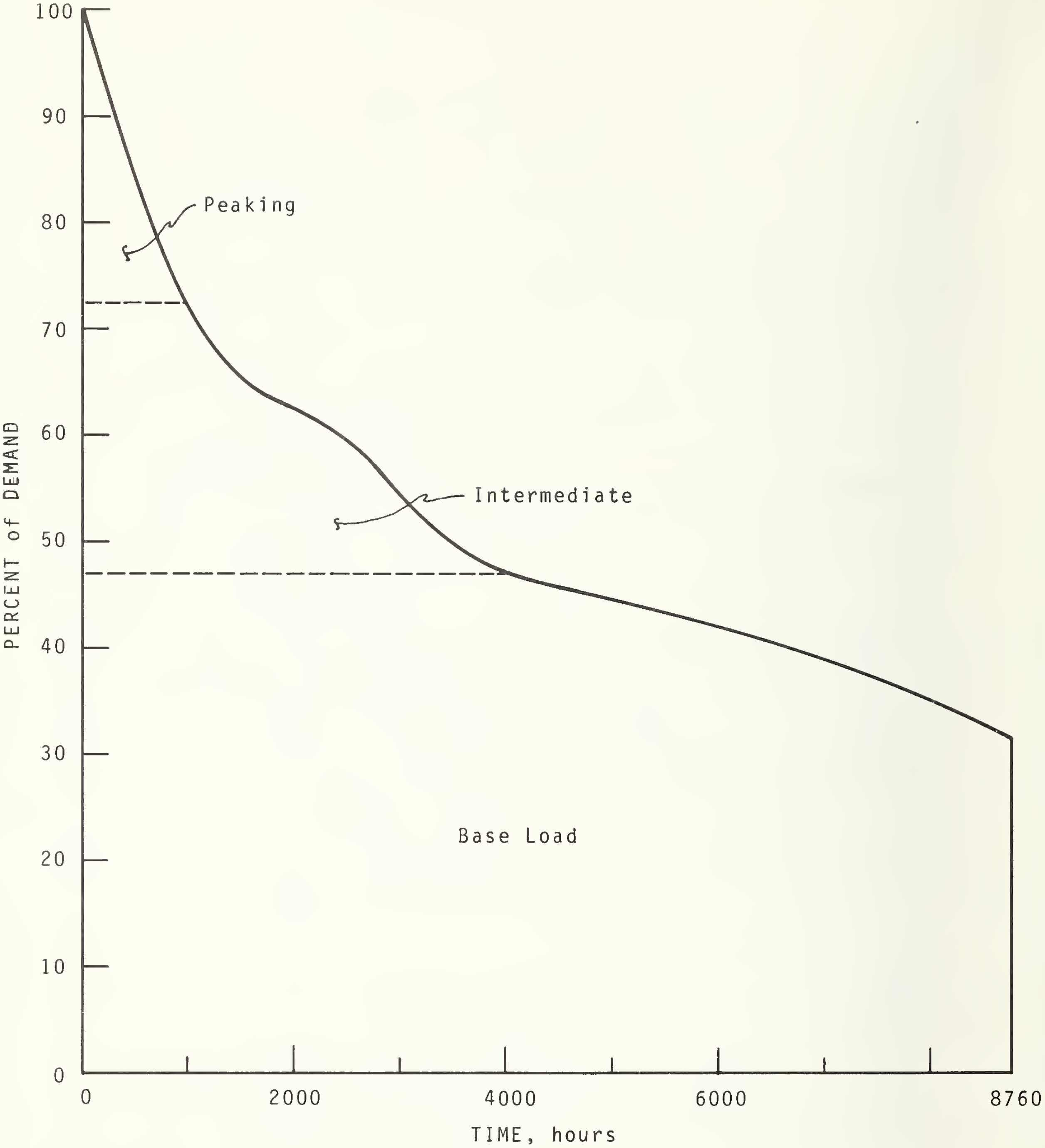

FIGURE 2.2: Typical Annual Load Duration Curve

Table 2.1 Peaking and Intermediate Power Plant Alternatives Considered in this Paper

UNIT	FUEL	ENERGY STORAGE MEDIA
Gas Turbines OR Fuel Cells OR Combined Cycle (Intermediate Duty Only)	Hydrogen: Electrolytic H_2, H_2 from Coal or Thermochemical Decomposition of H_2O	Liquid Hydrogen Compressed Gaseous Hydrogen Metal Hydride
	SNG (from Coal)	Liquid SNG Compressed Gaseous SNG
	Methanol (from Coal)	Liquid Methanol
Hydro Pumped Storage OR	Off-Peak Electricity	Potential Energy
Batteries OR		Electrochemical Energy
Superconducting Magnetic Energy Storage (SMES)		Electromagnetic Energy

be bought from the outside. In the latter case, we assume the hydrogen may be produced from coal or by thermochemical decomposition of water using nuclear reactor heat. It is assumed that both SNG and methanol are produced from coal.

The compressed gas concept uses off-peak electricity to drive a centrifugal compressor for pressurizing the storage vessel. When the unit is producing power, the gaseous fuel depressurizes through the compressor, making an electric motor a generator. Thus, some of the energy used to store the gas can be recovered; this reduces the total fuel requirement.

Energy storage systems considered include hydropumped storage, batteries and superconducting magnetic energy storage (SMES). We include pumped storage as a base case because it is the way some utilities store off-peak power today.

No attempt has been made to cover all of the possible ways of storing off-peak power. Two alternatives, briefly considered, appeared to be economically unattractive; these are capacitors and flywheels [6]. However, a recent article [7] gives some cost estimates for flywheels which make them more appealing if high strength, low cost materials become available.

One alternative studied by Korsmeyer [8] not considered here which might prove attractive is compressed air storage in combination with gas turbines. Air is compressed using off-peak power; then during turbine operation, the air is fed directly to the turbine. This would increase turbine efficiency by roughly 250% because a large portion of the energy generated by the turbine normally is used to compress the inlet air. Korsmeyer found large variations in estimated capital costs, especially mining costs. However, if the proper underground sites could be found for compressed air storage, this concept may significantly reduce peaking power costs.

Many variables affect power production costs, and we consider the influence of the following parameters:

1. unit size,
2. off-peak power costs,
3. fuel costs, and
4. equipment capital costs.

The parameters are varied over plausible ranges; in some cases, capital costs are considered from the standpoint of break-even charts.

Finally, there may be advantages to locating power units close to load centers [2,5]. Therefore, transmission credits can affect the relative attractiveness of the alternatives as shown herein.

2.2 ECONOMIC ANALYSIS

We take a simplistic approach in evaluating the economic feasibility of the various alternatives because each utility company is unique in demand requirements and in the make-up of generating components. Also, many of the cost data are too uncertain to justify a sophisticated analysis. (Appendix A gives sample calculations.)

2.2.1 Basic Assumptions

We assume that off-peak power is readily available within the distribution network for at least eight hours per day; this makes the type of base load plant immaterial in this study. It should be pointed out that the eight hours per day of off-peak power is realistic today but there may be less off-peak power in the future.

We assume that power production costs include three components:

1. fuel and/or off-peak power costs,
2. operating and maintenance costs (O & M), and
3. fixed charges on capital investment.

Fuel and power costs are simple functions of conversion efficiency. O & M costs include all maintenance, labor and operating costs, excluding fuel costs. Fixed charges cover taxes, depreciation, cost of capital, and return on investment. We calculate fixed charges using a capital recovery factor (which converts the initial capital cost to a series of equal annual payments) with a fixed charge rate of 15%/yr; this corresponds to an investor owned company [9].

To size the various components, we assume that the peaking and intermediate units must have the capacity to operate 10 and 16 hours per day, respectively. This method of estimating the capacity of an energy storage unit weighs heavily against those techniques with high capital costs. The reserve capacity is almost double the actual daily useage. In the case where a fuel is being produced and/or liquefied for storage, the flow rate is taken to be 75% of the maximum daily demand. This assumes that the remaining 25% can be made up during weekends when the demand is lower.

Finally, the cost of land is omitted and the working capital is considered negligible in terms of capital costs.

2.3 COST DATA

2.3.1 Power Generation Units

Table 2.2 lists the necessary cost data for the power generation units considered here. All costs are given in 1973 dollars. Gas turbine and combined cycle data are based on current operating technology [10]. We assume that turbine costs are independent of the fuel considered here.

Table 2.2 Cost Data for Power Generation Units

Unit	Capital Cost $/kW$_e$	O & M mills/kW-h$_e$	Plant Life Yrs.	Efficiency %
Gas Turbine	135 [10]	3.4 [10]	20	28[a] [10]
Fuel Cell	140-290[b] [12]	1.5 [11]	16,000 HRS [12]	51[a] [12]
DC-AC Inverter	45 [10]	--	20 [11]	97 [13]
Reformer	25 [12]	--	10 [11]	85 [11]
Combined Cycle	200 [10]	2.1 [10]	20	41[a] [10]

a. Efficiency is based on LHV

b. This is the cost of the fuel cell only. Ref. [12] gives costs of fuel cells plus inverters and reformer.

Fuel cell cost data are more uncertain because fuel cells have not been used by utility companies although they are supporting fuel cell development [11,12]. Since fuel cells produce DC power, DC-AC inverters are needed. The fuel cells being developed for utility applications use hydrogen and air [11]. Therefore, unless hydrogen is the fuel, a catalytic reformer is necessary to produce hydrogen from another fuel.

2.3.2 Fuel Production and Storage

Table 2.3 lists the economic data used in evaluating the economic feasibility of various fuels and storage schemes.

The primary means of producing hydrogen today is either steam reforming or partial oxidation of fossil fuels such as natural gas and naphtha [12]. As these feedstocks become more expensive and in shorter supply, coal will become the major source of hydrogen. Also, thermochemical decomposition of water [14,15] using nuclear heat may become economically attractive. The anticipated price range for hydrogen from these processes is 1.15 [16] to 1.55 $/MBTU* (HHV) [14]. The lower cost corresponds to hydrogen from coal at 4$/ton; if coal costs 6$/ton, hydrogen would sell at 1.30$/MBTU.

Electrolytic hydrogen costs depend primarily on power costs [17]; considering only power cost, electrolytic hydrogen costs 4.70$/MBTU if power costs 15 mills/kW-h. However, if off-peak power is available at less than 5 mills/kW-h electrolytic hydrogen becomes more competitive.

We use the cost data of Kincaide and Williams [17] for the electrolysis plant. In their work, they used equipment currently available which put a limit on component size. This makes the capital cost increase linearly with capacity. We assume that larger components will become available as needed because increasing sizes should not cause major technological problems. Hence, we assume that costs increase with size to the 0.8 power. The capital costs are based on a 10 ton/day plant with 33% utilization and an advanced cell design. As Kincaide and Williams point out, the optimum plant design depends upon power costs; this consideration is neglected here.

Of the three options for storing hydrogen, only cryogenic storage can be considered state-of-the-art for storing the quantities that would be required for utility applications. Liquefaction costs are from Hallett [18]; they have been increased 25% to account for inflation. The cryogenic storage cost is for an above-ground, double wall tank with evacuated perlite insulation [18]. This container has a boil-off rate of less than 0.1% per day. If higher boil-off rates are acceptable (2% per day), vessel costs can be cut by 60% [18]. The storage vessel is sized to hold three days supply of electrolytic hydrogen; storage vessels for the other fuels are sized to hold a ten day supply.

The centrifugal compressor cost for high pressure storage is estimated using Guthrie's [19] cost data. To size the compressor, we assume that it has a 60% efficiency, based on isothermal compression. In all the compressed gas storage calculations, we assume ideal gas behavior. The lower vessel cost is for depleted gas fields [20]; the higher cost is for above ground storage in 10 ft long by 10 ft diameter cylindrical pressure vessels [19]. We assume that the maximum pressure in underground storage is 1000 psia, and

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* MBTU = 10^6 BTU throughout this chapter.

Table 2, 3 Cost Data for Fuel Production and Storage

	Fuel Cost $/MBTU[a]	Capital Cost, K$	O & M K$/Yr	Plant Life Yrs	Power Consumption kWh_e/lb of Fuel
HYDROGEN					
Production					
Coal or Thermo-	1, 15 [16]	---	---	---	---
chemical decomposition	1, 55 [14]	---	---	---	---
Electrolysis	---	930·(lb/hr/833)$^{0, 8}$[b] [17]	0, 01 \$/lb H_2 [17]	25 [17]	19,0 [17]
Storage					
Liquefaction	---	39400·(lb/hr/20833)$^{0, 8}$ [18]	2380·(lb/hr/20833)$^{0, 65}$ [18]	20 [18]	4, 5 [18]
Cryogenic Storage	---	925·(lb/6x10^{6})$^{0, 90}$ [18]	2% of capital cost per year	20	---
Compressed Gas Storage	---	840·(HP/1000)$^{0, 82}$ [19]	5% of capital cost per year	20	60% of isothermal compression
High Pressure Vessel	---	0, 06 [20] - 10, 50 \$/ft^3 [19]	1% of capital cost per year	25	---
Hydride Storage	---	0, 50-1, 00 \$/lb FeTi [21] (See Text)	3 mills/kW-h_e	25	0, 88 [21]
SNG					
Production					
Coal	1, 00 [23]-1, 50	---	---	---	---
Storage					
Liquefaction	---	7980, (lb/hr/10602)$^{0, 56}$ [24]	5% of capital cost per year	25	1, 1 [20]
Cryogenic Storage	---	6, 6¢/lb [25]	2% of capital cost per year	25	---
Compressed Gas	Same as Compressed Gas Storage for H_2				
METHANOL					
Production					
Coal	1, 00 [26]-1, 50	---	---	---	---
Storage	---	53, 6 (lb/658000)$^{0, 63}$ [19]	3% of capital cost per year	25	---

a. Cost based on HHV of fuel; higher and lower heating values in BTU/lb, used in these calculations are:

	HHV	LHV
H_2	61, 030	51,570
SNG	23, 880	21,520
Methanol	9, 760	8, 680

b. Using the 0, 8 exponent involves certain assumptions, see text.

in aboveground storage, it is 2400 psia. To account for the added wall thickness of the pressure vessel, the vessel cost is increased by 15% of the base cost for each 100 psi of operating pressure [19].

Costs for hydride storage [21] are speculative because they are based on an as yet untested design. The process consists of the metal hydride unit operating at 35 atm and using hydrogen as the heat transfer fluid during charging and discharging. The estimated capital cost depends upon charging and discharging rate as well as the amount of hydrogen stored. Assuming iron titanium costs 1$/lb, it amounts to between 50 and 65% of the total hydride storage cost in peaking operation and even higher (70 to 80%) in intermediate duty. (See Appendix B for details of hydride storage costs). Hydride storage requires some power to drive compressors and pumps; this power demand is given in Table 2.3. The system also needs some thermal energy (~ 2000 BTU per pound of H_2 discharged) to heat the bed during discharging; we assume that waste heat is readily available at no charge for heating the bed.

Projected costs for making SNG from coal vary, but we anticipate that the selling price will be somewhere between 1.00 [23] and 1.50 $/MBTU (HHV).

As in the case of hydrogen, storage of SNG requires cryogenic processing. Liquefaction capital cost is based on Wenzel's [24] data for LNG peakshaving plants. The cryogenic container capital cost corresponds to an all steel, 600,000 barrel tank currently under construction [25].

We assume the capital cost per unit of container volume of compressed gas storage to be the same for both hydrogen and SNG. For equivalent energy storage at the same storage pressure, hydrogen requires larger containers and more compressor power than SNG.

The selling price of methanol from coal will probably be in the range of 1.00 [26] to 1.50 $/MBTU (HHV).

Of the three fuels considered, methanol is the simplest and cheapest to store. The storage capital cost is for cone roofed, carbon steel tanks [19].

2.3.3 Energy Storage Systems

Table 2.4 lists the cost data for the three energy storage systems considered here. The range in capital cost for pumped storage covers what a new facility might cost; costs above 250 $/kW make pumped storage unattractive [9].

Development in new types of batteries make their capital cost uncertain. The higher cost represents costs for present-day lead-acid batteries while the lower cost corresponds to the target selling price for lithium-sulfur batteries [5]. Battery life is based on lead-acid batteries [2]; future batteries might last 7 to 8 years [5] which would make them much more attractive. The total cost of a battery system must include a DC-AC inverter.

Superconducting magnetic energy storage technology is in its infancy; therefore, all cost data for SMES systems must be considered preliminary. Capital costs are based on 10.8 GWh_e of energy storage [27]. The capital cost depends upon the magnet geometry, solenoidal or toroidal, and the reinforcement, warm or cold. The solenoidal geometry is less expensive because it stores more energy per unit of superconductor than does the torus; depending upon the system, superconductor costs are between 20 to 35% of the total SMES cost. We assume O & M costs for SMES to be comparable to those of pumped storage.

Table 2.4 Cost Data for Energy Storage Systems

Unit	Capital Cost $/kW-h$_e$	O & M mills/kW-h$_e$	Plant Life Yrs	Efficiency %
Hydro Pumped Storage	200 $/kW	2 [9]	50	67 [9]
Batteries	20 - 50[a] [5]	1 [2]	5 [2]	70 [5]
Superconducting Magnetic Energy Storage	70 - 150[a] [27]	2	20	95 [13]

a. To obtain the total capital cost, the cost of a DC-AC inverter must be included (see Table 2.2).

2.4 ECONOMIC COMPARISON

2.4.1 Peaking Units

Table 2.5 lists the cost of producing peak power for the various alternatives. For ease of comparison, all three fuels are assumed to cost 1.25 $/MBTU (HHV). Tables 2.6, 2.7 and 2.8 present the component costs used to obtain Table 2.5. Using these supplemental tables and simple ratios, one can quickly estimate the effect of a component cost change on the total power cost. The effect of size is more complicated in many cases because costs are non-linear functions of capacity.

Based on Table 2.5, the least expensive ways to produce peak power are by using 1) pumped storage and 2) gas turbines using methanol as the fuel. Therefore, to make any of the other options competitive, costs must be lowered enough to reduce production costs to around 40 mills/kW-h if annual operating time is 1000 hours.

Considering the remaining energy storage systems first, we want to determine how they can be made competitive. For these discussions, we will hold plant size, operating time, and fixed charge rate constant. The remaining parameters affecting power costs for batteries and SMES are off peak power costs, capital costs, and transmission credits, i.e., credit for locating the units near load centers [2]. A simple calculation shows that to make batteries competitive, they must cost between 10 and 15 $/kW-h; this assumes reasonable off-peak power ($<$ 20 mills/kW-h) and transmission credits ($\leq$ 50 $/kW which corresponds to an 8 mills/kW-h credit for this case). Batteries could be competitive at 15 to 20 $/kW-h if battery life can be extended from five to eight years. Using the same ranges of off-peak power costs and transmission credits, SMES capital costs would have to be around 15 to 20 $/kW-h before they could produce peak power at 40 mills/kW-h.

The nearest competitor to the methanol gas turbine option is the methanol fuel cell system. Peak power costs are higher for the fuel cell systems using methanol or SNG because the fuel savings cannot offset the higher capital costs of the reformer-fuel cell-inverter system. Direct comparison of methanol-fueled gas turbine and fuel cell systems

Table 2.5 Base Case Peaking Power Costs, mills/kW-h

Capacity	100 MW
Operating Time	1000 h/yr
Cost of Off-Peak Power	5 mills/kW-h

POWER GENERATING UNITS

Fuel	Storage	Gas Turbines	Fuel Cells[a]
Hydrogen (el.)	Liquid	144.0	130.3
	Comp. Gas		
	A. G.[b]	29300	15500
	U. G.	144.1	128.3
	Hydride	153.8	135.0
Hydrogen (@ 1.25 $/MBTU)	Liquid	117.9	114.4
	Comp. Gas		
	A. G.	97400	51500
	U. G.	262.4	198.3
	Hydride	244.8	186.0
SNG (@ 1.25 $/MBTU)	Liquid	85.9	107.8
	Comp. Gas		
	A. G.	28900	19700
	U. G.	119.2	124.7
Methanol (@ 1.25 $/MBTU)	Liquid	42.8	74.2

ENERGY STORAGE SYSTEMS (1000 MW-h CAPACITY)

Pumped Storage	39.5
Batteries[c]	164.5
SMES[d]	254.1

[a] Assumes fuel cell cost is 290 $/kW.

[b] A. G. denotes above ground storage; U. G. denotes underground storage in a depleted oil or gas field.

[c] Assumes batteries cost 50 $/kW-h.

[d] Assumes SMES cost 150 $/kW-h.

Table 2.6a Component Peaking Power Costs for Hydrogen Fueled Systems Using Liquid or Hydride Storage

Component	Capital Cost, K$		Operating Costs, mills/kW-h					
			Fixed Charges[b]		O & M		Fuel/Elec.	
	GT[a]	FC	GT	FC	GT	FC	GT	FC
Power Generator	13500	33500	21.6	55.9	3.4	1.5		
Electrolysis Plant	12800	8070	19.8	12.5	2.4	1.3	22.4	12.6
Fuel Cost @ 1.25 MBTU							18.0	10.1
Cryogenic Storage Liquefier	41400	26000	66.1	41.6	2.5	1.7	5.3	3.0
Storage Tank								
3 days storage	267	183	0.4	0.3	0.0	0.0		
10 days storage	583	400	0.9	0.6	0.1	0.0		
Hydride Storage								
3 days storage	51800	30800	80.1	47.7	3.0	3.0	1.0	0.6
10 days storage	127800	74300	197.8	115.9	3.0	3.0	1.0	0.6

a. GT = gas turbine, FC = fuel cell

b. Fixed charges are calculated using capital recovery factor (fraction/yr) × Capital Cost ($)/Power (MW) / Operating time (h/yr) where the capital recovery factor is given by $FCR\,(1 + FCR)^{PL}/[(1 + FCR)^{PL} - 1]$ and FCR is the fixed charge rate and PL is plant life in years.

Table 2.6b Component Peaking Power Costs for Hydrogen Fueled Systems Using Compressed Gas Storage

Component	Capital Cost, K$		Operating Costs, mills/kW-h					
			Fixed Charges		O & M		Fuel/Elec.	
	GT	FC	GT	FC	GT	FC	GT	FC
Main Power Generator	10700[a]	25300	17.1	48.8	2.7	1.3		
Electrolysis Plant	10700	7200	16.5	11.2	1.9	1.2	17.8	11.0
Fuel Cost @ 1.25 $/MBTU							14.3	8.8
Compressor-Turbine	12000	8100	19.2	12.9	6.0	4.0	2.9	1.8
Storage								
Above Ground								
3 days storage	$13\text{x}10^{9}\$$	$7.1\text{x}10^{9}\$$	20850	11700	1350	712		
10 days storage	$45\text{x}10^{9}\$$	$23\text{x}10^{9}\$$	69500	36700	4500	2370		
Underground								
3 days storage	36500	22000	56.4	34.0	3.6	2.2		
10 days storage	121500	73200	188.0	113.3	12.2	7.3		

a. All costs, except where noted, are for underground storage.

Table 2.7a Component Peaking Power Costs for SNG & Methanol Fueled Systems Using Liquid Storage

Component	Capital Cost, K$		Operating Costs, mills/kW-h Fixed Charges		O & M		Fuel/Elec.	
	GT	FC	GT	FC	GT	FC	GT	FC
Power Generator	13500	36000	21.6	60.9	3.4	1.5		
SNG								
Fuel Cost @ 1.25 $/MBTU							16.9	11.1
Cryogenic Storage Liquefier	19700	15600	30.4	24.1	9.8	7.8	3.1	2.0
Storage Tank	340	220	0.5	0.4	0.1	0.0		
Methanol								
Fuel Cost @ 1.25 $/MBTU							17.1	11.3
Storage Tank	360	270	0.6	0.6	0.1	0.1		

Table 2.7b Component Peaking Power Costs for SNG Fueled Systems Using Compressed Gas Storage

Component	Capital Cost, K$		Operating Costs, mills/kW-h Fixed Charges		O & M		Fuel/Elec.	
	GT	FC	GT	FC	GT	FC	GT	FC
Main Power Generator	12500[a]	36000	20.0	57.9	3.2	1.4		
Fuel Cost @ 1.25 $/MBTU							15.7	10.6
Compressor-Turbine	5100	3700	8.2	5.9			1.0	0.7
Storage								
Aboveground	$13x10^9$$	$9.0x10^9$$	20600	14000	1300	904		
Underground	41600	28200	64.5	43.6	4.2	2.8		

a. All costs, except where noted, are for underground storage.

Table 2.8 Component Power Costs for Peaking Energy Storage Systems

Component	Capital Cost, K$	Operating Costs, mills/kW-h Fixed Charges	O & M	Elec.
Pumped Storage	20000	30.0	2.0	7.5
Batteries	54500	156.4	1.0	7.1
SMES	154500	246.8	2.0	5.3

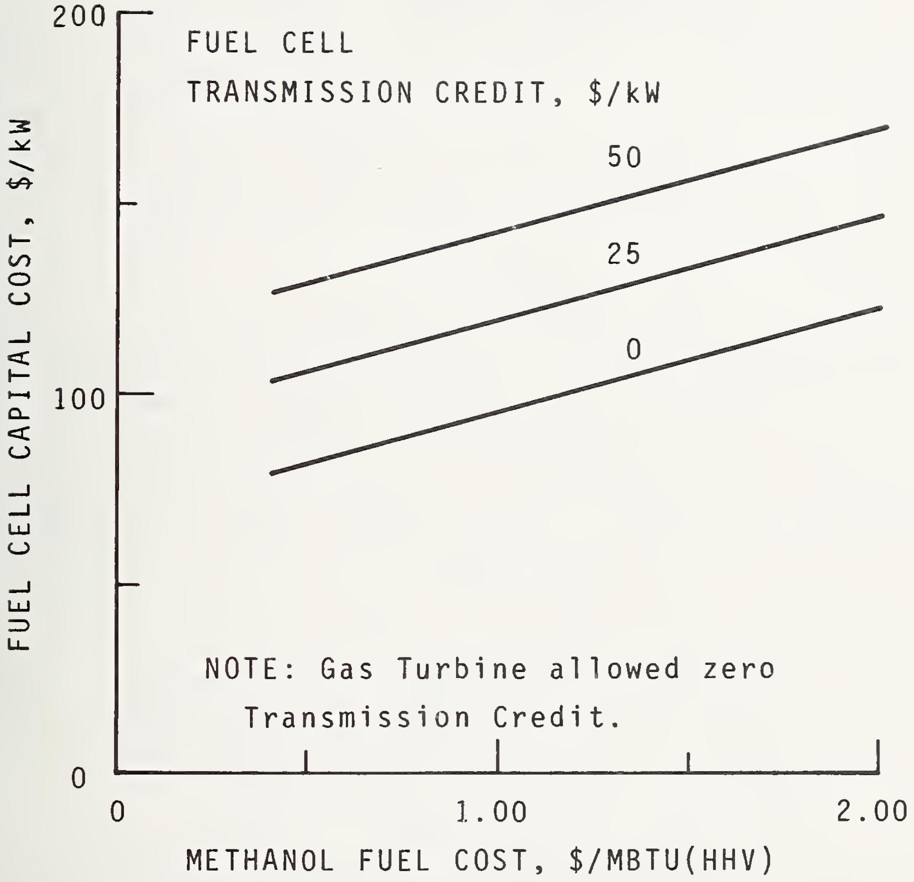

FIGURE 2.3: Fuel Cell Capital Cost Required to Make Fuel Cells Competitive With Gas Turbines.

gives break-even capital costs for fuel cells as shown on figure 2.3. The curves are based on gas turbine cost and efficiency remaining constant.

Under the stated assumptions, none of the remaining alternatives look promising for peak operations unless methanol costs over 3 $/MBTU. This is due to the high capital costs required for each alternative. Also, the equipment runs at roughly 30% of full capacity on an annual basis (assuming the units operate 8 instead of 24 hours per day). One alternative for the electrolytic hydrogen concept would be to run the electrolysis unit and liquefier at full capacity for 8 hours per day and sell the excess hydrogen. Considering the gas turbine option, a selling price of roughly 7 $/MBTU (including 1.90 $/MBTU for electricity at 5 mills/kW-h) would be required to make this option competitive with pumped storage.[1] However, the break-even selling price can be lowered by increasing plant capacity if there is sufficient off-peak power. Figure 2.4 shows the break-even selling price of gaseous hydrogen as a function of off-peak power cost and plant capacity factor. The plant capacity factor is the ratio of actual plant capacity to the base case capacity (2.2×10^4 lbs/hr for this case). The liquefier capacity remained constant in these calculations. Figure 2.5 shows break-even prices for producing liquid hydrogen.

The same type of calculations for fuel cells using electrolytic hydrogen shows that the break-even selling prices are roughly 2 $/MBTU higher than in the gas turbine case. This is caused by the high capital cost of the fuel cells and by the lower amount of excess hydrogen per kW-h output resulting from the fuel cells higher efficiency.

Considering storage techniques for hydrogen and SNG, cryogenic storage appears to be the most attractive while compressed gas storage in pressure vessels is the least attractive (at least at pressures less than 2400 psia). Hydride storage, assuming iron-titanium costs 1 $/lb, is more expensive than liquid storage if many days of fuel must be stored. If the cost of iron titanium drops to 0.50 $/lb [28], and if we store three days supply of hydrogen, hydride storage becomes competitive with liquid storage. On the other hand, no allowance has been made for recovery of the energy used in liquefaction while dehydriding energy was taken at zero cost. For example, it might be possible to use cold hydrogen gas to reduce the work required to compress the air fed to the gas turbine. As in the compressed air concept, this would increase turbine efficiency. However, it still would not make hydrogen competitive with methanol (at currently estimated costs of producing methanol from coal).

In the above discussions, we assumed plant capacity to be constant. Changing plant capacity does not alter the results; in using this simple analysis, peak power costs are independent of capacity for the energy storage systems and the methanol systems. Peak power costs for the other alternatives decrease slightly (< 10%) when plant capacity is doubled. The major effect of increased off-peak power cost is to make electrolytic hydrogen and the energy storage techniques look less attractive. To a lesser extent, it would decrease the attractiveness of liquid storage compared with compressed gas or hydride storage.

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[1] This assumes an annual operating factor of 0.9 for the electrolysis and liquefaction units.

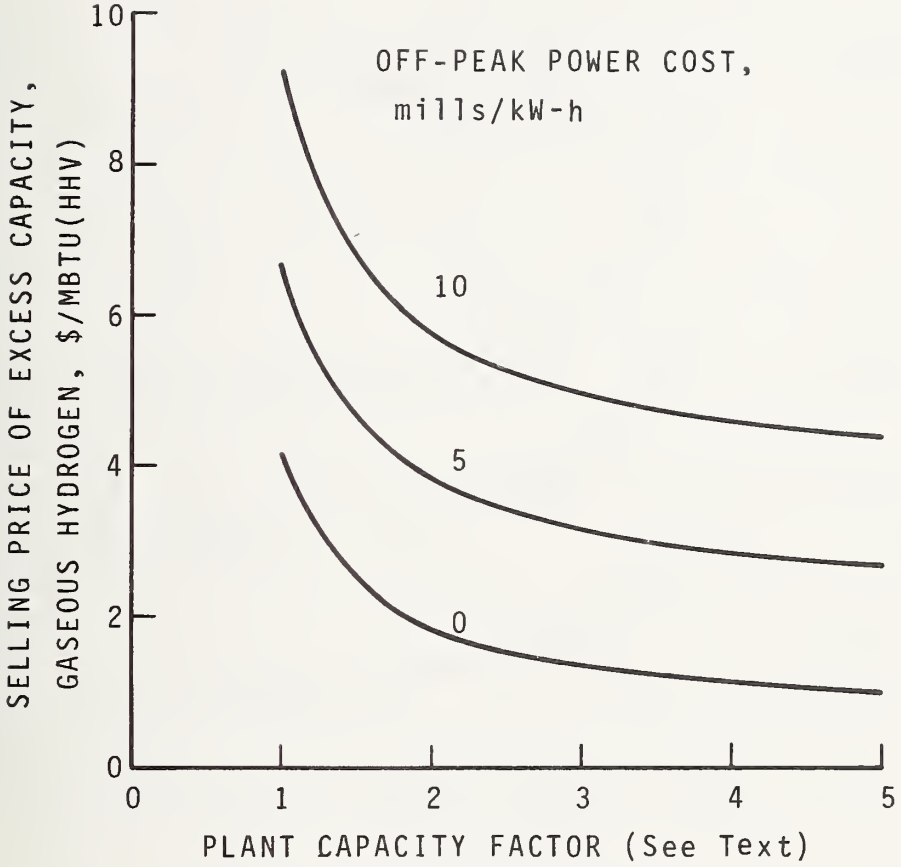

FIGURE 2.4: Selling Price of Gaseous Hydrogen Required to Make the Electrolytic Hydrogen Option Competitive With Pumped Hydro Storage.

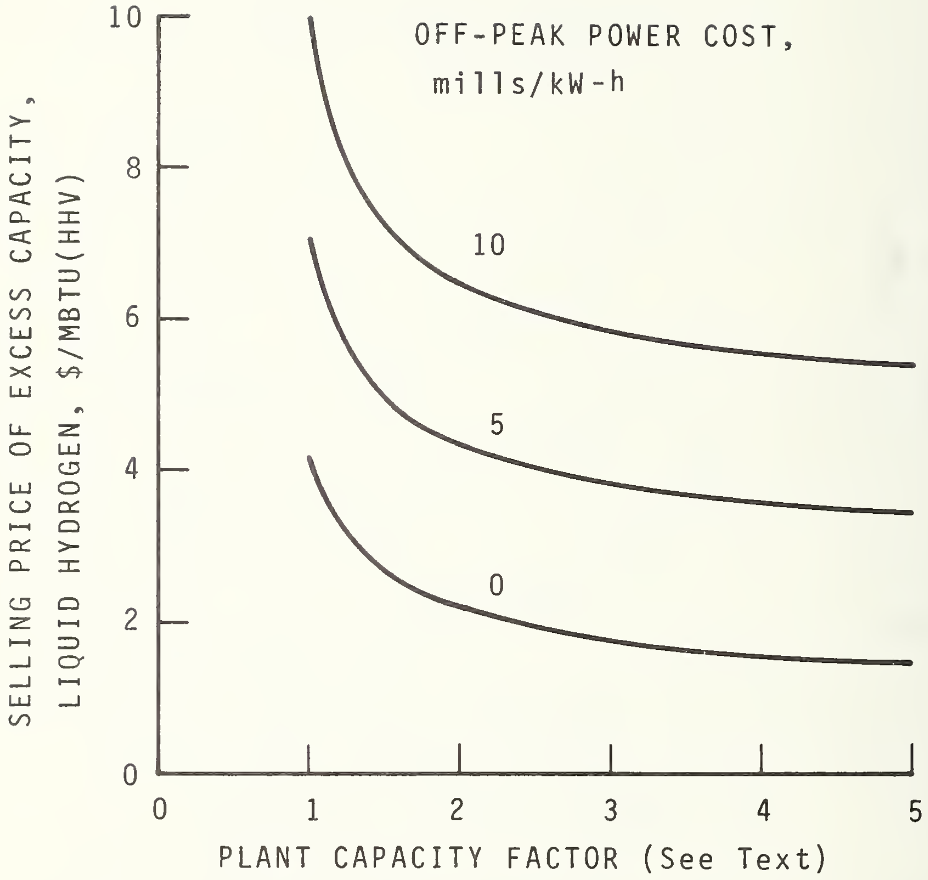

FIGURE 2.5: Selling Price of Liquid Hydrogen Required to Make the Electrolytic Hydrogen Option Competitive With Pumped Hydro Storage.

2.4.2 Intermediate Units

Table 2.9 gives intermediate power production costs for the various alternatives; component costs are listed in tables 2.10 through 2.12. For intermediate duty, power production costs must be around 17 to 20 mills/kW-h to compete with pumped storage. Operating intermediate units at 4000 instead of 1000 hours per year reduces fixed charges 75%. This is the primary reason for the intermediate power costs being lower than peaking costs.

To make batteries competitive for intermediate duty the capital cost would have to be less than 10 $/kW-h which is probably unrealistic. Because the batteries would have an eight hour charging time and 16 hour discharging time they would be more expensive than batteries used for peaking duty and would be less efficient [29].

As in the case for peaking, SMES capital cost would have to be less than 20 $/kW-h before they would become competitive for intermediate loading.

Of the power generating alternatives the methanol fueled combined cycle system is the most attractive. Compared to the gas turbine, the increased capital cost of the combined cycle unit is more than offset by the lower fuel and O & M costs. The fuel would have to be an unrealistic 30¢/MBTU before gas turbines would be competitive with combined cycle units.

Fuel cells in intermediate duty are less attractive for two reasons: 1) their high capital cost and 2) their short lifetime (4 years at 4000 hours per year). Lowering capital costs to 140 $/kW drops power costs by 13 mills/kW-h. Doubling the operating life lowers power costs by 9 mills/kW-h.

As in the case of peaking, liquid storage is the most attractive. However, in the electrolytic hydrogen options only above-ground storage is absolutely out of contention.

Compared to the peaking case, the option of selling excess electrolytic hydrogen is much less attractive. The small amount of excess hydrogen produced per kW-h is the reason. Also, from a realistic standpoint there probably will never be enough off-peak power to operate electrolysis units sized at capacity factors much greater than one.

2.5 CONCLUSIONS

2.5.1 Peaking Duty

Although the timing is unknown, at some future period the utilities will have to rely on fuels from coal to produce peak power. It is impossible to consider every possible option but based on this work, the most attractive future means of producing peak power is to use methanol made from coal and gas turbines or possibly fuel cells.

The next most promising alternative is probably lithium or sodium-sulfur batteries, providing their capital cost is around 20 $/kW-h. However, conventional lead-acid batteries are not feasible because of price and lead availability; if all of the lead mined in the U.S. during 1971 went into batteries, they would replace only 15% of the 1973 peaking capacity.

It is hard to tell which of the remaining alternatives are the most economically feasible. Before any of them can produce peaking power for 40 to 50 mills/kW-h, capital costs will have to be reduced significantly.

Table 2.9 Base Case Intermediate Power Costs, mills/kW-h

Capacity	400 MW
Operating Time	4000 h/yr
Cost of Off-Peak Power	5 mill/kW-h

Fuel	Storage	Gas Turbines	Fuel Cells	Combined cycle
Hydrogen(el)	Liquid	65.1	60.9	48.6
	Comp. Gas			
	A.G.	8900	4700	5400
	U.G.	64.9	61.1	51.1
	Hydride	67.2	63.6	51.6
Hydrogen (@ 1.25$/MBTU)	Liquid	51.1	53.7	40.0
	Comp. Gas			
	A.G.	29600	15700	18000
	U.G.	111.1	88.5	83.7
	Hydride	99.7	81.8	73.8
SNG (@ 1.25$/MBTU)	Liquid	36.2	48.9	29.7
	Comp. Gas			
	A.G.	8800	6000	6200
	U.G.	55.2	60.4	42.6
Methanol (@ 1.25$/MBTU)	Liquid	26.1	41.3	21.9

Energy Storage Systems (6400 MW-h Capacity)	
Pumped Hydro	17.0
Batteries	69.6
SMES	104.9

Table 2.10a. Component Intermediate Power Costs for Hydrogen Fueled Systems using Liquid or Hydride Storage

Component	Capital Cost, K$			Operating Costs, mills/kW-h								
				Fixed Charges			O & M			Fuel/Elec.		
	GT	FC	CC[a]	GT	FC	CC	GT	FC	CC	GT	FC	CC
Power Generator	54000	134000	80000	5.4	27.2	8.0	3.4	1.5	2.1			
Electrolysis Plant	56600	35600	41700	7.3	3.4	4.0	2.4	1.3	1.6	22.4	12.6	15.3
Fuel Cost (@ 1.25 MBTU)										18.0	10.1	12.3
Cryogenic Storage												
Liquefier	182700	114900	134600	18.2	11.5	13.4	0.5	0.4	0.4	5.3	3.0	3.6
Storage Tank												
3 days storage	890	610	700	0.1	0.1	0.1	0.0	0.0	0.0			
10 days storage	1950	1340	1520	0.2	0.1	0.1	0.0	0.0	0.0			
Hydride Storage												
3 days storage	248700	144500	173900	24.0	14.0	16.8	3.0	3.0	3.0	1.0	0.6	0.7
10 days storage	711800	407400	493000	68.8	39.4	47.7	3.0	3.0	3.0	1.0	0.6	0.7

[a] CC = combined cycle

Table 2.10b. Component Intermediate Power Costs for Hydrogen Fueled Systems using Compressed Gas Storage

Component	Capital Cost, K$			Operating Costs, mills/kW-h								
				Fixed Charges			O & M			Fuel/Elec.		
	GT	FC	CC	GT	FC	CC	GT	FC	CC	GT	FC	CC
Main Power Generator	42900	101200	67900	4.3	23.7	6.8	2.7	1.3	1.8	14.3	8.8	10.5
Electrolysis Plant	47100	31900	36600	4.6	3.1	3.5	1.9	1.2	1.4	17.8	11.0	13.0
Fuel Cost (@ 1.25 MBTU)										14.3	8.8	10.5
Compressor-Turbine	52200	35200	40500	5.2	3.5	4.0	1.6	1.1	1.3	2.9	1.8	2.1
Storage												
Above Ground												
3 days storage	$8.6\text{x}10^{10}$\$	$4.6\text{x}10^{10}$\$	$5.2\text{x}10^{10}$\$	8340	4400	5100	540	280	330			
10 days storage	$2.9\text{x}10^{11}$\$	$1.5\text{x}10^{11}$\$	$1.7\text{x}10^{11}$\$	27800	14700	16900	1800	950	1090			
Underground												
3 days storage	233000	140000	166800	22.6	13.6	16.1	1.5	0.9	1.0			
10 days storage	778000	468700	556000	75.2	45.3	53.8	4.9	2.9	3.5			

a. All costs, except where noted, are for underground storage.

Table 2.11a. Component Intermediate Power Costs for SNG & Methanol Fueled Systems Using Liquid Storage

Component	Capital Cost, K$			Operating Costs, mills/kW-h								
				Fixed Charges			O & M			Fuel/Elec.		
	GT	FC	CC	GT	FC	CC	GT	FC	CC	GT	FC	CC
Power Generator	54000	14400	80000	5.4	28.4	8.0	3.4	1.5	2.1			
SNG												
Fuel Cost (@ 1.25 $/MBTU)										16.9	11.1	11.6
Cryogenic Storage												
Liquefier	55600	44000	45000	5.4	4.3	4.3	1.7	1.4	1.4	3.1	2.0	2.1
Storage Tank	2100	1400	1500	0.2	0.1	0.2	0.0	0.0	0.0			
Methanol												
Fuel Cost (@ 1.25 $/MBTU)												
Storage Tank	1200	900	900	0.1	0.1	0.1	0.0	0.0	0.0			

Table 2.11b. Component Intermediate Power Costs for SNG Fueled Systems Using Compressed Gas Storage

Component	Capital Cost, K$			Operating Costs, mills/kW-h								
				Fixed Charges			O & M			Fuel/Elec.		
	GT	FC	CC	GT	FC	CC	GT	FC	CC	GT	FC	CC
Main Power Generator	50000	144000	75900	5.0	27.0	7.6	3.2	1.4	2.0			
Fuel Cost (@1.25 $/MBTU)										15.7	10.6	11.0
Compressor Turbine	22000	16100	16500	2.2	1.6	1.6	0.7	0.5	0.5	1.0	0.7	0.7
Storage												
Above Ground	$8.5\text{x}10^{10}$\$	$5.8\text{x}10^{10}$\$	$6.0\text{x}10^{10}$\$	8200	5600	5800	530	360	370			
Underground	$2.7\text{x}10^{8}$\$	$1.8\text{x}10^{8}$\$	$1.9\text{x}10^{8}$\$	25.8	17.4	18.0	1.7	1.1	1.2			

Table 2.12 Component Power Costs for Intermediate Energy Storage Systems

Component	Capital Cost, K$	Operating Costs, mills/kW-h		
		Fixed Charges	O & M	Elec.
Pumped Storage	80000	7.5	2.0	7.5
Batteries	338000	61.5	1.0	7.1
SMES	978000	97.6	2.0	5.3

2.5.2 Intermediate Duty

Of the options considered here for intermediate duty the methanol fueled combined cycle option is the most attractive. However, these alternatives will have to compete with coal fired power plants using stack gas clean-up and/or power plants fired by low BTU gas. The low BTU gas concept is attractive because it can use combined cycle systems whereas coal fired plants cannot.

2.5.3 Base Load Duty

Base load plants were omitted in this study because we were interested in energy storage concepts. However, at least two studies have considered hydrogen as a fuel for base load plants. Byron [30] considered hydrogen-air fuel cells as one of the possible advanced power generation systems. He concludes that this option could be competitive if pipeline hydrogen from coal costs around 1.25 $/MBTU and if fuel cell efficiency increases to roughly 70%.

Seikel et al. [31] evaluate hydrogen-oxygen combustion powered steam-MHD power plants. Their source of hydrogen is coal and they use an on-site liquid air plant to obtain oxygen. Based on their results, the hydrogen-oxygen MHD cycle is a competitive means of producing base load power. Also, since the system is essentially pollution free, the plant could be located close to load centers.

