

## HYDROGEN AND SYNTHETIC FUELS FOR THE FUTURE\*

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## INTRODUCTION

Early in 1972 the Energy R&D Goals Committee of the Federal Council on Science and Technology organized a study to assess a number of basic energy technologies which could favorably influence the U.S. future energy supplies. Various federal agencies sponsored eleven technical panels to perform this assessment and to prepare R&D plans for developing the priority technologies. The findings of one of these panels, "Hydrogen and Synthetic Fuels," sponsored by the USAEC, is the primary subject of this paper.

While there are currently serious problems in providing adequate electricity, the longer-term energy problems seem to be more associated with providing an assured supply of environmentally acceptable portable fuels. The importance of this supply is apparent when it is realized that electrical energy only meets about one-tenth of our end-energy needs today - the remainder is supplied from fossil fuels, mainly petroleum and natural gas.

While production of synthetic fuels requires thermal or electrical energy and thus may appear to complicate an already difficult problem, this energy can be obtained from domestic and, for the most part, clean sources, e.g., nuclear or solar. Further, because of low transport costs, synthetic fuels can be produced at remote, well-regulated plants and thus would not contribute to the primary pollution problems that exist in our urban centers. An additional consequence of such a system is that of conservation of our limited fossil fuel resources, particularly petroleum, so that they may be used as valuable chemical product feedstocks and in metallurgical processes. The synthetic fuels, especially hydrogen, may be consumed with very little or no air pollution as well as with higher conversion efficiencies and thus could be more attractive for urban uses than the fossil fuels in current use.

The intent of this paper is to summarize the findings<sup>(1)</sup> of the Synthetic Fuels Panel which evaluated the major aspects of new fuels systems, i.e., production, storage and transportation, end uses and an overall systems analysis. While the emphasis was on hydrogen and other fuels from nonfossil sources, a section on the use of coal to produce hydrogen and methanol is also included to help define the interim time period before our dependency on nonfossil fuels occurs.

The organization of the panel and the main contributors to the effort are given in the Appendix. The primary fuels considered, along with a listing of their significant characteristics, are given in Table 1.

## PRODUCTION OF FUELS

Perhaps the most critical factor influencing the viability of an energy system based on synthetic fuels resides in the production system, particularly in terms of the costs and the impact on the use of resources and on the environment. In considering the production of hydrogen from nonfossil primary energy sources four main processes are available - water electrolysis, thermal-chemical, biological, and radiolytic. Most current hydrogen production facilities are based on the use of fossil fuels, mainly natural gas and various petroleum fractions wherein the hydrogen source is partly from the hydrocarbon and partly from

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Table 1. Comparative characteristics of synthetic fuels

Fuel	Heat of combustion, low heating value (Btu/lb)	Heat of vaporization at b.p. (Btu/lb)	Relative fuel required to equal H <sub>2</sub> heat content		Density		Boiling point (°F)	Ease of storage <sup>d</sup>	Toxicity <sup>b</sup>	
			By wt	By vol	Liquid (lb/ft <sup>3</sup> )	H <sub>2</sub> <sup>a</sup> (lb/ft <sup>3</sup> )				Gas, STP (lb/ft <sup>3</sup> )
Hydrogen (H <sub>2</sub> )	51,600	194	1.0	1.0 (liq.)	4.4	4.4	0.005	-423	6 (liq.)	1
Ammonia (NH <sub>3</sub> )	8,000	590	6.4	0.6	42.6	7.8	0.043	-28	4	5
Hydrazine (H <sub>2</sub> H <sub>4</sub> )	7,200	540	7.2	0.5	62.4	8.9		236	3	6
Methanol (CH <sub>3</sub> OH)	8,600	474	6.0	0.5	49.7	7.1		149	2	4
Methane (CH <sub>4</sub> )	21,500	220	2.4	0.4	25.9	6.5	0.041	-259	5 (liq.)	2
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	11,600	360	4.4	0.4	49.7	6.5		173	1	3
Gasoline <sup>c</sup> (C <sub>8</sub> H <sub>18</sub> )	19,100	140	2.7	0.3	43.8	7.0		257	(1)	(4)

<sup>a</sup>Density of hydrogen in the fuel.

<sup>b</sup>Relative ranking.

<sup>c</sup>Included for reference only.

water. As these fossil fuels become more expensive and less available,  $H_2$  can be made from coal in which carbon is used to reduce water. As coal becomes more expensive, hydrogen could be produced on a massive scale by water electrolysis using nuclear, solar, or geothermal primary energy sources.

#### Water Electrolysis

Water electrolysis is a well established commercial process in which hydrogen and oxygen are produced by the passage of electricity through a conducting water medium. Figure 1, along with Table 2, gives a comparison of the actual performance of electrolysis cells to the theoretical energy requirements as a function of cell operating temperature.

The energy that must be supplied to the cell to cause the reaction  $H_2$  (liquid) +  $H_2$  (gas) +  $1/2O_2$  (gas) to proceed is the enthalpy of formation of water,  $\Delta H_{(g)}$ , and is equal to 68.32 kcal/mole at 25°C and 1 atmosphere. However, only the free energy of this reaction,  $\Delta F_{(g)}$ , equal to 56.69 kcal/mole, has to be supplied to the electrodes as electrical energy. The remainder is required as heat, and this can theoretically be provided as thermal energy from the surroundings, or from electrical losses within the cell.

The theoretical reversible voltage (defined by the free energy change) decreases with temperature, while the "thermoneutral" voltage (defined by the enthalpy change) increases slightly with increasing temperature. The actual performance is improved at elevated temperatures due to changes in the conductivity of the electrolyte and in the activity of the electrodes.

Efficiency of water electrolysis may be defined as the energy stored as chemical energy in the hydrogen ( $\Delta H$ ) divided by the electrical energy required to produce hydrogen. Throughout this report the LHV is used for  $\Delta H$ , since in most end uses the latent heat is not productive. Commercially available electrolysis plants operate at electrical efficiencies between 57% and 72%. The best demonstrated efficiency for advanced electrolysis cells is approximately 80%. Note that once the cell performance reaches the " $\Delta H$ " line on Fig. 1, operation below this voltage is theoretically possible and represents an apparent efficiency greater than 100% if only the electrical input is considered. As stated earlier, operation within the bounds of the  $\Delta H$  and  $\Delta F$  lines of Fig. 1 is quite possible, results in an "endothermic" cell, and thus requires the input of thermal energy at the cell's operating temperature.

The economic factors involved in the electrolytic production of  $H_2$  are illustrated in Fig. 2 and show the strong influence of the cost of the electricity used. The improvements in the cell efficiency that appear achievable, together with partial credit for the by-products, oxygen and deuterium, could allow a factor of two decrease in the production cost.

With such an electricity-intensive process as electrolysis, considerable leverage exists in decreasing the amount of power required per unit of production or in decreasing the cost of the power. Low-cost power as may be available from some few remaining remote hydroelectric sites would seem to be ideal for this use. Also, the use of off-peak power, particularly from a future, essentially all-nuclear system, would be an attractive power source. The advanced cells seem to be readily adaptable to operating with large power swings (variable cell current density) and can make use of the power when it is available or shed it when the electrical system requires it.<sup>(2,3)</sup> This latter characteristic could eliminate the need for a separate low use factor system for generating power to meet the peak demands. This characteristic also allows electrolysis plants to be coupled with intermittent energy sources, such as solar, winds, tides, etc.