2.6 HYDROGEN IN POWER GENERATION

Based on current and anticipated technology, the near-term use of hydrogen as a utility fuel appears unlikely. High capital cost for hydrogen systems is the major drawback. Even so, it is important to keep an open mind toward all the options; future technological advances and/or governmental regulations could alter the economic assessments and results presented here. For example, advances in thermochemical decomposition of water could keep hydrogen prices down compared to fuels from coal. Also advances in liquefaction technology and schemes to recover liquefaction energy could make it more competitive. (Chapter 1 discusses these topics). If antipollution factors become more important then hydrogen or hydrogen-oxygen systems will be more attractive.

The results that are presented here are based on current and near-term technology. As current technology improves or advanced technology develops these results will have to be reevaluated. The format used here allows rapid evaluation of the effect of technological progress on power production costs.

2.7 ACKNOWLEDGMENT

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2.9 APPENDIX A

Sample Calculation of Power Production Cost

The most difficult part of any economic analysis is obtaining reasonable cost figures; the calculations from that point on are usually straight forward. That is the case here; however, a sample calculation is in order because it clearly shows how we arrived at power production costs. For this example we choose a fuel cell using electrolytic hydrogen to produce 100 MW of peaking power and then make detailed calculations for the power generator and electrolysis plant. The peaking unit will operate 1000 h/year and the fuel cell life is taken as 16000 h, inverter life is 20 years and electrolyzer life is 25 years.

2.9.1 Power Generating Unit

Capital Cost: From Table 2.2 we obtain a capital cost of 290 \$/kW for the fuel cell and 45 \$/kW for the DC-AC inverter (no reformer is needed since we are using hydrogen as the fuel). The total capital cost of the unit is $\$335 \times 10^5$.

Fixed Charges: The fixed charge rate must be figured separately for the fuel cell and inverter because they have different plant lives. For the fuel cell we first need the capital recovery factor (CRF) which is

$$\mathrm{CRF} = \frac{\mathrm{FCR}\ (1 + \mathrm{FCR})^n}{(1 + \mathrm{FCR})^n - 1} \qquad \text{(A-1)}$$

where FCR is the fixed charge rate (15%/yr) and n is the plant life (16 years in this example). For the fuel cells CRF is 16.8%/yr and for the inverter it is 16.0%/yr. Multiplying the capital cost times CRF gives the size of the annual payment required to regain the initial capital investment after n years if the interest rate is the fixed charge rate. Fixed charges in terms of power production are

$$\mathrm{FC(mills/kW\text{-}h)} = \frac{\mathrm{TCC(\$)} \times \mathrm{CRF(yr^{-1})}}{\mathrm{P(MW)} \times \mathrm{T(h/yr)}} \qquad \text{(A-2)}$$

where TCC is the total capital cost, P is the power and T is the annual operating time. Then for the fuel cell and inverter

$$\mathrm{FC} = \frac{2.9 \times 10^7 \times 0.168 + 4.5 \times 10^6 \times 0.160}{100 \times 1000} = 55.9\ \mathrm{mills/kW\text{-}h.}$$

Operating and Maintenance Cost: O&M costs for the fuel cell are estimated to be 3.4 mills/kW-h. O&M for the inverter is assumed to be zero in this study.

Fuel and Power Cost: Since we are using electrolytic hydrogen there is no power or fuel charge here; however, we still need to calculate how much hydrogen is required for the plant. To produce one kW-h_e using a fuel cell with 50% efficiency we need

$$\frac{\mathrm{lb\ H_2}}{51{,}570\ \mathrm{BTU(LHV)}} \times \frac{3413\ \mathrm{BTU}}{\mathrm{kW\text{-}h}} \times \frac{1}{0.50} = 0.132\ \mathrm{lb\ H_2/kW\text{-}h.}$$

The flowrate is 0.132×10^5 lb/hr and the maximum consumption in one day is 1.32×10^5 lbs.

2.9.2 Electrolysis Unit

Capital Cost: From the above calculation we know the hydrogen consumption per day (1.32×10^5 lb). To size the plant we divide this number by eight (we assume an eight hour operating day) and multiply the result by 0.75 since the plant is sized at 75% of the maximum daily load. Thus we obtain 12375 lb/hr for plant capacity. From Table 2.3 the capital cost is $\$930 \times 10^3 \, (12375/833)^{0.8}$ or $\$8.07 \times 10^6$.

Fixed Charges: Using 25 years as the plant life for the electrolysis unit we obtain a capital recovery factor of 15.5%/yr. From Eq (A-2) we obtain fixed charges of 12.5 mills/kW-h.

Operating and Maintenance Cost: In this case O&M costs are taken as 0.01 $/lb of hydrogen produced. Since the fuel cell requires 0.132 lb H_2/kW-h, O&M costs are 1.3 mills/kW-h.

Fuel and Power Costs: No fuel is needed but a large amount of electrical energy is needed (19 kW-h/lb). Assuming power costs 5 mills/kW-h the cost of power per unit of energy output is 5 mills/kW-h x 19 kW-h/lb H_2 x 0.123 lb H_2/kW-h = 12.55 mills/kW-h. All of the other calculations can be made in a manner similar to the ones presented here.

2.10 APPENDIX B:

Hydride Storage Cost Data

As mentioned in the text, hydride storage is still in the developmental stage; therefore any cost estimates must be considered preliminary. Complete cost details for hydride storage were omitted in the text because the cost is a function of the charging and discharging flow rates, and the total amount of hydrogen stored. All numbers are based on cost estimates by R. J. Isler [21].

2.10.1 Cost Components Dependent Upon Amount of H_2 Stored

Hydride (FeTi): $38.75 \dfrac{\text{lb}_{\text{FeTi}}}{\text{lb } H_2} \times \dfrac{1\ \$}{\text{lb}_{\text{FeTi}}} = 38.75 \dfrac{\$}{\text{lb } H_2 \text{ stored}}$

Hydride Storage Vessel: (includes filters) $154.7 \, (\text{lb } H_2 \text{ stored})^{0.8} = \$$

Dissociation Energy: 1960 BTU/lb H_2 (taken at no charge in these calculations).

2.10.2 Cost Components Dependent Upon Discharge Flow Rate

Heat Exchanger: $1892 \, (\text{lb } H_2/\text{hr})^{0.65} = \$$

Recirculation Compressor: $993 \, (\text{lb } H_2/\text{hr})^{0.8} = \$$

2.10.3 Cost Components Dependent Upon Charging Flow Rate

Charging Compressor: $2233 \, (\text{lb } H_2/\text{hr})^{0.8} = \$$

Heat exchanger: $301 \, (\text{lb } H_2/\text{hr})^{0.65} = \$$.

CHAPTER 3

H_2 FUELED AUTOMOBILES

R. O. Voth

3.0 SUMMARY

There are no insurmountable technical problems that must be solved before hydrogen can be adopted as a synthetic fuel for use in transportation. Internal combustion engines, external combustion engines, and fuel cells either work best with hydrogen or are easily adapted to hydrogen fuel. The use of hydrogen in conventional or advanced engines tends to increase their efficiency while reducing polluting emissions. The cost of hydrogen and the cost of hydrogen storage onboard a vehicle are major economic barriers to the adoption of hydrogen fuel. Compressed gas storage is bulky and heavy and requires additional energy to compress the gas. The onboard storage of cryogenic liquid involves an expensive storage dewar, additional expense to liquefy gaseous hydrogen, and the venting of boiloff gases which, besides being a safety problem, adds to the operating cost of the vehicle. The onboard storage of hydrogen in a metal hydride is an economic unknown. The heavy weight of the hydride increases the energy consumed by a vehicle, thereby increasing the cost of operation, and the hydride requires a heat of dissociation which may or may not be available as reject heat from the onboard engine or fuel cell.

The following is a review of work being conducted on transportation power sources using hydrogen fuel and on methods of storing hydrogen on a vehicle. An economic comparison of the cost of operating a small intensively driven car for intercity use with various fuels, engines, and fuel storage methods is also presented.

3.1 INTRODUCTION

Currently, transportation consumes approximately 25 percent of the energy consumed in the U.S. Projections [1] indicate that transportation will continue to consume this portion although the portion used by the automobiles will decrease from the current 85 percent of the transportation total to 65 percent by the year 1990. The transportation industry is a major user of petroleum. It is now consuming approximately 55 percent of the oil used in the United States, and projections indicate this fraction will increase to 60 percent by the mid-eighties. The need to import petroleum products to meet this demand has caused many authorities to suggest the adoption of a synthetic fuel to be used for transportation. With a suitable primary energy source, hydrogen could serve this purpose.

The choice of synthetic fuel to be used by transportation is determined not only by economics but also by social and therefore political pressures to reduce polluting emissions. Because of the emission problem a purely objective decision on the type of synthetic fuel to be adopted by transportation is not possible.

The choice of hydrogen as a synthetic fuel is based on reduced emissions, adaptability of hydrogen fuel to current transportation power sources, and the ease of storing and distributing energy in the form of hydrogen; also, hydrogen offers a short-cycle ecological fuel, i.e., water-to-hydrogen-to-water. This chapter is primarily concerned with the adaptability of hydrogen as an energy source for transportation.

The following sections review the research work currently being conducted on heat engines and fuel cells. Also, a simplified analysis of the economics involved in the use of hydrogen fuel in an intercity automobile is presented.

3.2 SAFETY OF HYDROGEN FUEL

Before hydrogen can be adopted as a synthetic fuel for general use in vehicles, its ignition and flammability characteristics should be considered. These properties are used to design a hydrogen engine and to determine safety precautions involved in handling the fuel. Although liquid hydrogen involves cold temperatures (20.27 K) resulting in the freezing of human tissue exposed to the liquid, the properties of hydrogen of most concern are the gaseous ignition temperature and ignition energy, detonability limits, and flammability limits. Table 3.1 gives a comparison of the ignition and flammability characteristics of hydrogen with other fuels in air. Hydrogen in air displays a relatively high ignition temperature and a wide flammability range.

Table 3.1 Ignition and Flammability Properties

	Auto Ignition Temperature [2]	Limits of Flammability [2] Volume Percent of fuel in air		Stoichiometric Mixture [3] Volume Percent of fuel in air
	°C	Lower	Upper	
Hydrogen	585[4]	4.0	75	29.6
Gasoline	440	1.3	7.1	~1.3
Diesel fuel	225			~1.2
Methane	540	5.0	15.0	9.5
Methanol	385	6.7	36	12.3

Table 3.1 indicates that the flammability range for hydrogen is much wider than for gasoline but gasoline has a lower flammable limit. Thus, gasoline will burn at lower fuel-in-air concentrations but as the concentration increases hydrogen remains an explosive threat and gasoline becomes non-flammable. Based on the lower flammable limit hydrogen appears safer than gasoline. Based on the flammable range hydrogen appears more hazardous than gasoline. The time required to reach the lower flammable limit favors gasoline because hydrogen is much more volatile and/or stored at higher pressure; however, flammable hydrogen concentrations will also dissipate much more rapidly than gasoline-in-air as a result of buoyant forces. The wide flammability range makes even small leaks from a hydrogen fuel system into an enclosed area a safety problem. Assuming a 6.1 m (20 ft) x 6.1 m x 2.4 m (8 ft) garage enclosure, a leakage rate of .15 m^3/h or .00251 m^3/min would provide sufficient hydrogen in 24 hours to yield a flammable mixture in the garage. The garage would need to be free of leaks itself in order to contain the hydrogen for this period of time because of the rapid dispersion characteristics of hydrogen (high diffusion and buoyant leakage flows). Nonetheless, a hydrogen fuel system free of leaks is mandatory.

A more serious circumstance for a contained leak exists if the leak is of sufficient size to provide a detonable mixture within the enclosure. The detonability limits for hydrogen are 18-59 percent hydrogen by volume in air [5]. In the above enclosure a contained leakage rate of 0.679 m^3/h or 0.011 m^3/min would provide sufficient hydrogen to reach the lower detonability limit in 24 hours. Experiments with gaseous hydrogen-air mixtures have shown that a detonable mixture ignited by a strong detonation source or ignited while it is enclosed on three sides, may detonate resulting in severe explosive damage. Again, the high dispersion rate of hydrogen would tend to reduce the possibility of reaching a mixture of these proportions in the 24-hour period.

The high auto-ignition temperature of hydrogen-air mixtures would indicate that the mixture is difficult to ignite; however, the energy required to ignite hydrogen-air mixtures is an order of magnitude lower than that required by gasoline-air mixtures. A hydrogen fire can be initiated by an electrostatic discharge from a person even though the discharge is of such low intensity that the person would not feel the discharge.

The radiation from a hydrogen-air fire is 1 to 10 percent of that from a comparable hydrocarbon fire because of the low emissivity of the hydrogen flame. Besides the low emissivity, the radiation from a hydrogen fire is at a wavelength that is readily absorbed by the atmosphere; the radiation intensity therefore decreases rapidly with distance from a hydrogen fire. Also, smoke inhalation is a serious health hazard in hydrocarbon fires and non-existent in hydrogen fires.

Based on the flammability and explosive characteristics of hydrogen, any hydrogen system must be designed with great care if it is to be placed into the hands of the general public. Leakages of hydrogen must be virtually eliminated, and uncontrolled venting cannot be tolerated.

3.3 POWER GENERATING DEVICES FOR USE WITH HYDROGEN

In order to use hydrogen as a fuel for transportation, heat engines must be adapted to the fuel characteristics. The wide flammability limit, which was a detriment to safe handling, helps when hydrogen fuel is used in an internal (I.C.) or external combustion engine. Because of the wide flammability range of hydrogen, it is possible to run the hydrogen fueled I.C. engines fuel lean. Running the engine with excess air lowers the combustion temperature which in turn reduces the NO_x emission from the engine. Although the high auto ignition temperature of hydrogen-air mixtures would again indicate the mixture would be hard to ignite, the opposite is true. Fluffy deposits of carbon or other particles in the combustion chamber causes I.C. engines to backfire under certain conditions, probably because the hot deposits ignite the fuel mixture before the intake valve closes. The low energy required to ignite the hydrogen air mixture is the cause of the backfiring phenomenon. The tendency to backfire can be reduced by cleaning the combustion chamber, by using special cool-running exhaust valves and spark plugs, by running with fuel-lean mixtures, and carefully routing ignition wiring [32] or using a special distributor cap to ground spark plugs except when they are fired.

Since hydrogen fuel burns thoroughly, and since no hydrocarbons are involved in the combustion process, the exhaust constituents are water from the combustion process, oxides of nitrogen, and other atmospheric components. Griffith [36] has pointed out that exhaust emissions from hydrogen-fueled engines may contain low concentrations of hydrogen peroxide. Also, low concentrations of ammonia and hydrazine may possibly be produced in such engines. Although hydrogen-fueled engine exhausts have not been carefully analyzed for these contaminants, they are not considered [34] a significant threat to the use of hydrogen fuel.

3.3.1 The Internal Combustion Engine Using Hydrogen Fuel

A comprehensive history of the use of hydrogen to fuel internal combustion engines is presented by Billings and Lynch [6] and Weil [7]. Hydrogen, mainly from town gas rich in hydrogen, was used with I.C. engines as early as the 19th century. Even as early as 1923, the ability of hydrogen to run in an I.C. engine with a fuel lean mixture was recognized. High indicated thermal efficiencies were achieved with the fuel-lean mixtures. The engines used with the Zeppelin airships were converted to run on a partial charge of hydrogen in order to conserve the primary hydrocarbon fuel carried on board. Both spark ignition and compression ignition engines were partially fueled with hydrogen. The Great Britain Royal Airship Works also experimented with hydrogen fuel in their airships with equal success.

Because hydrogen is such an ideal fuel, two engines [8] are currently being developed that use a reaction chamber to convert a hydrocarbon fuel, water, and air to a mixture of hydrogen, carbon monoxide, and carbon dioxide. In one of the engines this gaseous mixture is inducted into the normal air and hydrocarbon mixture to improve combustion. The other engine runs on the mixture of reformed gases and air only. Both systems require water that is used in the reforming process, but the engines have demonstrated reduced emissions and slightly increased thermal efficiencies. The water can be obtained from onboard storage or condensed from the engine exhaust.

Different investigators have taken different approaches to the pure hydrogen-fueled internal combustion engine. The simplest conversion is to induct hydrogen into the intake air. By maintaining a fuel-lean mixture and varying the charge with an intake throttle valve, the thermal efficiency of the engine can be maintained at a high value while maintaining low NO_x emissions and a low probability of backfiring. The major problem with this approach is that the engine power per unit of displacement is reduced nearly 50 percent compared with a similar engine using gasoline. The compression ratio of the engine can be increased somewhat while maintaining the fuel-lean mixture to recover some of the power capability of the engine and to further increase its efficiency.

Another approach to the hydrogen I.C. engine is to inject water with the hydrogen to lower the combustion temperatures. With this approach the NO_x emissions can be maintained at a low value at richer fuel-air mixtures. With water injection, the output of the engine approaches 75 percent of a similar displacement gasoline engine without significant NO_x emissions or backfiring [9]. Exhaust recirculation is another approach to allow a richer fuel-air mixture without backfiring while maintaining low NO_x emissions. Again, the power per unit displacement is reduced below that of a gasoline engine by approximately 40 percent.

A combination of these methods would use lean fuel mixtures at part load on the engine to increase the efficiency of the engine and reduce the NO_x emission, while at peak loads the fuel-to-air mixture could be made richer with the addition of water or the use of exhaust gas recirculation in order to maximize output with low NO_x emissions.

Two other noteworthy experimental engines used a more direct method of injecting the hydrogen into the engine. The first used a modified single cylinder, small gasoline engine with the hydrogen injected directly into the combustion chamber [10]. The modifications of the engine included a mechanism to control a fuel injector valve and a boiling water cooling system to replace the normal air cooling. The fuel injection start time, the spark time, and the injection stop time could be adjusted in the experimental engine. Fuel flow to the engine could also be adjusted by varying the fuel supply pressure. Fuel supply pressure was as high as 66 atmospheres in some high-power output tests. Although fuel consumption of the engine was slightly higher than expected because of the additional valve-activating mechanism for the fuel injector and an incorrectly shaped combustion chamber, the NO_x emissions were a small fraction of the emissions obtained from gasoline tests.

Another engine tested with hydrogen fuel [11, 12] used a specially designed intake valve. When the intake valve opened, unthrottled air was inducted along with hydrogen from a special port installed in the intake valve seat. The engine power was changed by changing the amount of fuel inducted by varying the fuel supply pressure. At low power output, the combustible mixture was very fuel lean, and as power increased, the fuel mixture approached more nearly the stoichiometric mixture. Since the intake air is not throttled, the pumping losses are decreased and the part load efficiency of the hydrogen fueled I.C. engine behaves more like the higher part load efficiency of a Diesel cycle engine. The NO_x emissions from this engine were low at part loads, but at full load, exhaust gas recirculation or water injection would be necessary to reduce the NO_x emissions to an acceptable level.

A Diesel cycle engine to use hydrogen fuel has been proposed [13]. The Diesel cycle is distinguished by a constant pressure combustion process because the fuel is injected and burned during part of the power stroke of the piston. Ignition in a Diesel cycle is usually obtained by having high temperature air, obtained by compression, in the combustion chamber. Because of the high ignition temperature of hydrogen, a compression ratio of at least 55:1 is required for an ideal specific heat ratio for air of 1.4 to obtain the hydrogen auto ignition temperature. Since heat is transferred to the cylinder walls during compression, a more realistic compression ratio of 83:1 ($n = 1.35$) is required in order to obtain the desired compression ignition. Since these high compression ratios are not possible, the hydrogen Diesel cycle engine would require an auxiliary ignition source. An electric glow plug or other hot spot in the cylinder could provide the required ignition source. However, unless this ignition source were located to ignite the very first portion of the fuel injected, the cycle on a pressure-volume diagram would probably more closely resemble an Otto-cycle than a Diesel cycle.

3.3.2 External Combustion Engines

For external combustion engines such as the Stirling cycle engine, Rankine cycle engine, or gas turbine engine the only design problem different for hydrogen (from other fuels) is the design of the combustor. Because hydrogen is easy to burn, the burner design is relatively simple. Designing for minimum NO_x, a more difficult design, requires a uniform flame temperature without local hot spots [14]. Because hydrogen will burn readily with an excess of air, the NO_x emissions from a combustor using hydrogen should be less than can be obtained from a fossil fueled combustor. Since the combustion process is more readily controlled in a combustor than in an I.C. engine, considerable development of efficient burners is currently proceeding for the hydrocarbon fuels. Using hydrocarbon fuels, the NO_x emissions can be reduced to an equivalent of 0.18 g/mile with a Stirling cycle engine compared with the 1975/1976 requirements of 0.4 g/mile [15]. Using a hydrogen fuel combustor, the NO_x emissions will be at least as low as can be obtained with fossil fuels.

Gas turbines have been converted to hydrogen fuel. The first gas turbine to use hydrogen gas was a fossil fueled engine converted to hydrogen in 1956 [16]. The only major change required on the existing engine was an external heat exchanger to convert liquid hydrogen (the fuel used) to a gas before it was injected into the burners. Because of the excellent mixing and combustion properties of hydrogen, acceptable combustion efficiencies could be obtained with hydrogen in about one-quarter the combustor length required for hydrocarbon fuels. The turbine could operate with a combustion chamber temperature of less than 200°F, and under this condition the turbine turned so slowly that the first stage compressor blades could be counted. After the successful conversion, a gas turbine designed specifically for hydrogen was also built and tested. No problems with this turbine are reported although actual data are scarce because the original work was classified. Three successful flights of a twin-engine light bomber with one engine converted to hydrogen above 50,000 feet were accomplished by the NACA in 1957 [17]. No problems were encountered in the test flights.

The experimental results from both internal combustion and external combustion engines indicate that no significant technological breakthroughs are required. Although unburned hydrocarbons and carbon monoxides are not a problem with hydrogen fuel, NO_x is still a partial problem in air-breathing engines, but can be minimized by design modification. Combustion of hydrogen with oxygen eliminates the NO_x problem.

3.3.3 Fuel Cells

Fuel cells were conceived by Sir William Grove in 1839, but because the dynamo was coming into being around 1890, no serious battery development was accomplished until about 1944. At that time fuel cells came under active development because of the emerging space program and because fuel cells could theoretically yield a high conversion efficiency. Current development involves fuel cells for the power utilities, fuel cells for long life remote applications, fuel cell electrode development using less expensive materials, and fuel cells for space applications. Although significant amounts of development money have been spent on fuel cells, fuel cells are not generally available except as custom designs, and they are not generally used except in systems where the use of any other power source is impossible.

The basic fuel required for current fuel cells is hydrogen. In some of the applications being considered for fuel cells, hydrogen is provided by reforming heavier hydrocarbons. A specific example of this type of application is the current development of a fuel cell to be used as a peak power source for the electrical utilities [18].

The conversion efficiency of the fuel cell is one of its major advantages. At full capacity the conversion efficiency of a hydrogen-air fuel cell is slightly higher than that of a fully loaded heat engine. As the load decreases, the efficiency of the fuel cell increases while the efficiency of heat engines decreases. As a result the fuel cell will display significantly better efficiencies than heat engines in applications where the mean load is less than the full capacity of the power source. An economic analysis [19] of the fuel cell versus other heat engines is available with a definition of the economic size of the fuel cell versus capital costs and fuel costs to achieve the lowest overall operating cost.

Data concerning emissions from a fuel cell using a reformed hydrocarbon fuel are presented by Lueckel [18]. Table 3.2 is a sample of these data converted to g/mile assuming an average power consumption for a vehicle of 1 kW-h/mile [20]. Many of the emissions result from the dirty gas that was used as the fuel. If pure hydrogen were used as the fuel, the only emission would probably be the low NO_x pollutant.

The major disadvantages of the fuel cell are its high cost, heavy weight, and large volume. The high costs are a result of the one-of-a-kind production method of custom designs. Also current hydrogen-air fuel cells employ a platinum catalyst costing approximately $50/kW [21].

Table 3.2 Probable emission characteristics of a fuel cell powered vehicle using a reformed hydrocarbon fuel

	1976 Clean Air Act Requirements	Vehicle Emissions
Unburned Hydrocarbons	0.41 g/mile	0.104 g/mile
Carbon Monoxide	3.4 g/mile	not given
Nitrogen Oxides	0.4 g/mile	0.109 g/mile

Current costs of fuel cells vary from a high of $40,000/kW for the high reliability fuel cells for space use [22] to a low projected cost for the electric utilities fuel cell of $130/kW [18]. Cost projections based on the elimination of the platinum catalyst and the use of mass production techniques are as low as $18 - $30/kW [19]. All the above costs are for the full capacity output of the units and do not reflect the purchase of a higher capacity fuel cell for increased efficiency in a particular application.

Table 3.3 shows the weights and volumes of fuel cells compared with other more common power sources. The lead-acid battery has a high energy density; however, it lacks sufficient power density to be considered in most vehicle applications. The fuel cell has a relatively low energy density; however, it will supply power for as long as it receives fuel. The projected data for the dissolved methanol fuel cell indicates that it will have limited application in the transportation industry because of its large size and weight. Methanol or other petroleum fuel can be reformed to supply a hydrogen rich fuel for a hydrogen-air fuel cell; however, when the weight of the reformer is added to the weight of the fuel cell, the total weight approaches 25 - 40 kg/kW [19]. This high weight eliminates the use of a fuel cell with fuels other than hydrogen for small cars.

Although fuel cells are not fully developed, the high thermal efficiencies possible from fuel cells makes their use in transportation more desirable as fuel costs rise. Since hydrogen is a natural fuel for the fuel cell, the general availability of hydrogen would also increase the desirability of using the fuel cell in transportation.

Table 3.3 Range of fuel cell weights and volumes compared to other power sources

		Wt/Max. Power kg/kW	Vol./Max. Power m^3/kW
Low temperature hydrogen-air fuel cell with liquid electrolyte	from [21]	27.2	0.02 - 0.03
Projections	from [19]	15 - 20	
electrovan Oxygen-hydrogen	from [23]	9.6	
Low temperature hydrogen-air fuel cell with solid electrolyte	from [19]	10 - 15	0.005 - 0.015
Low temperature dissolved methanol fuel cell	from [19]	30 - 45	.06 - .09
I.C. Engine	from [3]	3 - 4.3	0.003
Lead-Acid Battery	from [24]	10 - 100	0.3

3.4 FUEL STORAGE ABOARD A VEHICLE

Although considerable research is being conducted on power sources for use in a vehicle, the major work being done on hydrogen fuel storage systems applicable to a vehicle is in the area of metallic hydride storage. Compressed gas storage and cryogenic liquid hydrogen storage are in widespread use and little research work is necessary in these areas except to match the storage container to the chosen power source; to perfect filling procedures, and in the case of liquid storage, to develop a safe system to vent boil-off gases. A prototype liquid hydrogen dewar for use onboard a car has been manufactured [35] and a liquefied-natural-gas dewar can easily be converted [26] to liquid hydrogen use. Compressed gas storage for vehicle use is too bulky and heavy to furnish the desired range from a vehicle. Several experimental vehicles are currently being fueled with liquid hydrogen [25,33,34] and a previous experimental car used liquid hydrogen and liquid oxygen to provide fuel and oxidant for a fuel cell [23]. No particular problem was encountered with the liquid storage except for some pulsating pressure from the vaporizer on the fuel cell vehicle. In general new designs using existing technology must be developed to handle the safe venting an filling procedures for the liquid containers; however, no technological breakthroughs are necessary to store liquid hydrogen aboard a vehicle.

Costs related to liquid storage involve the cost of the onboard container or dewar, the added costs of hydrogen due to the liquefaction process, and any additional costs involving venting of hydrogen overboard. A car-sized dewar for liquid hydrogen currently costs about $900.00 [26], and projections of $250 [27] to $500 [25] have been made for mass produced dewars of similar size. Unless the cost of liquefying hydrogen is written off to reduce transmission or storage costs, the selling price of liquid hydrogen will be $0.17/kg higher than the basic gaseous hydrogen costs. This added cost of the liquid fuel may be reduced slightly by recovering a portion of the liquefaction energy onboard the vehicle. The boiloff rate for the onboard dewar is determined partially by the cost of the dewar; however, with current technology a 1% boiloff per day should be achievable. Assuming an average range of 400 km for a vehicle, the 1% boiloff requires the vehicle to be driven an average of 4 km per day to use the boiloff gases. However, the average car is driven 42 km per day [1] and boiloff rate should not be a problem.

Hydrogen storage in a metal hydride does not have the extended history of compressed gas or liquid storage, but some general characteristics of metal hydrides have been measured. These characteristics are shown in table 3.4. Because of the heavy weights or high dissociation temperatures of most of the hydrides, the MgH or MgNiH are considered the most probable for use with a vehicle. Although the theoretical properties of the metallic hydrides are known, the performance degradation of the material with repeated usage has not been determined and even in carefully controlled experiments MgH could be loaded to only 80 percent of its theoretical capacity. Dissociation heat at the 1 atm equilibrium temperature may or may not be available from the heat rejected by the vehicle power source. Two investigators, [28 and 30], have theoretically determined the balance between the heat rejected by an I.C. engine and the heat required by MgH and they found the balance sufficient. Others [37] are more skeptical of the ability to use waste engine heat to dissociate the hydrides. The theoretical results [28,30] considered the possibility of increasing the available heat from the engine exhaust by decreasing the heat rejected to the engine cooling water. Also, to return a partially depleted and cooled MgH bed to operating temperature some hydrogen must be burned. Indications are that MgH requires a significant overpressure during loading to reduce the loading time to acceptable limits. The addition of the nickel catalyst reduces the required overpressure and the degradation of the material with time but also decreases the amount of hydrogen stored [29].

Another problem with hydride storage aboard a vehicle is the safety aspects of the storage medium. As magnesium is cycled to the hydride form and back to the pure form many times the material tends to form fine grains. The granular hydride becomes highly pyrophoric. Besides the hazards associated with handling large quantities of this material, the hazards of a magnesium fire following a vehicle accident with a partially depleted bed is severe. The adoption of any hydride, but especially of a hydride involving magnesium, for fuel storage aboard a vehicle may depend more on the hazards involved with the hydride than for other technical or economic reasons.

Cost factors are difficult to determine for the metallic hydride storage system because a working system has not been designed. In order to effectively use the reject heat from the vehicle power source, a highly efficient heat exchanger must be included in the hydride bed. Besides the expense of the heat exchanger, it may add significant volume and weight to the hydride bed.

Table 3.5 shows a comparison of the various methods of hydrogen storage with the storage of an equivalent amount of energy in gasoline and methanol. The unacceptability of compressed gas storage is apparent because of its large volume, heavy weight, and high capital costs. The volume required by the liquid hydrogen and the MgH storage is nearly the same although the weight of the hydride storage is considerably higher. MgNiH storage is significantly larger and heavier than that of liquid hydrogen or MgH. Gasoline storage is the best, followed by methanol and liquid hydrogen.

3.5 ECONOMIC ANALYSIS OF THE USE OF HYDROGEN FUEL FOR A SMALL AUTOMOBILE

In order to compare the possible power sources, fuels, and methods of storing the fuel, calculations were performed to determine the cost of operating a specific auto over a defined driving cycle. The type of auto selected was an intensively driven intercity vehicle because in this type of vehicle the high capital expense of a higher efficiency power plant can be amortized over a larger number of miles. Since projected fuel costs are high, a higher efficiency power plant should be best suited to an intensively driven vehicle.

The performance characteristics of this auto were chosen to be near that of a small, low powered car similar to the American sub-compact or small import car. Acceleration to 64.4 km/h (40 miles/h) was specified to be 12 seconds. The power calculated as necessary to achieve the required acceleration was sufficient for all other operating modes of the vehicle including a continuous cruising speed of 64.4 km/h. The basic car body and frame were assumed to weigh 680 kg with an additional load of 363 kg for passengers and baggage. The total weight of the car was varied in the calculations due to the varying storage weights of the fuel and corresponding engine weights. The total weight of the car ranged from 1160 to 2960 kg, depending upon the engine-fuel option selected.

Weights and costing factors for the defined car are shown in table 3.6. Most conventional materials were assumed to cost \$3.3/kg, as fabricated, while increased costs were used for non-conventional materials. The capital costs were amortized over their life (given in table 3.6) assuming 15 percent interest on the capital investment.

The driving cycle used to determine the required stored energy aboard the car was calculated using a time cycle of 8 hours. The car cruised at 64.4 km/h on level roadway for 60 percent of the 8 hours, accelerated to 64.4 km/h for 26.7 percent of the 8 hours, and decelerated to 0 km/h for 13.3 percent of the time. A total distance of 435 km was traveled during the driving cycle. For this driving cycle an average energy consumption of .23 kW-h/km was calculated for a vehicle weighing 1600 kg. This average energy consumption compares favorably with that calculated by Salihi [20] for the same weight vehicle performing according to the Federal driving cycle. No energy recovery was included during the deceleration periods.

Table 3.4. Properties of certain metal hydrides.

Initial and final composition	Dissociation Heat [28, 29] ΔH^f, kW-h/kg of H_2	Available wt % H_2	Equilibrium Temperature at 1 atm of H_2 (°C)	Cost [28] of metal per kg	Ratio of Dissociation Heat to low Heat of Combustion
$Li \longrightarrow LiH$	- 25. 0	12. 7	800	$18. 03	0.75
$Mg \longrightarrow MgH_2$	- 10. 3	7. 7	290	$ 0. 84	0.31
$Ca \longrightarrow CaH_2$	- 24. 1	4. 8	920	$ 4. 85	0.72
$Na \longrightarrow NaH$	- 13. 9	4. 2	525	$ 0. 66	0.42
$Mg_2NiH_{0.3} \longrightarrow Mg_2NiH_{4.2}$	- 8. 9	3. 5	250	$ 2. 20	0.27
$K \longrightarrow KH$	- 15. 7	2. 5	715	$ 0. 77	0.47
$UH_{0.95} \longrightarrow UH_{2.0}$	- 5. 6	2. 0	12	$ 8. 82	0.17
$FeTiH_{01} \longrightarrow FeTiH_{1.0}$	- 3. 2	0. 9	0	$ 4. 23	0.10

Table 3.5 Comparison of hydrogen storage methods to gasoline and methanol.

Fuel	Storage Method	Lower Heat Value (kW-h/kg)	Fuel Wt (kg)	Fuel Volume (m^3)	Energy Content* Including Container (kW-h/kg)	(kW-h/m^3)	Cost of Container
Hydrogen	Compressed Gas[1]	33.33	17.6	1.19	.612	447.44	$3160.
	Cryogenic Liquid[2]	33.33	17.6	0.249	10.15	1929.5	$250 - $900
	MgH_2 Hydride[3]	33.33	17.6	0.264	2.53	2219.7	$ 347.
	$MgNiH_2$ Hydride[4]	33.33	17.6	0.558	1.19	1050.2	$1398.
Gasoline	Liquid	12.92	45.36	0.0674	10.90	8548.8	$ 30.
Methanol	Liquid	6.20	94.5	0.1180	5.45	4896.8	$ 42.

* Total energy content was 586 kW-h

[1] Gas at 136 atm., 300 K

[2] Saturated Liquid at 1 atm absolute

[3] Cost of Mg Hydride - $0.84/kg [28]

[4] Cost of MgNi Hydride - $2.20/kg [28]

Table 3.6 Cost, weight, and life factors used to calculate operating costs for a specified auto.

	Weight	Cost	Life
1. Frame and Body	680.4 kg	\$2250	1 yr
2. Passenger and Baggage	362 kg	None	-
3. Internal Combustion Engine and Drive Train	4 kg/kW	\$3.31/kg	1 yr
4. Fuel Cell	18 kg/kW	\$20-\$160/kW	1-5 yr
5. Electric Motor and Controller	4.23 kg/kW	\$7.34/kW	2 yr
6. Fuel Storage	(kg)		
Hydrogen			
Liquid (Container)	$41.3 + 3.2\sqrt{\text{Wt of } H_2}$	\$15/kg	2 yr
MgNi Hydride	(Wt of H_2)/0.035	\$2.2/kg	2 yr
Mg Hydride	(Wt of H_2)/0.077	\$0.84/kg	2 yr
Hydride Container	0.136 x hydride wt.	\$3.3/kg	2 yr
Methanol	0.136 x Fuel Wt	\$3.3/kg	1 yr
Gasoline	0.18 x Fuel Wt	\$3.3/kg	1 yr

The equation used to calculate the energy requirements was taken from Austin [30] and modified to account for changing frontal area with car weight according to Ambs [31]. Including an acceleration term the final equation used was:

$$\frac{dV}{dt} = \frac{C_1 P}{(Wt)V} - C_2 \left[C_3 + \left(\frac{C_4}{Wt} + C_5 \right) V^2 \right] \qquad (1)$$

where

V is Velocity, km/h,

P is Power at the wheels, kW,

Wt is weight of Vehicle, kg,

$C_1 = 11,820.55$,

$C_2 = 32.24025$,

$C_3 = 0.02$,

$C_4 = 3.0906 \times 10^{-3}$,

and $C_5 = 1.3627 \times 10^{-6}$.

The power required during a constant velocity cruise was determined by solving the equation while setting dV/dt = 0. The power consumed during acceleration was determined by maintaining a constant P sufficient to accelerate a vehicle of selected weight to 64.4 km/h in 12 seconds. No power was consumed or recovered during the deceleration phase and only the distance traveled during this phase was of interest. The power required to accelerate a car of specified weight to 64.4 km/h in 12 seconds is shown on figure 3.1. Figure 3.2 shows the total energy required for the complete driving cycle of 8 hours versus the weight of the vehicle. In order to determine the size and thus the cost of the vehicle, a weight was assumed, and the motor sizes determined from the acceleration power requirement divided by a drive train efficiency. Then the fuel storage capacity was determined by dividing the total energy requirements over the 8-hour period by the overall efficiency of the power unit. If the final calculated weight did not agree with the initial assumed weight, a new weight was assumed and the calculation repeated. In the case of the I.C. engine, the drive train efficiency used was 80 percent. With the fuel cell the electric drive train efficiency together with the control unit was taken at 85 percent. Overall efficiency of the fuel cell and electric drive unit was taken as 50% [21]. The overall efficiency of the I.C. engine and drive train was varied in the calculations.

The fuel cell and electric drive unit weight was calculated by sizing the fuel cell to supply the total energy requirement of the 8-hour driving cycle, while the drive motor and control unit was sized to supply the required acceleration power. Lead-acid batteries were included to supply peak power requirements during the periods of acceleration.

Figures 3.3, 3.4, and 3.5 show the results of the cost analysis for three different fuel costs. The calculated costs on these figures are only fuel and capital costs and do not include maintenance or insurance costs. The total cost of car operation was reduced to a cost per kilometer of operation by dividing the annual costs by the assumed 161,000 kilometers driven per year. The cost of producing liquid hydrogen was taken at 0.205 $/kg. This cost was chosen as a lower-intermediate value from table 1.3 (Chapter 1) to account for some boil-off losses (10 to 20 percent of liquefaction costs) and an intermediate liquefaction efficiency.

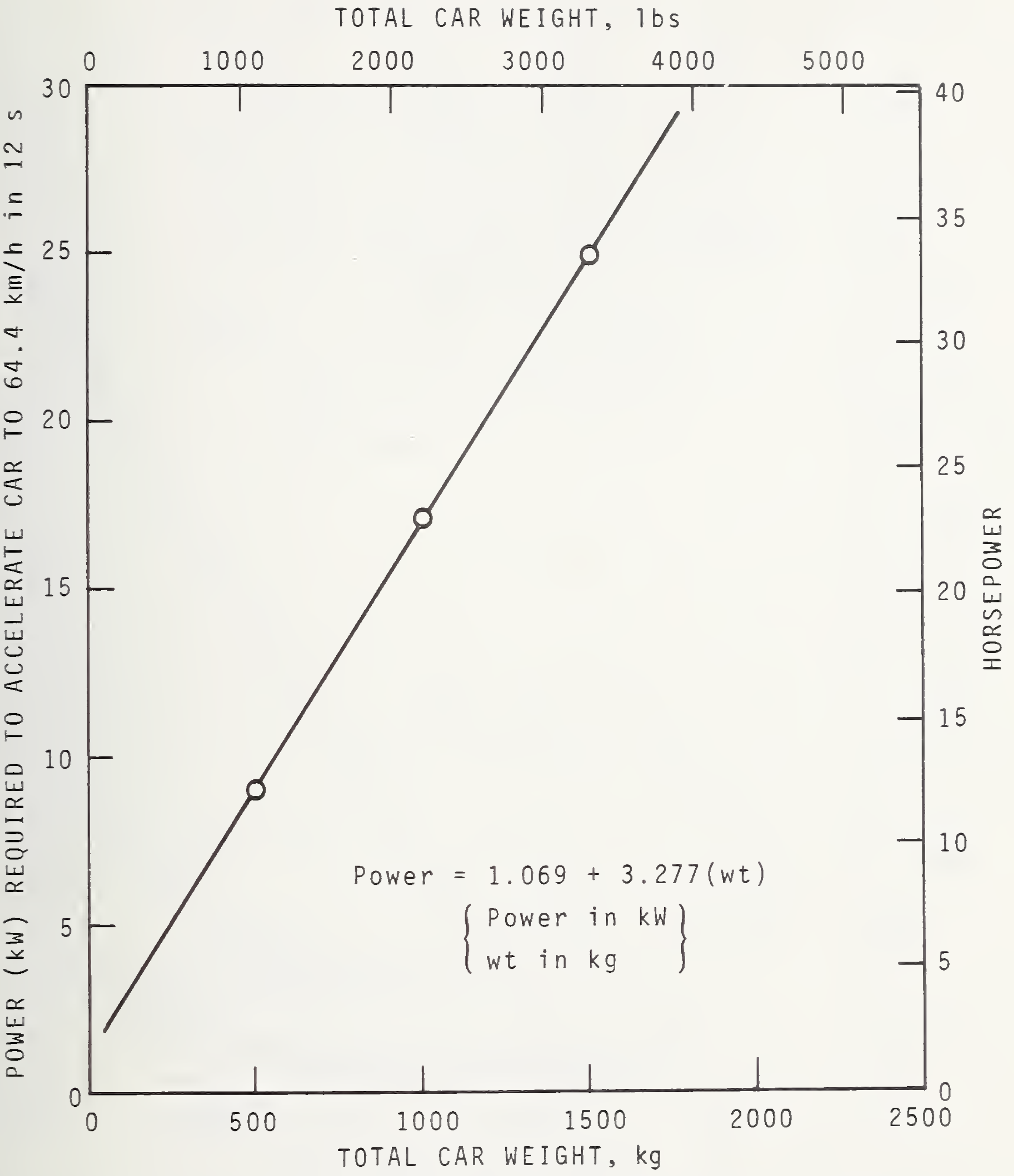

FIGURE 3.1 - Power Required at the Wheels to achieve 64.4 km/h in 12 seconds.

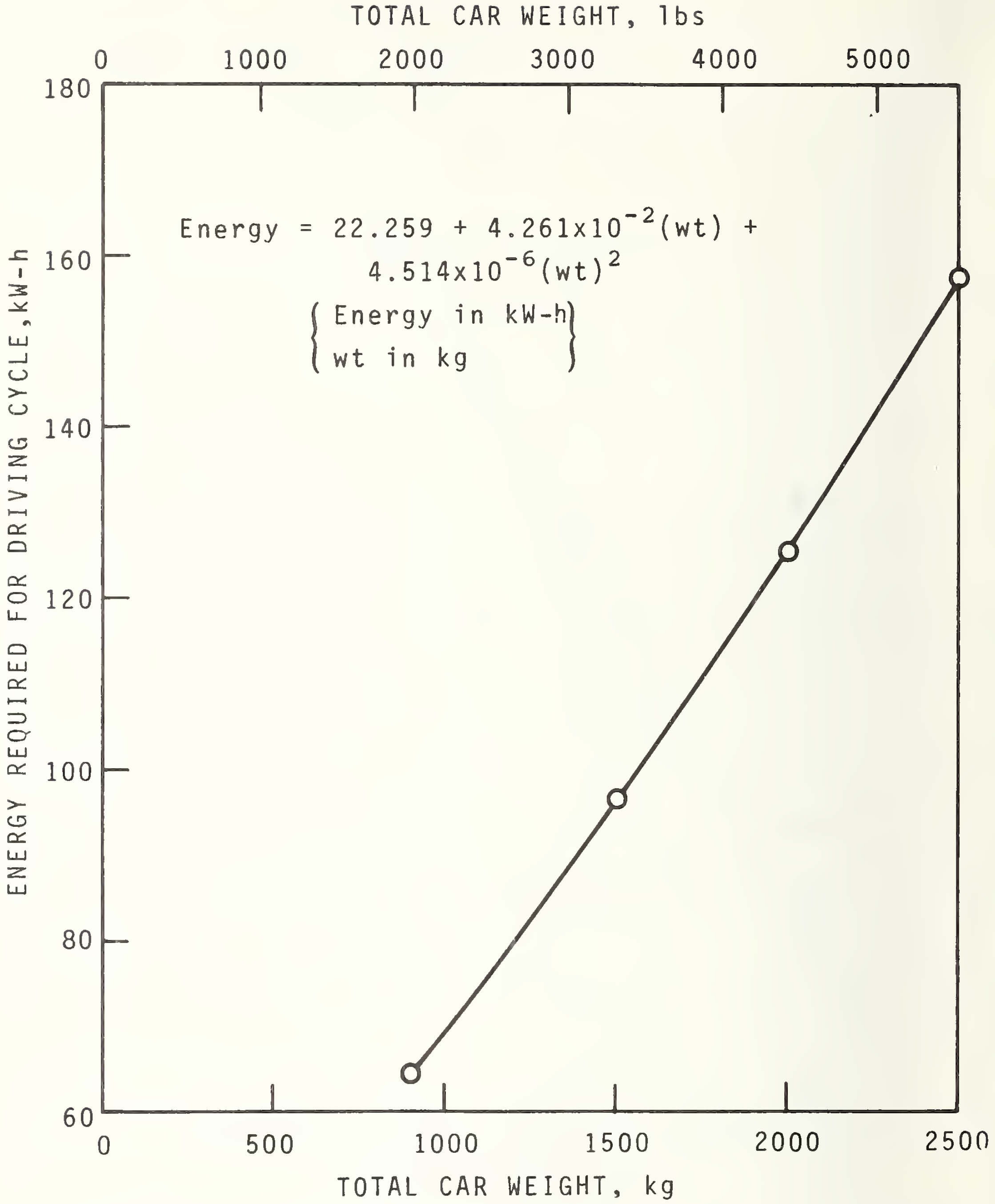

FIGURE 3.2 - Energy Required by Car for the Driving Cycle.

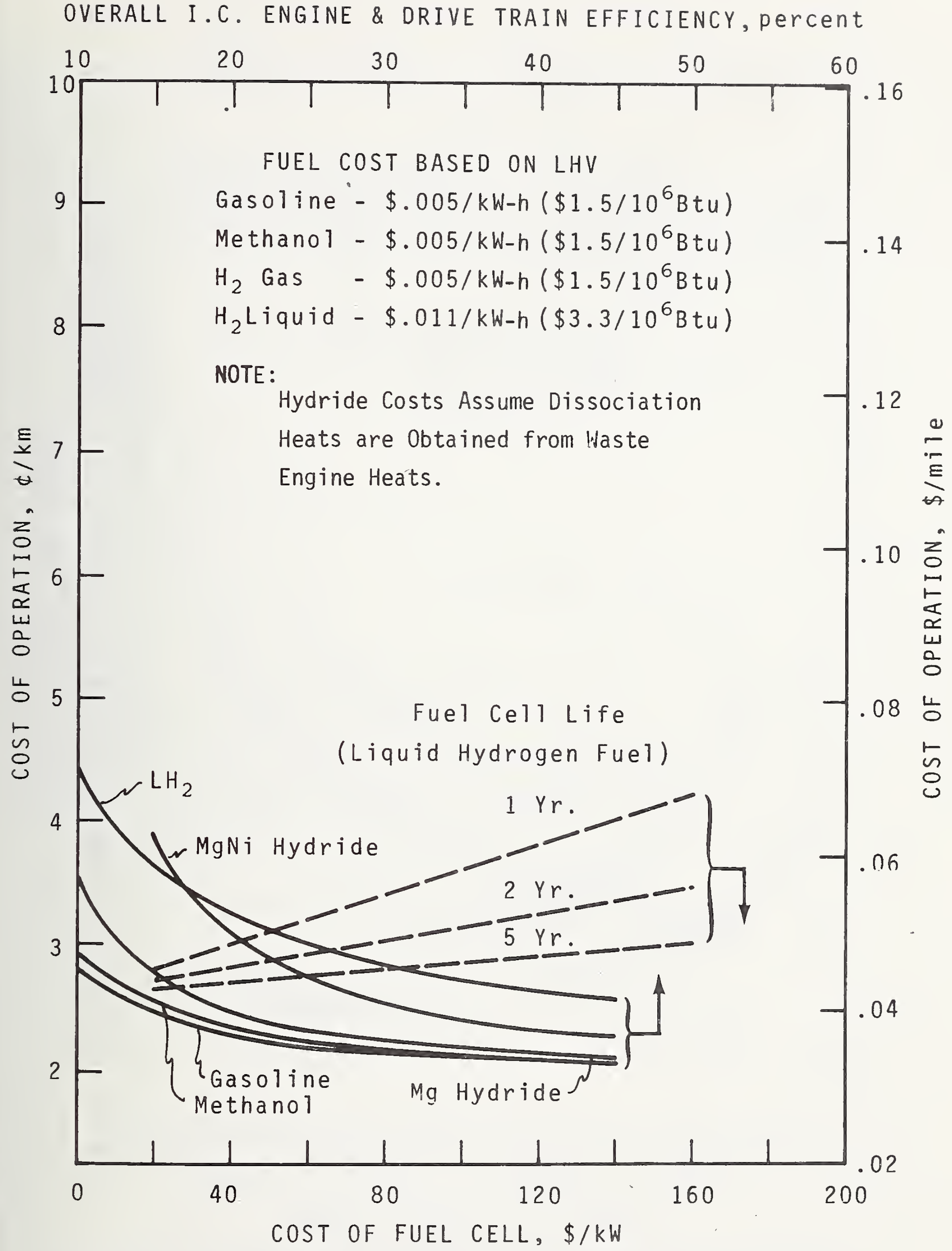

FIGURE 3.3 - Cost of Car Operation; Low Cost Fuel.

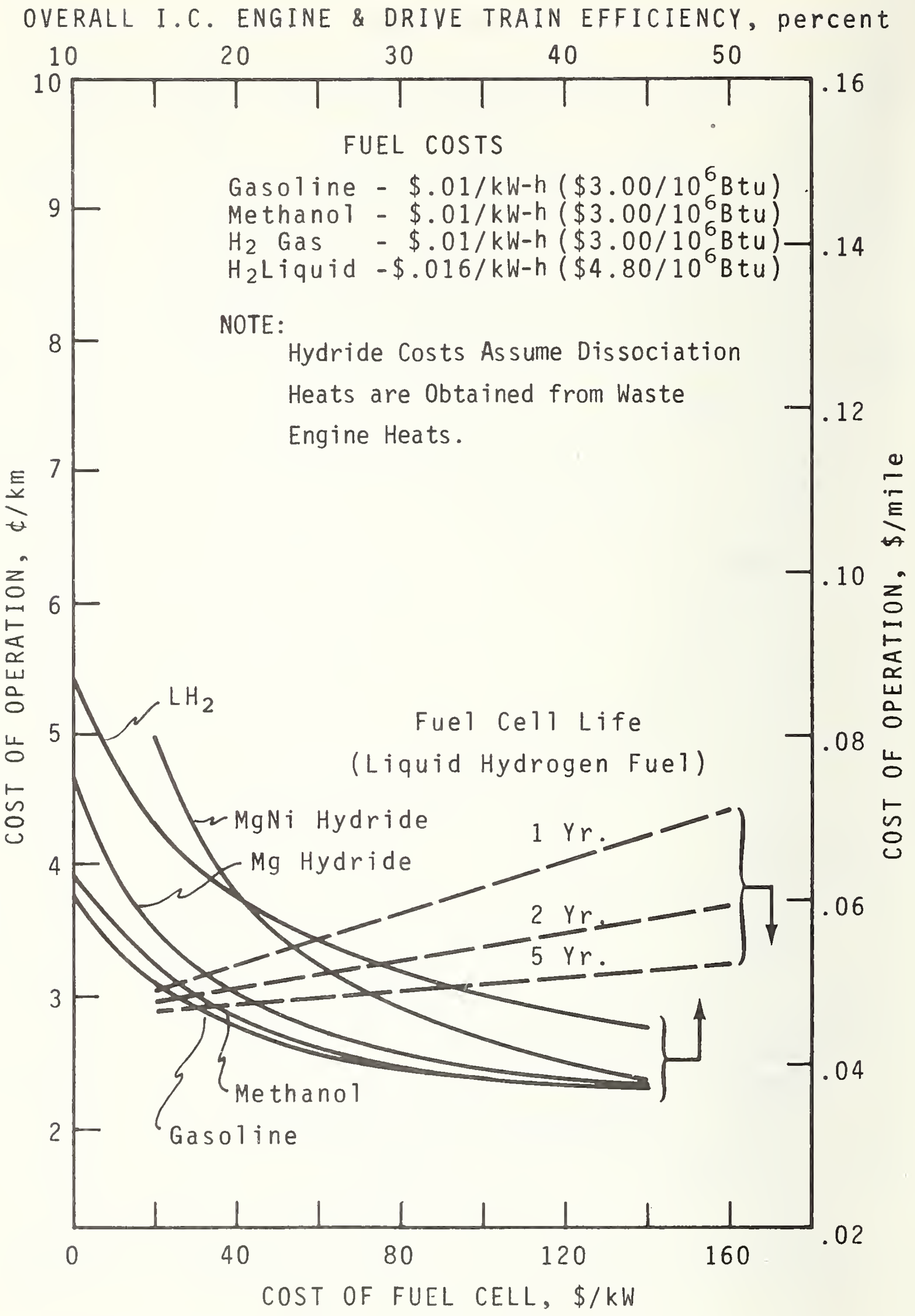

FIGURE 3.4 - Cost of Car Operation, Medium Cost Fuel

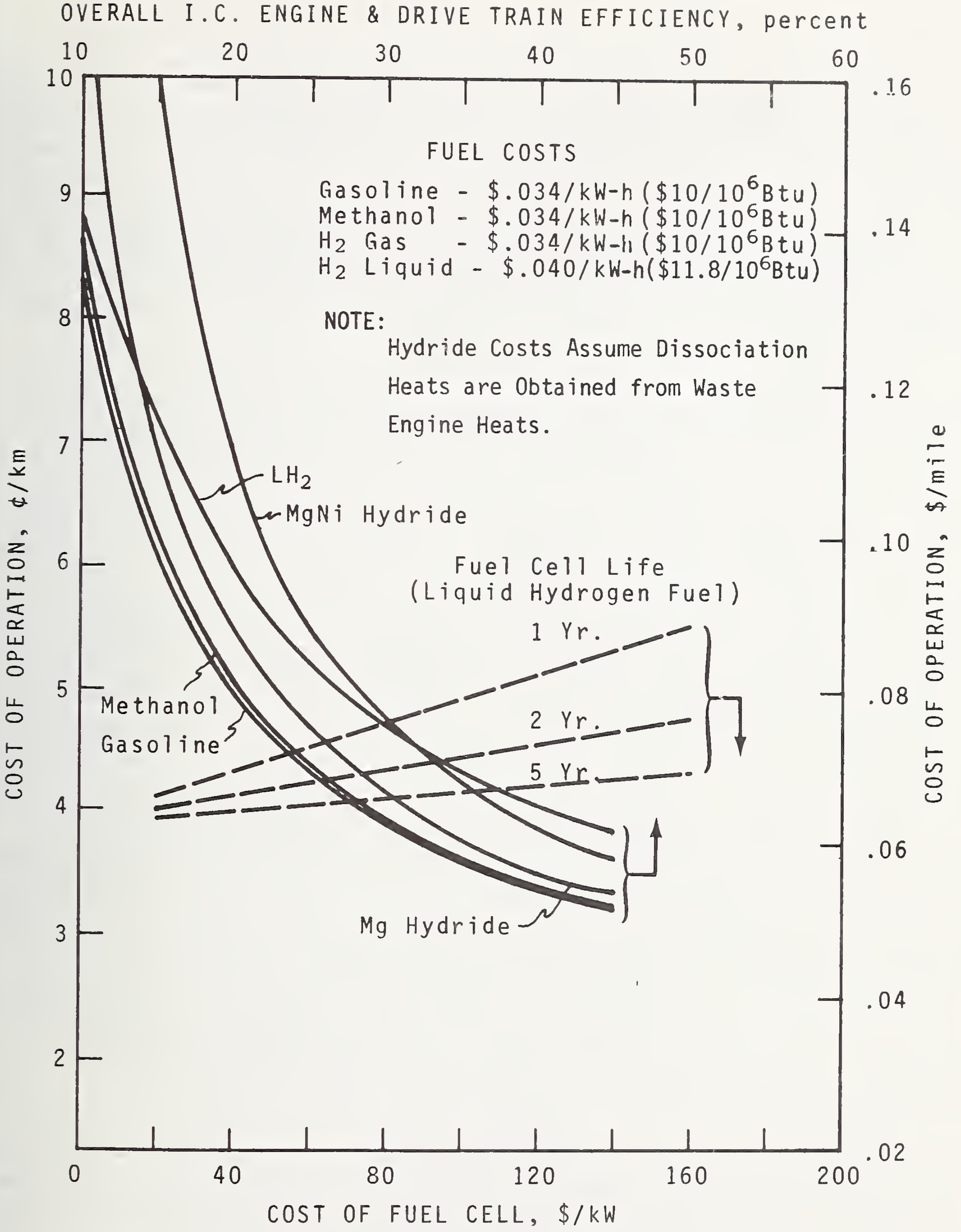

FIGURE 3.5 - Cost of Car Operation; High Cost Fuel.

The efficiency of the I.C. engine operating with gasoline or methanol fuel may approach 27 percent for a subcompact vehicle [19]. At least in the short term, the pollution controls on these engines may reduce their efficiency by 20 to 25 percent [1] resulting in an overall efficiency of 20 to 21 percent. Using hydrogen as a fuel for the I.C. engine should increase the efficiency of the engine to at least 27 percent. Although higher efficiencies [11,12,33,38] than those obtained using gasoline as a fuel have been observed for hydrogen fueled I.C. engines, most of the higher efficiency is due to a higher part-load efficiency, and at least for the car used in this calculation, the engine is of minimal size reducing the majority of the part-load advantage.

Gasoline costs are currently nearly \$.60/gallon (0.16 \$/ℓ), especially for the no-lead gasoline scheduled for use with a majority of the 1975 automobiles. Using 12.92 kW-h/kg as the lower heating value of gasoline and a density of 0.72 kg/ℓ, the current cost of energy is \$0.017/kW-h or one-half the cost of fuel used on figure 3.5. Using a fuel cost of \$.034/kW-h (figure 3.5) the most economical car using an I.C. engine would be the hydrogen fueled car (efficiency of the engine is 27 percent versus 21 percent for methanol or gasoline fuel) with the fuel stored in magnesium hydride. The only difficulty with this conclusion is that the theoretical performance of the magnesium hydride was used in the calculations, and indications are that it may be necessary to either burn hydrogen to supply a portion of the dissociation heat or that the hydride may poison or cake reducing its capacity [30]. Either one of the nonideal reactions of the magnesium hydride would increase the cost of operation of the car. Fuel cell powered cars with liquid hydrogen fuel would become competitive if fuel cells would cost less than \$60/kW and have a life of 1 year or have a cost of less than \$200/kW with a life of 5 years.

Table 3.7 presents a breakdown of the operating costs obtained for an I.C. engine driven car and for a car powered by a fuel cell costing 160 \$/kW. The gasoline and methanol fueled engines are assumed to be 20 percent efficient, the hydrogen I.C. engines are taken at a modest 25 percent efficiency and the fuel cell power plant is assumed to be 50 percent efficient. The effects of the heavy weights and high capital costs are reflected in the cost of operation for the fuel cell system. High fuel costs increase the cost of operating the liquid hydrogen fueled I.C. engine driven car while the heavy weight of the MgNi increases the cost of operating the car using the MgNi hydrogen storage system. In the breakdown, the costs of fuel were taken from figure 3.5 (high cost fuel).

No specific conclusion can be drawn from the economic study except that for low fuel costs the methanol and gasoline cars are the least expensive to operate. As the fuel costs increase, hydrogen fuel becomes more competitive. At high fuel prices, liquid hydrogen fuel with a fuel cell becomes more competitive if fuel cell costs can be reduced or if the life of a fuel cell can be extended. If cost of operation becomes competitive, the choice of fuel must be hydrogen because of the reduction in pollution from hydrogen-powered vehicles. As new engine designs evolve and cost factors are defined the approach outlined herein can be used to compare alternate synthetic fuels. Hydrogen must be considered a strong contender at this writing due to the inflationary trend of automotive fuel costs.

Table 3.7 Breakdown of costs for the various power plant concepts

Car	I.C. Engine Drive					Electrical Drive, Fuel Cell & Liquid H_2
	Gasoline	Methanol	Mg Hydride	Liquid Hydrogen	MgNi Hydride	
Efficiency, %	20	20	25	25	25	50
Total Wt, kg	1181	1226	1316	1218	1597	1498
Total Energy Required for Driving Cycle, kW-h	78.9	81.3	85.6	80.8	102	90.54
Cost of Fuel, Cents/km	3.086	3.181	2.68	2.985	3.194	1.777
Cost of Capital						
Body & Frame, Cents/km	1.609	1.609	1.609	1.609	1.609	1.609
Lead-Acid Batteries, cents/km						0.116
Fuel Cell, Cents/km						0.864
Control & Electric Motor Cents/km						0.168
I.C. Engine, Cents/km	0.298	0.310	0.265	0.246	0.318	
Fuel Tank, Cents/km	0.014	0.029	0.144	0.360	0.382	0.244
Totals	5.007	5.129	4.721	5.209	5.503	4.778

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CHAPTER 4

SURVEY OF MATERIALS FOR HYDROGEN SERVICE

J. G. Hust

4.0 SUMMARY

Hydrogen related materials requirements involve primarily: hydrogen embrittlement resistance, high and low temperature strength, wear and corrosion resistance, hydrogen and oxygen compatibility, and insulating materials. The problem of hydrogen-environment embrittlement, relatively unique to hydrogen service, introduces severe materials requirements and pervades essentially all phases of hydrogen production, transfer and storage, and applications. Low-cost, high-strength materials which are also embrittlement immune and resistant to corrosion, will be necessary in hydrogen production facilities and for transfer and storage systems. A strong need also exists for low-cost, light-weight storage systems and insulating materials for portable applications, such as for fuel tanks aboard automobiles and aircraft. Composite materials are strong candidates for these applications. Many materials, of course, exist which are applicable to hydrogen service, but low-cost materials are needed. In some instances, large uncertainty exists as to the compatibility of materials with hydrogen, primarily because of the embrittlement phenomena. In other cases, such as in proposed hydrogen production techniques, the materials problems cannot yet be defined because of uncertainty as to the method or process which will be adopted. Materials research should be directed toward: (a) compilation and critical analysis of existing low temperature, ambient temperature, and high temperature mechanical and thermal property data and embrittlement data for candidate structural materials, (b) compilation and critical analysis of low temperature insulation data, (c) establishment of standard embrittlement test procedures suitable for pertinent applications, (d) establishment of standard insulation test procedures and standard reference materials of insulation to facilitate these test procedures, (e) measurement of mechanical properties, thermal properties, embrittlement, and permeation of metals and non-metals (especially plastics) as indicated by (a), (f) measurement of thermal conductance of insulating materials using standardized test procedures, and (g) development of light-weight, high-strength, embrittlement immune materials for high pressure structural applications, of low-cost efficient insulations and development of hydrogen-oxygen catalytic materials.

4.1 INTRODUCTION

The fossil fuel energy shortage has created strong interest in alternate sources of energy and methods of energy storage. Fossil fuels, such as gasoline, natural gas, oil, and coal are portable and are used directly for transportation as well as for heating and electric power generation. Alternate sources of energy, such as nuclear, solar, and geothermal, are less portable or not portable at all. Their application tends toward an electrical economy which is less applicable to transportation needs.

If society is to retain all current modes of transportation, it is clear that a readily portable and storable energy carrier is needed. Fossil fuels have been the basis for such an energy carrier in the past, but as our resources are depleted, an alternate comparable energy carrier must be developed.

One of several portable energy carriers is hydrogen fuel [1]. It can be produced from water and is available almost anywhere on earth. This storable energy carrier is also ecologically clean and its closed re-use cycle, $H_2O \rightarrow H_2 + O \rightarrow H_2O$, can be measured in weeks as compared to the effectively open cycle of fossil fuels, measured in millions of years, if at all. It is emphasized that water is not an energy source but only a material which can be used effectively to produce an energy carrier (hydrogen fuel). The energy required to produce hydrogen by splitting water is theoretically comparable to the energy carried by the hydrogen produced.

Scores of papers have been written describing the production, storage and transmission, and applications of hydrogen as a fuel. Some of these are rather non-technical and speculative in nature, others relate principally to the aerospace program. The more detailed documentation on the feasibility, economics, and applications of hydrogen as a fuel for commercial and domestic use are by Hord [1], Gregory [2-6], De Beni and Marchetti [7,8], Winsche, et al. [9], Jones [10], and Maugh [11]. The most inclusive treatment is by Gregory [2].

These and other papers suggest that no insurmountable technical materials problems exist for the production, transfer and storage, and general use of hydrogen as a fuel. As a matter of fact, hydrogen has already been used in ground vehicles and aircraft to a limited extent, quite extensively as a 50% to 80% component in a gas mixture for domestic use in the form of "town gas" or manufactured coal gas, and most extensively in the aerospace program. The materials limitations are based primarily on economic considerations as described in later sections of this paper.

In anticipation of the development of a hydrogen fuel economy, we will consider materials problems associated with the production, transfer, storage, and use of immense quantities of gaseous, liquid, and possibly solid hydrogen, see for example reference [12]. The purpose of this paper is to review potential material (primarily structural and insulating materials) requirements involved in the production, transfer, storage, and use of hydrogen, including the containment of related chemicals in hydrogen applications. This review encompasses the containment of hydrogen under static as well as dynamic conditions, at temperatures from near absolute zero to high temperatures, which in some proposed devices exceeds the limits of present production materials, and at pressures from atmospheric conditions to thousands of atmospheres. In addition, attention is directed to materials requirements in the handling of oxygen by-product and the compatibility of materials in contact with some of the more corrosive chemicals used in the production and applications of hydrogen.

In section 4.2, hydrogen related materials properties are discussed, e.g., mechanical, thermal, and compatibility properties. Although a wide range of conditions is involved in a hydrogen economy, emphasis is directed toward those facets which are most unique to domestic and commercial applications of hydrogen. A lengthy section on hydrogen embrittlement is included to emphasize the significance of this phenomena in ambient as well as high temperature systems design. Other high temperature and pressure effects are slighted, since associated problems are common to other industrial processes and concomitant research and development. Low temperature insulation requirements and developments are reviewed.

Sections 4.3 through 4.5 are concerned with systems design requirements dictated by material embrittlement, low temperature effects, and compatibility, in hydrogen production, transfer and storage, and applications. Emphasis is directed toward those materials in direct contact with hydrogen, such as metal and plastic pipes, metal and composite storage vessels, seals, bearings, propulsion systems, and domestic appliances. Low temperature insulating materials and systems are discussed.

A materials survey similar to this is currently in progress at Stanford Research Institute under the direction of Neville Daniels [13]. Areas of emphasis will undoubtedly differ in these studies and in some instances viewpoints may be in conflict, but it is believed that the results of these two studies will supplement each other, resulting in a more thorough overview. Discussions have been conducted with Daniels and his associates regarding common areas of interest.

The quest for data on materials requirements included: computer searches of the NBS Boulder-Cryogenics Division Data Center, the NASA Cleveland Data Bank, and the Smithsonian Scientific Information Exchange Work-In-Progress File for information on hydrogen related problems, systems, and current research. Abstracts from the NASA Research and Technology Operating Plan Summary (1972) and An Inventory of Energy Research by ORNL (1972) were also searched. Approximately 1000 references resulting from these searches relating to hydrogen service and materials research were obtained and reviewed. In addition, discussions, both personal and by phone, were held with several dozen experts in materials research and cryogenic systems development. Considerable information was also obtained from members of the NBS Cryogenics Division.

The author has attempted to give due consideration to all pertinent aspects of a hydrogen economy, but it is unavoidable that a review of this scope reflects to some extent the author's personal interests. This work, therefore, should be considered a source of information gathered from workers in each discipline as reported in the published literature, contract reports, and summaries, and through personal contacts with these workers.

4.2 HYDROGEN RELATED MATERIALS PROPERTIES

Pertinent material properties can be divided into mechanical, thermal, electrical, and chemical properties. Each of these may have unique importance in particular applications. In structural design, economic, fabrication, and mechanical property considerations require the highest priority. In the presence of appreciable temperature gradients such as in the containment of cryogenic hydrogen, thermal properties (e.g., thermal conductivity, thermal expansion, and specific heat) are critical and significantly affect material selection. Chemical properties are considered significant here only in-so-far as they influence pertinent mechanical properties.

Of the previously mentioned range of conditions, temperature is the most significant from the standpoint of material property variation. Solids generally become stronger but less ductile as temperature decreases. For many metals, this loss in ductility is sufficient to eliminate them from low temperature applications (see, for example, Pearson [14]). The thermal conductivity and thermal expansion of most metals change appreciably with temperature, especially at low temperatures. Corrosion resistance decreases with increasing temperature and is a potentially serious problem in some of the proposed high temperature hydrogen production methods.

Because of their small size, hydrogen atoms readily dissolve into and diffuse through most materials. The diffusion and permeation of hydrogen in metals is a significant aspect of hydrogen embrittlement in metals. Hydrogen embrittlement produces severe mechanical property degradation of many metals and often results in premature structural failure by brittle fracture. It is most significant at ambient temperatures, less so at high temperatures, and negligible at cryogenic temperatures. Hydrogen-reaction embrittlement (see section 4.2.2) can be significant at high temperatures and in hydride storage applications.

The design of equipment for hydrogen service must include consideration of material compatibility, property variations (primarily as a function of temperature), and the degradation of these properties due to hydrogen embrittlement. The following sections elaborate on these property variations, concomitant design considerations, and related problem areas.

4.2.1 Temperature Effects

Excellent reviews and data compilations have been published on the temperature variation of mechanical properties of metals [15-27], polymers [18,21,23,28,29], and other non-metals [18,21,23]. Two basic requirements of a structural material that must be fulfilled are: (1) it must support a sufficient load (generally with a minimum deflection) and (2) it must be tough but not brittle. Of course, it should also be economic and readily fabricated. The first requirement implies a high strength material while the second implies ductility. For many materials, these requirements are somewhat in conflict, since as strength increases, ductility often decreases. At high temperature the increased ductility and lowered strength of most materials are significant factors in material selection. At low temperature the brittle behavior of materials is most important, and thus, fracture mechanics is of great importance. A myriad of mechanical properties of significance in material selection can be cited, such as hardness, modulus, strength, ductility, creep, fracture toughness, yield stress, offset strain, etc. Which of these are most important is determined by the particular applications. Often equipment must be designed to operate alternately at ambient and low temperatures or ambient and high temperature, thus requiring acceptable properties over extended temperature ranges.

The temperature dependence of some of the more important mechanical properties of transition metals can be classed according to the crystalographic structures, face centered cubic (fcc), body centered cubic (bcc), and hexagonal close packed (hcp).

Fcc transition metals are generally lower in strength but tend to remain ductile at low temperatures. Structural metals for low temperature applications are usually chosen from the fcc class, e.g., aluminum, copper, and nickel alloys as well as austenitic stainless steels. The fcc metals generally have low yield stress relatively independent of temperature, but the yield stress can be improved by cold work.

Bcc transition metals are hard, have high melting points, and thus are of considerable use at high temperatures. Iron, the most important and common of these, undergoes a crystal structure phase change at 910°C. The fcc, high temperature, or γ-phase exists above 910°C while the bcc, low temperature, or α-phase exists below. Bcc metals tend to become brittle at low temperatures, and thus are usually avoided for low temperature applications. Through the addition of various elements to iron, the α-γ transition temperature can be controlled. Additions of chromium, tungsten, vanadium or silicon among others raises the transition temperature and tends to stabilize the bcc structure. Additions of manganese, nickel, cobalt, or copper among others lowers the transition temperature resulting in a more stable fcc structure. With sufficient nickel, for example about 42%, a fully stabilized fcc alloy (austenitic steel) is obtained which remains stable to the lowest temperatures measured.

The hcp transition metals are not as readily classified as the bcc and fcc metals; some of them behave more like bcc metals while others have the properties of fcc metals. For example, tungsten is brittle at low temperatures, and zirconium and titanium remain ductile at low temperatures. Typical stress-strain curves for fcc and bcc metals are shown in figure 4.1 (data obtained from Fickett [19] and Kasen [39]).

Of the many physical properties, only a relatively few, other than mechanical properties, are important in structural applications. Probably the most significant are thermal expansion and density. Of lesser, but significant, relevance are thermal conductivity, specific heat, and thermal diffusivity. In fewer instances, electrical resistivity and dielectric properties are important in design.

The most extensive effort for the compilation of thermal properties of materials is the on-going work at the Thermophysical Properties Research Center, Purdue University, under the direction of Touloukian [30]. Other excellent compilations and papers are: thermal expansion of alloys by Clark [31], thermal properties of polymers by Schramm, et al. [29], specific heats by Corruccini and Gniewek [32], and thermal conductivity of materials by Childs, et al. [33]. Reviews on thermal properties of metals and non-metals are abundantly available; only the texts by Tye [34], Childs, et al. [33], and Touloukian [30] are cited. Density data on metals can be found in the ASM Metals Handbook [16].

A few summarizing remarks on thermal and electrical properties are given here. The thermal and electrical properties of metals and non-metals are generally strongly dependent on temperature. The thermal and electrical conductivities of pure metals at low temperatures are strongly dependent on the concentrations and types of impurities. The heat treatment or anneal condition also can significantly affect the low temperature values for both pure metals and alloys. Figure 4.2 illustrates the general temperature dependence of thermal conductivity for metals. Specific heat and thermal expansion are relatively insensitive to small composition changes in metals but heat treatment can produce significant changes in thermal expansion. See, for example, Clark's [31] data on AISI 633 annealed and precipitation hardened steel. High temperature properties are less sensitive to composition and heat treatment. Comparative behavior of thermal expansion is illustrated in figure 4.3.

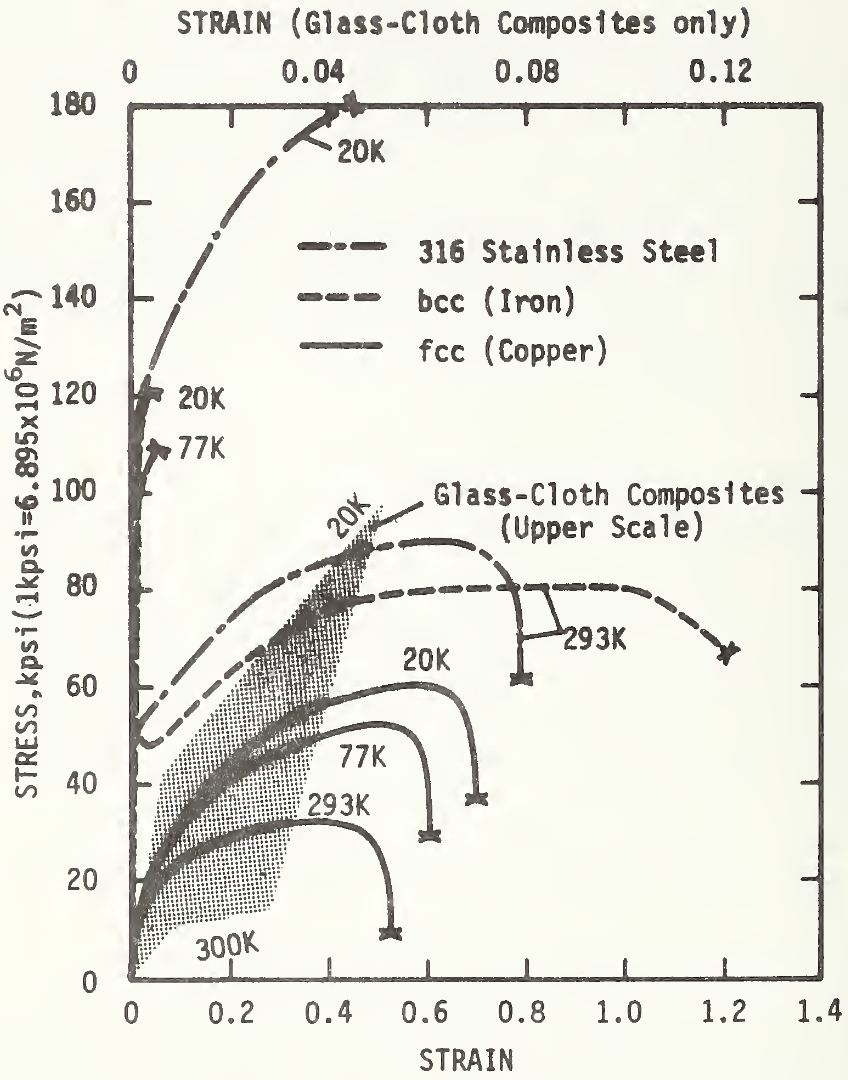

FIGURE 4.1 Tensile behavior of bcc and fcc metals and glass-reinforced composites.

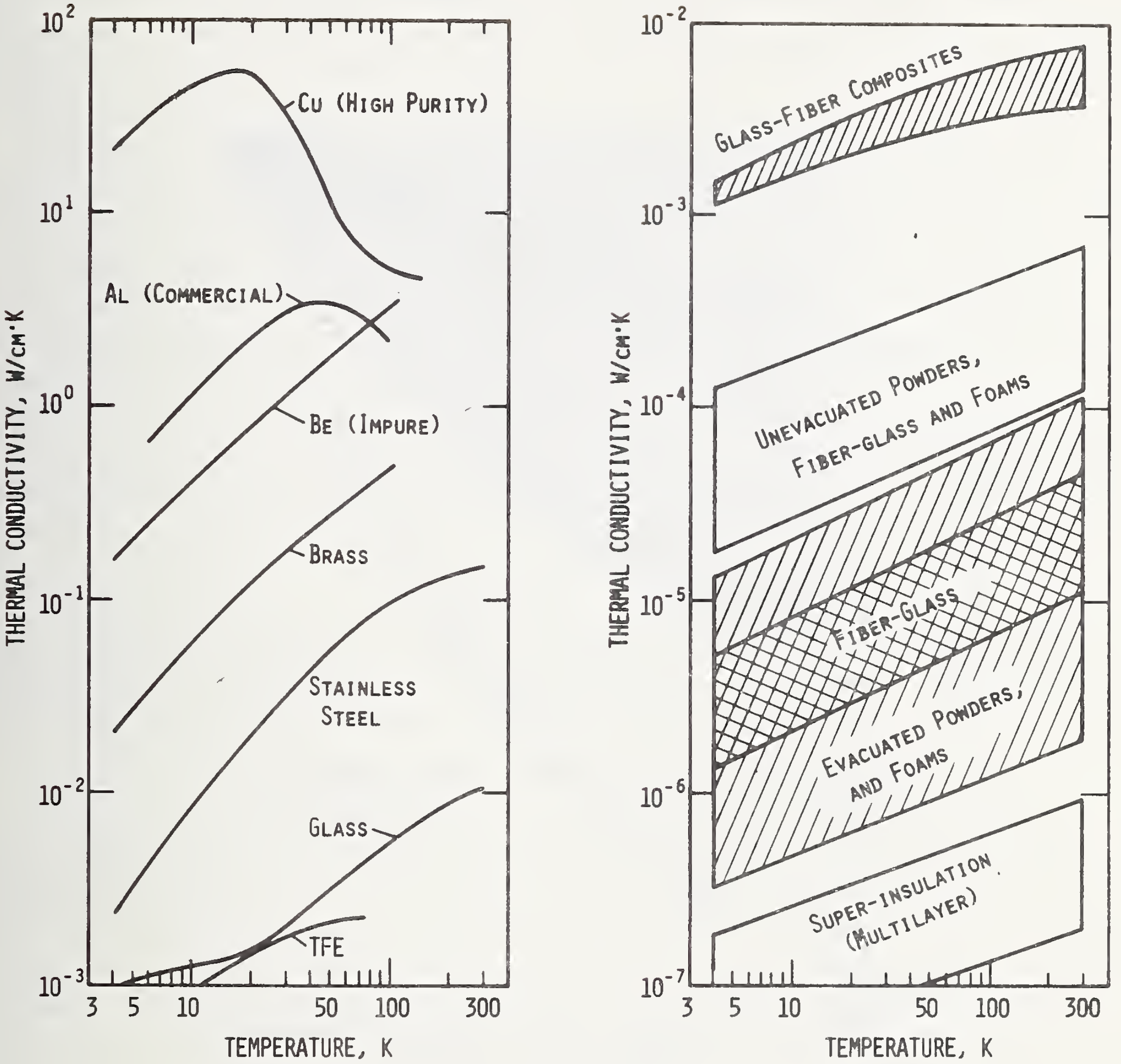

Figure 4.2 Thermal conductivity for several classes of materials as a function of temperature.

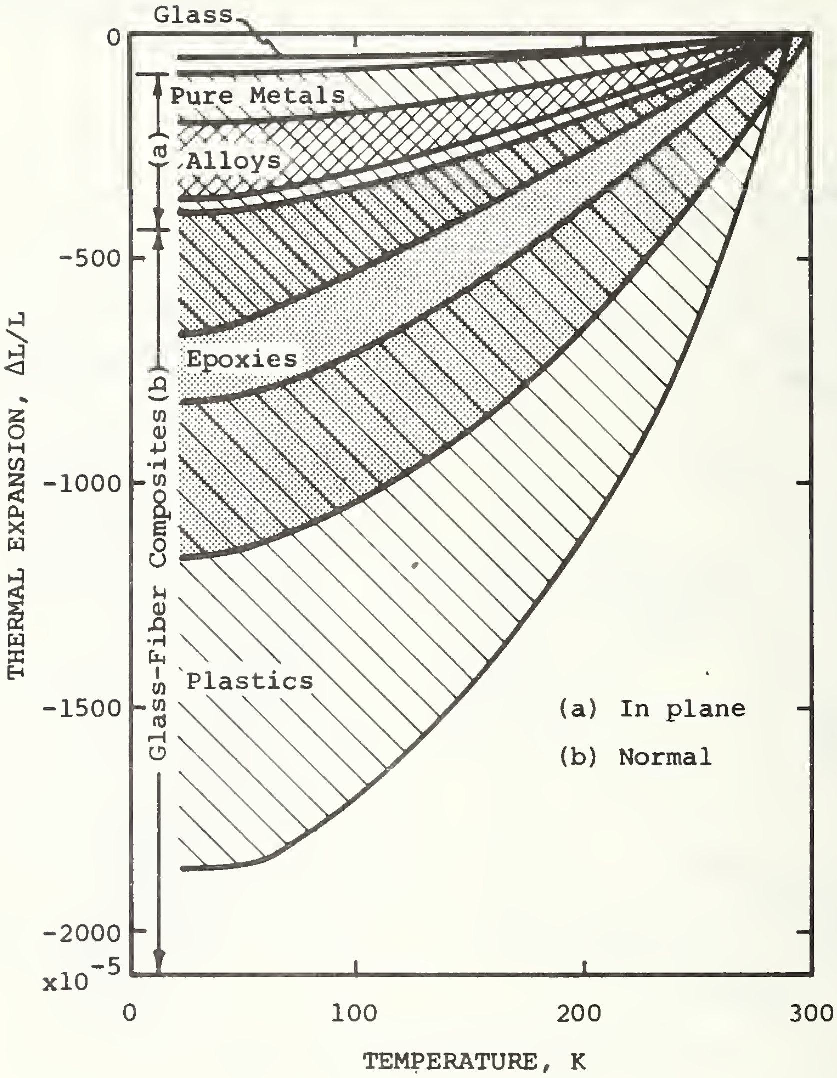

Figure 4.3 General behavior of the thermal contraction for several classes of materials.

Electrical resistivity data for pure metals are relatively abundant. The text by Meaden [35] contains extensive resistivity data and in addition is an excellent introductory treatise. Hall [36,37] has compiled the low temperature resistivity of selected pure metals. Electrical resistivity data sources for alloys are much more scarce, probably because of the lack of theoretical interest. A paper by Clark [38] contains low temperature data for selected alloys at low temperatures.

Non-metals, like metals, tend toward brittleness as temperature is lowered; a few non-metals remain sufficiently ductile at low temperatures to be structurally useful, e.g., polytetrafluoroethylene (TFE) and hexaflouropropylene (FEP). Creep in polymers is relatively large and can be a problem in certain applications. Non-metals often are useful in hydrogen applications involving insulations, supports, bearings, seals, and structural reinforcing composites. A review of the state-of-the-art on composites is presently being prepared by Kasen of this laboratory [39]. Composites range widely in mechanical properties depending strongly on fiber orientation, matrix material, resin, temperature, etc. In general, they have very high strength-to-weight ratios and may find extensive applications in high-pressure and low-weight vessels and pipes. Typical stress-strain, thermal conductivity, and thermal contraction data are illustrated in figures 4.1, 4.2 and 4.3, respectively.

An excellent review of the mechanical properties of non-metals, including polymers, foams, ceramics and glasses, and composites is given by Wigley [23]. Extensive polymer property data are tabulated in the Encyclopedia of Polymer Science and Technology [40], by Schramm, et al. [29], and reviewed by Serafini [28].

4.2.2 Hydrogen Embrittlement, Diffusion and Permeation

As indicated earlier, hydrogen readily diffuses into most engineering materials. The presence of atomic and molecular hydrogen can cause significant degradation of the mechanical properties, i.e., embrittlement, of most metals. Embrittlement is the most severe technological problem encountered in the containment of gaseous hydrogen. A vivid example is the failure of several 5000 psi, 1300 cubic foot hydrogen gas vessels [41]. One of these vessels developed a 50 inch long crack at a weld seam. Three similar hydrogen containing vessels failed, while several identical nitrogen containing vessels were operated without incident for several years. Such incidents could be avoided through the use of more compatible materials or more sophisticated vessel design, but this may not be economically feasible in a larger scale commercial facility. Jewett, et al. [41] and Voth [42,43] describe many failures due to material embrittlement in vessels and gauges. Failures have been observed at as little as one-tenth design pressure. These incidents are cited to emphasize the need for material research and development so as to obtain hydrogen compatible, inexpensive materials.

Although it has been known for about 100 years that hydrogen can seriously degrade the mechanical properties of metals [44], the exact mechanisms by which this occurs are not clearly understood. It is now believed that hydrogen embrittlement can be classified into three categories: (1) hydrogen-reaction embrittlement, (2) internal-hydrogen embrittlement, and (3) hydrogen-environment embrittlement. Hydrogen-reaction embrittlement occurs as a result of chemical reaction between hydrogen and the base metal or some alloying element of the metal. Metals such as titanium, zirconium, niobium, and tantalum (exothermic occluders) form irreversible embrittling hydride phases. The decarburization of steels and the formation of high-pressure water vapor in copper voids and methane in steel voids are other examples of hydrogen-reaction embrittlement.

Both internal and environmental-hydrogen embrittlement are due to hydrogen atoms dissolving into the metal. The most widely researched area of internal embrittlement is that caused by electrolytic charging such as in a plating, cleaning, or pickling baths. Internal-hydrogen and hydrogen-reaction embrittlement problems are often encountered in metal and petrochemical processing facilities. Any hydrogen containing chemical solution is capable of producing internal-hydrogen embrittlement.

Hydrogen-environment embrittlement signifies the degradation of mechanical properties occuring due to the presence of hydrogen at the surface of the metal. This is also referred to as external-hydrogen embrittlement. Both internal and external-hydrogen embrittlement are reversible so long as the hydrogen is removed before crack formation commences. Internal hydrogen can be removed by high temperature heat treatment. Hydrogen-environment embrittlement, although probably closely related to internal-hydrogen embrittlement, is the most unique to a hydrogen economy and is the primary subject of this section.

Several reviews and compilations of data on hydrogen-environment embrittlement exist [41,45-64]. It is clear from these reviews that controversy exists as to the exact mechanism operative in hydrogen-environment embrittlement. One argument leads to the conclusion that hydrogen-environment embrittlement is distinct from internal-hydrogen embrittlement, and other arguments lead to the conclusion that both are manifestations of the same mechanism. The main argument for distinctly different mechanisms is that delayed failure, failure at constant stress below the normal strength of the metal after a time which may be hours or days, occurs only through internal-embrittlement. Embrittlement due to hydrogen-environment is immediate, and no increase in embrittlement is seen with exposure times as long as 100 days [41,54,60,61]. Otherwise, the behavior of the two types of embrittlement is quite similar. It is noted that early internal embrittlement studies on Inconel 718 indicated no susceptibility to embrittlement, but recent hydrogen environment studies showed Inconel 718 to be severely embrittled [41].

The degree of hydrogen-environment embrittlement is dependent on the base metal and its alloying constituents, the microstructure of the metal, strain rate, the surface condition of the metal (cracks, notches, pits, etc.), stress, the strength level of the metal, impurities present in the hydrogen environment, and probably other parameters not yet investigated. It has often been suggested that, at least in the case of steels which are the most thoroughly investigated metal class, metals with a fcc structure are relatively immune to embrittlement while metals with a bcc structure are severely embrittled. It has been shown more recently that the crystal structure is less significant than the atomic structure [52]. More specifically, Louthan [52] has shown a close relationship between hydrogen solubility, and subsequently the degree of embrittlement, and the density of states at the

Fermi surface. Chandler and his associates at Rocketdyne [41,54,60,61] have compiled and reviewed all but the most recent hydrogen-environment embrittlement data. To avoid an overwhelming list of references, their reviews are the principal source of information here.