#### Thermochemical Processes

Electrolysis of water suffers from inherent thermodynamic limitations on the efficiency of initial conversion of thermal to electrical energy (currently ~30-40%) in addition to an expected maximum realizable electrolytic efficiency of about 80-90%. The large-scale needs for fuel therefore justify attempts to find processes that may exceed

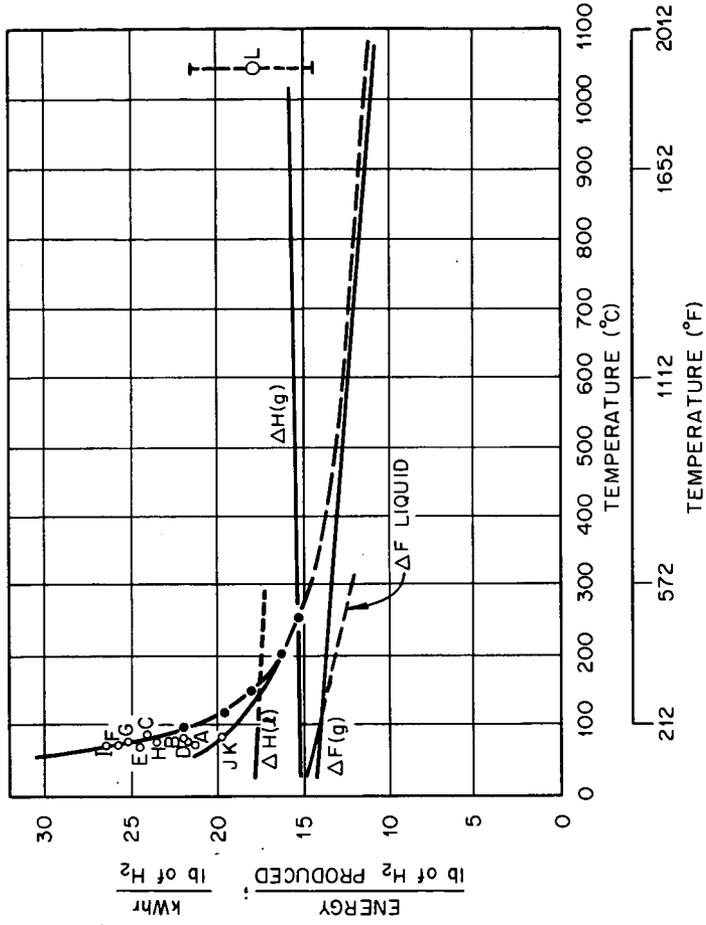


Fig. 1. Performance of water electrolysis cells compared to theoretical relationships. (See Table 2 for identification of A to L.)

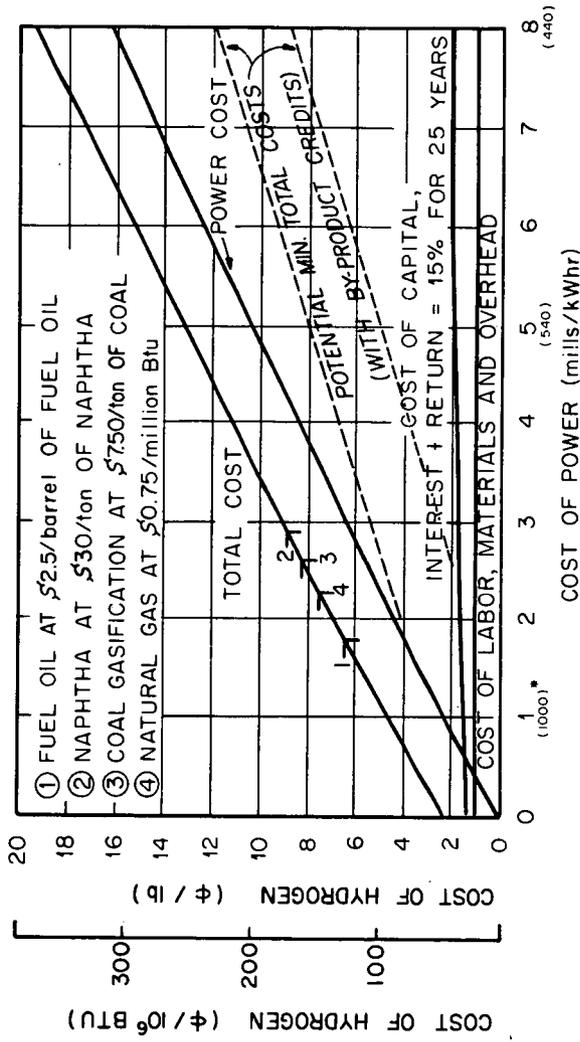
Table 2. Summary of electrolytic hydrogen plant equipment

Company/location	Cell name	Type	Cell Design				Experience			
			Current (A/cell)	Operating Voltage (V/cell)	Module (lb H <sub>2</sub> /day)	Precious metals (oz/cell)	Number of plants	Largest plant (lb H <sub>2</sub> /day)	Earliest plant (year)	Best atom plant (year)
A. Norsk Hydro Bodden, Norway	Hydro-Fuehranz	Filter press	140	1.778	1880	1	3	284,000	1927	Rjukan, Norway 1965
B. Lurgi Frankfurt, Germany	Zdanaky-Loma	Filter press	200	1.832	4200	440	32	22,000	1955 <sup>a</sup>	Cuzco, Peru 1958
C. DeSore Italy	DeSore	Filter press	280	2.00 <sup>b</sup>	4100	1	2	110,600	1958	Madag, India 1958
D. Pilsch-Baum Germany	Baum	Filter press	230	1.788	2600	13.5	200	UNK	1935	UNK
E. Electrolyser Corp. Canada	Stuart	Tank	200	2.04	40	0.03	1000	1,130	1930	Teleyne Wash Chang, Alabama, USA, 1971
F. Cominco Canada	Trail	Tank	80	2.142	38	0.1	1	77,000	1939	Trail, Canada 1939
G. Teledyne Isotopes USA	EGGS	Filter press	400	2.1	65	70	2	50	1968	Teledyne isotopes, USA, 1972
H. Demag Elektro- metallurgie ORH Duisburg, Germany	Demag	Filter press	82 to 175- 280	1.75- 1.95	900	1	57	177,000	1945	Awana Dm, Egypt 1960
I. Electric Heating Equipment Co. USA	Kent	Tank	115	2.2	28	0.1	100	1,610	1920	Hobart, Tasmania 1940
Cells being developed										
J. Teledyne Isotopes USA		Filter press	400	1.65	13	2000				Designed for military aircraft application
K. Teledyne Isotopes		Filter press	250	1.64	94	3000				Designed for nuclear submarine application
L. General Electric		Solid electro- lysis	360	1.2- 1.8		1				2000 <sup>o</sup> F, not now under development
M. Westinghouse		Solid electro- lysis	900	0.5 <sup>c</sup>		1				Used for CO <sub>2</sub> electrolysis in spacecraft atmosphere control system

<sup>a</sup>First Zdanaky-Loma plant.

<sup>b</sup>Before has indicated an ability to achieve 1.61 V on new cells.

<sup>c</sup>Assumes a fuel depolarized mode of operation, i.e., coal. Does not expect cell to be used as water electrolyser.



\* Cell current density, amps/ft<sup>2</sup>

Fig. 2. Production cost of hydrogen via water electrolysis.

the 25-35% overall thermal efficiency of electrolysis for hydrogen production. With the development of high-temperature nuclear fission reactors (and the potential development of fusion reactors), two conceivable processes for the production of hydrogen from water are: (1) thermochemical and (2) radiolytic. Solar or geothermal energy also are potential alternative heat sources for the thermochemical route. It should be recognized, however, that these high-temperature heat sources are also capable of more efficient conversion of heat to electricity so the ultimate overall electrolytic efficiency might approach 50%. Further, efficiency must be tempered with economics, reliability, safety, etc. to make meaningful comparisons between processes.

Various thermochemical hydrogen production routes have been investigated from the direct (high-temperature) dissociation of water to four- and five-step chemical reaction sequences, but none have been developed to the point of commercial utilization. In one set of reactions involving the reverse Deacon reaction followed by three sequential reactions of various vanadium chlorides, thermal efficiencies of 6 to 18% were computed<sup>(4)</sup> after allowing for all process energy requirements and losses. Higher efficiencies have been claimed by other investigators using different reaction sequences.<sup>(5)</sup>

#### Biological and Other Processes

Biological processes have been in use for the production of synthetic fuels in a limited manner for many years. Primary examples are the generation of methane from sewage and fermentation of grains and sugars to produce alcohol. In most cases, such systems are dependent on the diffuse solar energy input or the relatively slow processes of bacterial action and therefore may be difficult to scale up economically to the very large sizes required to meet a significant share of the future demand for fuels. A system for producing hydrogen via an interrupted photosynthesis process has been proposed and is currently being investigated. Based on preliminary estimates, a 500-tons-per-day hydrogen plant would require the solar input collected over an area of 22 square miles.

A number of other production possibilities were recognized, e.g., multistep chemical reaction followed by electrolysis, combined water electrolysis with coal gasification, using by-product oxygen, and radiolytic decomposition of water. Insufficient existing data were available to make comprehensive analyses of these processes.

The technologies and costs for the production of other synthetic fuels, specifically  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ , and  $\text{N}_2\text{H}_4$ , were shown to be well developed commercial processes. The long-range potential problem of a source of carbon (as CO or  $\text{CO}_2$ ) for methanol synthesis was believed to be available from the atmosphere, limestone, seawater or combustion of waste organic matter.

#### Waste Processes

Obtaining fuels from urban and agricultural wastes was briefly examined. Of the  $3 \times 10^9$  tons of solid organic wastes generated yearly in the U.S., about two-thirds are manure and over 80% are of agricultural origin. Total municipal and industrial wastes are about  $0.4 \times 10^9$  tons, half of which are currently collected for disposal by municipal agencies.<sup>(6)</sup>

A study prepared for the U.S. Department of the Interior's Bureau of Mines (BuMines)<sup>(7)</sup> indicates that more than half the total weight of these wastes is actually water. In 1971, the total amount of dry, ash-free organic waste produced in this country was only 880 million tons with about 136 million tons of dry organic wastes being readily collectable for conversion. This amount would have produced 170 million barrels of oil - roughly 3% of 1971 consumption of crude oil or 12% of imported crude. Alternatively, this amount of waste could have produced 1.36 trillion scf of methane, about 6% of 1971 consumption of natural gas. If all the wastes could be collected for this purpose, nearly 40% of our natural gas use could come from this source.

Among the problem areas which must be considered in developing synthetic fuels from wastes is the cleanliness of the fuels, i.e., the suitability of the fuels to unrestricted use as pipeline gas and the economic collection and storage of diffuse wastes sources, particularly agricultural wastes.

#### Agricultural Processes

Related to the use of waste processing is the production of fuels via intensive agriculture. The fuels that may be produced in this manner are ethanol from fermentation of grains, sugars, or starches, methanol from waste products, and wood from tree farms. The crop processing technology seems to be well developed, but the overall economics have been unfavorable due to the low cost of competing fossil fuels. The application of intensive agricultural methods (i.e., use of optimized nutrients, soil moisture levels, etc., coupled with a multiple crop climate), and the rising price of fossil fuels work toward making this scheme profitable. However, the relatively large amounts of land required to produce a significant fraction of our fuel requirements seem to preclude the use of this concept to areas of very specialized application, e.g., ethanol as a replacement for tetraethyl lead (10% in gasoline).\*

The use of wood obtained from a tree farm has been proposed<sup>(8)</sup> as a fuel for a conventional steam-electric power station. Preliminary computations indicate that an intensively farmed area of 400-600 sq mi would be required to continuously supply a 1000-MW(e) power station with wood fuel.

Although not usually considered agriculture, growing algae for fuel has often been proposed.<sup>(9)</sup> Here the fuel could be methane, but again the large land areas required suggest that such a system is not likely to meet a significant fraction of our total energy needs.

#### USE OF COAL

While the emphasis of the Synthetic Fuels Panel was directed toward nonfossil sources of portable fuels, some effort was devoted to the use of coal and lignite for the production of hydrogen and methanol. Many other studies and demonstrations are in progress to produce more conventional hydrocarbon fuels from coal which could be used for a comparative analysis.

The U.S. has been estimated to have had  $3.21 \times 10^{12}$  tons of coal at the end of 1969<sup>(10)</sup> or the equivalent of  $64.4 \times 10^{18}$  Btu of energy. Only one-half of this coal is believed to be recoverable; however, the U.S. total consumption of nonnuclear energy in 2000 has been estimated to be about  $131 \times 10^{15}$  Btu. A rough conservative assumption can be made that one-half of the energy in the coal could be delivered to end uses in the form of hydrogen and methanol. Thus, even if all nonnuclear energy were to be provided by hydrogen and methanol, coal could be the source of these two synthetic fuels for 120 years at the year 2000 consumption rate.

Two methods for producing hydrogen from coal were reviewed: steam-oxygen (Synthane) and CO<sub>2</sub>-acceptor. These processes give similar production costs; those for the CO<sub>2</sub>-acceptor process are shown in Fig. 3 as a function of the cost of the raw material. While these processes appear to be commercially viable, they have not been used in the U.S. due to the relatively lower cost of hydrogen available from natural gas and various petroleum fractions. In comparison to the production of methane from coal, hydrogen appears to offer a simplified flow sheet since no methanation step is required.

Methanol has been produced from coal in some parts of the world but not in the U.S. A two-step analysis of the manufacturing costs of (1) coal gasification and synthesis gas (H<sub>2</sub>, CO) purification and (2) methanol synthesis is summarized in Table 3. The cost of

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\* This requires  $8.8 \times 10^9$  gal of alcohol/yr or  $3.3 \times 10^9$  bushels of grain or about  $40 \times 10^6$  acres of land.

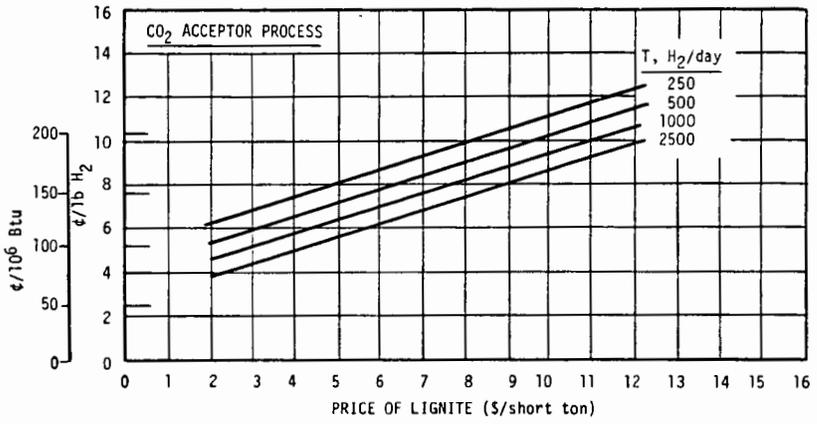


Fig. 3. Cost of producing hydrogen from coal.