The Rocketdyne group has shown that the degree of embrittlement is approximately proportional to the square-root of pressure until saturation occurs, which is generally several thousand pounds per square inch. Internal-embrittlement generally peaks near ambient temperatures and falls off both at high temperatures and at low temperatures. No hydrogen-environment embrittlement is expected at liquid hydrogen temperature with common structural materials. At higher temperature, such as encountered in engines, burners, and proposed hydrogen production equipment, both hydrogen-environment and reaction embrittlement problems are likely [41,65,66]. In addition, at high temperatures and pressures, the containment material will become saturated with hydrogen. If cooldown of the equipment is not controlled, to allow the internal hydrogen to escape by permeation, classical internal-hydrogen embrittlement may result at ambient temperature. Groeneveld [67] has observed blistering of A387 and A52 steels after cooldown from a high temperature and pressure hydrogen environment. Troiano [68] indicates that degassing by cyclic temperature control to remove hydrogen in refining operations is standard procedure. Gray [49] notes that embrittlement may also occur in a liquid hydrogen vessel if the ullage space material approaches ambient temperature.

Rate of strain is an important parameter in the degree of embrittlement exhibited. Low strain rates promote maximum embrittlement. Smooth surfaces are least susceptible to embrittlement. Metals conditioned to high strength levels are more susceptible to embrittlement than their lower strength counterparts. This effect is especially important in weldments or localized hard spots. Table 4.1 illustrates the relative degree of embrittlement of metal classes. The relative scale used is the same as that defined by Chandler, et al. [41]. Table 4.2, taken from a most recent publication by Chandler and Walter [69], illustrates more specifically the embrittling effects on metals as indicated by notched and unnotched strength ratios and unnotched ductility.

The purity of the hydrogen environment can have profound effects on the degree of embrittlement. Small amounts of oxygen, in some instances, have totally destroyed the embrittling capability of hydrogen. Small additions of SO_2, CO, and CS_2 are also effective in inhibiting hydrogen embrittlement. Chandler, et al. [41] and Fidelle, et al. [70] have investigated the effects of metallic and oxide coatings to inhibit embrittlement. Chandler, et al. [41] feel that an effective coating must have low permeability, be non-porous, adhere well to the substrate, and be ductile or self-healing. He has found that electroplated coatings of copper, gold, and silver are effective barriers. Chandler [71] is continuing his work on aerospace alloys and is also carrying on discussions with the Institute of Gas Technology to determine the significance of embrittlement on pipeline materials. He indicates that, although embrittlement is most important at ambient temperatures, creep and low cycle fatigue are affected at high temperatures. A286 stainless steel, for example, is relatively immune at room temperature but is appreciably affected at elevated

Table 4.1. Relative degree of hydrogen-environment embrittlement of classes of metals.

Degree of Embrittlement	Materials	Characterization
Extreme	High strength steels Nickel-base alloys	Large decrease in notch strength and notched and unnotched ductility. Some decrease in unnotched strength. Propagation of surface cracks.
Severe	Ductile, lower-strength steels Pure nickel Titanium alloys	Considerable reduction of notch strength and unnotched and notched ductility. No reduction of unnotched strength. Propagation of surface cracks.
Slight	Metastable 300 series stainless steels Beryllium-copper Pure titanium	Small decrease in notched Strength and unnotched ductility. Failure of unnotched specimens from within.
Negligible	Aluminum alloys Stable austenitic stainless steels Copper.	Essentially unembrittled with no surface cracks.

Table 4.2 Embrittlement of Metals by 68.9 MN/m^2 (10,000 psi) Hydrogen at Ambient Temperature, Chandler and Walter [69].

	Strength Ratio, H_2/He		Unnotched Ductility			
			Elongation Percent		RA* Percent	
Material	Notched (K_t=8.4)	Unnotched	He	H_2	He	H_2
18 Ni-250 MAR	0.12	0.68	8.2	0.2	55	2.5
410 SS	0.22	0.79	15	1.3	60	12
1042 QT	0.22	---	--	--	--	---
17-7PH SS	0.23	0.92	17	1.7	45	2.5
Fe-9Ni-4Co-0.2C	0.24	0.86	15	0.5	67	15
H-11	0.25	0.57	8.8	0	30	0
Rene 41	0.27	0.84	21	4.3	29	11
Electroformed Ni**	0.31	---	--	--	--	--
4140	0.40	0.96	14	2.6	48	9
Inconel 718	0.46	0.93	17	1.5	26	1
440 C	0.50	0.40	--	--	3.2	0
Ti-6Al-4V (STA)	0.58	---	--	--	--	--
430 F	0.68		22	14	64	37
Nickel 270	0.70		56	52	89	67
A-515	0.73		42	29	67	35
HY-100	0.73		20	18	76	63
A-372 Class IV	0.74		20	10	53	18
1042 Normalized	0.75				59	27
A-533-B	0.78				66	33
Ti-6Al-4V (annealed)	0.79		--	--	--	--
AISI 1020	0.79				68	45
HY-80	0.80				70	60
Ti-5Al-2.5Sn ELI	0.81				45	39
ARMCO Iron	0.86				83	50
304 ELC SS	0.87				78	71
305 SS	0.89				78	75
Be-Cu Alloy 25	0.93				72	71
310 SS	0.93				64	62
Titanium	0.95				61	61
A-286	0.97				44	43
7075-T73 Al Alloy	0.98				37	35
Incoloy 903**	1.00				50	47
316 SS	1.00				72	75
OFHC Copper	1.00				94	94
NARloy-2***	1.10				24	22
6061-T6Al Alloy	1.10				61	66
1100-0Al	1.40				93	93

Identification of a manufacturer and a manufacturer's product in this table has been necessary to make the results of this work meaningful and in no way implies a recommendation or endorsement by the National Bureau of Standards.

* RA=reduction in area

**Tested in 48.3 MN/m^2 (7000 psi) H_2

*** Rockwell International Corporation Trademark; tested in 40 MN/m^2 (5800 psi) H_2

temperatures (see also [72]). He also notes that little work has been done on crack growth at high temperatures. Chandler [41] says it is safest to assume a metal embrittles unless proven otherwise. Only aluminum alloys, austenitic stainless steels, and copper have been shown to be reasonably immune. Hydrogen embrittlement does not significantly affect elastic properties; most affected are tensile ductility, notch strength, fatigue, and crack behavior and creep.

Vented multilayer vessels have been used successfully to reduce failures due to embrittlement [73,74]. Filament-wound containers with an impermeable metal liner have been developed for aerospace applications [75-81]. These may be very useful in a hydrogen economy. Life prediction for high temperature hydrogen materials, based upon Nelson curves [82], has been common procedure to prevent unexpected failure. Extrapolation of these curves should be avoided.

No evidence has been presented which indicates serious embrittling effects of hydrogen on non-metals. However, very little work has been done in this area; the only work on non-metals compatibility is being done at White Sands Test Facility, New Mexico [83,84]. Preliminary results indicate that, of room temperature vulcanizing silicone rubber (RTV), polyvinyl chloride (PVC), polytetrafluoroethylene-hexofluoropropylene copolymer (FEP), polytetrafluoroethylene (TFE), glass filled TFE and cellulose acetate butyrate (CAB), only RTV is adversely affected by hydrogen. A slight charring of RTV was observed during hydrogen environment impact tests.

Thermal conductivity and electrical resistivity of pure metals can be strongly affected by impurities in solids, including gases such as hydrogen. In impure metals and alloys the effect is small and in most cases undetectable. Other thermal properties are not significantly dependent on hydrogen content. Structural design will not significantly depend on the effect of hydrogen on thermal and electrical properties.

Since hydrogen diffuses and permeates through materials and flows through crevices more readily than other gases, the often mentioned, potential problem of hydrogen leakage deserves attention. The permeation of hydrogen through metals is well below the level which would cause any safety or economic difficulty. Permeation through polymers, although much larger than through metals, is not expected to be a problem in plastic gas pipes. Figure 4.4 illustrates the approximate hydrogen permeabilities of metals and polymers. The principal area of concern for hydrogen leakage is in seals and cracks. Beck [46] reviews methods of low level hydrogen detection and quantitative measurements. These methods are useful both for permeation studies and for hydrogen content determinations. Powell, et al. [85,87] have recently described a very sensitive hydrogen content measuring device. Berman, et al. [88] have developed a thermochemical technique which is precise to 0.1 ppm, rapid, and is applicable to in-situ measurements. Jankowsky [89] has compared other test methods of hydrogen detection in metals.

4.2.3 Insulation

As envisioned, the hydrogen economy would involve large quantities of liquid hydrogen for convenient transport by ocean tankers, trucks, and by rail, for convenient storage, and for use in ground vehicles and aircraft. Liquid hydrogen, because of its low boiling temperature (20 K, -253°C) and its low volumetric latent heat of vaporization (7.5 kcal/liter),

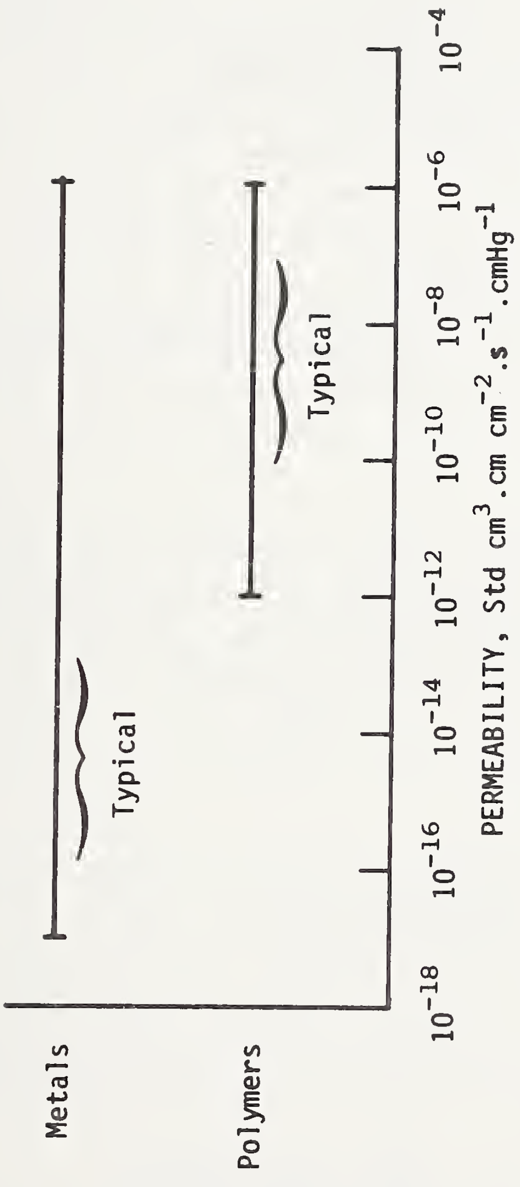

Figure 4.4 Permeability ranges of metals and polymers (ambient temperature).

must be extremely well insulated to minimize fluid boil-off losses.

Except for the relatively recent advent of multilayer insulation, few significant improvements in economic insulation technology are noted. Most of the recent hydrogen-insulation work is directed toward improved insulation systems rather than material development [73,74,90-110]. Recent reviews on insulation technology are extensive [73,111-115]. These describe systems of measurement, give comparative data on the thermal conductance of various insulations, comparative costs, weight, etc. Insulations commonly used for liquid hydrogen storage are vacuum with liquid nitrogen shield, and evacuated foams, perlite, silica gel, and superinsulation. Comparative heat losses are illustrated for these in figure 4.5. Thermal conductance is illustrated in figures 4.2 and 4.5.

For the lowest conductance insulations, such as superinsulation, a large proportion of the heat loss is through thermal bridges. Examples of these thermal bridges are structural supports, seams, and holes through which thermal radiation penetrates.

Not all systems will require the same degree of insulation quality. This is determined primarily by a trade-off between insulation system (material) cost and boil-off losses or hold time. For example, in an automobile storage vessel, the relative boil-off may be quite high because the tank is generally emptied in a few days at normal rates. In a large stationary storage vessel, relative boil-offs need to be small because of the large absolute losses involved. Thus, various insulation qualities will be required for different applications.

Although relatively small improvements can be predicted in insulation quality, these can be very significant economically because of the absolute magnitude of hydrogen losses in a hydrogen economy. More significant benefits are to be expected from improved insulation systems development. Standardizations of low heat flux measurements and the availability of standard reference materials would be beneficial in determining the most economic and effective insulating materials. The only effort related to the development of standard reference materials is that by Ludtke [116] to develop a series of low temperature transfer standards.

Thermal conductivities of insulating materials are strongly dependent upon the compaction (density) of the insulating material, the type and pressure of the gas on the insulation space, and the reflectivity of the insulation surfaces. Howell [117] indicates that the principal problems with insulations are: hydrogen permeation of internal foam systems and cell breakdown for external foam systems, insulation and bonding integrity under the stresses induced by thermal cycling, and vacuum leaks with superinsulation and other evacuated insulation systems. Thus, the principle insulation requirements are systems design improvements and measurement standardization.

4.2.4 Oxygen Compatibility

Regardless of the method used to produce hydrogen from water, oxygen is a by-product. Oxygen use has been growing at the rate of about 18% per year [118] (comparable to the growth of hydrogen production) and it is expected that this rate will persist or, more probably, increase. Mrochek [118] indicates a potential oxygen credit of 4$/ton of oxygen, but this is highly uncertain unless applications requiring huge amounts of oxygen are

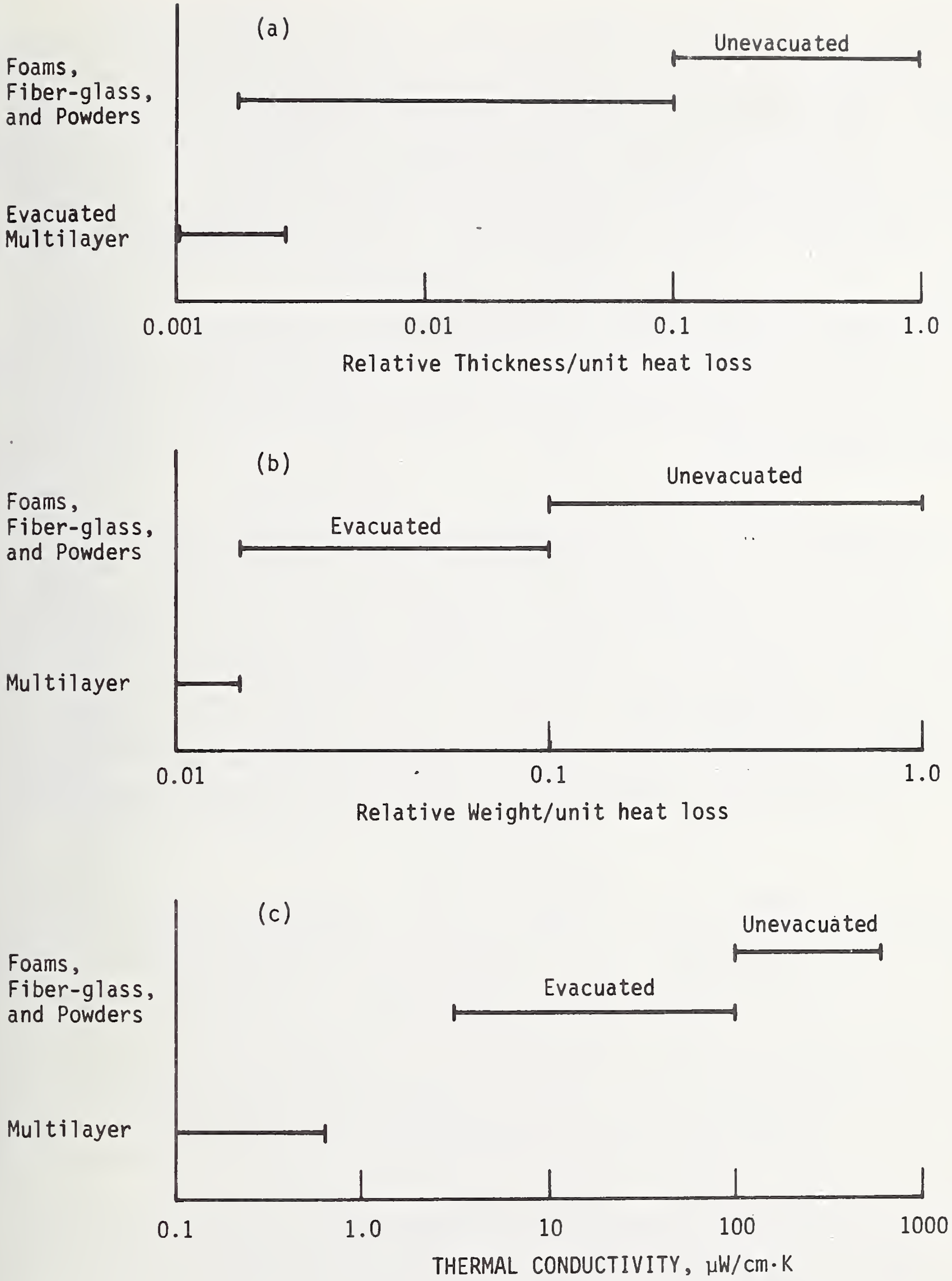

Figure 4.5 Comparative data for selected insulations.

developed. If this oxygen can be used we are faced with oxygen containment problems. Oxygen compatibility problems have been encountered in the space program and can be severe. The principal problem area is associated with the combustion (rapid oxidation) of the containment structural materials. It has been found that almost any material will burn in the presence of pure oxygen, especially at high pressures. This includes not only the common combustible materials but also metals and most other structural materials. A recent survey on the subject is cited [119]. This review confirms that the problems are significant, must be given serious attention in any high pressure or high temperature application, and cannot be ignored even at ambient conditions. The oxygen compatibility of metals and polymers has been investigated most extensively. Few polymers are compatible with high pressure oxygen. Metals are generally much more compatible, but the degree of combustibility varies widely from metal-to-metal. The degree of oxygen compatibility of ceramics is not extensively studied, but it is expected to vary widely according to the chemical composition of the ceramic. Oxide ceramics, for example, should be the most compatible and better than most metals.

4.3 MATERIALS REQUIREMENTS FOR HYDROGEN PRODUCTION

The primary sources of hydrogen gas production have been the steam reformation of natural gas, the petrochemical industry [120-122] and more recently from water by electrolysis [3,118,123]. As our dwindling fossil fuels are reserved for more essential purposes, more hydrogen will be obtained from water. Electrolysis of water requires an amount of electrical energy comparable to the energy stored in the hydrogen fuel produced. Thus, an immense electrical economy based on non-fossil fuels will need to be developed. This, in all probability, will be based on nuclear or solar power. Therefore, the materials requirements for the production of hydrogen fuel are closely linked with those of non-fossil fuel power generation as well. First, we direct our attention to the material requirements for the generation of hydrogen by electrolysis and other water decomposition processes.

4.3.1 Electrolysis

Water electrolyzer technology has developed to yield efficiencies of about 60% for large scale plants [4,11]. Gregory [2] points out that the maximum theoretical efficiency, based on electrical input energy, is 120%. The additional 20% comes from the thermal energy input to the electrolyzer. Since present efficiencies are only about 60%, it is reasonable to assume that sizeable gains in efficiency will occur with improved designs and materials. Efficiencies can be increased with the development of better electrode materials and configurations, to lower the overvoltage and internal resistance losses of the cells, and by operating the cells at higher temperatures and pressures. Kincaide [124] indicates an increase in efficiency of 15% is possible by operating at 700°C. It is noted that such increases in efficiency generally are accompanied by increased capital equipment costs. The structural material corrosion resistance requirements at increased temperatures will present a formidable materials development challenge. On the huge scale of production involved in a hydrogen economy, a few percent increase in efficiency represents billions of dollars in production cost savings per year in the U.S. alone.

Gregory [2] indicates that General Electric and Westinghouse are developing units for operation near 2000°F. Teledyne Isotopes is developing a high temperature unit for operation at a pressure of 3000 psi. Each of these involve materials corrosion and embrittlement problems because of the high temperatures and pressures.

Electrolyzers are generally built in modular form [2,124] and could be scaled-up readily to the plant size required at a nuclear power plant site without additional materials problems. The largest electrolyzer plants now operating are about one-tenth as large as will be required. The main materials requirements for electrolyzers are those affecting cost and longevity.

4.3.2 Thermochemical

Water can also be decomposed by thermochemical decomposition. Thermochemical decomposition is appealing since thermal energy can be utilized directly without first generating electrical energy, a thermodynamically inefficient conversion at present.

The production of significant proportions of hydrogen by direct thermal decomposition requires a temperature of about 2500°C [11] and is generally considered as impractical and inefficient with existing heat sources.

Significant effort is being devoted to the development of efficient, lower temperature, thermochemical decomposition processes [11,125-128]. These processes are composed of multi-step chemical reactions from water to hydrogen at temperatures below 1000°C [8,124,126]. The proposed chemical reactions involve highly corrosive chemicals, such as high temperature hydrobromic acid, further compounding the materials problem. Since the number of potentially useful processes is essentially limitless, no specific material requirements can be specified until a particular process is adopted. It is likely that structural material requirements related to thermochemical hydrogen production will include high-temperature strength, corrosion resistance, and relative immunity to hydrogen embrittlement. Potentially useful materials are noble metals, graphite, and ceramics, such as aluminum oxide [129,130].

4.3.3 Other Production Methods

Steam reforming of hydrocarbons is a common method of hydrogen production. The materials requirements for the extensively used method are well understood. Common structural steels find wide application in the petrochemical industry in spite of existing serious hydrogen-related materials problems [68].

Bockris [125] and Maugh [11] describe more exotic methods of hydrogen production. For example, the very high temperatures of a fusion reactor could be utilized to generate photons with the correct energy to decompose water. Because of the highly speculative nature of those techniques and the enormous basic developments which must precede their application, it does not seem prudent to speculate on potential material requirements.

4.3.4 Hydrogen Liquefaction and Solidification

Because of the low density of hydrogen gas, many volume-limited applications, such as ground and air vehicles, are not well suited to the use of hydrogen gas. Also, cross-country gaseous hydrogen transfer by truck or stationary hydrogen gas storage is impractical. Therefore, hydrogen is often liquefied or solidified to increase its density for more compact storage. Liquid or slush (mixture of liquid and solid particles) hydrogen is considered to be the most viable option for use in aircraft [6,92,131,132] and as a somewhat less attractive option for ground vehicles [11,133]. If these applications develop, a sizeable proportion (25%) of the total hydrogen usage will be in the form of liquid or solid. This liquefaction capability will dwarf present facilities [133].

Bartlit, et al. [133] indicate that the largest existing hydrogen liquefaction facility has a capacity of 60 tons/day. They feel that considerably larger plants can be built with no additional technology development.

Daniels [13] has indicated that a material problem with turbine blade tips may develop in large scale turbine expanders. Excessive blade erosion due to droplet impingement may result.

4.4 MATERIAL REQUIREMENTS FOR HYDROGEN TRANSFER AND STORAGE

Hydrogen produced at the power plant, possibly several miles at sea, must be transported to the user site. Because usage rate fluctuates widely, large storage facilities will be required for the storage of gaseous, liquid, or solid hydrogen. Hydrogen in gaseous, liquid, or slush form can be transported by pipeline or mobile tanks. Considerable experience has been gained in the space program on the transfer and storage of liquid hydrogen [42,73,74, 91,112,134-139]. This experience shows that hydrogen in large quantities can be handled safely with no serious materials problems.

4.4.1 Gaseous Hydrogen

The principal problems to be expected in the transfer and storage of gaseous hydrogen at ambient or high temperature are embrittlement and leakage. Embrittlement is most significant at high pressures and ambient temperature and is also significantly influenced by the purity of the hydrogen.

Relatively impure gaseous hydrogen has been handled for commercial and industrial applications for many years [2-5,8,133] with no serious material failures. Based on recent experimental results, this is partly because the hydrogen transferred is not of the extremely high purity used in the space program and in laboratory research. "Town gas" or "manufactured gas" used during the past decades in the United States and still being used abroad is approximately 50% hydrogen. Basilea, Italy distributes a gas containing 80% hydrogen for domestic use [133]. Gregory [2] and Daniels [13] indicate that Germany operates several hundred kilometers of hydrogen pipeline at a pressure of 200 to 700 psi. No special safety features beyond those for other flammable gases are used. The pipe is seamless steel St.35.29 grade, similar to SAE 1015. Other shorter hydrogen gas pipelines are in service such as the 8 inch diameter, 12 mile long pipeline, operated at 200 psi by Air Products and Chemical, Inc. in Houston. No booster compressors are found along any of the pipelines because of their relatively short lengths. Extensive storage experience also exists through the commercial use of hydrogen cylinders operated to above 2000 psi. These are hot-forged monolithic carbon steel cylinders; it is likely that the lack of hydrogen related incidents is due to the lack of severe metallurgical variations such as those produced in a weld zone.

Research has been conducted for several years at Battelle Memorial Institute [140] to determine the effects of cathodic hydrogen-charging on pipeline materials. Steels with 61 ksi to 181 ksi yield strengths were tested under laboratory conditions. They concluded that pipeline steel materials with yield strengths below 130 ksi would present no problems under the usual ground water conditions. Groenveld, et al. [140] also performed field studies of up to 8 years with buried sections of pipe. Their field results are consistent with the laboratory results. This is a study of internal hydrogen embrittlement. Based on the results of Chandler [60] on hydrogen environment embrittlement similar field tests for hydrogen-environment embrittlement should also be conducted on pipeline materials.

Although hydrogen transfer and storage systems are envisioned to be relatively low pressure (below 2000 psi), the storage pressures of hydrogen gas, in some instances, is much higher. And, in addition, the purity of the hydrogen can be very high. Both of these factors contribute significantly to the embrittlement problem. Several instances have been cited of failures of high pressure gaseous hydrogen storage tanks and gauges [41, 42,48,53,141,142]. Fortunately, none of these failures attained their full potential destructiveness, and loss of life and property damage has been relatively small. In many of these high pressure failures, material fracture has occurred far below design strength.

Embrittlement is the most serious material problem in a hydrogen economy and should receive considerable support for materials development and a more thorough understanding of hydrogen-environment embrittlement phenomena. Studies should be conducted on well-characterized research materials under controlled laboratory conditions and on specimens obtained from production run material; tests under actual field conditions. Embrittlement of hard spots and welds, including the heat affected zone, has been especially troublesome and must be closely scrutinized. Gaseous hydrogen-environment embrittlement has been researched primarily in connection with the NASA space program [41,50,51,53,54] but considerable work remains to obtain a complete understanding of the mechanisms involved, to be able to develop more immune materials, and to obtain design data for existing materials. Plastic pipelines for hydrogen transfer should be researched to determine if any degradation occurs and which materials are most compatible, especially from the standpoint of permeability. Another area which should be investigated is the effect of additives, such as odorants, to gaseous hydrogen. Additives may either enhance or inhibit crack growth of containment materials.

4.4.2 Liquid and Frozen Hydrogen

Commercial and government liquid and slush hydrogen handling experience has been primarily in conjunction with the NASA space effort and related research [73,74,76,112,120, 133-135,143]. The main research efforts in the space program have been directed toward pump, transfer line, storage vessel, and insulation development [77,78,91,134,138,139, 144-146].

Long distance transport of liquid hydrogen is now routinely accomplished with trucks (13,000 gallon capacity) and railroad tankers (28,000 gallon capacity). Because of the low density of liquid hydrogen (71 grams/liter) these vehicles are limited by volume, not weight. Boil-off losses of 1/4 percent per day are typical and for larger vessels the losses can be maintained at smaller levels. Over shorter distances (a few thousand feet), vacuum jacketed transfer lines of inside diameters up to 20 inches and pressures up to 2000 psi are in use [133]. Bartlit [133] also points out that reciprocating, centrifugal, and axial flow pumps for a wide range of pumping volumes have been developed. At the Nuclear Rocket Development Station in Nevada, for example, liquid hydrogen has been pumped at rates up to 35,000 gallons/minute. Based primarily on NASA experience, the principal technological material problems with liquid and slush hydrogen transfer have been with pump bearings and seals, and economic insulation techniques [92,142,144,146-150]. Because of the lack of extensive experience, pump wear problems for continuous long term slush hydrogen transfer are not definitive.

Storage vessels exceeding 500,000 gallons of liquid hydrogen are in use with boil-off rates on the order of 0.05%/day. This is equivalent to a hold time of over five years. The largest dewar built has a capacity of 900,000 gallons and Bartlit [133] indicates that no further materials development is needed to go to four or five million gallon capacity, which approaches the volume required for the needs of a hydrogen economy. The current cost of such vessels is about $2.00 per gallon capacity. It is likely that liquid hydrogen will be a strong contender in transportation applications. A liquid hydrogen storage vessel for automotive use has been developed [133]. It is estimated that on a mass production basis these will cost from 300 to $600. Research to develop lower cost structural materials, insulations, and fabrication techniques (such as the development of filament wound composite vessels) could result in substantial economic savings.

If hydrogen is generated at sea-based plants it must be transported to land for use. Large liquid hydrogen tanker ships or barges [151] similar to the liquid natural gas ships now in use [152], may be the most attractive form of transfer. The insulation requirements for a liquid hydrogen tanker will be more severe because of the lower boiling temperature; however, the weight requirements (structural strength) will be reduced because of the lower density of liquid hydrogen. Several million pounds of steel are used in the liquid containers of a large LNG tanker and huge quantities of insulation are also required. Similarly large quantities of steel and insulation are required for stationary storage vessels. The reduction in capital cost, through a few percent reduction in material costs because of new materials development, is an obvious benefit.

The economics of piping liquid versus alternate methods of delivering liquid hydrogen are examined in Chapter 6. Liquid hydrogen transfer through pipelines may be more economically feasible if it is combined with the transfer of electrical energy, via a low resistance or a superconducting transmission line [153,154]. Another combination is the transfer of liquid hydrogen, liquid natural gas, and electric power [133]. Novak [155] discusses a potential problem of cooldown flowrate limits imposed by thermal stresses. No technological material breakthroughs are required in these proposed applications, but improved low cost insulations, structural materials, and fabrication procedures may help to provide an economically competitive system.

4.4.3 Hydride Storage

Hydrogen can also be stored by chemically combining it with various metals as a hydride. With the application of heat the hydride is dissociated and hydrogen gas is released for use. Hydrogen densities larger than liquid hydrogen densities can be obtained by this method and, therefore, it is of strong current interest [156-160]. The main drawback at the present time, for mobile applications, is the very high overall weight and volume of such systems. Further research is warranted for the development of lightweight, inexpensive materials which absorb large quantities of hydrogen and readily liberate hydrogen at near-ambient temperatures and pressures. The concept of hydride storage systems is especially appealing for stationary applications.

4.5 MATERIALS REQUIREMENTS FOR HYDROGEN APPLICATIONS

The most prominent uses of hydrogen at present are in the petrochemical industry and in the production of methanol and ammonia [121]. Hydrogen is also used in rocket propulsion and in commercial hydrogenation. The experience gained through the space program has been monumental and the amount of liquid hydrogen used has dwarfed any other past applications [133,143]. Hydrogen has been used both in gaseous and liquid forms and preliminary research has been performed on the use of hydrogen in slush form because of its higher density [137,139,146,161-164]. Liquid and slush hydrogen are especially appealing for use in aircraft and space vehicles.

In a hydrogen economy the emphasis in applications would change such that the major portion of hydrogen would be used for space heating, commercial and domestic propulsion systems, and the generation of electric power; that is, almost anywhere that fuel oil, kerosene, gasoline, and natural gas are used today. The following sections discuss the materials requirements imposed by the use of hydrogen for such applications. Because the limitations of hydrogen-material compatibility are not yet well understood, considerable effort must be directed toward equipment, material, and regulatory developments before a hydrogen-economy can be realized.

4.5.1 Heating

Hydrogen can be used for heating with some modifications in existing heating systems. Space heating with hydrogen is appealing because of the potential of reducing flue heating losses and a resultant gain in heating efficiency. The compatibility of materials in existing systems has not been studied.

The advantages of using hydrogen for space heating can best be realized with conceptually new heating devices [165]. These devices would be based on flameless catalytic conversion of hydrogen and oxygen to water. Through the use of various catalysts one can achieve a wide range of combustion temperatures, ranging from temperatures in the cryogenic range to 3000°C. Thus one can visualize a wall radiator heating a room by catalytically combusting hydrogen in the wall at a temperature of 80°F or a burner on a stove operating at 212°F, etc. Most of the past work has centered on classical catalytic materials such as platinum and nickel but recent interest in the catalysis of the $H_2 - O_2$ reaction has brought other materials under investigation [166-174]. Some of the materials being studied are silicon carbide, thorium, platinum, nickel, silver, transition metal carbides, and copper.

The potential catalyst market in domestic applications is large and warrants sizeable materials research. Studies should be directed toward the development of economic catalytic materials for applications over wide temperature ranges.

4.5.2 Propulsion

The application of hydrogen fuel to propulsion, including automobiles, buses, trucks, boats, small ships, aircraft, and spacecraft, represents a major undertaking. However, the technical feasibility of converting conventional engines, both reciprocating and rotary, has been demonstrated [10,131,132,175-181]. These conversions include a railroad engine which operates on hydrogen fuel [182], but railroads are equally adaptable to electrical power. Large ships may be better propelled by nuclear power, except in special instances, such as fuel tankers where boil-off or part of the fuel load itself can be used for energy.

Experience with hydrogen operated engines is still limited, but it appears that problems will be minor except in high pressure (above 2000 psi) applications. Jewett, et al. [41] feel that many hydrogen-related materials problems will arise in the development of hydrogen fueled engines. They strongly recommend doing tests on components for hydrogen service equipment under operating conditions. Frick, et al. [65] have observed high temperature embrittlement on Udimet; water had no inhibiting affect. Udimet is a space shuttle main engine alloy. Quandt [183] is planning further research on hydrogen fueled gas turbines. The principal concern in this area is again related to embrittlement phenomena.

Bartlit [184] has indicated the LASL is undertaking an extensive project to convert an automobile to hydrogen fuel and to build a prototype refueling station. A liquid hydrogen tank for the vehicle is being built and impact tests are planned to test the material integrity. They feel the structural integrity should be sufficient to withstand impacts which an occupant can survive.

4.5.3 Electric Power Generation

Hydrogen will also find application for domestic and commercial electric power generation through the use of fuel cells and hydrogen fueled engines. The present efficiency of large fuel cells is about 60% and the maximum efficiency is 83.5% at 25°C [2,166]. Thus considerable improvement is possible through the development of more effective electrode materials, higher operational temperatures and pressures, and more efficient design. Similar to the existing situation for electrolyzers, a small percentage increase in efficiency can amount to millions of dollars in energy and cost savings.

Austin [166] performed an extensive survey of government sponsored research on fuel cells and this work is also an excellent sourcebook of information on the state-of-the-art and the principles of operation of fuel cells. Included in this work is a section on materials compatibility, listing many structural materials and their usefulness with various fuel cell chemicals. Some advances have been made since this review, but currently realized efficiencies suggest that his recommendations are still valid. He recommends research to improve the efficiency of fuel cells through the development of more effective electrodes and electrolytes. He also recommends research directed toward the reduction of the amount of expensive catalytic materials required, often platinum, and the development of less expensive catalysts. It has been indicated that the thickness of catalytic coatings has reached a lower limit (1 mg/cm^2) [13] thus necessitating cheaper materials for further cost reduction. Another area which requires attention is the effect of additives or impurities in hydrogen on catalytic materials. Poisoning of catalytic materials can seriously shorten the life of these materials. A more complete and recent review of fuel cell technology is presented by Berger [166a].

Fuel cell power capacities have increased into the kilowatt range, which are adequate for many domestic and industrial applications. Units with capacities in the megawatt range are currently under development. Such units will be used for electric power generation.

The application of hydrogen fueled engines to generate electric power has been described [144,176,177]. The materials requirements with these engines are the same as those described in the propulsion section.

In summary, materials requirements are dictated by higher temperature and pressure operations of fuel cells; improved, lower-cost catalytic materials; and, again, structural materials resistant to corrosion and embrittlement.

4.6 RECOMMENDATIONS

As indicated earlier, it is difficult to recommend specific research in a given area until existing data is critically evaluated and applications are well defined. Such a situation does not totally exist for the requirements of a hydrogen economy; however, based on the previously mentioned recent reviews on various phases of this subject, the following are recommended.

4.6.1 Structural Materials Research

(1) Perform on a continuing basis: compilations, reviews, critical analyses and evaluations, and select best materials on the basis of physical properties data and compatibility.

(2) Perform embrittlement studies over a wide range of applicable conditions on materials selected as a result of (1) to: (a) obtain a better understanding of embrittlement mechanisms, (b) determine how embrittlement depends on microstructure, temperature and pressure, stress, strain rate, composition and other pertinent parameters, (c) determine effective inhibiting additives and protective coatings, and (d) develop reliable and reproducible test methods for embrittlement characterization. Develop non-destructive test methods and life prediction techniques to detect or avoid incipient failure of structural material. Acoustic, eddy current decay, and other NDT techniques should be studied for application. Research should also be directed toward an evaluation of existing and new theories [186-190] of embrittlement.

(3) Perform mechanical and thermal properties measurements, especially at low temperatures, on existing materials lacking in characterization and on new materials, especially metals and composites and also polymers, ceramics and insulations.

(4) Develop new light-weight, high-strength materials for fabrication of vessels and transfer lines. Examine the applicability of composite materials (e.g., filament wound vessels) to domestic equipment. Direct research toward the development of low-cost, mobile vessels for application to automobiles, aircraft, and ocean tankers.

(5) Consideration should be given to novel designs, for maximum use of unique material properties and minimization of the developing material scarcity problem.

4.6.2 Insulation Research

(1) Improve standardization of low heat-flux measurement systems and develop standard reference materials to improve reliability of measurements and facilitate accurate intercomparisons.

(2) Perform research on existing and new insulation materials directed toward the development of lower cost insulations and more effective system designs to minimize heat losses, especially at thermal bridges.

4.6.3 Catalytic Material Research

Perform research on existing and new catalytic materials to obtain lower-cost, more efficient materials. Research should optimize the quantity of material required in a catalytic device and recovery systems should be studied for material conservation. The effect of hydrogen gas impurities and additives on the efficiency and life expectancy of catalytic materials should be studied. Methods of reactivating poisoned catalysts should be investigated.

4.7 ACKNOWLEDGMENTS

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4.9 APPENDIX

LIST OF RECENT AND ON-GOING HYDROGEN RELATED MATERIAL RESEARCH

Material research directed toward hydrogen applications is abundant. A listing of the recent and current research is desirable to plan future research. The literature collected for this investigation contains information regarding recent efforts. In order to obtain a more complete listing, the following files were also searched for hydrogen related materials research: Smithsonian Scientific Information Exchange, An Inventory of Energy Research by Oak Ridge National Laboratory, and the NASA Research and Technology Operating Plan. The more pertinent of these efforts are listed in that which follows. A listing of facilities, at which hydrogen related materials research has been recently conducted, is also included. The principal fields of interest are indicated. Because of the large number of investigations which pertain in some manner to the applications of hydrogen and oxygen, some significant omissions exist. For these unintentional omissions, the author apologizes.

4.9.1 Material Development Projects

Title: Thermodynamic and Other Studies of Metal/Hydrogen Systems
Contact: K. A. Moon
Institution: U.S. Army, Materials & Mechanics Research Center, Watertown, Boston, Massachusetts 02172

Summary: To obtain thermodynamic data for metal/hydrogen systems and to interpret the data in terms of interactions within the solids. Improved materials or material may result via: (1) Obtaining data directly applicable to materials design problems involving Ti, Zr, V, Nb, or Ta. (2) Improved understanding of interstitial solutes, H, B, C, N, and O, which profoundly affect strength, brittleness, and aging of metals. (3) Cooperation with other AMXRC investigators on more applied R&D involving joining or sintering techniques which employ metal hydrides.

Title: Composites
Contact: J. C. Freche
Institution: Lewis Research Center

Summary: The overall objective of this research is to develop fiber and laminate composite materials, structures, and components for various aeronautical applications. Temperature levels of interest range from cryogenic temperatures to over 250°F. The major objectives for the programs are as follows: (1) To develop or synthesize improved polymers suitable for use as matrix materials for temperatures up to 600°F. (2) To improve such properties of polymer matrices as thermo-oxidative stability, shear strength (in association with fibers) and toughness. (3) To develop carbon and boron fiber-polymer matrix composites with greater strengths, moduli, fiber matrix bonds and toughness.

Title: Interdisciplinary Laboratories for Materials Research
Contact: R. A. Lad
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objectives are to: (1) Obtain new understanding of the relationships between electronic, atomic, molecular and microscopic structures of solids and their useful mechanical, structural, electronic and chemical properties; (2) Employ the expertise existent in universities to obtain knowledge in these areas and to aid in determining the best directions to follow in improving existing materials and obtaining new materials of direct interest to NASA programs. Research topics include interatomic forces in solids, corrosion, diffusion, polymer rheology, composites, computer memory materials, hydrogen embrittlement, superconductivity, grain boundary mobility in ceramics, solid electrolytes, dispersion strengthening, electromigration, spacecraft coating materials, crystal growth, computer memory materials and others.

Title: Improved Performance Metallic Materials
Contact: H. Kato
Institution: U.S. Department of the Interior, Bureau of Mines, Albany, Oregon 97321

Summary: The objective is to develop metallic materials of construction specifically as follows: (1) Resistant to hydrogen embrittlement as encountered in pipeline steels contacting sour natural gas and oil. (2) Resistant to hydrogen fluoride-phosphoric acid media which may be abrasive aqueous liquids or humid vapors at temperatures to 200°C. (3) Resistant to chlorine and chlorine containing sulfur at temperatures to 650°C.

Title: High Strength Materials
Contact: V. F. Zackay
Institution: University of California, Lawrence Berkeley Laboratory, Berkeley, California 94720

Summary: Relationships between chemistry, microstructure and mechanical properties are being developed to allow design of materials with superior combinations of strength, ductility and toughness. The effects of lowering the stacking-fault energy (thereby producing various mixtures of austenite (gamma) and bcc (alpha) or hcp (epsilon) martensite) will be further studied with respect to mechanical properties and susceptibility to hydrogen embrittlement. Further corrosion, stress-corrosion cracking, hydrogen embrittlement and corrosion fatigue evaluations of several metastable austenites will be made to allow delineation of proposed fracture mechanisms. Accurate measurements of secondary incubation times for the thermally-activated process will be made as a function of stress intensity level and test temperature so that a mechanical-environmental analysis will be possible.

Other active facilities:

1. Institute of Gas Technology
   Chicago, Illinois
   Contact: D. P. Gregory

2. Naval Research Laboratory
   Washington, D.C.
   Contact: C. D. Beachem

3. North Carolina State University
   Raleigh, North Carolina
   Contact: R. B. Benson, Jr.

4. Oak Ridge National Laboratory
   Oak Ridge, Tennessee
   Contact: J. E. Mrochek

5. Sandia Laboratories
   Livermore, California
   Contact: J. H. Swisher

4.9.2 Hydrogen-Environment Embrittlement Projects

Title: Materials Environmental Compatibility for Space Shuttle
Contact: C. E. Cataldo
Institution: U.S. National Aeronautics & Space Administration, Marshall Space Flight Center, Huntsville, Alabama 35812

Summary: The objective of this study is to determine the effects of various environments anticipated during fabrication, storage, and flight of the shuttle on structural materials, both with respect to short term effects and long life effects. The studies covered under this RTOP include the effects of high pressure gaseous hydrogen on materials, flammability characteristics of materials in oxygen, corrosion susceptibility and outgassing characteristics of non-metallic materials.

Title: Fatigue, Fracture, and Life Prediction
Contact: G. Goodwin
Institution: U.S. National Aeronautics & Space Administration, Ames Research Center, Moffett Field, California 94035

Summary: The deleterious effects of stress corrosion on the mechanical properties of aircraft and spacecraft structural metals are being studied in order to develop analytical techniques and physical test criteria for predicting and minimizing such effects. In particular, an understanding of the embrittlement of metals by gaseous hydrogen will be sought.

4.9.3 Internal Embrittlement Projects

Title: Effect of Hydrogen on the Mechanical Properties of Titanium and Titanium Alloys for Use in Naval Aircraft
Contact: E. S. Tankins
Institution: U.S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: To study the effects of hydrogen absorbed at low temperatures on the embrittlement of various titanium alloys used in naval aircraft.

Title: Use of Nuclear Techniques to Study Naval Aircraft Materials and Processes
Contact: D. A. Lutz
Institution: U.S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: Fundamental studies of hydrogen embrittlement during chromium plating, of gas absorption by high temperature alloys.

Title: Electrochemical and Metallurgical Aspects of Environmental Stress Cracking of Alloys Used in Naval Aircraft Structures
Contact: J. J. Deluccia
Institution: U. S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: The phenomena of stress corrosion and hydrogen embrittlement of naval aircraft alloys in the simulated air-sea marine environment are being studied from a mechanistic standpoint.