Table 3. Economics of synthesis of 20,000 tons/day of methanol (MeOH) from coal

Item	Unit	Units /day	Cost		
			\$/unit	\$/day	¢/gal MeOH
Synthesis gas manufacture (Capital for plant: \$260 x 10 <sup>6</sup> )					
Coal <sup>a</sup>	Ton	26,000	7.00	182,000	3.02
Chemicals				1,000	0.02
Process water	10 <sup>3</sup> gal	6,250	0.20	1,250	0.02
Cooling water	10 <sup>3</sup> gal	346,000	0.02	6,920	0.11
Operating labor	Man-hr	960	4.00	3,840	0.06
Supervision				380	0.01
Maintenance				35,600	0.59
Overhead				<u>4,220</u>	<u>0.07</u>
Precapital manufacturing cost				235,110	3.90
Capital charges at 15%/year				<u>106,800</u>	<u>1.77</u>
Total cost				341,910	5.67 (99¢/10 <sup>6</sup> Btu)
Methanol synthesis from provided Syngas (Capital for plant: \$135 x 10 <sup>6</sup> )					
Steam	10 <sup>3</sup> lb	38,200	0.65	24,800	0.41
Fuel	10 <sup>6</sup> Btu	21,600	0 <sup>b</sup>		
Electricity	kWhr	100,000	0.01	1,000	0.02
Cooling water	10 <sup>3</sup> gal	540,000	0.02	10,800	0.18
Catalyst and chemicals				15,000	0.25
O&M labor and supervision				50,000	0.83
Overhead				<u>14,000</u>	<u>0.23</u>
Precapital manufacturing cost				115,600	1.92
Capital charges at 15%/year				<u>55,400</u>	<u>0.92</u>
Subtotal				171,000	2.84
Total cost				512,910	8.51 (148¢/10 <sup>6</sup> Btu)

<sup>a</sup>Combined raw material and fuel.

<sup>b</sup>Purge gas from synthesis gas plant.

producing the synthesis gas is seen to be the dominant cost and this, in turn, is largely dependent on the cost of coal. If lignite at \$2/ton were used, the total cost would decrease to 6.4¢/lb (\$110/10<sup>6</sup> Btu). The costs of the various fuels are summarized in Table 4.

#### STORAGE AND TRANSPORTATION OF SYNTHETIC FUELS

The technology and practice of storage and transportation of most of the fuels considered in this paper have been extensively developed and demonstrated on a significant scale. Hydrogen gas is being produced and distributed in and among refineries under conditions that would simulate a fuel gas production and distribution system. There are, however, no existing hydrogen transmission or distribution systems in which booster compressors are utilized. Liquid hydrogen equivalent to over 100 billion cu ft (STP) has been produced and distributed in support of the space program. Production of ammonia for fertilizer has reached a scale of distribution in which large interstate pipelines are now operating in addition to the extensive barge, rail, and truck systems that have been built to achieve economical distribution. Because of the seasonal nature of agricultural chemicals supply, large storage complexes have also been developed. Methanol has long been a basic tonnage petrochemical, and distribution by all means has been fully developed.

#### Storage of Fuels

The estimated investment for storing energy in the form of a synthetic fuel is illustrated in Fig. 4. The storage of gaseous hydrogen in pressure vessels appears to be non-competitive for the full range of storage capacity. This is due to the combination of low specific volume of the gas and high cost of the pressure vessel. The adaptation of gaseous storage might be enhanced by using the transmission line as an inventory device (line packing) — e.g., a pressure change from 750 to 1000 psia in 300 miles of 3 ft dia pipe can store the equivalent of  $5.2 \times 10^4$  million Btu. The volume and weight of a fuel storage tank containing  $2 \times 10^6$  Btu, the approximate size of an average automobile fuel tank, are given in Fig. 4. A tank of liquid (cryogenic) hydrogen would be twice as heavy, seven times greater in volume, and of much higher cost than an equivalent tank of gasoline.

It should be recognized that the storage costs shown are based on present technology and production techniques. With further development and use of mass production systems it is expected that the values shown for the unconventional types should decrease by as much as a factor of two.

The cost of a compression and/or liquefaction system should be added to the cost of storage in assessing the utility of hydrogen energy systems. The cost of hydrogen gas compression might typically be 15 to 50¢ per 10<sup>6</sup> Btu (.8 to 2.6¢/lb) for a wide range of delivery pressures and equipment utilization factors. The cost of hydrogen liquefaction might typically be \$1 to \$2 per 10<sup>6</sup> Btu (5.2 to 10.4¢/lb) for a wide range of system capacities and utilization factors. The electrical power requirement alone is about 5 kWhr/lb H<sub>2</sub>. These costs are usually more significant than tankage costs and must be considered in the design and evaluation of liquid H<sub>2</sub> storage systems.

Evaporation losses from large LH<sub>2</sub> tanks (~10<sup>6</sup> gal) are typically 0.03%/day while small mobile tanks may be from 1 to 10%/day. A possibility for circumventing some of the above costs and storage losses is the use of hydrides or compounds of hydrogen. Several hydride storage systems have been investigated and indicate that a large number of binary and tertiary metal systems are available for this use. Magnesium and alloys of Mg and Cu or Ni<sup>(11)</sup> will release H<sub>2</sub> at 1 atm at temperatures of from 440°F to 540°F. Also some intermetallic compounds of the composition AB<sub>5</sub>,<sup>(12)</sup> where A is a rare-earth metal and B is nickel or cobalt, are reported to absorb and desorb large quantities of hydrogen at near room temperature. Some compounds such as ammonia and hydrazine can be readily decomposed to yield H<sub>2</sub>. The hydrogen density in these compounds is from 1.5 to 2.0 times that of liquid hydrogen. Still lower effective heating values would, however, result since the heat of dissociation must be supplied, although in some applications waste heat may be utilized for this purpose.

Table 4. Summary of synthetic fuels production cost<sup>a</sup>

Fuel	Fossil-based process	Fuel cost (¢/10 <sup>6</sup> Btu)	Electrical (or other) based processes	Fuel cost (¢/10 <sup>6</sup> Btu)
Hydrogen	Natural gas, 40¢/10 <sup>3</sup> ft <sup>3</sup>	97	Water electrolysis	
	Coal, \$7/ton	132	Power, 8 mills/kWhr	368
	Lignite, \$2/ton	78	Advanced technology, 8 mills/kWhr	233
	(Liquefaction)	150)	Advanced technology + by-product credits, 8 mills/kWhr	174
Ammonia	Natural gas, 45¢/10 <sup>3</sup> ft <sup>3</sup>	157	Off-peak power, 2.5 mills/kWhr, adv. tech.	195 <sup>b</sup>
			H <sub>2</sub> via H <sub>2</sub> O electrolysis, 8 mills/kWhr	517
Hydrazine		~2100	H <sub>2</sub> via H <sub>2</sub> O electrolysis, 2.5 mills/kWhr	228
Methanol	Natural gas, 40¢/10 <sup>3</sup> ft <sup>3</sup>	158	H <sub>2</sub> via H <sub>2</sub> O electrolysis, 8 mills/kWhr (CO <sub>2</sub> from air)	~550
	Coal, \$7/ton (~27¢/10 <sup>6</sup> Btu)	148		
	Lignite, \$2/ton (~15¢/10 <sup>6</sup> Btu)	~125		
Ethanol	Petroleum feed stocks	~460	Fermentation from corn, \$1.25/bu	880
	Well-head gas	15 - 40	Urban and agricultural wastes	~115
Methane	LNG, imported	80 - 100		
	Coal	80 - 100		
Gasoline	Crude oil	105		

<sup>a</sup>Costs are based on 15% fixed charge rate and large plant capacities.

<sup>b</sup>Water electrolysis plant operated at a 0.3 load factor.