Title: Stress Corrosion and Hydrogen Embrittlement Characteristics of Missile Structural Materials
Contact: J. T. Davidson
Institution: U.S. Army, Ground Support Equipment Laboratory, Redstone Arsenal, Huntsville, Alabama 35809

Summary: To generate data on the susceptibility of precipitation hardening (PH) type stainless steel alloys to stress-corrosion failure. Of major interest will be those PH type alloys currently being utilized in Army missile systems as LANCE, DRAGON and TOW.

Title: Mechanism of Stress Corrosion Cracking 2841
Contact: H. H. Uhlig
Institution: Massachusetts Institute of Technology, School of Engineering, Cambridge, Massachusetts 02139

Summary: To study the nature of the metal-ion interaction and the function of the tensile stress involved in cracking. This project is concerned with the mechanisms involved in stress corrosion cracking. To determine whether cracks generated in mild steel or austenitic stainless by stress-corrosion are initiated and grow by local electrochemical action or whether a crack grows because the surface energy is reduced by the chemisorption of specific ions. To differentiate between stress-corrosion cracking and cracking by hydrogen embrittlement, and to clarify the role of interstitial impurities in the behavior toward hydrogen exhibited by vacuum-melted, cold-worked alloys of iron with metals such as nickel, cobalt, aluminum, or manganese.

Title: Navy Vehicle Design and Construction: Mechanisms of Hydrogen Embrittlement in Metals and Alloys Used in Naval Structures
Contact: H. K. Birnbaum
Institution: University of Illinois, School of Engineering, Urbana, Illinois 61801

Summary: This research undertakes to clarify the mechanisms by which hydrogen can embrittle metals and alloys, such as those used for Naval aircraft and ship structures. The investigators are to study crack initiation and propagation in niobium-hydrogen and iron-hydrogen alloys. Temperatures and hydrogen content are to be varied so that cracking may be studied in alloys both with and without the presence of precipitated hydrides. Acoustic emission techniques are to be used to follow crack growth and deuterium will be used as a substitute for hydrogen in certain cases to check diffusion constants and rates. Also, oxygen doping (which alters the diffusion rate of hydrogen in niobium) will be used to determine the effect of hydrogen diffusion rate on crack growth.

Title: Navy Vehicle Design and Construction: Investigation and Application of Strengthening Methods to Titanium Alloys
Contact: A. W. Sommer
Institution: Rockwell International Corporation, International Airport, Los Angeles, California 90009

Summary: This research project is aimed at providing needed strength improvements in titanium and its alloys. The mechanical properties will be determined to obtain the structure-property relationships. The interaction of hydrogen with dislocations in alpha titanium will be followed by internal friction measurements.

Title: Navy Vehicle Design and Construction: Mechanisms of Hydrogen Embrittlement in Metals and Alloys Used in Naval Structures
Contact: L. Nanis
Institution: University of Pennsylvania, School of Chemical Engineering, 203 Logan Hall, Philadelphia, Pennsylvania 19130

Summary: This research undertakes to clarify the mechanisms by which hydrogen can embrittle metals and high strength alloys, such as those used for Naval aircraft landing gear assemblies. Iron, nickel, and titanium base alloys are being given controlled hydrogen distributions while under tensile stress. Hydrogen distribution and permeation rate is being correlated with stress-strain behavior and fracture characteristics using conventional metallurgical techniques.

Title: Navy Environment: Study of Hydrogen Embrittlement Mechanisms in High Strength Steels
Contact: E. A. Steigerwald
Institution: TRW Incorporated, Cleveland, Ohio 44117

Summary: The objective of this research is to define the mechanisms by which hydrogen can embrittle high strength steels such as those used in landing gear of Naval aircraft and rocket motor casings. The mechanical properties of various high strength steels with and without hydrogen are being determined as a function of temperature, heat treatment, strain rate, specimen geometry, and testing environment. The evaluation of the mechanical behavior of these materials along with x-ray line broadening studies and permeability studies are being used to determine hydrogen embrittlement mechanisms and the factors which control the embrittlement process.

Title: Fundamental Corrosion Studies: Hydrogen Embrittlement
Contact: L. Nanis
Institution: University of Pennsylvania, Laboratory for Research on Structural Matter, 203 Logan Hall, Philadelphia, Pennsylvania 19104

Summary: To link stress and hydrogen distribution in the study of hydrogen embrittlement of steels by controlling of hydrogen distribution by electrochemical methods during actual mechanical testing. Tensile specimens of 4340 steel with controlled hydrogen distributions will be stressed to determine the interaction of hydrogen and microstructural features in embrittled material.

Title: Environmental Sensitivity of Structural Metals - Liquid Metal Embrittlement
Contact: P. Gordon
Institution: Illinois Institute of Technology, School of Engineering, 3300 S. Federal Street, Chicago, Illinois 60616

Summary: This research is an extension of on-going research on liquid metal embrittlement to include the methodology of fracture mechanics. The areas to be investigated include: (1) The effect of prior deformation on the fracture behavior of metals. (2) The role of grain boundaries as the path for fracture propagation. (3) Experimental and theoretical studies of materials hysteresis.

Title: Stress Corrosion and Hydrogen Embrittlement in Desalination Equipment
Contact: Prof. A. R. Troiano
Institution: Case Western Reserve University, School of Engineering, University Circle, Cleveland, Ohio 44106

Summary: This program examined the resistance to SCC and hydrogen embrittlement in saline solutions of high strength aluminum base alloys, austenitic and martensitic stainless steels and monel.

Title: Investigation of the Effects of Hydrogen on the Structural-Mechanical Properties of a Titanium-2 Nickel Alloy
Contact: R. E. Westerman
Institution: Battelle Memorial Institute, P.O. Box 999, Richland, Washington 99352

Summary: Determine the effects of hydrogen on the tensile, fatigue crack growth, fracture, and acoustic emission behavior of 0.040 in. thick Ti-50A and Ti-2Ni strip.

Title: Stress Corrosion and Hydrogen Embrittlement in Desalination Equipment - Environmentally Induced Brittle Delayed Failure
Contact: Prof. A. R. Troiano
Institution: Case Western Reserve University, School of Engineering, University Circle, Cleveland, Ohio 44106

Summary: This program explores the SCC of a variety of alloys exposed to saline solutions as related to a hydrogen embrittlement mechanism.

Title: The Effect of Electrochemical Factors on the Stress-Corrosion Cracking of Titanium
Contact: J. F. Gloz
Institution: Ohio State University, School of Engineering, 190 N. Oval Dr., 102 Administration Bldg., Columbus, Ohio 43212

Summary: Current research is aimed at determining the amount and effect of hydrogen introduced into titanium under various electrochemical conditions. Also the effect of alloying additions on the hydrogen concentration is being examined. A new and relatively simple technique for determining low hydrogen concentrations in metals is being developed.

Title: Hydrogen Embrittlement - Steel
Contact: C. G. Interrante
Institution: U.S. Department of Commerce, National Bureau of Standards, Washington, District of Columbia 20234

Summary: This new project is undertaken to establish limiting conditions in respect to strength levels, hydrogen content or effective hydrogen pressure, and temperature for the changeover from microcrack propagation fracture behavior to fracture by ductile rupture.

Title: Hydrogen Embrittlement in Prestressing Steels
Contact: D. Bailey
Institution: University of Newcastle Upon Tyne, Newcastle Upon Tyne, England, United Kingdom

Summary: The effects of composition, heat treatment, polarization potential, electroplating, and environmental conditions on the development of hydrogen embrittlement in prestressing steels is being studied.

Title: Research on Corrosion and Inorganic Protective Coatings for Naval Aircraft Use
Contact: S. J. Ketcham
Institution: U.S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: Research into instrumental methods to detect hydrogen embrittlement with emphasis on design of a portable version of the permeation apparatus for in-situ measurements (so-called barnacle electrode); hydrogen permeation studies on steels and titanium alloys; characterization of corrosion behavior of composites, both metal fiber/metal matrices and metal fiber/organic matrices; research on coating systems to minimize corrosion and embrittlement; and study of mechanism of cadmium embrittlement of high strength steels.

Title: Analysis of the Ductile-Brittle Transaction Temperature in Fe-Binary Alloys
Contact: W. W. Gerberich
Institution: University of Minnesota, School of Engineering, Institute of Technology, Minneapolis, Minnesota 55414

Summary: A systematic study of both the flow and fracture characteristics of binary alloys of iron is proposed so that the following salient factors involved in the ductile-brittle transition temperature may be evaluated. (1) Atom size effect. (2) Metallic bonding effect. (3) Concentration dependence. (4) Dislocation dynamics as applied to both flow and fracture. In addition, several preliminary studies of dislocation and cracking mechanisms as associated with slow crack growth processes are being carried out. One of these, associated with hydrogen embrittlement, promises to provide considerable insight into the stress gradient effects on hydrogen diffusion.

Title: Effect of Environment on Fracture Behavior
Contact: H. H. Johnson
Institution: Cornell University, School of Engineering, 242 Carpenter Hall, Ithaca, New York 14850

Summary: A detailed characterization of hydrogen "trapping" in iron and steels is essential to an improved understanding of hydrogen brittleness and some stress corrosion phenomena. Particular experimental attention is directed to the temperature dependence of the trapping parameters. Identical strength levels will be obtained by two different processing routes, cold working and quenching and tempering. The first produces a microstructure resistant to stress corrosion; the quenched and tempered microstructure is more susceptible.

4.9.4 Hydride Embrittlement Projects

Title: Precipitation and Dispersion Hardening in Hexagonal Alloys
Contact: Dr. N. S. Stoloff
Institution: Rensselaer Polytechnic Institute, School of Engineering, 110 - 8th, Troy, New York 12181

Summary: This research has as its primary objective the study of the role of second phases in the plastic deformation and fracture of metals of hcp structure. Tests to determine whether hydride cracking during plastic deformation limits strength at high hydrogen levels will involve prestrain at 77 degrees K, followed by tests at 298 degrees K. The role of oxygen in supressing cross-slip in hafnium-hydrogen alloys also will be investigated.

Title: Fatigue Behavior of BCC Metals
Contact: Prof. N. S. Stoloff
Institution: Rensselaer Polytechnic Institute, School of Engineering, 110 - 8th, Troy, New York 12181

Summary: The objective of the proposed work is to determine the resistance of polycrystalline high purity vanadium to cyclic deformation. The test program will eventually be extended to vanadium-hydrogen alloys.

Other Active Facilities (all types of embrittlement)

1. Alcoa Laboratories
   Alcoa Center, Pennsylvania
   Contact: P. D. Hess

2. Atomic Energy of Canada
   Chalk River Nuclear Laboratory
   Chalk River, Ontario, Canada
   Contact: C. E. Ells

3. Atomic Energy of Canada
   Whiteshell Nuclear Research Establishment
   Pinava, Manitoba, Canada
   Contact: A. Sawatzky

4. Battelle Memorial Institute
   Columbus, Ohio
   Contact: T. P. Groeneveld

5. Bethlehem Steel Corporation
   Bethlehem, Pennsylvania
   Contact: H. E. Townsend

6. Boeing Company
   Seattle, Washington
   Contact: R. G. Bassett

7. Brown-Boveri
Baden, Switzerland
Contact: M. O. Peidel

8. Cambridge University
Cambridge, England
Contact: G. C. Smith

9. Case-Western Reserve University
Cleveland, Ohio
Contact: A. R. Troiano

10. Caterpillar Tractor Co.
Peoria, Illinois
Contact: R. L. Straus

11. Carnegie-Mellon University
Pittsburgh, Pennsylvania
Contact: I. M. Bernstein

12. Cornell University
Ithaca, New York
Contact: H. H. Johnson

13. Drexel University
Philadelphia, Pennsylvania
Contact: H. C. Rogers

14. Frankford Arsenal
Philadelphia, Pennsylvania
Contact: F. E. Sczerzenie

15. French Atomic Energy Commission
Pruyeres-Le-Chatel, France
Contact: J. P. Fidelle

16. Imperial College of Science and Technology
London, England
Contact: P. R. Swann

17. Institute of Gas Technology
Chicago, Illinois
Contact: D. P. Gregory

18. Lehigh University
Bethlehem, Pennsylvania
Contact: S. J. Hudak

19. Martin Marietta Coporation
Baltimore, Maryland
Contact: R. M. Latanision

20. Massachusetts Institute of Technology
Cambridge, Massachusetts
Contact: R. M. N. Pelloux

21. McDonnell Douglas Corporation
St. Louis, Missouri
Contact: T. C. Grimm

22. NASA - Ames Research Center
Moffett Field, California
Contact: H. G. Nelson

23. NASA - Lewis Research Center
Cleveland, Ohio
Contact: J. R. Stephens

24. National Bureau of Standards
Boulder, Colorado
Contact: R. P. Reed

25. National Bureau of Standards
Washington, D.C.
Contact: C. Interrante

26. Naval Facilities Engineering Command
Washington, D.C.
Contact: R. A. McCoy

27. North Carolina State University
Raleigh, North Carolina
Contact: R. B. Benson, Jr.

28. Naval Research Laboratory
Washington, D. C.
Contact: C. D. Beachem

29. Pennsylvania State University
University Park, Pennsylvania
Contact: H. Pickering

30. Rockwell International
Rocketdyne Division
Canoga Park, California
Contact: W. T. Chandler

31. Rockwell International, Science Center
Thousand Oaks, California
Contact: N. E. Paton

32. Sandia Laboratories
Livermore, California
Contact: J. H. Swisher

33. Savanah River Laboratories (DuPont)
Aiken, South Carolina
Contact: M. R. Louthan

34. T. R. W., Inc.
Cleveland, Ohio
Contact: C. S. Kortovich

35. University of Wisconsin
Madison, Wisconsin
Contact: D. Westphal

36. University of Illinois
Urbana, Illinois
Contact: H. W. Birnbaum

37. University of Maryland
College Park, Maryland
Contact: C. C. Chen

38. University of Paris
Orsay, France
Contact: J. P. Laurent

39. University of Minnesota
Minneapolis, Minnesota
Contact: W. W. Gerberich

40. University of California
Los Angeles, California
Contact: A. S. Tetelman

41. University of Technology
Loughborough, Leics, England
Contact: R. Haynes

42. U.S. Steel Corporation
Monroe, Pennsylvania
Contact: R. A. Oriani

43. Westinghouse Research Laboratory
Pittsburgh, Pennsylvania
Contact: W. G. Clark

4.9.5 Embrittlement Inhibitor Projects

Title: Inhibition of Hydrogen Embrittlement in Alloys
Contact: K. E. Parr
Institution: U.S. Army, Structures and Mechanics Laboratory, Redstone Arsenal, Huntsville, Alabama 35809

Summary: This research effort is directed to the gathering of experimental data to evaluate the effectiveness of a thin nitrided surface layer in subduing or stopping hydrogen embrittlement in the Ti-6Al-4V alloy.

Title: Navy Environment: Hydrogen Embrittlement of High Strength Steels
Contact: H. W. Pickering
Institution: Pennsylvania State University, School of Earth Sciences, 201 Shields Bldg., University Park, Pennsylvania 16802

Summary: The objective of this research is to assess methods of reducing hydrogen embrittlement damage in high strength steels used in naval structures by control of surface properties. Techniques will be investigated for modifying the surface of steels in order to reduce (A) the rate of hydrogen adsorption, (B) the ease of hydrogen absorption, and (C) the diffusivity of hydrogen. Methods of approach will include specific solute additions to surfaces, hydrogen getter surface layers, and inhibitor layers. The ability of these methods to control hydrogen entry and transport will be assessed by electrochemical methods, permeation measurements, and fractography of ruptured specimens.

4.9.6 Hydrogen Diffusion Projects

Title: Controlled Thermonuclear Research - General Research and Development Studies of Deuterium and Tritium Management for Thermonuclear Reactors
Contact: R. C. Vogel
Institution: U.S. Atomic Energy Commission, Argonne National Laboratory, Lemont, Illinois 60439

Summary: This program involves an in depth study of the mechanisms and rates of diffusion of hydrogen isotopes through a wide variety of materials of potential utility in the construction of fusion reactors. In the early stages, hydrogen permeabilities will be measured for niobium and vanadium as a function of both temperature and hydrogen partial pressure. The interactions of hydrogen with these materials will also be investigated by x-ray and micrographic techniques.

Title: Lattice Dynamical Theory of the Diffusion Phenomena
Contact: B. N. Achar
Institution: U.S. Atomic Energy Commission, Argonne National Laboratory, Lemont, Illinois 60439

Summary: The theory of diffusion of interstitials will be studied in greater detail. Numerical applications will be made to diffusion of hydrogen and deuterium in palladium.

Title: Diffusion of Interstitial Components in Titanium and Zirconium Alloys
Contact: S. J. Hruska
Institution: Purdue University, Materials Science Center, Executive Bldg., Lafayette, Indiana 47907

Summary: The objective of this research was to determine the Ti-Zr phase diagram with greater precision and to measure the diffusivity of hydrogen in Ti-Zr alloys.

Other Active Facilities

1. Institute für Eisenhüttenkunde
   der Rheinsch-Westfälschen
   Technischen-Hochschule
   Aachen, Germany
   Contact: K. W. Lange

2. NASA - Ames Research Center
   Moffett Field, California
   Contact: H. G. Nelson

3. University of Nebraska
   Lincoln, Nebraska
   Contact: D. L. Johnson

4.9.7 Hydrogen and NDT Failure Detection Projects

Title: Development of an Electrochemical Device for In-Situ Determination of Embrittling Hydrogen Content in Naval Aircraft Steel Components
Contact: D. Berman
Institution: U.S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: To develop an electrolytic contact cell for the determination of hydrogen in high strength steel aircraft structures and to correlate this with the degree of embrittlement.

Title: Study of Acoustic Stress Wave Emission Phenomena and Its Application to the Early Detection of Corrosion and Fatigue
Contact: R. Klinman
Institution: U.S. Navy, Air Vehicle Technology Department, Warminster, Pennsylvania 18974

Summary: To study the fundamental mechanisms of acoustic stress wave generation and propagation in order to improve applicability of the method for detection and investigation of stress and intercrystalline corrosion cracking, hydrogen embrittlement, and fatigue phenomena.

Title: Nuclear Microprobe Hydrogen Detection Technique
Contact: G. M. Padawer
Institution: Grumman Corporation, S. Oyster Bay Rd., Bethpage, New York 11714

Summary: To acquire capability for detection and analysis of hydrogen at surface of high strength metallic critical aerospace weapons systems parts.

Title: Applicability of Backscatter Mossbauer Effect to NDT for Hydrogen Embrittlement of Navy Materials
Contact: R. C. Folweiler
Institution: Sanders Associates, Inc., 701 Concord Ave., Cambridge, Massachusetts 02138

Summary: Provide a convenient, practical technique for the appraisal of the deterioration modes of high strength steel. Hydrogen embrittlement, stress-corrosion hydrogen and residual stress are the principal controllable factors of Navy materials.

Title: Stress-Corrosion Behavior of Prestressed Wires
Contact: S. Elices
Institution: Center for Public Works Studies, Madrid, Spain

Summary: The behavior of high-quality steel wires is being determined under different conditions; stress, corrosion brittleness through hydrogen, and cathodic polarization. An easy and rapid test procedure, which is representative of the above phenomena, is to be developed for use as a standard specification in Spain.

Other Active Facilities

1. Naval Air Development Center
   Warminster, Pennsylvania
   Contact: D. A. Berman

2. Oak Ridge National Laboratory
   Oak Ridge, Tennessee
   Contact: G. L. Powell

4.9.8 Hydrogen Production and Transmission Projects

Title: Energy Conversion, Energy Storage and Reconversion
Contact: W. L. Hughes
Institution: Oklahoma State University, School of Electrical Engineering, Whitehurst Hall, Stillwater, Oklahoma 74074

Summary: To develop a family of systems for storing electrical energy and thereafter re-utilize the stored energy in various ways. In storage, major emphasis has been in the development of high-pressure (1000 to 3000 PSI) moderate temperature (300 to 400 degrees Fahrenheit) electrolysis cells, fuel cells and rechargeable fuel cells for the storage of electrical energy in the form of high-pressure hydrogen gas (other alternatives include hydrides and liquid hydrogen).

Title: Thermochemical Hydrogen Production
Institution: Institute of Gas Technology, Chicago, Illinois

Summary: Hydrogen can be produced by the decomposition of water using the heat generated in a nuclear reactor. Multi-step chemical processes are being theoretically and experimentally examined. All intermediate chemicals are recycled so that the overall reaction scheme produces only hydrogen and oxygen with water as the only raw material. A number of different reaction schemes have been considered. Two of them have potential promise and are being analyzed in more detail.

Title: Energy Conversion and Storage
Contact: W. L. Hughes
Institution: Oklahoma State University, School of Engineering, 101 Gunderson Hall, Stillwater, Oklahoma 74074

Summary: The original prime objective of the project was to develop an economical commercial electrolysis-fuel cell, the purpose of which would be to utilize off-peak electric energy and water in the electrolysis mode to produce oxygen and hydrogen which would be stored.

Title: Production of Hydrogen from Water
Contact: J. L. Russell
Institution: Gulf General Atomic, Inc., San Diego, California

Summary: To discover and develop closed thermochemical cycles for producing hydrogen from water.

Title: Ocean Sited Power Plants
Contact: W. E. Heronemus
Institution: University of Massachusetts, School of Engineering, Amherst, Massachusetts 01002

Summary: The augmented effort will be applied to marine system conceptualizations and feasibility studies of power generation from ocean temperature differences where the boiler and condenser temperatures are about 75-85 degrees F (tropical surface waters) and 35-45 degrees F (bottom waters below 2000 feet), respectively. All components of a system will be conceptualized and evaluated including hulls, heat exchangers, pumps, pipes, electrolysis of water to hydrogen fuel, etc., for a 100-400 MW central power stations moored in the Gulf Stream.

Title: A Hydrogen Energy Distribution System
Institution: Institute of Gas Technology, Chicago, Illinois

Summary: This study was undertaken to assess the feasibility of producing hydrogen from nuclear energy and to determine whether any technical roadblocks exist which would prevent its long-distance transmission and its in-city distribution and utilization.

Other Active Facilities

1. General Electric Company
   Schenectady, New York
   Contact: A. R. H. Wentorf

2. Euratom C.C.R.
   Establishment of Ispra, Italy
   Contact: C. Marchetti

3. Los Alamos Scientific Laboratory
   Los Alamos, New Mexico
   Contact: Mel Bowman

4.9.9 Hydrogen Storage Projects

Title: Chemical Energy Storage
Contact: J. M. Burger
Institution: Public Service Electric and Gas Company, 80 Park Place, Newark, New Jersey 07101

Summary: Develop a reliable, low cost chemical energy storage device to store electrical energy during off-peak times and to deliver electrical energy for a duration of 10 to 12 hours during heavy-load times. Also included is the development of a gas electric two-way transformer system utilizing hydrogen storage to produce electrical energy or pipeline gas.

Title: Vacuum Shell Cryogenic Tankage Fabrication for Possible Orbit to Orbit Shuttle Use
Contact: J. Kennedy, T. Nicastro
Institution: Signal Companies Incorporated, 1010 Wilshire Blvd., Los Angeles, California 90017

Summary: Technical objective: The purpose of this effort is to fabricate a vacuum jacketed tank with application to long term storage of liquid hydrogen. After fabrication and delivery of the tank to the AFRPL a test program will be initiated to determine thermodynamic performance of the tank using liquid hydrogen.

Title: Cryogenic Storage Technology
Contact: C. A. Aukerman
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The general objectives of the programs under this RTOP are to provide technology for various aspects of cryogenic thermal protection systems. The specific areas covered by these programs are: (1) shadow shields for liquid hydrogen tanks, (2) a liquid hydrogen mixing unit, (3) cryogenic tank supports, and (4) integrated thermal protection systems. In each area, the objective is to demonstrate the feasibility of a new concept for improving the capability to store liquid hydrogen in space vehicles.

Title: Tankage Development and Evaluation
Contact: G. T. Smith
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: Design and fabrication of low cost, high performance reliable pressure vessels for upper stage vehicles. Characterization of the growth of flaws which are deep with respect to the material thickness. Both critical and subcritical flaw growth data will be obtained in both aggressive and inert environments.

Title: Metal Hydrides
Contact: J. J. Egan, D. R. MacKenzie
Institution: Brookhaven National Laboratory; Upton, New York 11973

Summary: We plan to obtain PTC or exchange data or both on the hydrides of such metals as the alkaline earths, thorium, zirconium alloys, vanadium alloys, AB5-type and other rare earth alloys, and perhaps some ternary alloys. As regards hydrogen storage, experiments are planned which will increase our knowledge of the effects of minor components of alloys on hydride reservoirs in conjunction with energy sources which will be investigated both by engineering analysis and if possible with actual bench-scale integrated systems.

4.9.10 Propulsion Systems Projects

Title: Non-Polluting Engine Program
Contact: J. Agost, also with H. C. Wieseneck, Rockwell International Corporation
Institution: Commonwealth Edison Company, 3500 N. California Ave., Chicago, Illinois 60632

Summary: Commonwealth Edison Co., and Rocketdyne Division of North American Rockwell Corp. are working on this joint plan to install an experimental "rocket" powered or non-polluting engine (NPE) to produce peaking power electricity at Edison's Joliet Station.

Title: Advanced H-O Power System Technology
Contact: D. G. Beremand
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: This activity is directed toward the continued investigation and advancement of Hydrogen-Oxygen Turbine engine technology. This work is in support of advanced H-O Space Power Systems (such as advanced Shuttle APU's) as well as the widening interest in non-polluting H-O ground power systems. Potential areas of investigation include Stoichometric H-O engines with water-injection-cooled combustors, utilization of water-cooled turbines, and materials development for hydrogen turbines.

Title: Space Shuttle Auxiliary Propulsion
Contact: D. L. Nored
Institution: U. S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objective of this program is to provide improvements in the technology of engine components for the auxiliary propulsion system of the space shuttle. The major portion of this work will be devoted to advancements in the thruster assembly, including the injector, thrust chamber, igniter, and valves. The operating conditions for experimental work are selected to fit the particular requirements of the space shuttle. This includes operation with gaseous hydrogen/gaseous oxygen propellants at thrust levels in the range from 1500-2000 pounds, chamber pressures from 100-150 psia, and appropriate ranges of propellant inlet pressure and temperature.

Title: Space Storable Propulsion Technology
Contact: E. W. Conrad
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objective of this program is to provide component, subsystem and system design criteria for propulsion systems using moderate cryogenic (space storable) and deep cryogenic (hydrogen) propellants to demonstrate the performance and technology readiness of propulsion modules using both propellant types for simulated mission of up to 1200 days.

Title: Advanced Liquid Rocket Propulsion Component Technology
Contact: J. W. Gregory
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objective of this program is to provide improvements in the technology of liquid rocket propulsion, including (1) turbomachinery, (2) feed systems, (3) injectors and thrust chambers, and (4) associated instrumentation. In turbomachinery, the major efforts will be devoted to investigation of axial flow pumps, inducer design, cavitation in cryogenic propellants.

Title: Advanced Combustors and Fuels
Contact: J. H. Childs
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: Research will be conducted on film cooling of combustor liners, multiple jet penetration and mixing, new types of fuel injectors, and short-length, bleed-type combustor inlet diffusers. Concluding research will be done on fuel system components and handling techniques for liquid methane and liquid hydrogen fuels.

Title: Space Systems Propulsion
Contact: M. J. Saari
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objective of this study is to provide a point design of an LH_2/LO_2 engine of about 10,000 pounds thrust.

Title: Development of a Pollution Free Hydrogen-Fueled Automobile
Contact: R. R. Adt, Jr.
Institution: University of Miami

Summary: The object of this work is to optimize the design of the hydrogen-fueled engine, fuel storage and delivery system.

4.9.11 Bearings, Seals and Lubricants Projects

Title: Bearings, Seals, and Lubricants
Contact: R. L. Johnson
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: Basic materials and lubricants studies as well as experiments and analyses with actual components in vacuum, cryogenic, inert gas, and low viscosity fluid environments will be conducted. The potentials of self-lubricating materials and film deposition methods are being explored. Experiments and analyses of promising types of fluid film bearings and seals for gas and low viscosity liquid applications are underway.

Title: Shuttle Lubrication, Bearings and Seals
Contact: R. L. Johnson
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: Materials and lubricants selection, development, design, theory, analysis and experimentation of bearings and seals will be performed under extreme conditions associated with (A) engine and (B) vehicle components subject to lubrication, friction, wear, and hydraulics problems. Rolling element bearings and face type seals for hydrogen pumps of shuttle engines will be operated under conditions simulating problem areas.

4.9.12 Fuel Cells Projects

Title: Direct Energy Conversion Research
Contact: M. Altman, G. L. Schrenk, H. Wroblowa
Institution: University of Pennsylvania, School of Engineering, 107 Towne Bldg., Philadelphia, Pennsylvania 19104

Summary: Electrocatalytic Materials for Oxygen Electrodes. Involves an investigation of the electrochemical behavior and of structural changes occuring in doped Cu, Au alloys during oxygen reduction in low temperature alkaline cells, aiming at development of a stable oxygen electrode containing no noble metals of Group VIII and outperforming platinum based electrodes. The second goal is an examination of the theory of Bocciarelli which led to construction of new electrocatalysts for oxygen and hydrogen electrodes.

Flow-Through Systems. The research covers the theory of flow-through electrodes by including the diffusional effects hitherto neglected: development of a method of determination of the electro-active surface area of porous electrodes and production of low catalyst load flow-through and gas diffusion electrodes.

Applied Surface Physics. Transport phenomena of electrons through surfaces will be investigated with emphasis on applications in field ion microscopy and electrocatalysis. This will involve research in the kinetics and quantum mechanics of surface reaction, adsorption/desorption processes, and tunneling through multi-layer adsorbates, both in vacuo and in the presence of solvents.

Title: Reactive Sensitivity of Fuel Cell Gas Mixtures
Contact: J. S. Greer
Institution: M S A Research Corporation, Evans City, Pennsylvania 16033

Summary: Mixtures of gases arising during the routine operation of candidate naval fuel cells such as hydrazine-peroxide and hydrogen-oxygen types will be examined with respect to the effect of pressure on their flammability limits. Where flammability is observed, the ignitibility characteristics of the system will be studied as a function of pressure. Ignition will be effected by spark, compression and thermal gradient. In addition, the effect of selected catalysts and hypergolic (e.g., peroxide vapor) impurities on the flammable mixtures will be observed. Negotiations are underway for an experimental study of the effects of high pressure (in the range of 10,000 psi).

Title: Low Cost Matrix for Hydrocarbon Fuel Cell
Contact: B. S. Baker
Institution: Energy Research Corporation, Bethel, Connecticut 06801

Summary: The purpose of this contract is to develop an H_3PO_4 matrix technology. Suitable matrices must be structurally and chemically invariant in hot H_3PO_4, be composed of low cost raw materials, and be capable of inexpensive mass production. A second part of this contract will examine low cost CO tolerant anodes for indirect hydrocarbon/air fuel cells. Those materials exhibiting desirable characteristics will then be tested in single H_2/air cells. Small amounts of platinum and platinum alloys will be supported on carbon and the resulting electrodes tested with H_2-CO mixtures.

Title: Fuel Cell Safety
Contact: H. B. Urbach
Institution: U.S. Navy, Ship Research and Development Laboratory, Annapolis, Maryland 21402

Summary: Provide improved safety characteristics of candidate naval fuel cell powerplants by development of data on material and component design selection and safety criteria guidelines applicable to power supplies for deep submergence vehicles, and underwater habitats.

Title: Thermocatalytic Hydrogen Generation from Logistic Fuels
Contact: O. F. Kezer
Institution: U.S. Army, Mobility Equipment Research and Development Center, Fort Belvoir, Virginia 22060

Summary: The objective of this investigation is to produce a lightweight, efficient gas generation system operating on logistic hydrocarbon based fuels capable of producing hydrogen for a fuel cell reactant. The first phase of this investigation is the derivation of fundamental design and operational parameters for thermocatalytic hydrogen generators.

This effort will be centered around the investigation of basic parameters, techniques and materials, applicable to the design and operation of thermocatalytic hydrogen generation systems. This includes an investigation of the effect of fuel, catalyst, and temperature on the products formed and will also involve a study of the mechanism of hydrocarbon cracking.

Title: Regenerative Fuel Cells Follow-On for Satellite Secondary Power
Contact: J. K. Stedman
Institution: United Aircraft Corporation, Hartford, Connecticut 06118

Summary: Build an exploratory development base to support advanced development of a 20 watt-hr/lb hydrogen-oxygen regenerative fuel cell for energy storage for synchronous orbit applications.

Title: Twenty watt-hr/lb Regenerative Fuel Cell (EOS)
Contact: R. Costa
Institution: Xerox Corporation, 3452 E. Foothill Blvd., Pasadena, California 91107

Summary: To develop an energy storage system capable of long life (5-7 years) cyclic storage and release of 20 watt-hours or more of electrical energy per pound of storage system on board synchronous orbit satellites. To design, develop, test and evaluate a single cell (nominal 1 volt unit) regenerative hydrogen-oxygen fuel cell (about 350 ampere-hour capacity) utilizing a KOH electrolyte matrix and concentric electrodes in a cylindrical configuration.

Title: Twenty watt-hr/lb Regenerative Fuel Cell (P+W)
Contact: J. Stedman, Pratt & Whitney Aircraft Div.
Institution: United Aircraft Corporation, Hartford, Connecticut 06118

Summary: To develop an energy storage system capable of long life (5-7 years) cyclical storage and release of 20 watt-hours or more of electrical energy per pound of storage system on board synchronous orbit satellites. To design, develop, test and evaluate an integrated regenerative hydrogen-oxygen fuel cell stack utilizing separate electrodes for charge and discharge and KOH critical components and a functionally complete regenerative fuel cell system.

Title: Electrode-Electrolyte System for H_2-Air Fuel Cell
Contact: O. J. Adlhart
Institution: Englehard Industries, Inc., Newark, New Jersey

Summary: The technical objective is to attain 180 ma/square centimeters from fuel cells using a simulated cracker fuel (90 percent hydrogen, 10 percent methane plus trace of carbon monoxide) and air as the oxidant at voltages of .60 or higher after 2000 hours. Total noble metal catalyst loading are not to exceed 8 mg/square centimeters.

Title: Electrochemical Power Devices
Contact: H. J. Schwartz
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: Emphasis will be placed on technology leading to an advanced H_2-O_2 fuel cell system for space shuttle applications.

Title: Low Cost Cathode Catalysts
Contact: B. S. Baker
Institution: Energy Research Corporation, Bethel, Connecticut 06801

Summary: The objective of this contract is to demonstrate high performance with low cost fuel cell air electrodes. The specific goals are to develop cathodes with a catalyst cost equivalent not more than $150/kW based on performance after 500 hours of constant current drain in H_3PO_4 electrolyte.

Title: Hydrogen-Oxygen Fuel Cells for Underwater Applications
Contact: D. R. Gormley
Institution: U.S. Department of Defense, Naval Ship Research and Development Center

Summary: The objective of this work is the exploratory development of naval hydrogen-oxygen fuel cell powerplant modules over the range of 2 to 20 kW with capabilities reaching 20 lb. and 0.2 cu. ft. per kW rated output, 0.8 lb. consumables per kW, and a maintenance free life of 3000 hours.

Title: Fuel Cell Materials for Underwater Power Sources
Contact: J. R. Bowen
Institution: U.S. Department of Defense, Naval Ship Research & Development Center, Naval Ship R&D Laboratory, Department of Machinery Technology, Annapolis, Maryland 21402

Summary: Study the electrochemical and compatibility behavior of candidate fuel cell materials for application in fuel cell power plants operation in deep-sea pressures as high as 10,000 psi. Present efforts involve materials for hydrogen-oxygen and hydrazine-hydrogen peroxide fuel cells.

Title: Energy Storage and Generation
Contact: W. L. Hughes, H. J. Allison, R. G. Ramakumar
Institution: Oklahoma State University, School of Electrical Engineering, Stillwater, Oklahoma 74075

Summary: Research and development on high pressure electrolysis, high temperature and high pressure hydrogen-oxygen fuel cells, and development of a family of electric alternators for which output frequency is independent of prime mover shaft speed, physical size is about 1/4 that of conventional system (for same output frequency, power and efficiency).

Title: Corrosion-Resistant Materials for Electrochemical Cells
Contact: H. P. Silverman
Institution: TRW, Inc., TRW Systems, One Space Park, Redondo Beach, California 90278

Summary: Methods for determining compatability of materials with fuel cell electrolytes and the environment of electrochemical cells will be investigated.

Title: Evaluation of Phosphoric Acid Matrix Fuel Cells
Contact: O. J. Adlhart
Institution: Engelhard industries, 113 Astor Street, Newark, New Jersey 07114

Summary: To reduce the catalysts cost/kW of H_2-air fuel cells were expanded to include the examination of other reactants such as methanol and propane. Elevated temperatures, as high as 250 degrees C, shall be used in order to increase the oxidation rate of hydrocarbons.

Title: Regenerative Hydrogen-Oxygen Fuel Cell Systems
Contact: H. J. Allison, R. G. Ramakumar
Institution: Oklahoma State University, School of Electrical Engineering, Whitehurst Hall, Stillwater, Oklahoma 74074

Summary: Testing and development of rechargeable hydrogen-oxygen fuel cells.

Title: Family of Open Cycle Fuel Cell Power Plant Development
Contact: T. Shillet
Institution: United Aircraft Corporation, Pratt & Whitney Aircraft, 400 Main Street, East Hartford, Connecticut 06108

Summary: To design, develop and fabricate 1.5 kW fuel cell power plants and to design 0.5 kW, and 5 kW power plants.

Title: Electrode-Electrolyte System for H_2-Air Fuel Cell
Contact: O. J. Adlhart
Institution: Engelhard Minerals & Chemicals Corporation, Engelhard Industries Division, 113 Astor Street, Newark, New Jersey 07114

Title: Fuel Cell Electrodes
Contact: D. Laverty
Institution: Brunswick Corporation, Materials Research Laboratory, Needham, Massachusetts 02102

Title: Thin Electrode Fuel Cells
Contact: J. Batzold
Institution: Esso Research & Engineering Company, P.O. Box 8, Linden, New Jersey 07036

Summary: The objective is to develop high performance alkaline, hydrogen-oxygen fuel cell electrodes based on the technology developed under National Aeronautics and Space Administration grant NSG-325. Principally, efforts will be directed towards reduction of electrode thickness, amount of catalyst and production problems for a given performance level.

Title: Hydrogen-Oxygen Power Systems
Contact: D. G. Beremand
Institution: U.S. National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Summary: The objectives are to develop technology readiness for a hydrogen-oxygen APU to provide hydraulic and electric power for the space shuttle vehicle, and to evaluate the performance potential and applicability of hydrogen-oxygen dynamic power systems for other space and ground applications.

CHAPTER 5

INSTRUMENTATION FOR CRYOGENIC HYDROGEN FUEL

T. M. Flynn

5.0 SUMMARY

This chapter surveys state-of-the-art technology for cryogenic hydrogen instruments. Recommendations for future work are outlined: adaptation of existing technology to commercial applications, development of new technology and integrating liquid hydrogen measurements into the National Measurement System (NMS) are future priority tasks.

Since measurements are the basis of technology, and dictate the fineness of our physical observations and control, it is apparent that this part of hydrogen technology is lagging. Our three conclusions are: 1) little is being done to bring the hydrogen instrumentation technology of the space program to the market place, 2) if it were, adequate primary instruments and facilities do not exist to bring this part of the NMS under control, and 3) no concerted effort exists to explore the consequences or exploit the opportunities of new technological opportunities.

These conclusions appear to apply generally to each area of cryogenic instrumentation, although, of course with varying degrees of severity. Specific analyses and conclusions appear in each major instrumentation area in the following sections of this chapter. The broad conclusions are:

Pressure transducers are normally placed in a temperature controlled environment near room temperature. Some available pressure transducers are capable of performing satisfactorily at low temperatures, but new types such as piezoelectric, diode, electrokinetic, etc. may perform equally well or better. It is, therefore, necessary for the purpose of comparison that all pressure transducers be tested at low temperatures and at various frequencies to determine their potential for hydrogen use. Because pressure sensing devices are widely used (differential pressure flow meters, level gauges, and vapor pressure thermometers) and because their cryogenic behavior is quite different from that of normal use, a systematic, well documented testing program is presently needed.

Temperature measurements are unquestionably in better shape than any other hydrogen measurements. Adequate calibration facilities exist as well as a large body of knowledge that together help keep this part of the NMS in control. Industrial type platinum resistance thermometers are routinely used, for instance. Improvements in their interchangeability would be desirable, as well as some simple thermometry for crude temperature indications and the monitoring of process trends.

Level detectors for liquid hydrogen were extensively developed during the space program, but it is remarkable how little space hardware is actually used in the commercial sector. A deliberate effort to adapt space instrumentation to commercial and industrial applications seems worthwhile.

Primary instruments and facilities to calibrate liquid level devices do not exist, and accordingly it is questionable whether this part of the NMS is in control. Furthermore, a large body of knowledge and experience needs to be developed to move with assurance from

this relatively clean measurement to the practical measurement question of how much does the tank really contain?

Density is an inferential measurement, and as such, it should be traceable to a national standard, such as a national density reference system. Primary instruments to calibrate densitometers do not exist.

Several physical principles of hydrogen density measurement have been brought well forward by the space program. Notable are the capacitance, vibration, and nuclear radiation attenuation schemes. Microwave methods are recently moving to the forefront. It is felt that the pressing need now is to: a) commercialize these instruments for routine engineering applications and b) provide an adequate national reference system.

Flow - There is no shortage of physical principles upon which to base a hydrogen flowmeter. Depending on the need, they range from simple pressure drop meters to sophisticated mass reaction types. Flow, however, is a derived quantity and as such flowmeters require traceability to a reference system to establish credibility. Thus flowmetering needs fall into four categories: 1) flow reference systems, 2) possible use of substitute fluids for calibrations, 3) extension to large flow rates, 4) standard codes and practices.

The latter requirement is basic to each area of instrumentation as hydrogen technology moves into the marketplace and becomes an influential member of the NMS.

5.1 INTRODUCTION

The national space program developed not only a complete technological base for cryogenic instrumentation, but also many specific instruments themselves for particular tasks in hydrogen propellant loading and utilization. Nothing remarkable has been done, however, to bring these instruments to the market place for commercial and industrial use. A recent survey of the Smithsonian Science Information Exchange, Inc., revealed two hydrogen instrumentation projects. One was the development of a nuclear magnetic resonance (NMR) flowmeter for the USAF, and the other was a modest NBS effort.

Thus one component of the problem of hydrogen instrumentation is that it is largely static. Not much has been accomplished technically since the peak of the space program, perhaps since 1969, or earlier, and surely there is little evidence of the commercialization of these instruments.

A second part of the problem arises from the way hydrogen measurements fit into the NMS. As long as only a single agency or one sector of our economy (NASA, the aerospace industry) were using essentially all of the results of their own measurements, then that part of the NMS was internally consistent and in harmony with itself. Now however, the prospects are that hydrogen is becoming commercialized and moving to the market place and thus external consistency as well as internal consistency is now required to make this part of the NMS work. Primary instruments and facilities to calibrate the derived quantities -- liquid level, density, and flow -- do not exist. Unlike pressure and temperature, this part of the NMS is chaotic and needs to be brought under control.

The third part of the problem is perhaps a derivative of the first. Because the field is static, a crucial question is not being asked: are there predictable technological developments that will either create a need for new hydrogen instruments or possibly provide an altogether new measurement means?

5.2 PRESSURE

Pressure measurements in cryogenic systems have, for years, been made by simply running gage lines from the point where the pressure measurement is desired to some convenient location at ambient temperatures and attaching a suitable pressure-measuring device such as the familiar Bourdon gage.

This system works quite well for most applications; however, there are disadvantages to this straightforward approach that may introduce problems in many systems. The two most important are (1) reduced frequency response and (2) thermal oscillations. In addition, heat leak, uncertainties in hydrostatic head within gage lines, and fatigue failure of gage lines could become significant in some applications. Such problems associated with pressure measurement at cryogenic temperatures could be eliminated by installing pressure transducers at the point of measurement, thereby doing away with gage lines. For these reasons, we shall consider in the following discussion primarily those pressure transducers which have an electrical output, and which can be "flush mounted" directly on the cryogenic component under consideration.

5.2.1 Pressure Transducers

All pressure transducers, regardless of their particular type, share three major subassemblies: (1) a force summing device which converts the force or pressure to a displacement, (2) a mechanical link to transmit this displacement and perhaps amplify it, and (3) an electrical conversion device.

The force summing device may take any of several forms. It may be, for example, a diaphragm, whether flat, corrugated, or encapsulated. It may also be a bellows, or a Bourdon tube, whether circular or twisted, or simply a straight tube which is stressed under pressure.

The link may simply be a straight bar which transmits this displacement directly, or it may be an involved series of linkages which magnifies the original displacement.

The electrical conversion device can also take many forms. It may be a variable capacitor whose plate spacing depends upon the displacement and, hence, pressure. It may be a variable potentiometer in which the position of the wiper arm is determined by the displacement and, hence, pressure. It may be any of several variable reluctance or variable inductance devices. It may also comprise a piezoelectric element, a strain gage, or a linear variable differential transformer (LVDT).

Like all instruments, the output of a pressure transducer depends not only on the primary input, in this case pressure, but also upon extraneous effects, such as the effect of temperature on its various components. Erroneous pressure readings can be caused by both steady state temperature effects and temperature gradient, or thermal shock effects.

5.2.2 Steady State Temperature Effects

Steady state temperature effects can be measured by simply calibrating a pressure transducer at two or more different fixed temperatures, after a sufficient amount of time has elapsed such that every component of the transducer is at the same temperature. There will generally be noted both changes in sensitivity and also zero shifts. Dean [1] modeled pressure transducers in an analytical form and demonstrated that the sensitivity shift is primarily due to the differences in the thermal expansivities of the several components which make up the transducer, and especially due to change in the elastic modulus as a function of temperature. Likewise, the zero shift can also be attributed to the difference in the thermal expansivities of the several components of the pressure transducers, but the more significant effect in this case is the change in the dimensions of the components due to changes in temperature. If the electrical conversion device is used in some form of a bridge network, additional zero shifts can occur from the inability of the bridge to perform adequate common mode rejection.

5.2.3 Thermal Shock Effects

So far we have been assuming that the pressure transducer is experiencing a uniform temperature throughout its many components. The effect of temperature gradients across a pressure transducer can be measured by applying no pressure to the pressure transducer, but subjecting it to a thermal shock by plunging it into a liquid cryogen. What is observed is purely the thermal shock, or thermal gradient, effect. Some pressure transducers are known to suffer a permanent deformation, or offset, after being returned to their normal operating temperature. It has been noted that many pressure transducers would, in fact, be quite good thermometers.

Such erroneous readings can be explained if one considers a typical pressure transducer that is made up of a bellows, a link, and a linear resistor. Under conditions of thermal shock, the bellows will reach the new temperature environment at a different rate than the linear resistor. The difference in the expansivity of these materials are drastically different over a wide temperature range. Therefore, the contributions of the expansivities of these components to the sensitivity coefficient is changed from the design condition, causing a sensitivity shift. A compensating resistor is often placed in the bridge in order to perform a common mode rejection to compensate for the temperature dependency of the elastic modulus of the bellows. Unfortunately, this compensating resistor is often several inches away from the bellows, so that its temperature gradients are quite different from that member. In fact, if temperature gradients are expected for a pressure transducer installation, it may be beneficial to remove the electrical compensation, as the error thus induced may far exceed the error due only to the temperature dependency of the elastic modulus.

The temperature gradient effect also causes zero shift. These zero shift effects are usually dissipated with time as all of the members of the pressure transducer reach the same temperature.

5.2.4 Methods of Avoiding Temperature Effects on Pressure Transducers

The most common solution to temperature effects is to avoid extreme-temperature environments. When the pressure instrumentation point is subjected to such temperatures, the standard procedure is to run tubing from the pressure source to a remote, stable temperature location. This is good procedure if the instrument engineer is interested in a frequency response of the order of 10 Hz.

Another approach is to flush-mount one pressure transducer in the extreme environment and another at the end of a tube as discussed above. The object is to measure static pressure levels with the tube-mounted pressure transducer and dynamic pressures with the flush-mounted transducer. The hope is that the temperature-shock contribution to dynamic response will be small or of low enough frequency to separate easily.

A perhaps better but more complicated solution for cryogenic application is shown in Figure 5.1. A short thin-walled tube connects a cryogenic transfer line or tank to a pressure transducer. A heater and a thermostat are attached to the transducer, regulating the temperature to perhaps 27°C. Insulation surrounds the transducer. Tube length is long enough to reduce the power requirement to the heater to a few watts, hopefully without excessively reducing the frequency response. It is important that the heater and tube connection be arranged so that temperature gradients do not exist in the transducer. The transducer must be oriented so that the liquid cryogen does not flow into the diaphragm.

5.2.5 Pressure Summary

Temperature, as an extraneous variable, can have a profound effect upon pressure transducers, altering both the sensitivity of the instrument and its zero setting. Sensitivity shifts are primarily proportional to the spring constant and thus the Young's modulus temperature dependency of the force summing member-be it a diaphragm, a bellows, a Bourdon tube, or a capsule. Zero shifts are primarily due to dimensional instability caused by temperature changes of the pressure transducer components, including the case or frame. Temperature gradient effects are the combination of the above effects while the transducer component temperatures are varying.

Proper design can reduce zero shift by locating the electrical sensing element so that dimensional changes are not detected as an input. Sensitivity shifts can be electrically compensated assuming a resistor can be found that has the desired resistance-temperature properties. Unfortunately there is not much that can be done about temperature gradient effects except to avoid them. Component material and compensating resistors that are carefully chosen for steady state temperature conditions lose their relationships under transient conditions. However, it may be helpful to place the compensating resistor as close to the force summing element as possible. Avoiding temperature gradients is a matter of heat transfer. Under cryogenic conditions enough insulation must be used to greatly extend the thermal time constant of the system.

Of all the measurements made on cryogenic systems, surely one of the most common must be that of pressure measurement. Pressure measurements are made not only to determine the force per unit area in a system, but also to determine flow rate (head type meters), quantity

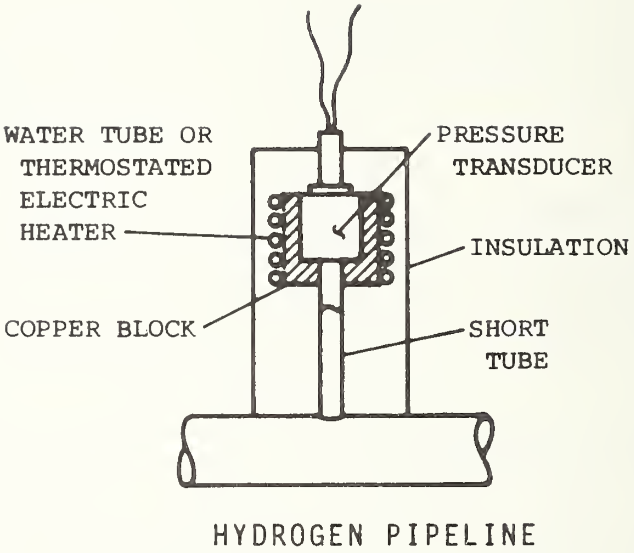

FIGURE 5.1 - Temperature- Regulated Pressure Transducer for Cryogenic Installation.

(differential pressure liquid level gages), and temperature (vapor pressure or gas thermometers). Pressure measurements are thus fundamental to the smooth running of much of this part of the National Measurement System (NMS).

While it is agreed that some available pressure transducers are capable of performing satisfactorily at low temperature, other types, e.g., piezoelectric, diode, inductance, reluctance, and electrokinetic devices may perform equally well or better. It is, therefore, necessary for the purpose of comparison, that all pressure transducers types be tested at low temperature and at various frequencies to determine their potential for cryogenic use. Because pressure sensing devices often behave quite differently (from ambient conditions) in a cryogenic medium, a systematic, well documented testing program is presently needed before all types can be evaluated and compared.

A cryogenic calibration system with varied capabilities is essential for the successful completion of such a program described above. The details of such a system have been described by Arvidson [2].

5.3 TEMPERATURE

Most engineering measurements are made with metallic resistance thermometers, nonmetallic resistance thermometers, or thermocouples. Gas thermometers and vapor pressure thermometers find little practical engineering application, and hence are mentioned only briefly in the following paragraphs. A recent compilation of the commercial availability of thermometers is given in "Measurements and Data" [3].

5.3.1 "FLUID" THERMOMETRY

Gas Thermometry. Constant-volume gas thermometry is familiar as a technique for accurate realization of the thermodynamic temperature scale. In such work the P-T behavior is made as linear as possible by minimizing the extraneous volumes in the manometer and the connecting tubing. Troublesome corrections for these extraneous volumes decrease with decreasing bulb temperature inasmuch as the proportion of gas in the bulb increases. On the other hand, gas imperfection increases with decreasing temperature.

If, however, the sensing bulb is made small as compared to the external volume of the system at ambient temperature, the characteristic is far from linear, the sensitivity increasing greatly as the bulb temperature decreases. By using a Bourdon gage to show the pressure in this device, a simple gas thermometer is achieved which is useful for such purposes as monitoring the cool-down of cryogenic apparatus.

In order to obtain accurate results in gas thermometry it is necessary to correct for (1) the imperfection of the gas, (2) the effect of the "nuisance volume" or the volume of gas which is not at the temperature being measured, (3) the change of volume of the bulb with changing temperature, (4) variations in the amount of gas adsorbed on the walls of the gas thermometer bulb, and (5) the thermomolecular pressure gradient encountered at extremely low pressures. Accordingly, for engineering applications, gas thermometry is recommended for indicating the approximate temperature, or temperature trend. For precision temperature measurements, the corrections required are usually too bothersome.

Precision Gas Thermometry falls in the category of fundamental thermometers rather than empirical thermometers. It is much too demanding for common use.

Vapor-Pressure Thermometry. As is well known, vapor pressure is a sensitive but non-linear function of temperature providing convenient means for thermometry in limited ranges of temperature which, unfortunately, do not join to provide continuous coverage of cryogenic temperatures. For example, the range from 40 K to 50 K is above the range of neon and below that of oxygen and nitrogen. Within its limits, however, this type of thermometer is very accurate. In fact, one of the greatest advantages of vapor-pressure thermometers at low temperatures is their extreme sensitivity in the range over which they can be used. A temperature change of 1 Kelvin will result in a sizeable pressure change.

These thermometers are most accurate in the area of the normal boiling point of the liquid used, and hence could be very useful, albeit over a very limited temperature range.

Hydrogen is especially troublesome because of the dependence of vapor pressure upon ortho-para composition; however, hydrogen vapor pressure thermometers have been successfully used under carefully controlled conditions where high accuracy over a very narrow span was sought.

Advantages of this type of thermometry are that it is sensitive, can have good time response, is not affected by magnetic fields, and needs no calibration. The primary disadvantage is that it can be used only between the triple point and critical point of the fill liquid.

5.3.2 Metallic Resistance Thermometry

Since the resistivity of an element or compound varies with change in temperature, it has in many instances been used as a simple and reliable temperature-measuring device. Many elements or compounds, however, are not suitable for use in low-temperature resistance thermometry since they lack one or more of the desirable properties of an ideal resistance thermometer. These properties include:

1. A resistivity that varies linearly with temperature to simplify interpolation.
2. High sensitivity.
3. High stability of resistance so that its calibration is retained over long periods of time and is not affected by thermal cycling.
4. Capability of being mechanically worked.

While there exist a number of metals that are more or less suitable for resistance thermometry, platinum has come to occupy a predominant position, partly because of excellent characteristics, such as chemical inertness and ease of fabrication, and partly because of custom: that is, certain desirable features such as ready availability in high purity and the existence of a large body of knowledge about its behavior have come into being as its use grew and have tended to perpetuate that use. Its sensitivity down to 20 K and its stability are excellent. Its principal disadvantages are (1) low resistivity, (2) insensitivity below about 10 K, and (3) a variation of the form of the resistance-temperature relation from specimen to specimen below about 30 K.

The significance of the first item is that the excellent sensitivity in the liquid-hydrogen region cannot be realized unless the resistor has a high ratio of length to cross-sectional area. If it is a wire, it must be long and thin, which results in a bulky and delicate resistor coil and complications in supporting and insulating it. If it is a film, nonreproducible behavior due to differential contraction stresses between the film and substrate is difficult to prevent.

The second disadvantage can be avoided only by using a different metal in which the lattice vibrations persist to lower temperatures, inasmuch as these are responsible for the temperature-dependent part of the resistivity: that is, a low value of the Debye parameter θ_D is required. Indium has been proposed and ought to have useful sensitivity almost down to its superconducting transition at 3.4 K. However, attention has been diverted from it by the advent of successful germanium thermometers, and it has undergone little or no commercial development.

The third disadvantage is at present the most troublesome one since it can demand that each thermometer be separately calibrated.

A variety of platinum resistance thermometers (PRT) designed for engineering applications is now available. As with other transducers, these devices are subject to extraneous effects (noise). In this case, we wish to measure only the temperature dependence of the resistivity. However, we may also unwittingly measure the strain dependency as well. To avoid this, the engineering thermometers are built to imitate the strain free construction of the precision laboratory type thermometers.

There are two basic designs for engineering use: immersion probes and surface temperature sensors. The immersion probes feature a high purity platinum wire encapsulated in ceramic, or securely attached to a support frame. Features such as repeatability after thermal shocks, time response in different environments, interchangeability, and mechanical shock tolerance differ between companies and specific designs. For the most part, the specifications below represent typical values which might be used in preliminary designs, but exact specifications must necessarily come from the manufacturer. The repeatability of the typical immersion sensor is usually certified to be about ± 0.1 K at the ice point after several thermal cyclings to cryogenic temperatures. For most thermometers this repeatability figure is conservative. The time response is particularly difficult to assess in a general way because it depends critically upon the design and on the method of testing. Flowing water, oil, or cryogenic liquids are often used as the test medium. The time response of the capsule type PRT was previously given as 2 to 7 seconds, which meant that in this time the sensor had reached the equilibrium temperature of the system (ignoring I^2R heating). In the case of the industrial PRT, dynamic systems are frequently encountered. Convention has been to define the time response of a thermometer to be the time it takes the sensor to reach 63.2% of the temperature of a step function temperature change. With this definition of the time constant, a typical range of values for this type of resistor is 0.1 to 3 seconds. Interchangeability is measured in terms of errors involved when more than one thermometer is used with a single R versus T relationship. This becomes a major concern in operations where control resistors must be replacable without system interruption, and where data reduction and calibration expense must be minimized. Interchangeability is ordinarily specified at a given temperature, i.e., the resistance of the thermometers will not vary more than a specified amount at a certain temperature. Immersion type sensors may generally be specified to have the same ice point resistance to within an equivalent of about ± 1.5 K; surface sensors show slightly worse interchangeability, ± 4 to 5 Kelvins at 0°C. Some manufacturers provide different grades of interchangeability for particular models. Even after specifying a particular resistance value at a given temperature, the slope of R versus T, which depends on purity and strain, may vary from one thermometer to another.

The second type of industrial sensor is broadly known as a surface temperature sensor, whose geometry is such that they make good thermal contact with surfaces of various shapes. Sensors are available for clamping around small tubing, fitting into milled slots, and clamping under bolt heads. The principle advantages of these thermometers are that they are small, typically 0.25 cm x 1.25 cm x 1.25 cm with perhaps a factor of two variation in any dimension.

Both the immersion and the surface sensors are available in versions which have built-in bridge circuits. These bridge circuits allow adjustments to be made on individual sensors to increase the interchangeability. Two, three, and four lead configurations are available in both the surface and immersion sensors. Joule heating must be guarded against in all types of resistance thermometers by limitation of the measuring current.

5.3.3 Non-Metallic Resistance Thermometry

A number of semiconductors also have useful thermometric properties at low temperatures. A semiconductor has been defined as a material the electric conductivity of which is much less than that of a metallic conductor but much greater than that of a typical insulator. There are, however, at least three distinct differences between semiconductors and pure metals as resistance thermometers. First, the sensitivity, $(1/R)(dR/dT)$, of a semiconducting thermometer in its useful range is usually much greater than that of a pure metal thermometer. Second, the temperature coefficient of resistivity of semiconductors is negative whereas for pure metals it is positive; for example, the dR/dT for a typical semiconductor is -50×10^{-3}/K at 273 K, whereas for platinum at the same temperature it is 4×10^{-3}/K. Thus the resistance of a semiconductor decreases with increasing temperature while the opposite is true for a pure metal. Third, as mentioned in the definition for a semiconductor, the resistivity of a semiconductor is usually several orders of magnitude greater than that of a pure metal. Consequently, a semiconducting thermometer element is usually short and of relatively large cross section, so that its resistance will be readily measurable.

The most promising semiconductors seem to be germanium, silicon, and carbon. The latter, though not strictly a semiconductor, is included in this group because of its similarity in behavior to semiconductors.

Of the three, germanium has received by far the most attention, and germanium resistance thermometers are now available from several commercial sources. The resistance element is usually a small single crystal. Inasmuch as the resistivity is high, the element can be short and thick. It is mounted strain-free in a protective capsule. Because of this combination of features, the germanium thermometer is both rugged and reproducible.

The major disadvantage associated with the use of germanium thermometers is the lack of a simple analytical representation. Each thermometer must be calibrated by comparison at many points in the range of interest if the inherent reproducibility of the thermometers is to be utilized.

Thermistors (thermally sensitive resistors) are essentially resistors made up of sintered metal oxides. Frequently used materials are nickel, manganese, and cobalt oxides. The temperature-resistance relationship for this type of resistor has a negative slope much like the carbon or germanium resistors. The fact that these resistors are becoming increasingly popular in measurement and control circuits is attested to by the number of companies selling them [3]. The reasons for the increasing use are in part: 1) they are small which tends to make the time response significantly less than one second, 2) they are typically high resistance units which reduces the overall effect of lead resistances, and 3) their temperature-resistance characteristics are dependent on materials and procedures which allows thermometers to be developed which are particularly sensitive in limited ranges of temperature.

There are, of course, disadvantages also. Items 2) and 3) above may be considered as disadvantages as well as an advantage: any one thermistor is not usable over a wide range of temperatures due to its resistance becoming exceedingly high. The temperature dependent behavior of thermistors is similar to that of the semiconductors discussed above. Manufacturing processes allow the tailoring of thermistors to be useful over a wide range of temperatures.

5.3.4 Thermocouples

Thermocouples have the familiar advantage that the temperature-sensing junction can be reduced in size to almost any desired extent, so that the disturbance to the object being sensed can be made very slight, and the response time can be very fast. They also have a familiar disadvantage, namely, that rather small voltages must be measured. This disadvantage is accentuated at low temperatures where the thermoelectric power, dE/dT, is usually smaller than elsewhere. In addition, they have a less familiar but very serious disadvantage, namely, that the net emf depends not merely on the materials nominally used for the two wires but also on material inhomogeneities which, if located in a temperature gradient, will introduce parasitic voltages. These inhomogeneities may arise from variations in chemical composition or may consist of crystal lattice imperfections introduced, for example, by kinking the wires. Their presence can be detected by various tests but cannot readily be corrected for, so that testing merely serves to indicate whether a given wire should be discarded or not.

The emf-temperature relationships of thermocouples are seldom simple over wide ranges and, hence, functional representation is not usually attempted. Instead, a tabular relationship obtained by careful calibration of a thermocouple representative of a particular type is adopted as a standard, and the fabrication of thermocouples of this type is controlled to duplicate within close limits the characteristics of the standard. Where the emf-temperature relation must be known more closely, the user may calibrate the thermocouple at a few well-spaced temperatures and, by reference to the standard table, construct a graph of emf differences. Then, by interpolating in this graph, a correction to any measured emf can be found, and by entering the standard table at the corrected emf, the temperature is found. Some thermocouples commonly used in the hydrogen region include:

1. Gold (2.1 atomic % cobalt) vs. copper: Large thermoelectric power; the gold-cobalt alloy tends to be less homogeneous than other commonly used materials and is unstable if heated above 70°C.

2. Constantan vs. copper: Good homogeneity is possible.

3. Constantan vs. iron, or Chromel vs. Alumel: Advantageous only where the thermocouple is required to be used at both low and high temperatures.

Copper also has serious disadvantages: (1) Its thermal conductivity is very high. This property reaches a maximum around 20 K and at this point may be from two to five times greater than at room temperature. Now, the temperature of a thermocouple junction is determined partly by the heat conductance of the contact between the junction and the object or fluid to be measured. If the contact is noncrystalline and nonmetallic, its conductance will be low and will decrease with decreasing temperature. This would be true if, for example, the thermocouple were used to measure the temperature of a fluid or vapor, or if it were used to determine the temperature of a solid surface to which it was glued or clamped without metallic contact. Conversely, the conductance of the copper wire is high and increases with decreasing temperature (down to 20 K). Thus, the temperature of liquid hydrogen provides a bad set of conditions under which it is difficult to eliminate the heat flow and hence the temperature difference across the contact. (2) The thermoelectric power of copper is very sensitive to transition-metal impurities and especially to iron at low temperatures. Both of the above disadvantages of copper can be avoided by substituting a suitable alloy for it. The alloy, silver (0.37 at.% gold) called silver-normal is currently being used.

5.3.5 Temperature Summary

Figure 5.2 summarizes some representative characteristics of the best known types of cryogenic thermometers.

The terms "reproducibility" and "accuracy" require some explanation. By reproducibility is meant the variability observed in repeating a given measurement using the best present-day laboratory techniques. Changes produced on thermal cycling of the thermometer to and from ambient are included in this parameter. By accuracy is meant the significance with which the thermometer can indicate the absolute thermodynamic temperature. This includes errors of calibration as well as errors due to nonreproducibility, the former usually being much more significant.

The approximate numbers given for these quantities represent good current practice. It may be possible to do better by extreme care. On the other hand, in most engineering measurements a lower order of accuracy is permissible, and this may allow relaxation of certain requirements such as strain-free mounting of resistors, homogeneity of thermocouple materials, purity of vapor-pressure fluid, sensitivity and accuracy of associated instruments, etc.

Some Approximate Characteristics of the Most Widely
Used Classes of Thermometers

TYPE	RANGE K	BEST REPRODUCIBILITY °K	BEST ACCURACY[a] °K	RESPONSE TIME Sec	RELATIVE SIZE[b]	
RESISTANCE THERMOMETERS						
Platinum	10-900	10^{-3}-10^{-4}	10^{-2}-10^{-4}	0.1-10	3	
Carbon	1-30	10^{-2}-10^{-3}	10^{-2}-10^{-3}	0.1-10	2	
Germanium	1-100	10^{-3}-10^{-4}	10^{-2}-10^{-3}	0.1-10	2	
THERMOCOUPLES						
Gold-Cobalt vs Copper	4-300	10^{-1}-10^{-2}	10^{-1}	0.1-1[c]	1	Down to a
Constantan vs Copper	20-600	10^{-1}-10^{-2}	10^{-1}	0.1-1[c]	1	few mills dia
VAPOR PRESSURE						
Helium	1-5	10^{-3}-10^{-4}	10^{-3}	0.1-100	4	
Hydrogen	14-33	10^{-3}	10^{-2}	0.1-100	4	1 cm^3 and up
Nitrogen	63-126	10^{-2}-10^{-3}	10^{-2}	0.1-100	4	
Oxygen	54-155	10^{-2}-10^{-3}	10^{-2}	0.1-100	4	

a-Including nonreproducibility, calibration errors and temperature scale uncertainty

b-From 1 (smallest) to 4 (largest)

c-Bare junctions

Figure 5.2 Summary of Cryogenic Thermometry

For temperatures above about 20 K, the metallic resistance thermometers are more sensitive than the nonmetallic resistance thermometers. Temperatures above 20 K can be measured routinely with an industrial type platinum resistance thermometer with an accuracy of better than 100 mK and time responses somewhat better than 1 second. Accuracy at the millidegree level requires a precision capsule type PRT and careful calibration.

Carbon thermometers are generally used for low temperature measurements ($T < 80$ K) when accuracies of ± 0.1 K or ± 1% of the absolute temperature are needed. Millidegree accuracy is attainable using germanium resistance thermometers at temperatures below 20 K. The primary drawback to germanium thermometers is that no simple analytical representation is available which represents the resistance versus temperature characteristics even for a given class of doped germanium crystals. A many point comparison calibration is required if all the inherent stability of the resistor is to be utilized.

Vapor pressure and gas thermometry offer sensitive methods of temperature measurement with the advantage that no calibration is necessary. Further advantages are that these transducers are not sensitive to magnetic fields or electric fields. In the case of vapor pressure thermometers, the time response may be made comparable to the resistance thermometers.

A sensible recommendation about which type to use cannot be made without knowing the specific measurement requirements. The generalization most likely to hold true, however, is the following: For crude temperature indications and monitoring trends, a gas thermometer will probably be suitable. For more accurate work, vapor pressure or resistance thermometry is recommended. For engineering application in this latter area, the need is for inexpensive devices that do not call for unique calibration.

5.4 LIQUID LEVEL

Liquid level is but one link in a chain of measurements necessary to establish the contents of a container. Other links may include volume as a function of depth, density as a function of physical storage conditions, and, sometimes discerning useful contents from total contents (e.g., pumpable liquid vs. liquid and dense gas contained). Fortunately, the actual discernment of the liquid-vapor interface (liquid level) is often the strongest link in this measurement process due to the significant progress made here in the course of the space program. Liquid level determinations are essential to propellant loading, management, and utilization, and to other diagnostic or control functions, such as engine cut off. As a result of this intense interest, hydrogen liquid level measurements can be made with an accuracy and precision comparable to that of thermometry, for instance, and often with greater simplicity.

This period of development led to many different physical embodiments of liquid level sensors, and there are as many ways of classifying these devices as there are authors who write about them. One classification is by the principle of operation. This groups sensors according to the physics of the device, usually an impedance measurement (or mismatch) in some region of the electromagnetic spectrum. By this scheme, liquid level sensors are grouped as acoustic, optical, thermal, magnetostrictive, etc. This classification is helpful if one is developing new instruments and needs to search the electromagnetic spectrum for a new type.

Another classification which includes the above is useful if one is interested in the outcome rather than the input. Here, sensors are grouped by whether the output is discrete, or digital (point sensors) or whether the output is a continuous analog of the measurand (continuous sensors).

We shall use this latter classification understanding from the outset that the principle of some point sensors can be stretched to make continuous sensors (e.g., capacitance measurements), and that no one type is intrinsically better than another for all cases. Special requirements of the particular application and engineering trade-offs will govern the choice. This chapter will conclude with some comments on the need for further research and development in this area.

5.4.1 Point Liquid Level Sensors

All liquid level sensors depend for their operation on the fact that there be a large property change at the liquid vapor interface, a significant change in density, for example. This may not always be the case if the fluid is stored near its critical point, for instance, or if stratification has built up after prolonged storage. Be that as it may, point level sensors are tuned to detect a sharp property difference and give an on-off signal. Several of the more commonly used types are described below.

The thermal or hot wire type senses the large difference in heat transfer coefficient between liquid and vapor. Since the heat transfer coefficient is much larger in the liquid than it is in the vapor, one can expect, for a given power input, that the transducer will have a different temperature and hence resistance in the liquid than in the vapor. It is this change in electrical resistance which is actually sensed in a wheatstone bridge, and hence these devices can be made both simple and fast. Protection in the form of a stillwell is usually provided to prevent splashing or drops falling on the hot wire (sensing element) from causing a false indication. Small platinum wires, solid carbon resistors and thin-film carbon resistors are examples of sensing elements that are used.

The capacitive type depends upon the difference in dielectric constant between the liquid and vapor which is essentially a function of the fact that the liquid is more dense than the vapor. This sensor is usually made in the form of a bulls-eye, with alternate rings forming the plates of the capacitor, and are installed so that the plane of the rings is parallel to the liquid vapor interface. Detection is accomplished much like the hot-wire sensor, above, but in a capacitance bridge rather than a wheatstone bridge.

The optical type senses the change in refractive index between the liquid and vapor, which of course is closely related to the dielectric constant and density.

This type of transducer contains a light source and a light sensitive cell which are isolated from one another but which do communicate down a prism. The prism is cut in such a way as to have total internal reflection when in gas, and yet let the light escape when in liquid. This is possible since there is a difference in the index of refraction of the liquid and the vapor, and since the critical angle for total internal reflection depends upon the index of refraction. This type of transducer has a very high in-out signal ratio, for the light detector is almost totally illuminated or not.

There are also several acoustic or ultrasonic devices which depend upon the fact that the damping of the vibrating member is greater in the liquid than in the vapor. Often, a magnetostrictive element is driven at a constant power and is more or less dampened depending whether it is in liquid or in vapor. The end of these sensors is about the size of a quarter dollar, but this does not in any way indicate the limit of its resolution. These devices can be tuned to detect only a fraction of the total damping that would occur upon total immersion so that their sensitivity can be much smaller than the total end of the device. Piezoelectric versions of this acoustic type liquid level sensor are also available.

5.4.2 Continuous Liquid Level Sensors

Figure 5.3 illustrates several types of continuous liquid level sensors. Shown schematically are: (a) a direct weighing scheme, (b) differential pressure, (c) capacitance, (d) acoustic and (e) nuclear radiation attenuation.

Direct weighing schemes have indeed been used for hydrogen, but have been handicapped by the fact that the weight of the container is often large compared to the weight of the contents. In modern weigh-facilities the weight of the tank rarely exceeds the weight of the contents (when the tank is full). Calibrated balance weights and strain-gage load cells are most commonly used in this application.

Differential pressure measurements are simple to visualize, but difficult to realize for liquid hydrogen. The "signal" is low due to the very low density of hydrogen and the "noise" is high due to boiling and potential thermal oscillations at the lower pressure tap. Also, the unknown level of the liquid in the gage lines can introduce hydrostatic head errors.

Capacitance sensors are widely used for the continuous measurement of the level of liquid hydrogen. They do not truly follow the interface but sense the total contents of the container. That is, the dielectric constant of the gas phase contributes to the output signal, as well as that of the liquid phase. This can be a serious source of error in hydrogen as the density of the cold gas (and hence its dielectric constant) is significant compared to that of the liquid. This problem is especially troublesome in nearly empty tanks, but is often compensated for by either: (a) segmenting the capacitor and ignoring the output from those sensor sections located in the vapor phase as the liquid level drops or (b) installing a few point sensors at critical levels and routinely calibrating the continuous sensor against them. Rod-to-blade and concentric tube configurations are most common in this type of sensor.

In the acoustic device shown, the liquid itself is used as the transmitting medium. In this case, a transmitter feeds an electric pulse to a transducer where it is converted to an acoustic pulse traveling at sonic velocity to the liquid-vapor interface, reflected back at the same speed to the transducer, where it is reconverted to an electric pulse,

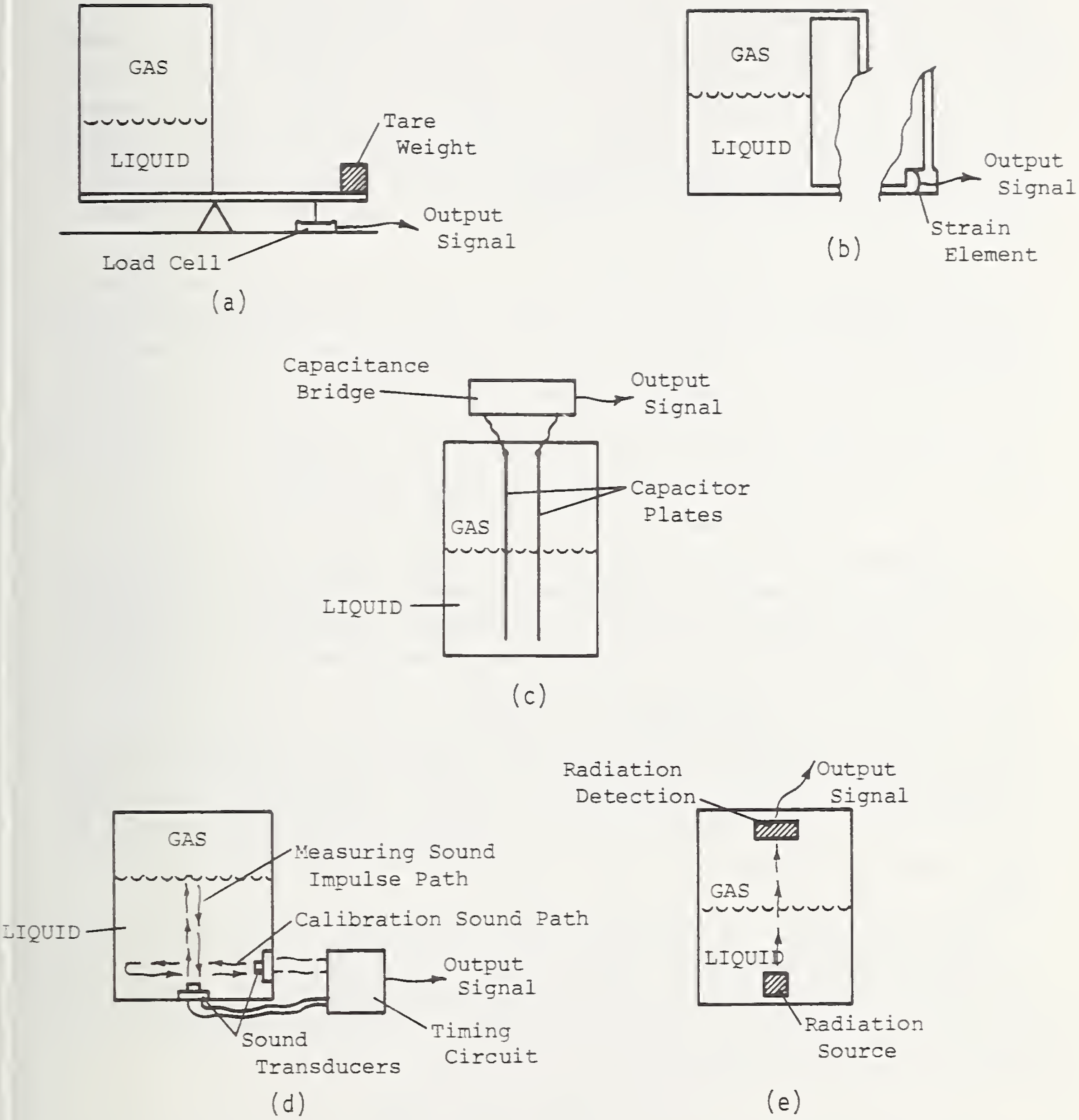

FIGURE 5.3 - Continuous Liquid Level Sensors.

and finally sent to a receiver. Knowing the velocity of sound in a given liquid, the pulse transit time from transmitter-to-interface-to-receiver becomes an indication of liquid level. In order to eliminate extraneous interfaces that may be caused by vapor bubbles in the liquid, a tubular still-well often is used to isolate the measured fluid column from such physical distrubances. Bubbles also may be suppressed by slight pressurization of the vessel immediately prior to any measurement. Sometimes an acoustic racetrack of known path length and variable time of flight is included to provide a measure of the density of the fluid. The product of the two measurements tends to give an indication of the mass of the fluid contained in the tank.

Nuclear Radiation Attenuation (NRA) has found some success in oxygen and nitrogen systems, but comparatively little use for hydrogen. This is so because hydrogen is nearly transparent to the commonly available sources of nuclear radiation, while the tank walls are relatively "thick" to the same radiation. Hence the fundamental signal to noise ratio is inherently low. Hydrogen does absorb beta radiation rather well, but then "windows" of beryllium or equivalent light metals must be placed in the tank walls. On the whole, this technique seems too sophisticated for simple engineering measurements.

Not shown, because the system consists of inserting a simple dipole antenna into the tank, is RF cavity detection. In this system microwave energy is introduced into a tank so as to energize it by setting up electromagnetic fields throughout the entire volume of the tank. The tank interior is a dielectric region completely surrounded by conducting walls. Such a system is called a cavity, and the resonant frequencies established are the normal theoretical modes of the cavity. Considerable development work has been done very recently on both uniform density fluids, and non-uniform density fluids and this technique continues to show considerable promise for both mass-gaging and level-gaging in a variety of cryogenic fluids, including hydrogen. RF transmission characteristics through coaxial cables can also be used to detect liquid levels by measuring the time of flight of a RF pulse through the cable [4,5]. This latter technique is called time domain reflectometry (TDR).

Heated platinum wires or ribbons have been used as continuous liquid level sensors in cryogenic fluids but have found little application in hydrogen service. With continuing improvements in superconducting materials it may soon be possible to use a superconducting wire to detect liquid level in hydrogen containers -- in the absence of magnetic fields, materials already exist that are suitable for operation up to 23 K.

5.4.3 Liquid Level Summary

Extensive development of liquid hydrogen level detectors took place during the space program, but it is remarkable how little space hardware is actually used in the commercial sector. A deliberate effort to adapt space instrumentation to commercial and industrial application seems worthwhile.

Primary instruments and facilities to calibrate liquid level devices do not exist. Unlike pressure or temperature measurements, this part of the national measurement system is chaotic and needs to be brought under control.

5.5 DENSITY

Density measurements are closely akin to liquid level measurements because: 1) both are often required simultaneously to establish the mass contents of a tank, and 2) the same physical principle may often be used for either measurement, since, as noted, liquid level detectors sense the steep density gradient at the liquid-vapor interface. Thus, the methods of density determination include the following techniques: direct weighing, buoyancy, differential pressure, capacitance, optical, acoustic, ultrasonic, momentum, rotating paddle, transverse momentum and nuclear radiation attenuation. Each of the principles involved will be discussed along with its relative merits and shortcomings.

5.5.1 Direct Weighing Method

The direct weighing method of density determination measures the volume and weight of the mixture to obtain density. Although direct weighing is not considered a field-type instrument, it could serve as a primary calibration standard. Some of the advantages of this method are the simplicity of the equipment, repeatability, good frequency response, and the lack of dependence of pressure, temperature, and fluid inhomogeneities on the measurement. A disadvantage of direct weighing is the poor sensitivity, due to the fact that the entire system must be weighed or nulled out.

5.5.2 Buoyant Force Method

Density of a fluid may be measured by the buoyant force of the fluid upon a submerged plummet. This method is ideally suited for static laboratory use and involves relatively simple equipment. The drawbacks of the buoyancy method are slow response, poor sensitivity, and the need to make a remote reading of a mechanical displacement.

5.5.3 Differential Pressure Method

The differential pressure method measures the pressure of a vertical column of the fluid which, along with the height of the column, gives the density. Advantages of this method are: relatively simple equipment, small component size, and the possibility of application as a field type instrument.

This method has several disadvantages. The method is dependent upon two separate measurements, pressure differential and fluid liquid level. Errors in the accuracy of either of these two separate measurements will affect the over-all method accuracy. Because of the extreme low density of liquid hydrogen, the accuracy, the sensitivity, and the hysteresis of the differential pressure measurement will be adversely affected. This method also requires a sophisticated electronic system to compute the average fluid density.

5.5.4 Capacitance Method

The determination of density through capacitance measurements depends upon the fact that the dielectric constant and density are related for simple fluids, such as hydrogen, by the well-known Clausius-Mossotti function:

$$P = [(\varepsilon - 1)/(\varepsilon + 2)](1/\rho).$$

Where P is the macroscopic polarizability in units of induced dipole moment per unit mass per unit applied field, and ε and ρ are the dielectric constant and density in cgs units.

Thus, a measure of the dielectric constant (capacitance measurement) is a direct measurement of the density. Disadvantages include the well known problems of making good capacitance measurements in the field without stray signals and erroneous temperature effects.

5.5.5 Optical Method

The optical method utilizes the relationship of spectral absorption to fluid density. The density of hydrogen can be measured by measuring the amount of spectral absorption, caused by the fluid, of an incident light source.

$$\rho = \frac{1}{u\ell} \ln \frac{I_o}{I}$$

where:

ρ = density of fluid

u = absorption coefficient

ℓ = light path length

I = measured intensity after passing through length ℓ

I_o = incident intensity.

Using the infra-red spectrum, this method can determine the density of liquid hydrogen because a number of spectral absorption lines exist in the range of 4100 to 5100 wave numbers for these fluids. Such a method should have good frequency response, adequate sensitivity, and not be restricted to homogeneous fluids. However, the problem of providing optical windows may be overwhelming.

5.5.6 Acoustic Method

The acoustic method utilizes the fact that the velocity of propagation of a sound wave in a fluid is directly related to the fluid density:

$$c = \sqrt{K/\rho}$$

where:

c = velocity of propagation of a sound wave

K = bulk modulus, a constant for a particular fluid

ρ = density of the fluid

Solving the above equation for the fluid density yields:

ρ = K/c^2, or

ρ = Kt^2/ℓ^2, where

ℓ = distance between the sound wave transmitter and the sound wave receiver, and

t = time required for the sound wave to travel distance ℓ.

Thus, fluid density is measured by measuring the time required for the sound wave to travel from the sound wave transmitter, through the fluid, to the sound wave receiver.

This method has been used for both static and dynamic fluid density measurements with some success. Advantages of this method include a good frequency response and the fact that there are no moving parts located in the fluid.

This method has several disadvantages such as a low signal to noise ratio, the fact that fluid turbulence and fluid non-homogeneity will cause spurious echoes, and a bulky instrument is required. Also, temperature effects that influence the fluid vessel geometry may adversely affect performance.

5.5.7 Ultrasonic Method

The ultrasonic method measures the impedance of a crystal vibrating in a fluid; this impedance can be related to the fluids density. For instance, a piezoelectric crystal, in torsional vibration, immersed in a fluid, has its electrical impedance related to the fluid density by:

$$\rho = \frac{\pi}{f_o} \left(\frac{m}{s}\right)^2 \frac{(K_1 R - K_2 R_o)^2}{\mu}$$

where:

ρ = density of the fluid

f_o = resonant frequency

m/s = mass to surface ratio

R = impedance of the crystal at its natural frequency

R_o = impedance of the crystal at its natural frequency in a vacuum

μ = viscosity of fluid

The terms K_1 and K_2 may be considered constant over a small fluid viscosity range. For density measurements where the fluid viscosity range is <u>appreciable</u>, a more general equation is applicable:

$$\rho = \frac{\pi}{f_o} \left(\frac{m}{s}\right)^2 \frac{(\Delta f_{total} - \Delta f_o)^2}{\mu}$$

where:

Δf_{total} = bandwidth at the half power point

Δf_o = bandwidth at the half power point in a vacuum

For most density measuring applications the fluid viscosity range is not too great, therefore the first equation is applicable. In this case, sufficient accuracy is generally achieved solely by measuring the impedance R and neglecting the term R_o. With this, fluid density is related to impedance by:

$$\rho \propto R^2.$$

This ultrasonic method of density measurement has advantages that include excellent frequency response and sensitivity. Disadvantages of this method include the delicate nature of the apparatus, the requirement of a quiescent fluid medium, and the viscosity dependence.

5.5.8 Momentum Methods

Density can be measured by several momentum methods. The density of the fluid is obtained by measuring fluid flow rate and fluid flow momentum.

For instance, the rotating paddle method is based on the principle that an aerodynamic foil, if rotated through a fluid, will experience a measurable drag which can be related to density. The rotating paddle serves a two-fold purpose: density measurement and stirring of the mixture. The equipment required is relatively simple. Disadvantages include low frequency response and sensitivity, and the presence of moving parts in the fluid.

Density of a fluid can also be measured by the angular momentum method, which measures the angular momentum of a rotating fluid and relates this momentum to density. As in the rotating paddle method, the angular momentum method measures the density and stirs the mixture. The equipment required is relatively simple. Disadvantages of this method include the presence of bulky, moving parts in the fluid and the lack of any known investigation into the method's applicability to a static fluid density measurement.

One particular hydrogen momentum densitometer depends upon the fact that the mass of any vibrating system is a primary factor in determining the dynamic characteristics of the system. If the system is designed so that the fluid flowing through it measurably affects the vibrating mass, a means of measuring fluid densities will have been provided.

The dynamometer, sensing the force exerted by passage of the fluid, generates a signal, (E_{ac}), in phase with the motion and proportional to the maximum force, or:

$$E_{ac} \sim F_{max} \sin \omega_f t \; .$$

If E_{ac} is rectified, the resulting signal, (E_{dc}), is proportional to the maximum force, or:

$$E_{dc} \sim F_{max} \; .$$

The final relation for the fluid density takes the form:

$$\rho = a + b' \; E_{dc}$$

where:

a and b' are experimental constants.

This method will, hence, determine fluid density with the fluid in either a static or dynamic condition.

Advantages of this method are in its frequency response, repeatability, and linearity. This method also has advantages of being unaffected by fluid pressure effects, is not dependent upon fluid homogeneity, and can be made fluid-material compatible.

This type of densitometer has been evaluated in oxygen and nitrogen systems but application to liquid hydrogen will require higher sensitivities.

5.5.9 Nuclear Radiation Method

The nuclear radiation method utilizes the adsorption of radiation energy by the fluid medium interposed between a radiation source and a radiation detector.

Typically, this method for hydrogen employs a beta or low energy gamma radiation source so focused to impinge on the radiation detector placed on the opposite side of the fluid container. The fluid may be in either a static or a dynamic condition. The adsorption of a collimated radiation beam from the radiation source in the matter interposed between the radiation source and the radiation detector is given by:

$$I = I_o \exp(-VT)$$

where:

I = intensity at receiver

I_o = intensity of source

V = linear adsorption coefficient

T = thickness of the adsorber.

V, the linear adsorption coefficient, is related to the density of the matter interposed between the source and detector by the expression:

$$\frac{V}{\rho} = \sigma$$

where ρ is the apparent or combined density of the matter interposed between the source and detector. In this case ρ is the combined density of the fluid container, ρ_c, and the fluid, ρ_f. σ is the mass adsorption coefficient which for a particular fluid and container is a constant.

The fundamental adsorption equation may now be written in the form:

$$I = I_o' \exp(-K\rho_f)$$

where:

$$I_o' = I_o \exp(-\rho_c T_c \sigma_c)$$

$$K = \sigma_f T_f.$$

For a fluid container having a fixed geometry, the intensity of radiation received by the detecter is related to the density of the fluid inside the container by:

$$\frac{dI}{I} = -K \rho_f.$$

Thus, a linear change in fluid density causes a linear change in output signal.