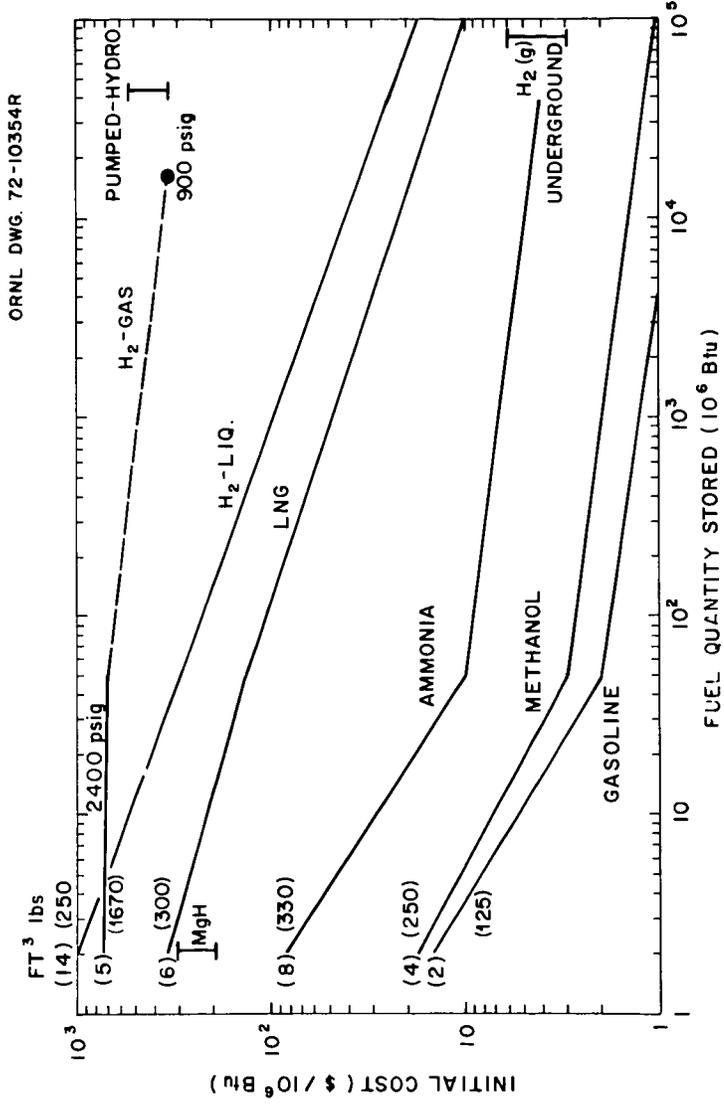


Fig. 4. Investments costs for storage of energy.

### Fuels Transportation

The costs of transporting various forms of energy in a near-urban environment are summarized in Table 5. An average cross-country cost for natural gas transmission today is reported to be 1.5 to 1.7¢/10<sup>6</sup> Btu per 100 miles.<sup>(13)</sup> Hydrogen transmission cost would be 2.6 times this cost since compressor size and horsepower must be considerably increased and a more expensive fuel (hydrogen) used to power the compressors. By increasing the pipeline operating pressure from the "usual" 750 psia to 2000 psia, this factor could be reduced to about 1.5. Further, the average pipeline distance for hydrogen is likely to be less than for natural gas so that the total costs of delivery may be nearly equal.

The advantage in pipelining fuels is the ability to scale this type of system up to very large capacities with the resultant effect of the economy of scale being to lower unit-energy transfer cost. The use of pipeline transport of thermal energy will therefore be superior for the transmission of energy over long distances and/or transmission of very large blocks of energy. Relative to natural gas, the volumetric flow of hydrogen must be quite high because of its low specific heat content, although the low molecular weight compensates considerably, resulting in similar system performance. The primary penalty in transmitting hydrogen over methane is the increased cost of recompression which amounts to a relatively small fraction of the cost of a transmission system in a near-urban environment. This penalty may be offset by the potential efficiency gain of hydrogen energy conversion devices and the resultant flow decreases in the hydrogen energy transmission system. An area of concern in the transmission of hydrogen, however, is in the admission of this gas into older existing mains since the leakage coefficient is three to six times that of methane. Techniques of sealing older natural gas systems would therefore have to be developed to avoid their total replacement in transition to use by hydrogen.

### USE OF SYNTHETIC FUELS

End uses for hydrogen and other synthetic fuels were examined for the major energy use sectors, i.e., industrial, urban, transportation and electricity generation.

#### Industrial

Industrial uses for H<sub>2</sub> are mainly as a chemical as in ammonia production and in petroleum refining. Iron ore reduction could potentially require large amounts of hydrogen as will most coal processing schemes. Its use as an industrial fuel appears, technically, to be unlimited. Further, if a dual pipe (hydrogen and oxygen) system were available, or as dictated by economic tradeoffs, with oxygen from an air liquefaction plant, process steam could be produced directly. With this arrangement, a simple pipe-combustor-attenuator (as a closed system) would be substituted for the current massive water tube steam generators.

Of the other synthetic fuels methanol appears the easiest to adapt to industrial fuel uses - in fact, is already (as "methyl-fuel")<sup>(14)</sup> being evaluated as a boiler fuel. Because of its toxicity and poor combustion properties, ammonia would be less suitable for this use. It may, however, be readily dissociated to H<sub>2</sub> and N<sub>2</sub> which for many applications would be an attractive fuel.

#### Urban

Although some system revisions would be required, hydrogen appears to be substitutable for any natural gas use and, at the same time, with improvements in use efficiency. Conversion to a hydrogen system should be possible with only a minor amount of capital expenditure. Although gas distribution systems already exist, they may require some upgrading to meet leakage and increased flow requirements, and gas burners would require modification. Safety problems associated with the use of hydrogen are comparable with those associated with the use of natural gas. An education program will be required to familiarize the public with the use of hydrogen.

Table 5. Energy transmission - relative transportation costs  
(near-urban environment)

	Volume (10 <sup>6</sup> Btu/hr)	Size	Investment per 100 miles (10 <sup>6</sup> \$)	Total cost, operating plus investment <sup>d</sup> per 100 miles (¢/10 <sup>6</sup> Btu)
H <sub>2</sub> gas	21,000	36-in. pipe	68 <sup>b,c</sup>	5.7 <sup>c</sup>
NH <sub>3</sub>	21,000	36-in. pipe	62 <sup>b,c</sup>	5.0 <sup>c</sup>
CH <sub>3</sub> OH	21,000	30-in. pipe	52 <sup>b,c</sup>	4.2 <sup>c</sup>
Natural gas	21,000	36-in. pipe	62 <sup>b,c</sup>	5.1 <sup>c</sup>
H <sub>2</sub> Liquid	550	3-in. pipe	79 <sup>d</sup>	250.0
H <sub>2</sub> Liquid	1,800	1,100,000-gal barge	2.4	6.9
H <sub>2</sub> Liquid	62	13,000-gal trailer	0.15	34.0
Electric (superconducting line)	13,600	4,000-MVA line	140	19.3
Electric (aboveground)	8,500	2500 MW, 750 kV	30	8.3
Electric (belowground)	8,500	2500 MW, 345 kV	~300	~100

<sup>a</sup>Unit cost assumption: 100% utilization of facility, 15% = fixed charge rate (depreciation, interest, return on investment), operating power 6 mills/kWhr.

<sup>b</sup>Reported pipeline costs can vary by as much as a factor of 4, depending on terrain, congestion, etc.

<sup>c</sup>For cross-country straight lines, 50% reduction is likely.

<sup>d</sup>No reliquefaction included.

As for the industrial sector, methanol could readily find use as a residential/commercial fuel, but ammonia use would probably be more difficult.