This method has a distinct advantage in the fact that no moving parts are inside the fluid container. This method can be highly repeatable, and have little hysteresis error.

Primary disadvantages, besides those inherent to any radiation measurement include the need for windows transparent to the radiation (or long counting times) and the need for a fairly long adsorption path.

5.5.10 Density Summary

Density is an inferential measurement, and as such, it should be traceable to a national standard, such as a national density reference system. Primary instruments to calibrate densitometers do not exist.

Several physical principles of hydrogen density measurement have been brought well forward by the space program. Notable are the capacitance, vibration, and nuclear radiation attenuation schemes. Microwave methods (see Section 5.4.2) are recently moving to the forefront. It is felt that the pressing need now is to: a) commercialize these instruments for routine engineering applications and b) provide an adequate national reference system.

5.6 FLOW

There are three basic types of flowmeters which are useful for liquid hydrogen. These are the 1) pressure drop or "head" type, 2) the turbine type, and (3) the momentum type. We shall discuss each in turn.

5.6.1 Head Meters

This type of meter embodies the oldest method of measuring flowing fluids. The distinctive feature of head meters is that a restriction is employed to cause a reduction in the static pressure of the flowing fluid. This pressure change is measured as the difference between the static heads on the upstream and downstream sides of the restriction.

Theoretical development of the flow equations for head type meters may be found in publications of the ASME [6]. A simple expansion of Bernouilli's theorem leads to an equation of the form:

$$V \sim \sqrt{g\Delta P/\rho}$$

where V is the velocity, ρ the density, g the gravitational constant and ΔP the pressure drop. The form of the solution is independent of the particular embodiment of the flow restriction, whether it be an orifice plate, venturi, or flow nozzle.

The appeal of these meters in cryogenics is more than simplicity and stems from the possibility of eliminating the necessity for calibration, if proper design, application theory and practices are followed. Design methods for orifices, flow nozzles, and venturi tubes are available in publications of the ASME [6]. Recommended practice for flange-mounted sharp-edge orifice plates can be found in publications of the ISA [7] and ISO [8].

These recommendations which were developed for water can be corrected for thermal contraction of the flow device and used to provide suitable flow measurements at cryogenic temperatures. Reynolds number increases caused by the low viscosity of cryogens are treated in the conventional way, i.e., by adjustment of the head meter discharge coefficient.

The characteristics of this class of meter are as follows. The device is strictly a volumetric meter, that is, it can of itself give no information regarding mass flow rate. With appropriate pressure sensing, the range can be extended up to 10 to 1. It is the very nature of these devices that they generate a decrease in pressure by accelerating the fluid. If we are dealing with a saturated cryogen, then this sudden decrease in pressure could lead to vapor formation (cavitation) in the flowing stream and an erroneous flow measurement.

Richards et al. [9] addressed themselves to the problem of potential cavitation in head meters designed for cryogenic flow. Richards made many attempts to obtain points off the calibration curve with the upstream static pressure lower than the equilibrium vapor pressure. In spite of the fact that the downstream static pressure was as much as 10 inches of mercury below the vapor pressure, all of the points fell on the calibration curve within the accuracy of the experiments. Although these particular experiments showed no ill-effects attributable to cavitation, it is good design practice to maintain static liquid pressures within the meter well above the fluid saturation pressure. In spite of all shortcomings, head meters are widely used and quite reliable.

5.6.2 Turbine Type Meters

The turbine-type volumetric flowmeter is probably the most popular of the various flow-measuring instruments. This is partially due to a lack of direct mass-measuring flowmeters, although the simple mechanical design and the demonstrated repeatability are sufficient merits of their own.

The turbine-type volumetric flowmeter is a simple mechanism which consists of a freely spinning rotor having N blades, each inclined at an angle α to the axis of flow. The rotor is supported in guides or bearings mounted in a housing which forms a section of the pipeline. The angular velocity (rpm) of the rotor may be detected by one of a number of methods; e.g., a permanent magnet encased in a rotor body will induce an alternating voltage in an inductive pickup coil mounted on the housing, or the core of the pickup coil may consist of a permanent magnet and the rotor constructed of a magnetic material so that the change in magnetic circuit reluctance, as each rotor blade passes the coil core, causes an alternating current to be induced in the coil. Capacitive and photoelectric methods of observing rotor rpm have also been used. The primary requirement, however, is that the angular velocity of the rotor be directly proportional to volumetric flowrate, or more correctly, to some average velocity of the fluid in the pipe. A mathematical description of the turbine-type flowmeter is given by

$$\omega = \frac{V \tan \alpha}{R} = \frac{Q}{A_{\lambda} - A_{r}} \, \frac{\tan \alpha}{R}$$

where ω is the rotor angular velocity, V is the average flow velocity at the rotor blades, α is the rotor blade angle with the pipe axis, R is the average radius of rotor blade center of pressure, Q is the volumetric flow rate, A_λ is the internal cross-sectional area of housing, and A_r is the maximum cross-sectional area of rotor.

Deviations from this idealized mathematical expression can be expected because of (1) retarding forces on the rotor such as fluid drag, mechanical friction from rotary and thrust bearings, and transducer magnetic drag, (2) velocity profile variations, and (3) swirl of the incoming fluid stream.

A variation of the turbine type meter is the "twin turbine" type. In this case, two turbines of different blade pitch are coupled together by means of an elastic restraint. Because of the difference in pitch, they would tend to revolve at different speeds. However, this is prevented by the elastic coupling, so that they do revolve at the same speed, but with a "phase angle" between them. The magnitude of the phase angle is a measure of the flow rate, and is said to be, in fact, a measure of the mass flow rate.

The turbine type flowmeter is widely used for several reasons. It is, first of all, a simple mechanism. It generally is of a minimum physical size, therefore it is lightweight. This means a minimum mass to cool. It has a flow range of 10 to 1. The electrical signal output is easily converted to digital, hence readily adaptable to telemetry systems. It is self-propelled (fluid flow supplies the driving force) and no electric driving motors are required. In case of bearing failure, which could jam the rotor, no further impedance to flow results. There are no shaft or electrical seals required between the fluid and the meter exterior. It has a record of good repeatability, and the meter has had extensive use.

While the turbine-type flowmeter has the above advantages, there are certain considerations which must be made when using the flowmeter in hydrogen service. For instance, turbine meters can be damaged by excessive rotor speed from gasseous or two-phase flow. As with some other meters with moving elements, protection must be provided through proper piping design, venting, bleeding and cooldown procedures. Screens are sometimes installed in the pipeline downstream of these meters to collect turbine blades in the event of an overspin failure. Such screens are good insurance against damage to expensive pumping equipment, etc. that may be located downstream of the turbine meter. Other considerations governing turbine meters are: thermal effects which may cause dimensional changes of the rotor blade and hence rotor speed; and change in the average velocity profile due to changes in fluid viscosity [10]. Also, there is some pressure drop across these meters and they are subject to cavitation-induced errors as are the head meters.

To achieve the full potential of the turbine meter as a flow measurement element in cryogenics, the meter must be calibrated at the cryogenic temperature and with the fluid intended for use.

5.6.3 Vortex Shedding Meter

The vortex shedding meter is also a single-phase fluid rate-velocity meter, like the turbine meters, but in a distinct class by itself.

The phenomena upon which it is based is the Karman vortex trail and its application to the measurement of flow of liquids and gases is fairly recent [11], probably because only recently have sensors become available to detect the vortices.

The Karman vortex trail is used to explain certain phenomena associated with the flow around cylinders, ellipsoids, and flat plates. For flow around a cylinder, for instance, at Reynold's numbers above about 20, eddy's break off alternately on either side in a periodic fashion. Behind the cylinder is a staggered, stable arrangement or trail of vortices. The alternate shedding produces a periodic force acting on the cylinder normal to the undisturbed flow. The force acts first in one direction and then in the opposite direction. Let f represent the frequency of this vibration in cycles per unit time, D the diameter of the cylinder and V the undisturbed velocity. Experiments have shown values of the dimensionless Strouhal Number, fD/V, to vary between 0.13 and 0.27.

If the frequency of the vortex peeling approaches or equals the natural frequency of the elastic system consisting of the cylinder and its supports, the cylinder may have a small alternating displacement normal to the stream flow. (The vibration of some smoke stacks, the vibration of some transmission lines, and the fatigue failure or progressive fracture of some transmission lines have been attributed to this resonance phenomenon).

Such a meter was evaluated on liquid nitrogen at NBS [12]. It consisted of a bluff body located normal to the flow stream and basically measured the average velocity of the flow passing through the pipe. The frequency f of the vortex shedding was given approximately by

$$f = \frac{0.27\ V}{D}\ , \text{ Hz}$$

where V is the velocity in feet per second and D is the nominal meter diameter in feet. The bluff body was in the shape of a modified delta with its base facing upstream.

The vortex sensors consist of electronically self heated resistance elements whose temperatures and therefore resistances vary as a result of the velocity variations adjacent to the body. These velocity variations reflect directly the action of the vortices as they peel off from the downstream edge of the bluff body.

The precision of this meter was quite good (approximately 1/2 percent, 3σ), but the range of linearity was found to be about 5 to 1 rather than the expected 10 to 1. Since these meters are quite new to cryogenic service, one can reasonably hope their performance to improve with further experience. They have the advantage of no moving parts at the low temperatures and therefore require minimum maintenance. The meter factor (pulses/gallon) depends only on the inside diameter of the pipe and the width across the bluff body face. Cryogenic evaluation is limited, but performance on liquid nitrogen and oxygen shows promise.

5.6.4 Momentum Mass Flowmeters

Mass reaction or momentum flowmeters are of three types. There are those in which an impeller imparts a constant angular momentum to the fluid stream and then the variable torque on a turbine which removes this momentum is measured; there are those in which an impeller is driven at a constant torque and then the variable angular velocity of the impeller is measured; and those in which a loop of fluid is driven at either a constant angular speed or a constant oscillatory motion and then the mass reaction measured.

One type of mass reaction flowmeter is shown in Fig. 5.4. The cylindrical impeller and turbine are coaxially mounted in the fluid conduit, but each on a separate shaft. The axial vaned impeller imparts a constant angular momentum to the fluid while the axial vaned turbine removes the angular momentum. A measure of the torque on the turbine, which is elastically restrained, is a measure of the mass flow rate. This flowmeter employs rotating elements in the fluid stream. Some consider the use of such rotating elements in a cryogenic fluid stream a disadvantage since they are subject to mechanical failure. Experience has shown however that the probability of such a failure is quite remote.

Another type of these mass reaction flowmeters is shown in Fig. 5.5. A single axial vaned impeller is used in conjunction with a hysteresis drive and an exterior mounted drive motor. Torque is maintained constant and the impeller speed is varied inversely with the mass flow rate. A measure of the impeller speed is a measure of the mass flow rate. This scheme has the characteristics of high resolution at low flow rates and decreasing resolution as the flow rate increases. This flowmeter also employs a rotating element in the fluid stream. The previous remarks concerning moving elements in a cryogenic fluid stream apply here also.

Still another type of mass reaction flowmeter is shown in Fig. 5.6. This flowmeter consists of a closed loop through which the fluid flows, a means of driving the closed loop in a constant manner, and a means of measuring the mass reaction. Instead of rotating the loop, as shown in Fig. 5.6, the loop is driven in an oscillating fashion, thus the measured mass reaction has an oscillating value. This oscillation of the loop eliminates the need for rotating seals. While this flowmeter does not employ moving parts that are located in the fluid stream, it does require a mechanical movement of the flow loop itself which some consider a disadvantage.

The above described mass reaction flowmeters have in common the fact that momentum must be imparted to the fluid stream and require that the mass reaction due to this momentum be measured to determine the mass flow rate.

The performance of these flowmeters were determined in a NASA sponsored flowmeter evaluation program [13]. From the results of this program it appears that several cryogenic mass flowmeters have been developed that are capable of liquid hydrogen mass flow measurement accuracies on the order of ± 0.5 percent. There appears to be degradation of mass flow measurement accuracy however when subjected to a two-phase flow.

There are several other concepts of cryogenic fluid flowmeters that are available or are in development. Since they were not evaluated in the previously mentioned NASA-sponsored program, definitive performance results, on the scale of the previously discussed mass flowmeters, are not yet available. These flowmeters are inferential mass flow measurement devices having in common measurements of fluid density and fluid volume flow or fluid volume flow-induced momentum.

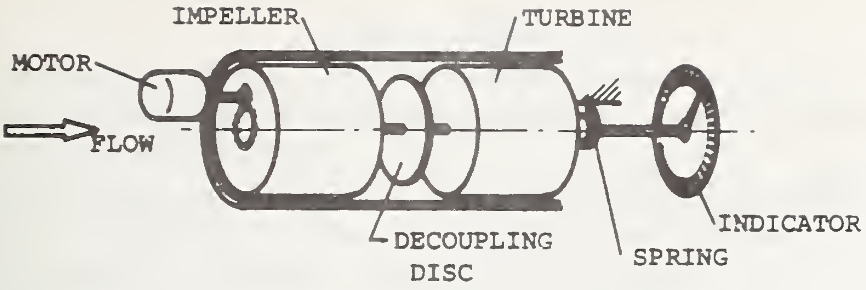

FIGURE 5.4 - Axial Flow Transverse Momentum Mass Flowmeter.

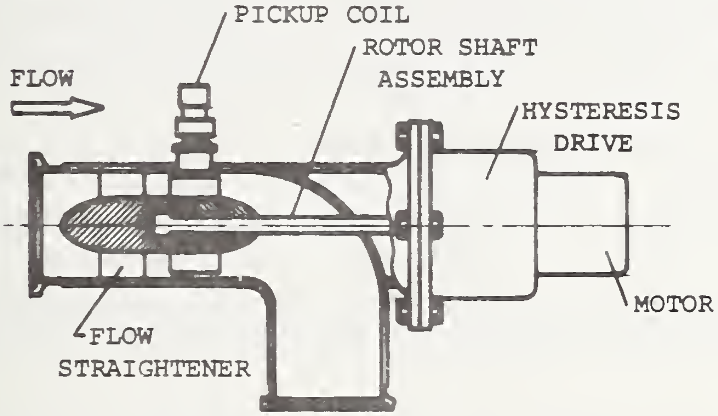

FIGURE 5.5 - Axial Flow Transverse Momentum Mass Flowmeter.

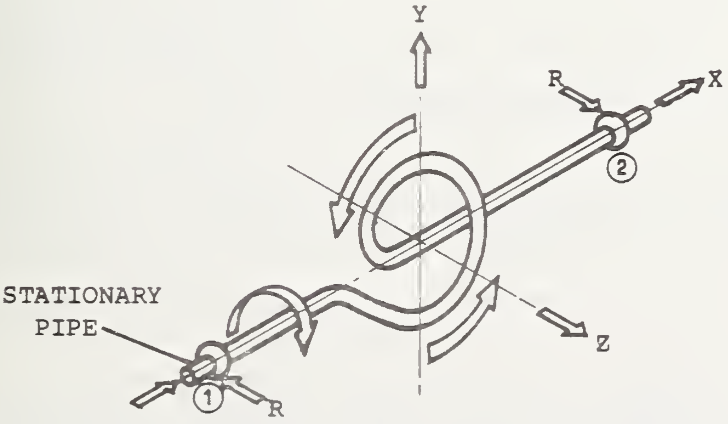

FIGURE 5.6 - Gyroscopic Transverse Momentum Mass Flowmeter.

5.6.5 Flowmeter Summary

There is no shortage of physical principles upon which to base a hydrogen flowmeter. Depending on the need, they range from simple pressure-drop meters to sophisticated mass reaction meters.

The need is thus not for more types of meters, but rather stems from the problem common to every type. Namely, flow is a derived, not an intrinsic, quantity. As such, every flowmeter will require traceability to a reference system to establish its credibility. The general needs were perhaps best articulated in four categories by Mann [14]:

1. Flow Reference Systems. A study should be initiated to identify those systems that are currently available to document the flow range, pressure and temperature capabilities, precision and accuracy relative to basic standards and multiple test fluid capability. After establishing location and capability, a system of interlaboratory comparisons should be initiated by exchange of test meters and performance data for these test meters as obtained on each reference system. This interlaboratory comparison using reference test meters would identify systematic errors existing with respect to individual facilities relative to the entire reference measurement system.

2. Substitute Fluids. A concerted program should be inititated and designed to determine the appropriateness of the use of substitute fluids for cryogenic flow metering calibrations. This would include a program designed to determine the reasons for water calibration errors experienced at cryogenic temperatures as well as experimental evidence that other fluids (such as liquid nitrogen) may be used as a test fluid in place of liquid hydrogen.

3. Large Flow. General purpose flow reference systems are at the present time restricted to less than 200-300 gallons per minute. The trend for flow measurement is to higher and higher flow rates in excess of these values. The severity of modern constraints placed on design and operation and the requirements both economical and technological for mass flow measurements to total uncertainties of less than one percent, suggest that a fresh look be taken at establishing a general purpose cryogenic flow research center. Such a center would include as process fluids: water, liquid oxygen, liquid methane, liquid nitrogen, liquid argon, and liquid hydrogen. Flow range should extend to 3.8 m^3/s (60,000 gpm) with provision for pressure and temperature controls.

A cryogenic flow research center of this size and scope would impact on present oxygen and hydrogen aerospace requirements, short term (10-20 year) energy importation programs (LNG), and long term requirements of a hydrogen-based energy system. The latter has tremendous potential in providing and distributing energy in an environmentally attractive form using many existing fossil fuel type systems, but will require high density liquid storage systems to make it a workable concept in certain cases.

4. Uniform Performance Method. Standard tests or codes should be developed and adopted where possible for cryogenic flow measurement. The number of experimental points, treatment of experimental data and reporting of error should be standardized to provide common and effective criteria for meter evaluation.

In short, this branch of the National Measurement System needs to be brought under control, and such a program of quality assurance would have far ranging benefits, extending greatly beyond only hydrogen technology itself.

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CHAPTER 6

TRANSMISSION OF HYDROGEN

C. F. Sindt

6.0 SUMMARY

Transmission and transport of hydrogen were studied to determine the most economical method of delivering liquid hydrogen. From economical considerations alone, hydrogen should not be liquefied for transmission or transport except when delivery is across more than 200 km of ocean or unless hydrogen is to be used as a liquid. In practice, hydrogen is frequently liquefied to facilitate transport, i.e., it is liquefied for convenience of transport and delivery. When the final use requires liquid hydrogen, it can be transmitted as gas or liquid, or the energy can be transmitted as electricity to produce hydrogen gas and to liquefy it at the final destination. Costs of transmission, production, and liquefaction must all be considered before the most economical method of delivering liquid hydrogen can be determined in any specific delivery system.

For this study a 1200 MW electrical power plant was the assumed source of electrical power to produce hydrogen gas and to run the liquefier. Because the electrical power generation may occur some distance from the delivery terminal, liquid hydrogen transmission distances of 80 and 1600 km were used in this analysis.

Costs of delivered liquid hydrogen were determined for the following energy transmission systems: gaseous hydrogen pipeline, liquid hydrogen pipeline, electrical power line, electrical power line combined with liquid or gas pipeline, truck and rail transport of liquid, and liquid transport by ocean tanker. The systems that combine electrical power lines and gas or liquid pipelines used the electricity to liquefy gas or to pump and refrigerate liquid in the pipeline. The costs of delivered liquid hydrogen varies with electrical power costs; hydrogen costs were calculated for electrical costs ranging from 5 to 45 mills/kW-h_e. For a transmission distance of 80 km and electricity costs of 12 mills/kW-h_e, the lowest delivered cost of liquid hydrogen was 19 mills/kW-h_t; the transmission system was the combined gas pipeline and electrical power line. For 1600 km distance and 12 mills/kW-h_e electricity costs, the lowest delivered cost of liquid hydrogen was 22 mills/kW-h_t; the method of transport was ocean tanker. The lowest cost for hydrogen transmission over land was obtained with the combined gas pipeline-electrical power line system (23 mills/kW-h_t). Truck and rail transport of liquid were more costly for both 80 and 1600 km distances, but they may be preferable because they accommodate widely separated delivery sites.

6.1 INTRODUCTION

Transmission costs of hydrogen have been reported by others [1-3] and some comparisons have been made of costs to deliver hydrogen as liquid and gas. Gregory [1] has performed detailed cost analysis of hydrogen gas transmission. Johnson [2] compares costs of gas transmission and costs of transporting liquid in barges. He also gives some comparative costs of transporting liquid and costs of delivering liquid hydrogen produced from coal gasification and from nuclear power. From the data of Gregory and Johnson, it is apparent that hydrogen should not be liquefied for transport over land if the end use does not require liquid. We, therefore, did not analyze costs for delivering gaseous hydrogen but concentrated on cost analysis for delivering liquid hydrogen to those users who require hydrogen in liquid form.

Transport or transmission costs alone do not reflect the total cost of delivery of liquid hydrogen. The complete system of production, liquefaction and transmission must be considered because of the significant differences in the energy consumed in the different systems. To obtain a comparison of the conventional methods of delivering liquid hydrogen, eight systems were analyzed using six methods of transmitting or transporting energy over two distances. To keep the comparison of the systems on an equal basis, it was assumed that a 1200 MW electrical power plant supplied energy to the systems, but no specific energy sources for the power plant were considered. Each system was then analyzed to determine the cost of delivering liquid to the user's storage dewar as a function of the cost of the electrical power.

6.2 SYSTEM DESCRIPTIONS

The approach taken was that the hydrogen was to be produced by electrolysis using power generated by some large electrical power plant such as a nuclear or solar plant. Since solar power was considered, and sea-power plants are normally far at sea, the transmission distance of 1600 km (approximately 1000 miles) was used as well as 80 km (50 miles). The 80 km would be more typical for a nuclear plant.

The systems were evaluated for both transmission distances to get relative costs for liquid at the destination. The systems considered were: (1) liquid hydrogen production at the power plant and liquid transmission in a vacuum-and-Perlite insulated pipe; (2) production of hydrogen gas at the power plant, gas pipeline transmission with parallel electric power transmission to run the liquefier at the destination; (3) production of gas at the power plant, gas pipeline transmission with gas used from the pipeline at the destination to produce the liquefier power requirements; (4) electric power transmission to the destination, gas produced by electrolysis and liquefied at the destination; (5) gas and liquid produced at the power plant with truck transport of liquid; (6) gas and liquid produced at the power plant with railroad transport of liquid; and (7) gas and liquid produced at the power plant with ocean tanker transport of liquid. The last two systems were not considered for the 80-km transmission because railcar turnaround is a problem for such short hauls and therefore does not compete with trucks, and for 80 km the large ocean tankers are not competitive with off-shore pipelines. The seven methods of transmission are depicted in figure 6.1.

6.3 SYSTEM ANALYSIS

To evaluate the methods of transmission to deliver liquid hydrogen to the user, the integrated system, not just the transmission method, must be considered. The approach used was to assign a power plant size of 1200 MW and to then size the components to fit this power source. The first assumption was that the plant was devoted strictly to production of hydrogen liquid and that it operated at an average load factor of 90%. All equipment was sized to take 100% of the power plant output. The second consideration was that the cost of producing electricity varied depending on the power plant, fuel, location, etc. Since cost of power is a major item in all systems, the analysis was made for

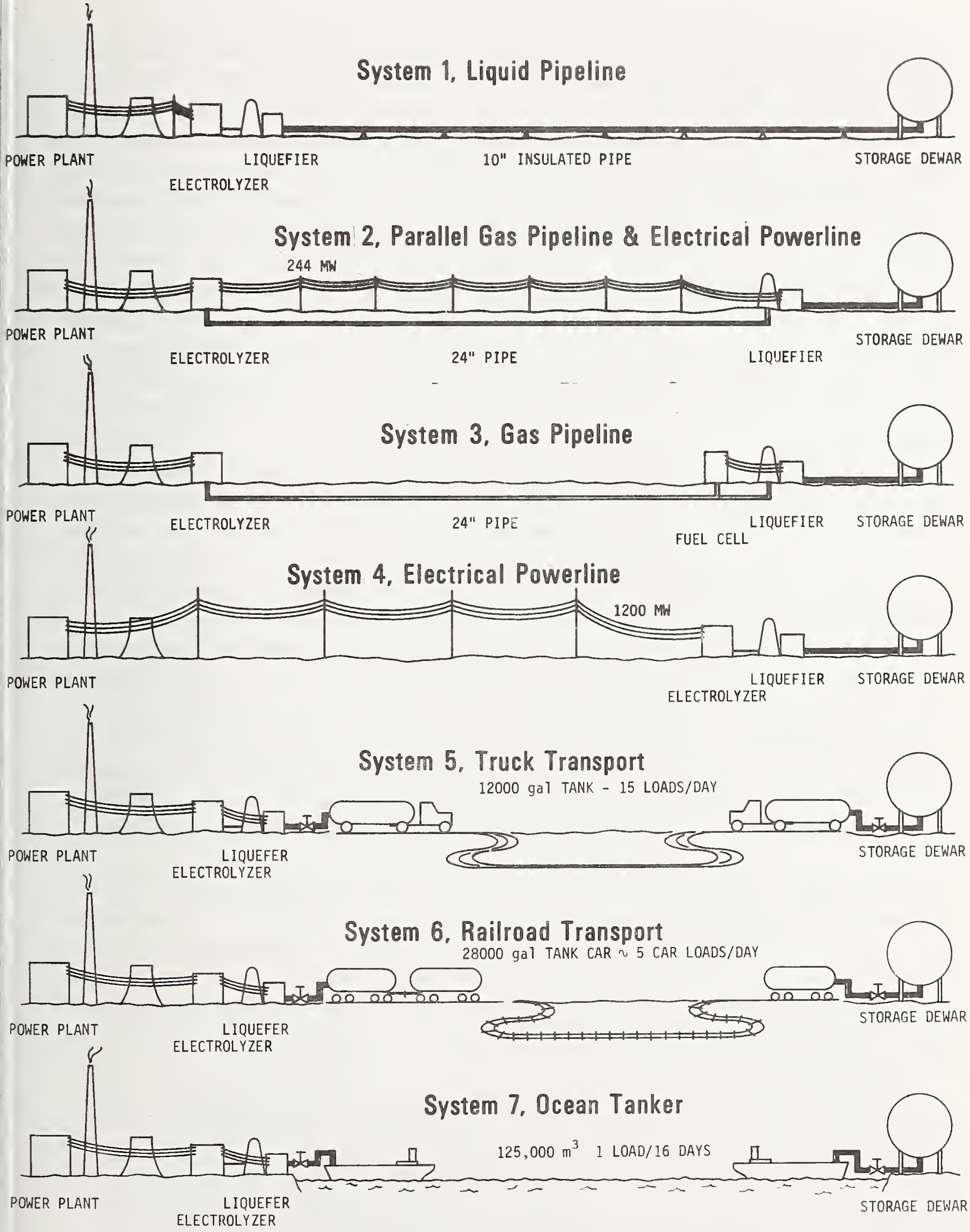

Figure 6.1 Hydrogen supply systems.

electrical cost of 5 to 45 mills per kW-h. Cost of gas and power lines was taken from Gregory [1] and the Federal Power Commission Report [4]. Other costs used for the study are given in Chapter 2.

The cost of the liquid hydrogen transmission pipeline (system 1) was estimated as $490 per meter of length. The line size selected was 25 cm (10 inches) in diameter with 15-cm-thick insulation. Construction and installation costs were not available, as no such line of the length considered has been used; therefore, the cost of installation was considered to be near those of a power line. These costs were used because the installation of the liquid line was aboveground to facilitate maintenance of vacuum and access for replacing sections. The aboveground installation costs include purchase and clearing of right-of-way, and construction of supports for the line. Although support structures would be much smaller than for power lines, they would be much more frequent. This was the rationale used to justify the relatively large installation cost for liquid hydrogen lines versus gas pipelines.

The 80-km-long liquid hydrogen line was sized so that no pumping or refrigeration stations were required along the way. The liquid was pumped to 2.02 MPa pressure at the liquefier, then cooled enough so that normal boiling point liquid arrived at the end of the 80-km line. This required the 15-cm-thick insulation.

The use of slush hydrogen was considered, but the constraint of delivering normal-boiling-point liquid was met without adding the slush-producing equipment.

The selection of the line diameter was not optimized for minimum energy consumption, but was selected to keep the velocity reasonably low so that the pressure drop in 80 km could be met without excessive pumping pressures. A very detailed analysis would have included transfer line costs as a function of pipe diameter and pressure loss, and then balanced these costs with energy consumption for pumping and refrigeration. It was felt that this type of detailed analysis was not warranted unless this preliminary comparison of hydrogen transmission costs indicated that the liquid hydrogen pipeline was a good choice.

For system 2 the gas transmission costs for a 24-inch (61 cm) pipe [1] were used with appropriate adjustments for total gas flow. For the 80-km line, the gas compressors were considered to be located at the power plant and to be driven electrically. The electrical power transmission costs were taken from The Federal Power Commission Report [4], adjusting for the relatively short distance. The electric power line must supply approximately 244 MW, so the costs for a 230 kV line were used. Energy losses in the power line were negligibly small for this analysis.

The gas pipeline for system 3 was nearly the same as for system 2, since the change in the required flow was not significant for cost evaluation. The big difference between systems 2 and 3 was the back conversion of hydrogen gas to produce electricity to run the liquefier. This conversion includes a significant loss of energy due to inefficiency. Because fuel cells are estimated to be about 50% efficient, a fuel cell was considered as the means of converting the hydrogen to electrical energy.

System 4 used a 500 kV power transmission line which is near peak efficiency at 1200 MW. Electrical losses were small but significant and so they were included.

Data for trucking costs for system 5 were taken from Eifel [5] and from current charges for trucking of liquid hydrogen. The costs of trucking LNG given by Eifel [5] were thought to be valid for liquid hydrogen since equipment and regulations for hauling are very similar.

Railroad costs from Eifel [5] were used for system 6 for the 1600 km transmission distance. The railroad and trucking costs were adjusted for inflation which has occurred since 1968.

Ocean shipping costs for system 7 were taken from the current shipping contracts for LNG. These contracts include the cost of operation and of docking.

For the 1600 km transmission of hydrogen, the systems are very similar to those for 80 km except refrigerators and pumps are required every 80 km for system 1, and in systems 2 and 3 compressor stations are required every 105 km. Of course, electrical losses were greater for the electrical transmission lines in systems 2 and 4.

Another system similar to system 1, identified as system 1A, was also analyzed for the 1600 km distance. This system, which is a liquid pipeline with a parallel electrical power line to supply power for the refrigerators and pumps, was considered when it became evident that system 2 outperformed system 3. In system 1A a large portion of the power is required to run the refrigerators and pumps so that the delivered energy is still low but it is greater than system 1: In system 1 the inefficiency of converting the hydrogen back to mechanical power to run the refrigerators and pumps is very significant and reduces the delivered energy by a considerable amount.

For systems 5, 6, and 7, the gas produced during cooldown of the transport tanks was recycled through the liquefier. The liquid vaporized at delivery by transfer losses and cooldown of the receiving hardware was considered lost from the liquid system; in practice, an effort would be made to recover this gas.

The costs computed were costs of production (not selling costs) and consider the total cost of capital, including interest, insurance, etc. to be 15 percent. Also, the costs are only representative of actual costs for average installations. Actual costs vary considerably; for instance gas line and power line costs may vary as much as 300% due to the area of installation.

6.4 RESULTS

The condensed results of the analysis are presented in table 6.1. System 2 is the least expensive means of supplying the liquid on shore for both distances considered.

It is evident from the table that the systems delivering the most energy per year are also those that deliver liquid hydrogen at the lowest cost. The largest single cost item for most of the systems is the cost of electrical power and all of the systems were limited to the same amount of electrical power. Thus, delivered energy is representative of overall system efficiency.

For the 80 km transmission, liquid piping (system 1) and total electrical power transmission (system 4) are competitive. The total gas pipeline transmission of system 3 suffers from the inefficiency of back converting gas to mechanical power to drive the

Table 6.1 Costs of Delivering Liquid Hydrogen 80 km and 1600 km from Power Plant. Electric Power (All Systems Use 1200 MW @ Cost of 12 mills/kW-h_e) (Costs are mills per unit of delivered energy based on the high heat value)

	SYSTEM	ELECTROLYZER			LIQUEFIER			TRANSMISSION					TRANSPORTATION		DELIVERED LIQUID HYDROGEN	
								Gas or Liquid Pipeline		Electrical Powerline						
		Size (kg/h)	Cost of Electricity (mills/kW-h_t)	Capital and (O&M) Cost (mills/kW-h_t)	Size (kg/h)	Cost of Electricity (mills/kW-h_t)	Capital and (O&M) Cost (mills/kW-h_t)	Size (I.D.)	Capital and (O&M) Cost (mills/kW-h_t)	Size (MW)	Cost of Electricity (mills/kW-h_t)	Capital and (O&M) Cost (mills/kW-h_t)	Size (kg/load)	Total Cost (mills/kW-h_t)	Total Cost (mills/kW-h_t)	Delivered Energy (kW-h_t/yr)
80 km	1. Liquid Pipeline	22285	12.70	1.13	22285	3.49	1.53	25 cm	1.44						20.3	6.9×10^9
	2. Parallel Gas Pipeline and Electric Powerline	22581	12.88	1.13	22280	3.30	1.45	61 cm	0.06	244	.03	0.20			19.1	7.0×10^9
	3. Gas Pipeline*	28359	21.10	1.78	17275		5.16*	61 cm	0.13						28.1	5.4×10^9
	4. Electric Powerline	22365	12.91	1.13	22365	3.31	1.39			1200	.22	0.78			19.8	7.0×10^9
	5. Truck Transport	22180	14.30	1.31	24400	4.00	1.65						3080	0.84	22.1	6.2×10^9
1600 km	1. Liquid Pipeline	22285	31.95	2.76	22285	8.76	3.41	25 cm	72.5						119.4	2.8×10^9
	1A. Parallel Liquid Pipeline and Electric Powerline	16920	16.92	1.64	16920	4.28	1.84	25 cm	39.51	302	.36	2.26			67.0	5.3×10^9
	2. Parallel Gas Pipeline and Electric Powerline	21850	13.04	1.14	21550	3.25	1.39	61 cm	0.79	270	.56	3.03			23.2	6.7×10^9
	3. Gas Pipeline*	28350	21.41	1.82	17035		5.16*	24 cm	1.65						30.0	5.3×10^9
	4. Electric Powerline	19990	12.87	1.14	19990	3.25	1.45			1200	2.12	15.27			36.0	6.2×10^9
	5. Truck Transport	22180	15.14	1.33	24400	4.21	1.74						3080	11.63	34.0	5.8×10^9
	6. Railroad Car Transport	22180	15.14	1.33	24400	4.21	1.74						9165	5.26	27.7	5.8×10^9
	7. Ocean Tanker	22400	13.60	1.19	22400	3.60	1.54						8.8×10^6	1.83	21.8	6.6×10^9

* Includes 367 MW fuel cells to power the liquefier at 3.64 mills/kW-h_t

NOTE: The higher heat value (HHV) of liquid hydrogen is 2.77 kW-h_t/ℓ = 10.47 kW-h_t/gal liquefier. Even though trucking (system 5) appears costly, it may be highly favored because of the flexibility of delivery locations and because no new technology is required (such as development of fuel cells and large hydrogen compressors for gas pipelines). Also, the liquid transfer losses of the truck system at delivery may be reduced below present day losses by improved procedures and hardware. The transfer losses at delivery were considered an entire loss from the system. In actual practice, this gas would very likely be sold or used locally. This same argument holds true for the truck, railroad and ocean tanker systems for the 1600 km distance.

For the 1600 km distance, the railroad system (system 6) is third lowest in cost; however, with improved transfer systems and use of boiloff gas, it could be more competitive with the gas-electric system (system 2). The railroad system does not require new technology.

Since the cost of electrical power generation varies significantly with location, method of generation, cost of fuel, etc., the costs of producing and delivering liquid hydrogen were determined for power costs ranging from 5 to 45 mills per kW-h. These costs are shown in figures 6.2 and 6.3.

For the 80 km distance, the truck transmission seems to increase at a higher rate than systems 1, 2, and 4; therefore, trucking may not be a good compromise if power costs are relatively high.

For 1600 km distance, railroad costs remain second to system 2 for the range of electrical power costs and may be a good compromise. System 1A, using liquid transmission and a parallel electric power line, still is not competitive because of the high costs of the insulated pipeline and the high capital and operating costs of refrigerators stationed every 80 km. The most economical means of moving very large quantities of liquid is by ocean tanker if the source and use points are seaports.

A separate analysis was made to compare the system of transmission of hydrogen gas via offshore high pressure pipeline to the system of liquefaction and ocean tanker shipment. The cost for long distance offshore pipelines was estimated from one such line that is to be constructed at a projected cost of 3.1×10^6 \$/km. Using this cost, a distance of 1600 km, a cost of 12 mills/kW-h_e for electricity, and current shipping costs for LNG, the ocean tanker shipping of liquid hydrogen was found to be less expensive than piping gas for delivery of hydrogen in either liquid or gaseous state to a seaport.

6.5 CONCLUSIONS

As long as electrical power costs are below 15 mills/kW-h_e, the most practical means of supplying liquid hydrogen to users within about 100 km of the power plant is probably by truck. This method offers more versatility in that trucks can deliver to many different users. If the use is at a single installation, such as an airport, the gas pipeline with a parallel power line to run the liquefier is probably the best choice. This system has the added advantage of placing the liquefier so that any boiloff gases from storage, from transfer, and from detanking operations can be recovered and reliquefied.

If the transmission distance is long, 1000 to 2000 km, the railroad delivery is attractive. As for the short haul trucking case, it is more versatile in delivery, since two or more large and widely separated users can be supplied with very little additional cost. If

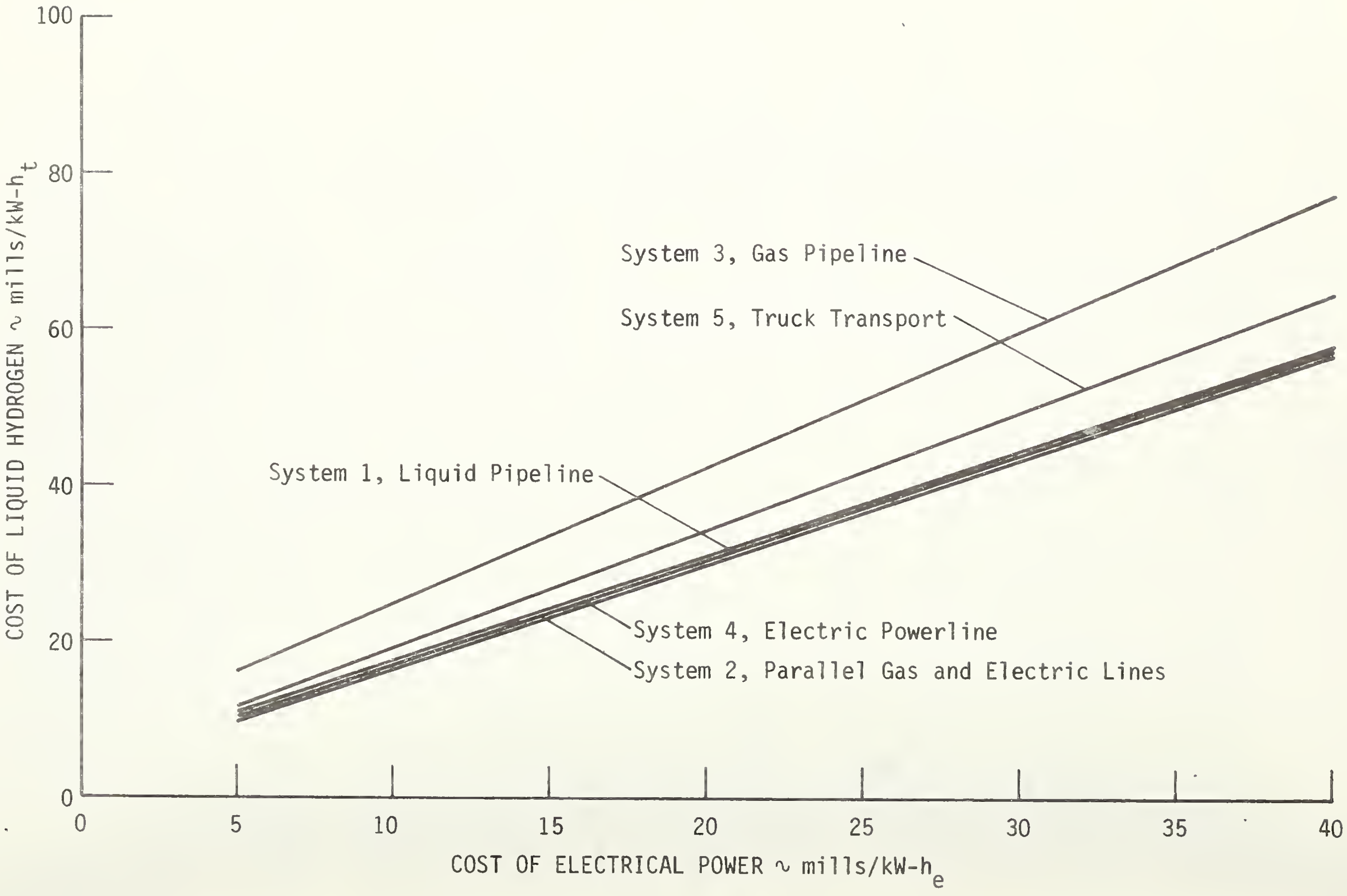

FIGURE 6.2 Cost of Liquid Hydrogen (HHV) at 80 km From Power Plant. HHV=High Heat Value.

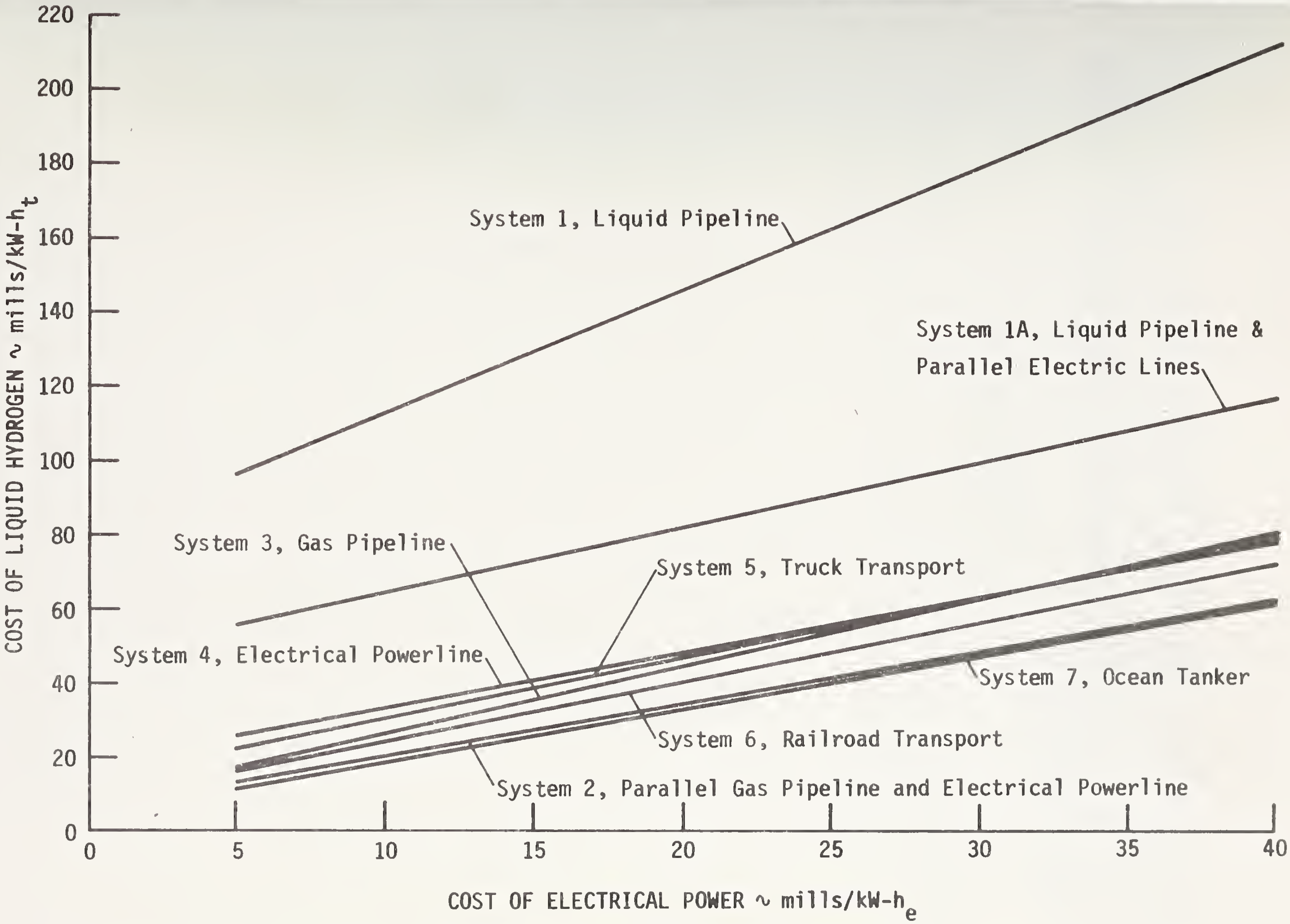

FIGURE 6.3 Cost of Liquid Hydrogen (HHV) at 1600 km From Power Plant. HHV=High Heat Value.

all use is confined to a single airport or all users are close to a large storage dewar, the gas pipeline with the parallel electric power line looks to be most efficient and practical; again, the liquefier is located so that boiloff gas from heat leak and liquid transfer can be reliquefied. For hydrogen transmission across the ocean, liquefying and shipping is the most attractive.