#### Transportation

Hydrogen, with air from the atmosphere or with oxygen supplied on board, offers an impressive potential for fueling future transportation systems. Due to hydrogen's high gravimetric heat of combustion,  $\sim 2\ 1/2$  times greater than conventional hydrocarbon fuels, it is an attractive fuel for aircraft. As a liquid, its low density ( $\sim 1/10$  that of jet fuel) and low temperature ( $-423^\circ\text{F}$ ) do, however, present some design and operating problems. Improvements in air transport efficiency are potentially great, e.g., a recent analysis<sup>(1)</sup> of a hydrogen-fueled subsonic commercial transport showed that a 30% decrease in takeoff weight is possible. With high-speed aircraft substituting hydrogen for jet propulsion fuel could give a 45% increase in payload at a Mach 3 cruise condition. For hypersonic aircraft ( $> \text{Mach } 4$ ) the use of liquid hydrogen is probably mandatory due to its unique cooling capabilities and attractive chemical properties, e.g., noncoking.

For ground transport hydrogen appears to be substitutable for existing fossil fuels, but sizable problems are evident relative to fuel tankage and logistics. Large fleet-operated trucks or buses or high-speed trains appear to be the easiest to adapt to hydrogen fuel. The clean-burning characteristics of hydrogen offer an additional option to overcoming the polluting effects of internal combustion engines.

Hydrogen-oxygen fired steam cycle power plants may be of special interest to nuclear-powered ships, to provide large amounts of reserve speed, for example. For submersibles this power plant's completely condensible exhaust (water) offers a number of system advantages.

Of the other synthetic fuels, methanol and ammonia show some promise for the ground transport sector with methanol the more attractive fuel. Its main advantages are that it shows promise as a long-term, high quality, domestically produced, portable fuel, particularly as a replacement for gasoline. Since it is basically a high-octane, clean-burning fuel (without additives), it can be used in high-performance engines with apparently relatively simple exhaust treatment and thus compensate, in part, for its low heating value. Its current relatively higher cost, low heat of combustion and higher volatility appear to be the primary obstacles to its widespread use today.

#### Electricity Generation

The use of nonfossil synthetic fuels for electricity generation would seem to apply only in special situations such as to meet a relatively remote small requirement or as a part of an energy storage power peaking system.

One possibility is that electricity will be generated near the load center from hydrogen fuel or hydrogen-oxygen taken from pipelines as it is transmitted long distances from remote production sites. Both thermomechanical systems and nonthermomechanical systems appear plausible for converting hydrogen energy into electrical form. Examples are gas turbines, magnetohydrodynamic generators, and fuel cells.

Hydrogen is expected to be a very favorable fuel for gas turbine operation, permitting increased turbine inlet temperatures to be reached, provided that the excellent cooling virtues of hydrogen can be used to keep metal temperatures under control. If cryogenic hydrogen is used, precooling of inlet air and/or compressor intercooling might be advantageous in increasing efficiency and/or output. Efficiencies of 35% are anticipated for the hydrogen-air turbines. The hydrogen-oxygen turbine offers the ultimate in cycle efficiency and may exceed 60% with several generations of development. The hydrogen-oxygen turbine also prevents any air pollution since the exhaust is pure water and may be condensed, i.e., since air is not used in the combustion process, no  $\text{NO}_x$  can be formed.

Primarily in the space program, hydrogen has found limited use in fuel cells with either air or oxygen to produce electricity. Commercial fuel cells are being developed by Pratt & Whitney as part of the TARGET\* program using air and hydrogen derived from natural gas. With a pipeline source of hydrogen, this technology could be readily adapted for its direct use and would in the process realize significant improvements in cell efficiency and in lower operating costs. Efficiencies of the prototype units using reformed natural gas and air are 35 to 40%. Using hydrogen with large units, efficiencies up to 55% are projected and using hydrogen and oxygen a 60% efficiency (AC power out/heat energy in) should be realized. Fuel cells fueled with hydrogen should produce electricity with only minimal air pollution, since the main waste product is water vapor. Waste heat would be rejected to air and with few moving parts (cooling fan and pump) their operation is quiet; further, they exhibit a characteristic of maintaining high efficiency at part load, i.e., down to ~25% of design load.

Fuel cells have also been proposed for supplying utility peak power needs using hydrogen fuel (and oxygen) produced electrolytically during low demand periods. Overall efficiencies (electricity in/electricity out) with today's technologies will probably be under 30%, but with possible future technologies the efficiency could approach 50%. As an alternative to pumped hydro storage, it does offer a flexibility of location and a compact plant which may become an important consideration for peaking facilities. Other fuels, e.g.,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ , have been used to a limited extent in fuel cells, both directly and after dissociation.

#### SYSTEMS ANALYSIS

The purpose of the systems analysis effort<sup>(16)</sup> in this short-term study was to identify system concepts which would show the typical resource, economic, and environmental impact of implementing hydrogen in selected sectors of the energy system. The concepts evaluated are listed below:

1. The use of hydrogen, generated with available off-peak electricity, as a clean fuel in the transportation sector (auto, diesel, or aircraft).
2. The use of hydrogen produced from coal, as an alternate clean fuel in the transportation sector.
3. Energy transport and distribution from remote central station sites to urban areas via hydrogen in pipelines.

It was estimated that the amount of available off-peak power in the year 2000 could satisfy: (a) 50% of the automotive, (b) 50% of the aircraft, or (c) all of the diesel fuel requirements. In one case where the off-peak fossil-generated power (for the production of  $\text{H}_2$ ) was shifted to nuclear (part base load), a decrease of over 20% in petroleum imports was projected. The impact of this change on environmental factors is illustrated in Fig. 5 showing a decrease in chemical pollutants with an increase in radioactive wastes.

Another systems analysis example computation shown in Fig. 6 compares the cost of delivering hydrogen for residential energy needs to an all-electric case. As thermal energy hydrogen is less expensive than electricity due to lower transmission and distribution costs as well as savings resulting from a better utilization of the primary energy plant. If all of the hydrogen were converted back to electricity in fuel cells, the total costs would exceed the all-electrical case. If, however, an energy mix of four parts thermal to one part electrical were used to meet residential needs, hydrogen would become an attractive energy source. Also shown in this figure are the estimated costs for producing hydrogen with off-peak nuclear power and from coal at both \$7/ton and \$17/ton.

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\* Team to Advance Research for Gas Energy Transformation.