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CHAPTER 7

SOLAR ENERGY--LIQUID HYDROGEN

C. F. Sindt

7.0 SUMMARY

Using a solar collector area of about 110 m^2, year-round single-household energy needs in Boulder, Colorado, can be provided if the excess energy collected in summer is converted to and stored as liquid hydrogen for use in the winter; all space heating, hot water, and electricity needs can be supplied. The system to collect the energy, produce the hydrogen, and store it as liquid is complex; therefore, to be economical, it must be large enough to serve a community of 100 or more households. Ten major components are needed for the system; however, all except the solar collector and hydrogen-air fuel cell are commercially available.

The solar energy-liquid hydrogen system discussed herein has some advantages over more conventional solar energy systems. Several of these advantages are: (1) the system has redundancy for supplying energy for space heating, hot water, and electricity, so it will provide the required reliability for utilities; (2) the system is self-contained and does not depend on energy sources external to the system during normal operation; and (3) if the solar collector does fail, emergency energy can be supplied from an external source in the form of liquid hydrogen.

Cost of energy delivered by the system will very likely be competitive with other energy sources in the future. At solar collector costs of \$30 per square meter, the energy costs are about 1.5 times present electricity costs and at \$20 per square meter, the energy costs are about twice present energy costs for a Boulder home using propane and electricity.

7.1 INTRODUCTION

In the northern half of the United States, the greatest part of the insolation occurs nearly six months out of phase from the greatest need for energy. To make solar energy a practical year-round total energy source in these regions, long term storage of this energy must be accomplished in a method compatible with other energy sources and compatible with community development.

A preliminary study indicates that sufficient solar energy can be collected in some areas of the United States (such as the Missouri Valley, the Rocky Mountains, and the Southwest region) to supply all of the residential energy needs of the average household using 110 to 150 m^2 of solar collector per residence. A solar system will provide the energy for space heating, hot water, and electricity. To provide all three, the system must store summer energy for winter use. The excess summer energy is stored as chemical energy in the form of liquid hydrogen. The liquid is burned in the winter to make up the energy deficiency which occurs because of the low winter insolation.

The solar energy-liquid hydrogen system is complex and is not economically feasible as a single resident unit. It is more suited as a public utility supplying a minimum of approximately 100 residences or an apartment complex of 100 households per energy plant. Because energy for space heating must be distributed as a hot fluid--to keep heating efficiency high--the more condensed the community the less energy lost to pumping, heat transfer, etc. Energy systems to supply 100 average households were analyzed.

7.2 SYSTEM DESCRIPTIONS

Two solar energy systems were evaluated for comparison. One system stores energy as liquid hydrogen; the other systems stores energy as heat in aluminum oxide.

The first system (the solar energy-liquid hydrogen system) consists of ten components. The largest and most costly component is the solar collector. The collector considered is of the concentrating type as heat is required at temperatures to 755 K. A heat storage unit is required that is capable of storing all of the heat accumulated during the longest day of the summer and storing this heat at temperatures to 755 K. A heat engine such as a Rankine or Stirling engine converts the heat in excess of that required for space heating to mechanical energy. The heat engine drives a dc generator which supplies power to an electrolyzer to electrolyze water. The hydrogen from the electrolyzer is then liquefied and stored in a dewar. Dewar boil-off gas is used in a hydrogen-air fuel cell to produce electricity for the households when the generator is not running. Heat rejected from the heat engine is used to heat water for domestic use. The system is depicted in figure 7.1.

The operation of the system during the four seasons is generally as follows. During the summer, heat is collected during the day and some is used immediately to run the engine to generate electricity and produce liquid hydrogen. The remainder of the daytime heat is stored to be used during the night to run the engine and hydrogen producing equipment. Because insolation is not constant, the short term heat storage is used so that the liquefier will run nearly continuously. Boil-off hydrogen gas during this time of year is reliquefied. Electricity for household use is taken from the generator and hot water from the rejected engine heat.

During the spring and fall, when space heating is required intermittently, hydrogen is produced less frequently and only when excess heat is available. Thus, the heat storage unit is used to store the energy in excess of the household requirements and when the storage is near maximum, hydrogen is produced until the storage is at the lower temperature limit. When the generator is not running, electricity is produced using boil-off gas in the fuel cell.

In winter, if the sun shines, the solar collector produces nearly enough energy to meet the average space heating requirement. When it is cloudy, hydrogen is burned to supply heat and hot water. The fuel cell supplies electricity using boil-off gas or gasified liquid. This arrangement provides for carrying the great excess of summertime energy into the winter in the form of chemical fuel.

The second system studied (the solar energy-heat storage system) stores heat energy in aluminum oxide at two temperatures. The system consists of a concentrating solar collector, a low temperature heat storage unit, a high temperature heat storage unit, a heat engine, an electrical generator, and a hot water heater -- see figure 7.2. Most of the solar energy

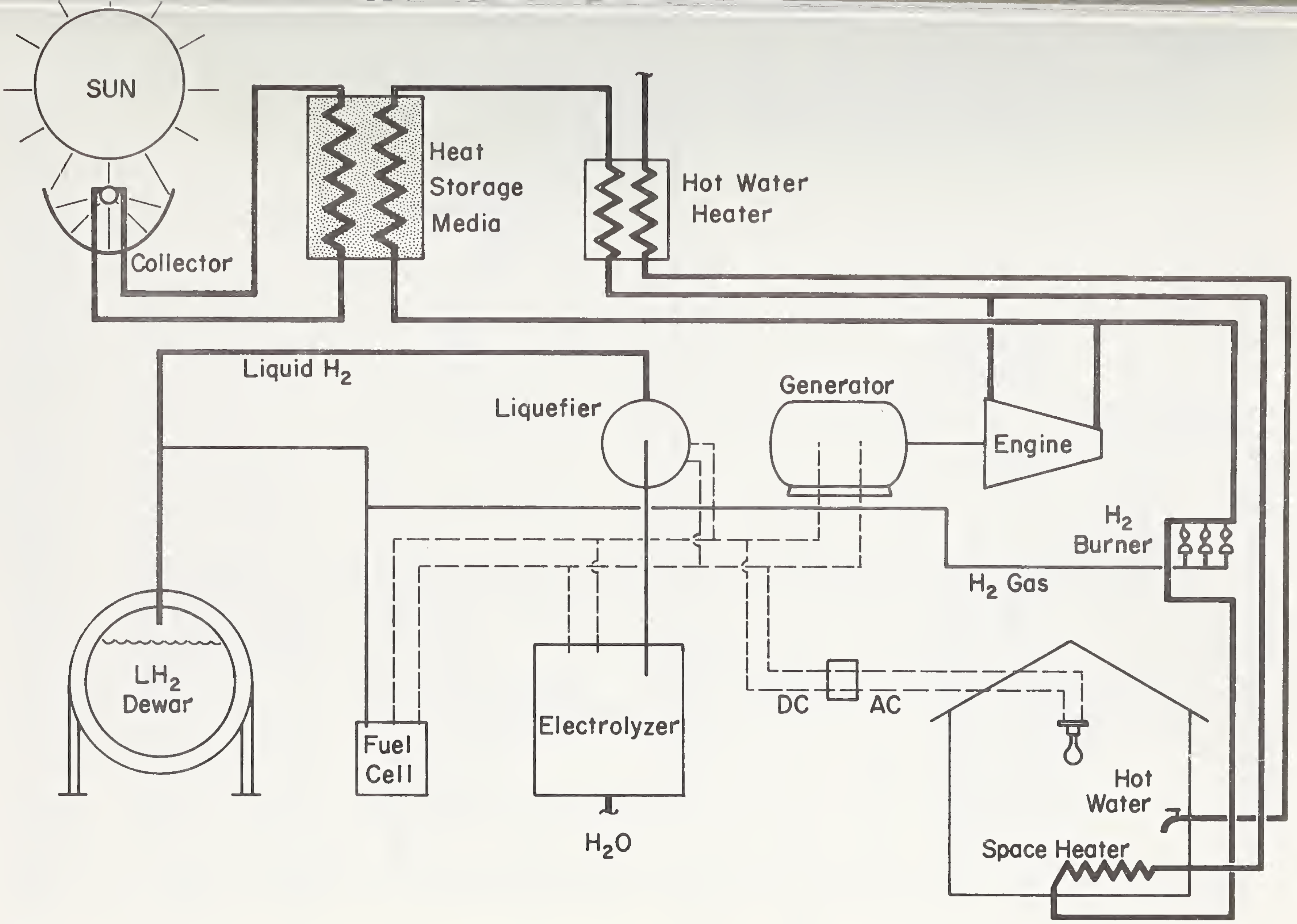

Figure 7.1 Solar-liquid hydrogen energy system.

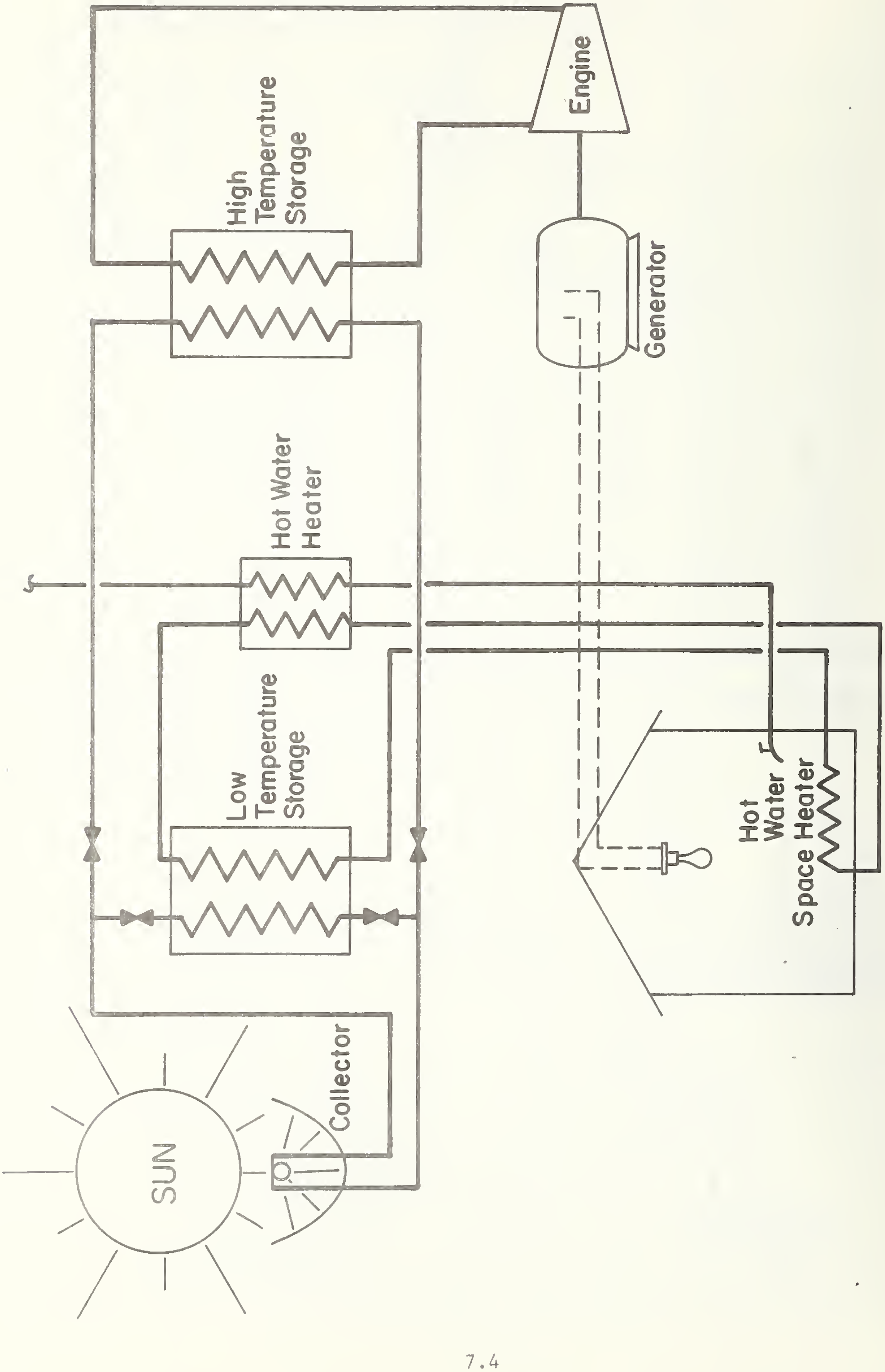

Figure 7.2 Solar energy system.

collected in this system is stored at low temperature (360 to 755 K) for space and hot water heating. The rest of the energy is stored at high temperature (645 to 755 K) and is used to run the heat engine to drive the electrical generator. The solar collector and the heat storage units must be large enough to supply the required heat, hot water, and electricity needs for a specified period of cold, cloudy winter days.

7.3 SIZING SYSTEM COMPONENTS

To size the system components, the energy requirements of the average household were needed. These were taken from a paper by P. A. Achenbach [1]. The data presented are from a subpanel report on total energy systems [2] and are for Baltimore, Maryland. These seasonal data were adjusted to a Boulder, Colorado environment by using the ratio of the sums of the respective geographic degree-days[1] during the heating seasons. The monthly heating loads for Boulder were obtained by using the appropriate fraction of this total heating load as determined by the number of degree-days in each month.

No change was made to the cooling loads. The cooling loads were assumed to be evenly distributed over the months of June, July, and August. Hot water and electricity loads were assumed to be the same as those given for Baltimore.

Design trade-offs can be made in sizing units such as the solar collector, heat storage, electrolyzer, and liquefier. Two extremes in solar collector sizes were analyzed in the study.

The system using the smallest solar collector assumed that all energy collected over and above the daily requirements was converted to liquid hydrogen and is one of the systems described in section 7.2. For this system, the heat storage unit was small and was primarily used to run the engine; therefore, the assumed operating temperature levels of the heat storage were 645 to 755 K. The heat storage media was assumed to be aluminum oxide. The storage unit was sized so that the liquid hydrogen producing equipment would operate 24 hours a day during the summer. The heat engine, generator, electrolyzer and liquefier were sized to use this energy at maximum output. The fuel cell was sized to carry 200% of the average monthly load with air conditioning. The liquid hydrogen storage dewar was sized to accommodate the maximum amount of liquid that would accumulate if all of the excess energy were converted to liquid, i.e., enough hydrogen to last through 21 cold, sunless winter days. This dewar contains enough liquid, as of January 1, to last 12 cold (sunless) winter days. A cold winter day was assumed to use 150% of the average December day heat load.

The solar collector was assumed to be as small as possible so that just enough energy is collected to run the system during an average year. The solar collector configuration used was a parabola of revolution with an assumed collection efficiency of 70% of the incident radiation. A concentration ratio of about 120 is required to attain the desired temperature of 755 K. The total monthly insolance and the average percentage of possible sunshine were taken from Strock [3]. The resulting available energy per square meter is given in table 7.1.

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[1] The degree-days for a given day are equal to the difference between the daily mean temperature (in degrees F) and a reference temperature of 65°F. The degree days in any period are the sum of the daily degree-days.

The second system uses the largest solar collector, no hydrogen storage and requires two temperature levels of heat storage, one for space heating and one for electrical generation. The heat storage media was also aluminum oxide. Since space heating can use temperature as low as 360 K or lower, this energy was assumed to be stored at temperatures ranging from 360 to 755 K. The energy storage for the generation of electricity was taken at temperatures of 645 to 755 K. The high temperatures were used to keep the heat engine efficiency at a reasonable level. The heat engine was therefore assumed to operate with input temperature from 645 K to 755 K and rejection temperatures at 340 K. The assumed thermal efficiency was 30% which is high for the lower temperature but reasonable for the maximum temperature. This system was then sized to provide energy storage for a maximum of 8 cold winter days.

Table 7.1 Solar heat at Boulder, Colorado, per month

Month	$W\text{-}h/m^2$
Jan.	98,667
Feb.	111,288
Mar.	166,629
Apr.	185,480
May	208,775
June	205,353
July	208,775
Aug.	185,480
Sept.	166,629
Oct.	111,288
Nov.	98,667
Dec.	92,018

7.4 ESTIMATED PERFORMANCE OF SYSTEM COMPONENTS

Each component of the system was assigned efficiencies comparable with existing equipment or in the case where equipment is not available, efficiencies were assigned similar to the values predicted by those developing the equipment. The efficiencies used were 90% for heat exchange, 80% for combustion, 30% for engine and generator combined, 78% for electrolyzer, 51% for the fuel cell, 30% for the liquefier and 70% for the solar collector. Of all efficiencies estimated, the solar collector is the least credible as no data were available for this type of collector.

7.5 COMPARISON OF THE OPERATION OF SYSTEMS

Since the hydrogen system is complex, system operation will require full-time monitoring. The collector temperature must be higher than the temperature of the storage unit before heat can be added. The heat in storage must be compared to the projected space heating requirements before the decision is made to run the liquefier since liquefaction includes several low level efficiencies that result in greater energy losses. In the summer the liquefaction rate would need to be adjusted so that the operation is as near continuous as possible since warmup and cooldown of the liquefier represent energy losses.

Several features of the hydrogen system do provide for advantages over the simpler system of dual temperature storage. The most significant advantage is that the liquid hydrogen system can be fueled from an exterior source in the event of a component failure or an extended local cold, cloudy period of weather. The fuel cell and the hydrogen-fired boiler could assure continuous supply of electricity and heat as long as liquid hydrogen was provided to the liquid storage dewar. This dewar has a capacity to handle 21 cold winter days or 30 days of average winter-day energy consumption.

The second operational advantage is that the system normally has a minimum of 12 cold winter days energy on hand as of January 1, where the nonhydrogen system can store only an 8-day supply. This 8-day supply of energy requires that the heat storage be at a maximum. To get maximum heat storage, more than 16 totally sunny and consecutive days are required preceding the 8 cloudy days. This is an unlikely series of events.

A third advantage of the liquid hydrogen system is that there is redundancy in the heat and electrical supply in the event of a solar collector failure or an engine-generator failure. The hydrogen-fueled boiler can provide space heating and the fuel cell provides electricity. In the event of a fuel cell failure, the generator could be run from the hydrogen-fueled boiler and the heat engine.

Stand-by heat and power sources could be supplied for the non-hydrogen system at additional costs.

7.6 COSTS

Capital, operation, and maintenance costs of each unit were determined from information taken from the literature. These costs are given in chapter 2. The cost of capital, insurance, and profit was assumed to be 15% and was amortized over 20 years. This amortization time may be extensive for some components such as fuel cells and solar collectors. Data on fuel cells are not available because commercial units have not been in existence many years. Also, no data exists on solar collectors of the highly concentrating type required. Because of this lack of substantiated data, the 20-year period was assumed as the most reasonable for all equipment. The unit cost that could not be estimated with any degree of confidence was that of the solar collector. Since the solar collector is the major cost item and actual costs were not known, a study of the effect of solar collector cost on final energy cost was made for \$20 to \$110 per square meter of collector. The capital costs of the other items used for the analysis are given in table 7.2. The resulting cost per kilowatt hour of energy versus cost per square meter of solar collector is shown in figure 7.3 for three systems. The liquid hydrogen system and the system designated as an 8-day dual temperature system are the two systems described earlier. The 4-day single temperature system is a conventional non-hydrogen solar system considered for comparison. In this system all heat is stored at 645 to 755 K and a maximum of 4 sunless, cold winter days of energy is stored. Also, for comparison purposes, the current operating costs for similar households using electricity with natural gas, heating oil and propane are shown and the separate cost of the electricity is shown. As is evident from the figure, the total energy costs are very sensitive to the cost of the solar collector,

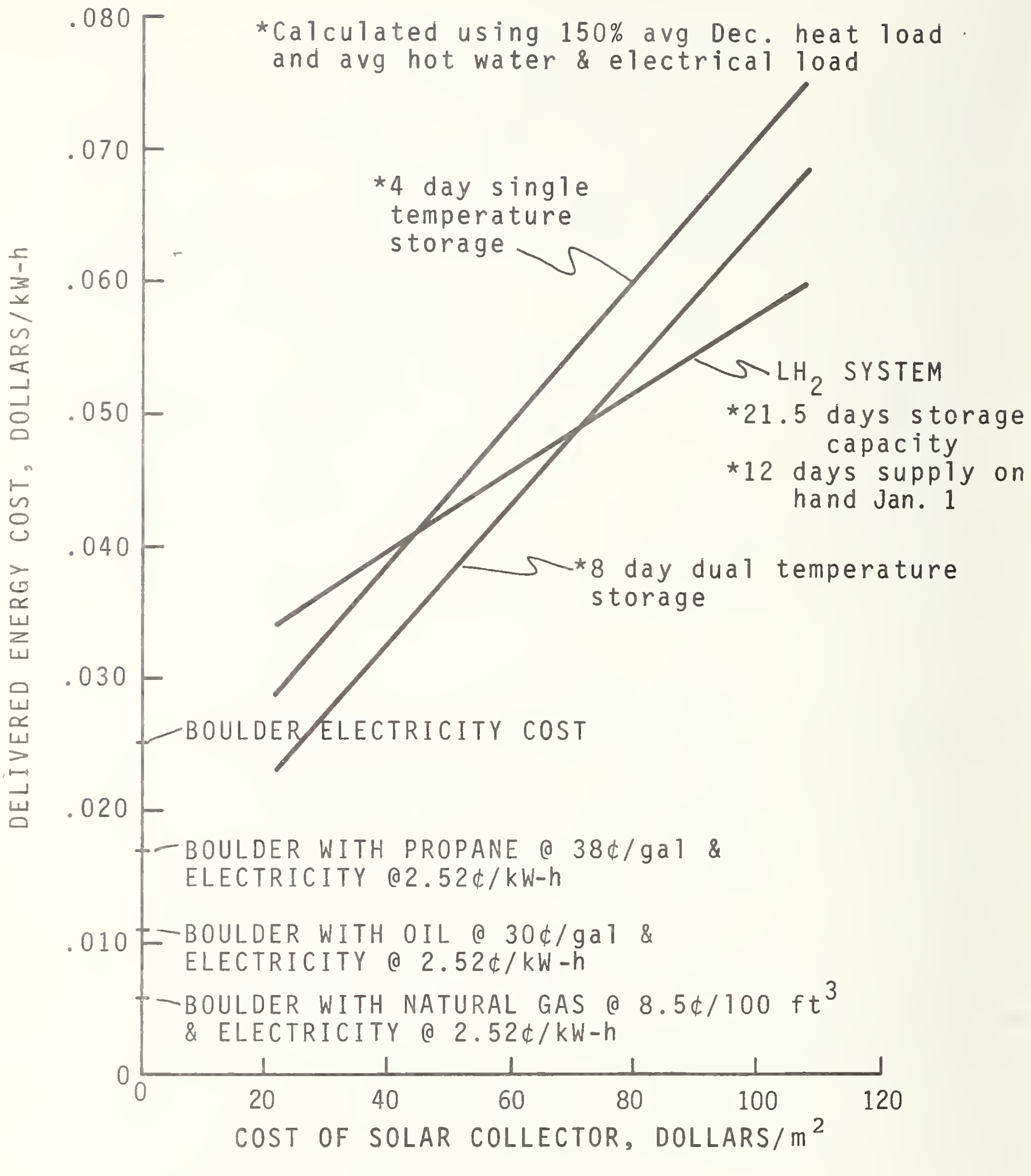

Figure 7.3 Cost of energy versus solar collector costs.

and the energy costs for the solar systems considered are all higher than current energy costs where solar collector costs exceed $20 per square meter. The hydrogen system is competitive with the other solar systems in the range of 40 to 70 dollars per square meter solar collector costs and also provides the previously mentioned advantages.

Table 7.2 Size and cost of solar energy system per residence (based on system components sized to service 100 residences)

Unit	Size	Cost
Heat storage tank	3.85 m^3	$ 769.
Al_2O_3	15,495 kg	$ 900.
LH_2 Dewar	4500 liters	$ 1340.
Engine and generator	15.46 kW	$ 471.
Electrolyzer	24.3 kg/h	$ 1035.
Liquefier	2.27 kg/h	$ 3000.
Fuel cell	2.45 kW	$ 678.
Cost (less solar collector)		$ 8193.

Although many solar collector costs are proposed as low as $15 per square meter, only the very simplest flat plate collector costs can approach this value, and these collectors provide energy at maximum temperature well below that required to run efficient heat engines. These collectors also collect less energy per unit area; therefore, they must be larger to collect the same amount of total energy. Since power generation is less efficient using lower temperatures, the low temperature system requires more energy than a high temperature system and, therefore, a larger solar collector. Thus, large area, low temperature collectors are required and land costs become important. It was not determined if the low temperature system produces electricity at lower costs than a high temperature system because low temperature heat engines are not currently available. Consequently, the conventional high temperature heat engine was selected for analysis.

Electrical energy can also be supplied using photovoltaic cells, but the current state-of-the-art results in very expensive units of low efficiency. Again, there is a trade-off if the photovoltaic cell can be produced cheaply. The trade-off occurs between large areas of low efficiency cells versus less area of a higher efficiency solar collector system. The current cells convert solar energy to electricity at efficiencies of 5 to 7% while the efficiency of the electrical system proposed is about 20%. The proposed system includes storage capability for cloudy days and for night time. To provide full-time power in a photovoltaic system, batteries or some other electricity storage media would be needed. Cost comparisons of these systems were not justified at this time since their are no real cost data for photovoltaic cells for commercial use.

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CHAPTER 8

INDUSTRIAL APPLICATIONS OF HYDROGEN

W. R. Parrish

8.0 SUMMARY

Large quantities of hydrogen are consumed in a variety of industries. Most of the hydrogen is used in ammonia and methanol syntheses, hydrocracking, and hydrotreating. Smaller quantities of hydrogen are needed in manufacturing drugs, processing metals, and hydrogenating fats and oils.

Hydrogen consumption is expected to double by 1985; however, large scale coal liquefaction and shale oil processing will greatly increase the demand.

8.1 INTRODUCTION

In 1972, U.S. industries consumed roughly 6.5 x 10^9 kg of hydrogen [1]. More than 98 percent of this gas had a purity of less than 99.5 percent. The majority of the low purity hydrogen went into petroleum refining and the production of ammonia and other chemicals. High purity hydrogen (> 99.5 percent) was used in manufacturing drugs, processing metals, and hydrogenating fats and oils. Table 8.1 gives a rough breakdown of hydrogen usage during 1972. Based on a 20-year trend, hydrogen consumption will nearly double by 1985; however, two future technologies, coal liquefaction and shale oil production, could greatly increase the demand.

Table 8.1 Estimated usage of hydrogen in 1972.[1]

Process	%
Ammonia Synthesis	35
Hydrocracking	30
Hydrotreating	21
Methanol Synthesis	8
Other	6

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[1] These estimates are from Harper [1].

8.2 PETROLEUM REFINING

There are two processes in refineries which use large quantities of hydrogen: hydrotreating and hydrocracking.

Hydrotreating uses hydrogen to reduce sulfur compounds in petroleum fractions to H_2S, which is easily removed, and to upgrade lubricating oils and kerosene. The process consumes roughly 500 cubic meters of low purity hydrogen for each cubic meter of hydrocarbon liquid processed. The primary source of hydrogen for hydrotreating is catalytic reforming, a process which increases the octane rating of gasoline components.

Hydrocracking is a catalytic process of increasing the hydrogen-to-carbon ratio of high-boiling petroleum fractions such as low quality heating oil and tars. Thus, it converts low value materials into the more valuable lighter hydrocarbons by breaking down long-chained molecules. The process requires 4600 to 5000 cubic meters of hydrogen for each cubic meter of feedstock converted. Based on current trends and anticipated expansion plans, hydrocracking will constitute the largest single use of hydrogen in this country.

8.3 AMMONIA PRODUCTION

Each year, ammonia production consumes more hydrogen than any other process. It takes around 20 cubic meters of low purity hydrogen to produce 1 kg of ammonia. Over 75 percent of the ammonia is converted into fertilizer, and most of the remainder is used to manufacture explosives. Currently, natural gas is the major source of hydrogen for ammonia production.

8.4 OTHER USES OF HYDROGEN

In addition to the above processes, hydrogen is used to produce various other chemicals, the major one being methanol. Methanol is used as a solvent and as an intermediate for the production of many other chemicals. To a lesser extent hydrogen is used to produce oxoalcohols, cyclohexane, hexane, and many others.

Hydrogen plays a major role in the hardening of vegetable and fish oils e.g., the production of margarine. Hydrogenating fatty acid oils, primarily cottonseed and soybean oils, produces lard, oleo margarine, and shortening. Nonedible hardened oils are used in the soap industry and to a lesser extent in leather dressings, electrical insulations and pharmaceutical ointments.

Hydrogen is important in metallurgical ore reduction and annealing, in glass manufacturing, and in drug synthesis. However, these applications consume small quantities of hydrogen when compared to petroleum refining and the production of ammonia and methanol.

8.5 FUTURE USES OF HYDROGEN

It is impossible to foresee all of the future applications of hydrogen in industry; however, shale oil upgrading and coal liquefaction represent major potential consumers of hydrogen. Whereas petroleum stocks usually contain sulfur compounds, shale oil can contain up to two percent nitrogen as well as one percent sulfur [2]. Therefore, shale oil has to be hydrotreated to remove the nitrogen and sulfur before it can be used as a fuel oil or processed to make more valuable liquids. The hydrotreating requires roughly 3700 cubic meters of hydrogen per cubic meter of shale oil [2].

In terms of hydrogen consumed per unit of stock processed, coal liquefaction will constitute the largest use. To produce one cubic meter of synthetic liquid requires roughly 13,000 cubic meters of hydrogen, nearly 25 times more than required in hydrotreating. So, when coal becomes a major source of hydrocarbon liquids, vast quantities of hydrogen will be needed.

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CHAPTER 9

HYDROGEN FUEL LITERATURE

Neil A. Olien

9.0 SUMMARY

The Cryogenic Data Center has as its mission the identification, acquisition, storage, retrieval and critical evaluation of information and data on the properties of materials at cryogenic temperatures. In addition, an information service is provided for the entire field of cryogenics.

In 1973 a survey was made of the world's technical publications in order to add to our present coverage so that we can adequately review those publications containing information on hydrogen. Prior to this the coverage was adequate for cryogenic hydrogen, but it was necessary to add to the review in the energy field to locate hydrogen-fuel information. In addition, a retrospective search has been made to locate papers in the literature prior to 1973. This search is nearly complete and the results have been incorporated into a preliminary bibliography on hydrogen-fuel. A more complete version of this will be available in December 1974.

The Cryogenic Data Center has now published and distributed four copies of a quarterly literature survey entitled Hydrogen-Future Fuel. This is completed each August, November, February and May. Each issue lists some 300-500 references under 40 subject headings. An author index is included with each issue.

The Cryogenic Data Center has been working with the Aerospace Safety Research and Data Institute (ASRDI) of NASA since 1970 in an effort to compile all available information on cryogenic fluid safety. The initial effort was on oxygen, but was expanded to include hydrogen in 1972. This effort has resulted in the location and careful indexing and abstracting of over 500 safety-related papers on hydrogen safety. This information is now available for searching using an on-line search system operated by ASRDI.

A major data compilation is now underway which will produce a Hydrogen Properties Handbook. This effort is also sponsored by ASRDI and will provide a single source, internally consistent set of data for the thermophysical properties of hydrogen.

9.1 INTRODUCTION

All surveys, reviews and state-of-the-art assessments begin with, and must ultimately rely on the literature covering the field. The purpose of this chapter is to summarize the efforts made to provide an adequate coverage of the published, report and patent literature dealing with the possible widespread use of hydrogen as a fuel. There has, therefore, been a large amount of cooperation between various groups within the Cryogenics Division as regards the information covering the field of hydrogen fuel.

9.2 THE CRYOGENIC DATA CENTER

The Cryogenic Data Center was established [1] in 1958 to assist the staff of the Cryogenics Division and other organizations within the National Bureau of Standards, other Government Agencies, industry, and universities in keeping up with the flood of information in this multi-disciplinary field. The field of cryogenics is, after all, defined by a temperature range rather than by subject or discipline.

From its inception the Center has been divided into two operational groups -- a Documentation Group to provide information services in the field of Cryogenics and a Data Evaluation Group to compile and critically evaluate thermophysical properties data of the technically important gases. The latter group has produced Standard Reference Data for the properties of helium [2], nitrogen [3], hydrogen [4] and argon [5], is completing work on hydrogen and is beginning work on fluid mixtures. In addition a long term project, supported by the NBS - Office of Standard Reference Data, has produced tables of transport properties data for monatomic and polyatomic fluids [6,7] in the dilute and dense phase regions. This effort also will soon become directed toward mixtures.

The Documentation Group maintains a thorough and systematic review of the current published, report and patent literature by means of a regular review of over 350 primary publications, supplemented by a cover-to-cover scan of some 30 abstracting services. The first step in the operation of this information system is the preparation of a weekly Current Awareness Service for the Cryogenics Industry. All important references listed in this service are entered into an automated information storage and retrieval system. The most important step in this entry process is careful subject indexing by professional scientists and engineers. Once the information is in the information system it is available for retrieval by means of a number of access points and thus provides the basis for a number of information products.

During the winter and spring of 1973 the staff of the Data Center made a thorough survey of the world's technical literature to determine how best to cover the hydrogen fuel field. The result, which was instituted in July 1973, was a net change of nearly 100 primary publications and 10 abstracting services reviewed. The new material being added to the information system to cover hydrogen amounted to an increase of over 20 percent (7500 - 8000 documents are entered in a normal year). This increase was not possible, of course, with a fixed budget and staff. The new additions were offset by reducing the coverage in certain areas of solid state physics, notably the semiconductor field. This redirection of effort during the past year has been a great success and quite healthy for the Cryogenic Data Center. This new expanded coverage for hydrogen fuel has also been incorporated into the Current Awareness Service and appears there under Section III - Energy.

9.3 SERVICES AND PRODUCTS OF THE CRYOGENIC DATA CENTER

The Cryogenic Data Center provides a number of services and products, most of which are available on a cost reimbursable basis.

a) Current Awareness Service -- a weekly bulletin averaging 8 - 10 pages listing new publications in the fields of low temperature physics and chemistry, cryogenic engineering and energy. Each issue contains a subject index. It has been published each week since 1964. Subscriptions are available from the National Technical Information Service, Springfield, Virginia 22151. Price: \$20/year-domestic; \$25/year-foreign (includes airmail delivery).

b) Superconducting Devices and Materials Quarterly -- published each January, April, July and October since 1968. This is a joint publication including participation from staff of the Office of Naval Research, the Naval Research Laboratory and Superconducting Technology, Inc. Each issue includes approximately 300 - 500 references divided into 41 subject areas and includes an author index. In addition a summary of the important papers in each issue is included. This is written by Dr. Robert A. Kamper of the NBS-Cryoelectronics Section and has proved to be a useful and popular column. Subscriptions are available from the National Technical Information Service, Springfield, Virginia 22151. Price: $20/year.

c) Liquefied Natural Gas -- published each January, April, July and October since 1970. This publication is sponsored by the American Gas Association and covers this new and rapidly expanding industry which is closely related to the hydrogen-fuel industry. Each issue includes 100-300 references listed under 25 subject headings -- an author index is included as well. Subscriptions are available from the National Technical Information Service, Springfield, Virginia 22151.) Price: $20/year.

d) Hydrogen - Future Fuel is a new periodical which has been distributed in August, November, February and May since August 1973. This publication is a direct result of the efforts described in section 9.2. It is obvious that a comprehensive publication could not be produced in August 1973 when the effort was started in July. The first issue tapped the information contained in the Cryogenic Data Center's information system and was, in essence, a selected bibliography of liquid hydrogen technology. Since then, issues have listed mainly new references in the field. Each issue contains 300 - 500 references listed under 40 subject headings and includes an author index. Subscriptions are available without cost by writing to: Mr. Neil A. Olien, Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302.

e) Specialized Bibliographies -- The information bank maintained by the Cryogenic Data Center now contains over 80,000 carefully indexed references in the field of cryogenics. These include 20,000 references to the properties of fluids, 35,000 references to the properties of solids, 15,000 references on processes and equipment (including a very complete selection of U.S. Patents) and 10,000 references to instrumentation and metrology. This information bank can be tapped to provide specialized bibliographies on any subject. The searches are made by the same professional staff that index the documents. This results in bibliographies containing maximum information with minimum volume. Searches start with a minimum of $35 and average about $45. For further information contact Neil A. Olien, Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302, or telephone (303) 499-1000, ext 3257.

f) Fluid Properties Computer Programs -- The Data Evaluation Group has developed a number of general purpose computer programs for fluid properties which are made available on a cost reimbursable basis. For further information see Table 9.1.

g) Specialized Bibliographies -- In order to expand the usefulness of the Data Center's information bank we have begun a series of widely useful bibliographies. Two of interest here are:

Liquefied Natural Gas Technology, October 5, 1973, Order No. COM-74-10324 - $7.00, Foreign $9.50. Energy and Superconductivity, March 20, 1974, Order No. COM-74-10713 - $7.00, Foreign $9.50.

Send Orders to:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22151.

In addition to these we have prepared a summary bibliography on hydrogen-fuel. This is still a preliminary publication because it does not yet contain all of the results of the efforts described in chapters 1 through 8. A more complete bibliography will be available in December of 1974. Requests should be directed to: Neil A. Olien, Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302.

9.4 HYDROGEN SAFETY INFORMATION

The Cryogenic Data Center has cooperated with the Aerospace Safety Research and Data Institute (ASRDI) of the National Aeronautics and Space Administration (located at Lewis Research Center, Cleveland, Ohio) since 1970 in an effort to locate, catalog, carefully index and evaluate the literature relevant to cryogenic fluid safety. Initially this effort was directed toward oxygen safety, but has since been expanded to include hydrogen and beginning October 1, 1974 methane and LNG. ASRDI has developed a sophisticated information system of which the information we have supplied on cryogenic fluid safety, comprises a major part. In the near future, the ASRDI information bank will be available, through a nationwide computer network, on a real-time basis.

9.5 HYDROGEN PROPERTIES HANDBOOK

The Data Evaluation Group, with funding from NASA-ASRDI, is currently completing a major compilation of the thermophysical properties of hydrogen. This will be similar to a handbook [8] of oxygen properties prepared two years ago. The hydrogen effort will bring together under one cover, data which are scattered throughout the literature. Even more important the data will be made internally consistent and will be extended into regions for which data presently do not exist. The manuscript and associated tables will be completed by October 1974. The medium of publication is a NASA Special Publication which should be available in early 1975. The computer programs used to generate the tables will be made available by NBS at cost.

Table 9.1 PROPERTY DATA AVAILABLE FROM THE NATIONAL BUREAU OF STANDARDS

Fluid	Document	Program Name	Program		Range		Input	Output
			Type	Acy*	P	T		
Ar	NBS-NSRDS 27	AR PROPS	BWR, 16	1	1000 atm	TP-300 K	P-T, ρ-T	P, ρ, T, S, H, U
CO	NBS TN 202	CO PROPS	BWR, 16	1	400 atm	70-300 K	P-T, ρ-T	P, ρ, T, S, H, U
D_2	NBS Report-Unpublished	D_2	BWR, 24	1	400 atm	TP-300 K	P-T, ρ-T	P, ρ, T, S, H, U
F_2	NBS TN 392	SAMPLE, PVT F_2	Poly Int	1	24 MN/m²	TP-300 K	P-T	$P, \rho, T, S, H, U, C_p, C_v, \left(\frac{\partial P}{\partial T}\right)_\rho, \left(\frac{\partial P}{\partial \rho}\right)_T, W$
	No reference	Never issued	BWR, 24	2	240 atm	TP-300 K	P-T, ρ-T	P, ρ, T, S, H, U
He	NBS TN 631	HE PROPS (71)	BWR, 87	1	1000 atm	LP-1500 K	P-T, ρ-T	$P, \rho, T, S, H, U, C_p, C_v, \eta, \lambda$ and others
	NBS Report-Unpublished	HE PROPS (70)	BWR, 35	2	1000 atm	LP-1500 K	P-T, ρ-T	$P, \rho, T, S, H, U, C_p, C_v, \left(\frac{\partial P}{\partial T}\right)_\rho, \left(\frac{\partial P}{\partial \rho}\right)_T, W$
	NBS TN 154	HE PROPS (62)	BWR, 17	3	100 atm	3-300 K	P-T, ρ-T	P, ρ, T, S, H, U
H_2	NBS Mono 94	THERMO or VALUES	Poly Int	1	340 atm	TP-100 K	P-T	$P, \rho, T, S, H, U, C_p, C_v, \left(\frac{\partial P}{\partial T}\right)_\rho, \left(\frac{\partial P}{\partial \rho}\right)_T, W$
	NBS TN 130	PROP TRS and	BWR, 16	2	340 atm	33-300 K	P-T, ρ-T	P, ρ, T, S, H, U
		PROP LIQ	BWR, 16	2	340 atm	TP-32 K	P-T, ρ-T	
	In Preparation	H2HIP	BWR	2	700 atm	TP-700 K	P-T, ρ-T	$P, \rho, T, S, H, U, C_p, C_v, W, \eta, K$
(Para)(Equi)	NBS TN 625	TAB CODE	Lin Int	3	5000 psi	TP-6000 R	P-T, P-H	$P, \rho, T, S, H, U, C_p, C_v, K, \eta, W$
Para	NBS TN 617	H_2 PROPS	BWR, 17	1	10,000 psi	180-6000 R	P-T, ρ-T	(all of above plus, $\theta, \Phi, \beta, P_r, \sigma, \gamma$ and others)
			THERMO	1	10,000 psi	TP-180 R	P-T	
CH_4	NBS Report In Preparation	METHERM 4	Non-Ana	1	10,000 psi	TP-500 K	P-T	$P, \rho, T, S, H, U, C_p, C_v, \left(\frac{\partial P}{\partial T}\right)_\rho, \left(\frac{\partial P}{\partial \rho}\right)_T, W$
Ne	ASME Advances 65 R-346	NE PROPS	BWR, 18	1	200 atm	25-300 K	P-T, ρ-T	P, ρ, T, S, H, U
N_2	NBS TN - In Preparation	N_2 PROPS	BWR, 32	1	10,000 atm	64-1900 K	P-T, ρ-T	Same as H_2, O_2 and He
O_2	Stewart,	O_2 PROPS	BWR, 32	2	340 atm	65-300 K	P-T, ρ-T	$P, \rho, T, S, H, U, C_p, C_v, W$
	J. Res. 70, R-559	PVT 02	Poly Int	1	340 atm	TP-300 K	P-T	$P, \rho, T, S, H, U, C_p, C_v, \left(\frac{\partial P}{\rho T}\right)_\rho \left(\frac{\partial P}{\partial \rho}\right)_T, W$
	NBS TN 384	PVT 02 & TEST	Poly Int	1	5000 psi	TP-600 R	P-T	(all of above & $\theta, \Phi, \beta, Pr, \alpha, \gamma, K, \eta$ and others)

* Acy - A relative indication of accuracy. 1 = Best accuracy, 3 = Poorest accuracy

We feel that this Handbook will serve as the "Standard" data for hydrogen. This will make it particularly useful as it will serve as the same data base for everyone when cycles and processes involving hydrogen are compared. It is obvious that meaningful comparisons cannot be made between competing systems unless a common data base is used.

This summarizes the efforts, products and services of the NBS-Cryogenic Data Center for providing information services to the cryogenics industry and particularly that part associated with the energy field. The emphasis of the Data Center's efforts is on the low temperature portion of the hydrogen fuel field, although we do cover higher temperature areas when those areas are related to cryogenic hydrogen.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The National Bureau of Standards played a vital role in developing hydrogen technology for the space age and is now engaged in efforts to adapt and improve this technology for the commercial use of hydrogen fuel. This document is a summary report on selected hydrogen-fuel topics and was prepared to identify cost and technical barrier to the commercial use of hydrogen fuel and to generate reference data for policy-planning, decision-making and design. Cryogenic hydrogen fuel technology is emphasized in the economic and systems analyses reported herein. Using the best available technical and economic data, hydrogen fuel is not currently cost competitive with alternate fuels; however, we must not reject hydrogen on the basis of current economic comparisons. Increased efficiencies of production, liquefaction, and energy conversion may drastically change these comparisons-of-today as will increased fossil fuel prices and more stringent environmental and pollution constraints. Hydrogen appears currently marketable in certain integrated utility systems, in transoceanic transport of energy produced far at sea, and is a necessary element in a wide variety of growing industrial processes and in the liquefaction of coal. This publication identifies research and development needs within selected areas of NBS competence and future research plans are outlined.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Conservation; conversion; cost; cryogenics, economics; embrittlement; energy; hydrogen; industrial, instrumentation, liquefaction; literature; materials; production; solar; storage; transmission; transportation; utilities.

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