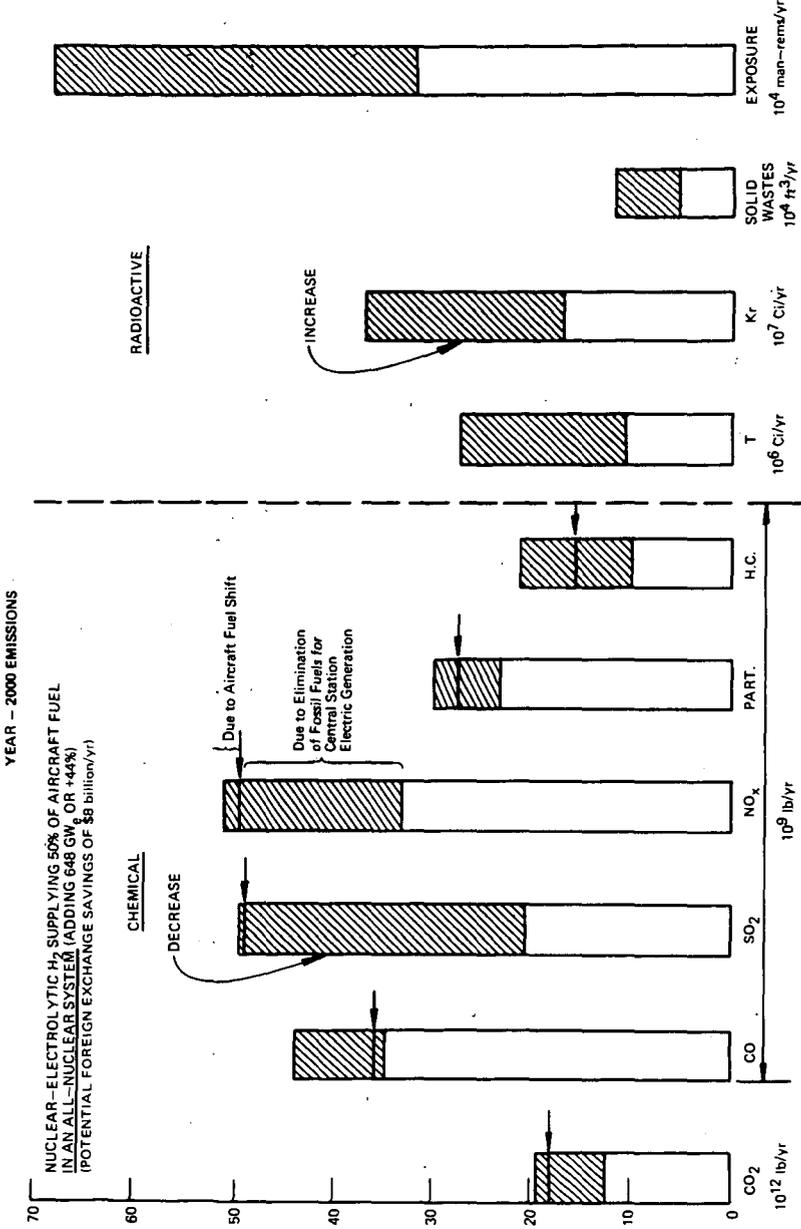


Fig. 5. Systems analysis - emission tradeoffs.

ORNL-DWG 72-12744

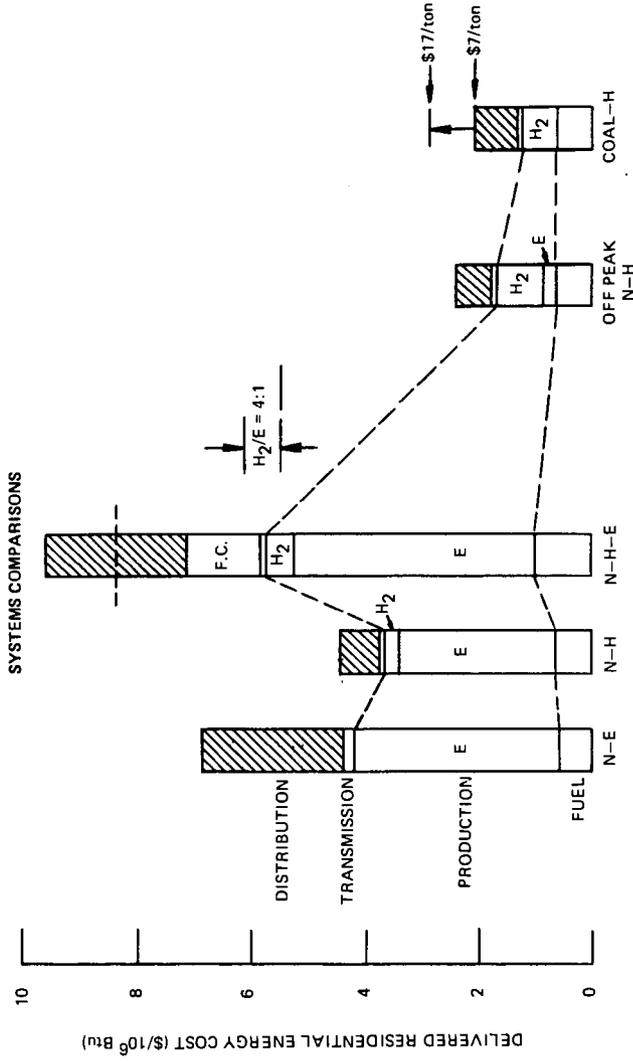


Fig. 6. Cost of delivered energy.

## CONCLUSIONS AND RECOMMENDATIONS

The primary sectors of an energy system based on nonfossil synthetic fuels were examined on the basis of readily available information. The main overall conclusion reached was that these fuels can have a significant beneficial long-term impact on the energy problems facing the U.S. Hydrogen is a particularly attractive synthetic fuel for the following reasons:

1. It is essentially clean burning, the main combustion product being water.
2. It may be substituted for nearly all fuel uses.
3. It can be produced from domestic resources.
4. It is available from a renewable and universal raw material -- water.
5. Nearly all primary energy sources, nuclear, solar, etc., may be used in its production.

The main obstacles to its use as a universal fuel are its high cost relative to the current low prices for fossil fuels and, for some applications, the unresolved problems of handling a low density or a cryogenic fluid. Safety considerations, while important, are not believed to present a serious technical obstacle to its widespread use.

The panel believed that most of these economic problems could be resolved by appropriate R&D programs. The recommended R&D programs were divided into two categories: those which could have a near-term, by 1985, impact on the nation's energy problems and those which would be of significant impact after this date. The near-term tasks which were identified are:

1. Development and demonstration of methanol from coal as an automotive fuel.
2. Development and demonstration of H<sub>2</sub> as an energy storage medium for electric utilities use in supplying peak power demands.
4. Development and demonstration of the production of gaseous and liquid fuels from urban and agricultural waste products.

Assuming a reasonable funding level,\* these programs are projected to require up to a five-year research and development effort. The methanol task would establish the technology and economics of both the production from coal and/or lignite as well as the end use in automobile engines. Since auto transportation represents the biggest single user of petroleum, the successful implementation of this program could have a significant impact on the oil import and air pollution problems. Tasks 2, 3, and 4 also appear to have near-term viability and would likewise relieve the demand for natural gas and petroleum.

The research and development program identified to achieve the longer-term impact is as follows:

1. Use of hydrogen as a transportation fuel, particularly for aircraft and for specialized ground vehicles.
2. Hydrogen production investigations.
3. Long-distance transmission and bulk storage of hydrogen.
4. Public safety studies.

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\* The panel developed recommended R&D funding levels, but these are not yet available for publication.

## 5. Overall systems analyses.

It is estimated that a five- to ten-year research and development program would be required to establish the feasibility of using hydrogen as a transportation fuel. This program would give particular emphasis to fuel tankage and logistics and their interrelationships to engine and frame considerations.

Hydrogen production investigations to improve the water electrolysis process, as well as to investigate new methods such as thermochemical and biological, could involve a five- to ten-year program. Long-distance transmission and bulk storage of hydrogen, including system studies, design optimizations, and component development, are estimated to require a continuing effort of at least five years.

Public safety and overall system analysis are envisaged as long-term, relatively low-level efforts, but ones which are essential to a smooth implementation period as well as to form the base for a well coordinated research and development program. It is expected that most of the long-term tasks will require concerted work well beyond the initial feasibility efforts outlined above, but will depend strongly on the results obtained by the end of the research and development period.

In general, the panel concluded that the main obstacle to the use of hydrogen as a universal fuel is an economic one, and that an extensive and long-range research and development program could do much to narrow the gap between its cost and the cost of fossil fuels. The cost of fossil fuels, because of declining resources and increasing environmental protection requirements, should increase at a higher rate than the cost of producing the synthetic fuels, and this will also contribute to improving the relative economic position and shortening the implementation period for the adoption of the hydrogen-based economy.

It is clear that our fossil fuels will ultimately be depleted and that reliance must then be placed on the nonfossil synthetic fuels. When this will take place or when a transition from coal-based to nuclear- or solar-based fuel should begin is suggested as a critically important topic for a future, more detailed study.

## APPENDIX

The following members of the study panel on nonfossil synthetic fuels and fuel cells, together with other contributors listed below, were responsible for the preparation of this report. The work was sponsored by the AEC under the cognizance of the Division of Reactor Development and Technology.

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## HYDROGEN GENERATION BY SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS

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A number of recent studies (1 - 11) have concluded that hydrogen is a most promising future means of energy storage and transmission, as fossil fuel supplies diminish and nuclear energy usage increases. These conclusions are based on the premise that a reliable, efficient and cost-effective means of generating hydrogen from water will be available. Electrolysis is presently the most practical generation method, and offers the greatest promise of meeting required capital and operating cost objectives without requiring a major technological break-through. The most common water electrolysis units in the past used a liquid caustic (potassium hydroxide) electrolyte and were relatively inefficient and required frequent maintenance. During the past five years, however, the General Electric Company has developed a unique solid polymer electrolyte (SPE) water electrolysis technology. The SPE system combines high efficiency with exceptionally long, maintenance free life (over three years of continuous operation have been accumulated to date on one of the early single-cell units). While this development was prompted primarily by requirements for oxygen generation in aerospace and submarine life support systems, the design can readily be adapted and scaled to large-size hydrogen generation plants.

It is the purpose of this paper to summarize the present and projected capabilities of the SPE water electrolysis technology, and to consider the applicability of the SPE technology as a generator of hydrogen for use as a fuel, for energy transmission, and for energy storage.

In view of the considerable attention given the "future hydrogen economy", it would seem important that a projection of the costs of the potential hydrogen applications in that economy be considered. This paper attempts to deal with such considerations in a manner that is not overly dependent upon indeterminate factors such as future energy costs, location of nuclear plants, etc. This has necessitated that the respective analyses be kept somewhat general and simplistic.

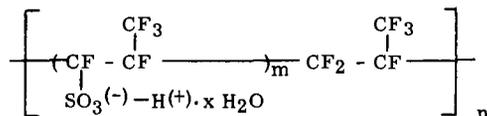
SOLID POLYMER ELECTROLYTE TECHNOLOGY

Details of the technical background describing the performance improvements, demonstrated operating lifetimes, and hardware developments related to this technology have been previously described (12). The following is a summary of this technology and its inherent characteristics.

Solid Polymer Electrolyte

The electrolyte used in the SPE electrolysis cell is a solid plastic sheet of cation exchange membrane about 12 mils thick. This membrane when saturated with water is an excellent ionic conductor ( $\leq 15$  ohm-cm resistivity) and is the only electrolyte required. There are no free acid or alkaline liquids in the system. A typical cell is shown schematically in Figure 1.

The ion exchange membrane (SPE) is a perfluorinated sulfonic acid membrane which has all of the stability and performance requirements for a long-lived electrolysis system. Chemically, the polymer approximates:



Ionic conductivity is provided by the mobility of the hydrated hydrogen ions ( $\text{H}^+ \cdot x \text{H}_2\text{O}$ ). These ions move through the polymer sheet by passing from  $\text{---SO}_3^-$  to  $\text{---SO}_3^-$ . The sulfonic acid groups  $\text{---SO}_3^-$  are fixed and do not move, thus the concentration of the acid remains constant within the SPE.

Water is supplied to the oxygen evolution electrode (anode) where it is electrochemically decomposed to provide oxygen, hydrogen ions, and electrons. The hydrogen ions move to the hydrogen evolving electrode (cathode) by migrating through the SPE. The electrons pass through the external circuit to reach the hydrogen electrode. At the hydrogen electrode, the hydrogen ions and electrons recombine electrochemically to produce hydrogen gas.

An excess of water is usually supplied to the system and recirculated to remove any waste heat.

The gases are generated at a stoichiometric ratio of hydrogen and oxygen at any pressure required of the system. The SPE can withstand large differential pressures ( $> 1000$  psid) as well as high generating pressures which can easily be attained simply by back-pressuring the system.

The use of the SPE results in the following advantages:

- a) The cell can operate with high differential pressures ( $> 1000$  psid) in addition to high gas generating pressures.
- b) The concentration of the electrolyte is fixed and the electrolyte is not mobile.
- c) There is no possibility of acid carry-over into the effluent gas.
- d) There are no corrosive electrolytes to control or leak in the system.
- e) The electrolyte is essentially invariant in operation.
- f) The acid SPE electrolysis unit results in a minimum power requirement per unit of gas generated.

#### Catalytic Electrodes

An additional feature of the SPE water electrolysis cell is the simplicity of the catalytic electrodes. Since the electrolyte is a solid, the catalytic electrodes are not required to retain the electrolyte and may therefore be optimized for catalytic activity at minimum cost. Presently, a thin layer of platinum black ( $1 - 5 \text{ mg/cm}^2$ ) is attached to the

SPE surface to form the hydrogen electrode and a similar layer of a proprietary alloy catalyst forms the oxygen electrode. The improvements in the oxygen electrode catalyst over the past five years have resulted in substantial reductions in the voltage requirements for a fixed hydrogen generation rate. These improvements are shown in Figure 2.

#### Stack and Hardware Design

Figure 3 illustrates the basic components of a cell. The design uses a flat gasket concept for sealing the gas compartments and manifolding the feed water and generated gases between cells. The active area of the membrane is supported by expanded screening on each side. This screening forms the hydrogen and oxygen/water compartments and provides sufficient membrane support to allow operation at 500 - 1000 psid across the membrane. Bipolar current collection is maintained between each cell by means of the screen layers contacting a 3 mil separator sheet.

These cells are in turn stacked between end plates as shown in Figure 4. The particular hardware shown in this figure has operated for more than 12,000 hours with no change in operating characteristics.

Generally the metallic components within the cells are either titanium alloy or niobium to eliminate corrosion. Titanium alloy would be used almost exclusively for ground applications to take advantage of its lower cost. As can be seen, this particular design concept can readily be scaled-up either in terms of the number of cells in a stack or the area of a cell. SPE fuel cell stacks of 78 cells have been made and tested for over 5000 hours. Likewise, 1 x 2 ft fuel cells have been tested. One unit with approximately 1 x 0.5 ft cells has operated for more than 15,000 hours without problems.

#### Present SPE Water Electrolysis Capability

Status of the SPE water electrolysis technology in 1972 - 1973 is best depicted in Figure 5, which shows the performance attained with "state-of-the-art" SPE electrolysis cells. The cell used to determine these curves has operated for 7000 hours to date with no change in its performance capability.

Based upon this technology, an electrolysis stack operating at 1000 ASF would require 22.2 KWH to produce a pound of hydrogen. Capital costs would be \$3000/lb/hr of hydrogen capacity (equivalent to \$167/KW capacity based upon the higher heating value of hydrogen).

#### Projected SPE Water Electrolysis Capability

Titterington et al (12) have examined the potential for further reductions in both energy requirements and the capital cost of producing hydrogen by SPE water electrolysis. Figures 6 and 7 summarize these projections.

The projections through 1985 are straightforward extensions of the present SPE technology. Input energy reductions will be obtained through further anode improvements and the increase in operating temperature to 300°F. The SPE has been operated at this temperature for 800 hours and has been shown to be stable at this temperature condition. Capital cost reductions will be achieved by modest reductions in the quantity of noble metal required per cell and the use of lower cost hardware materials. For example, materials are presently available to achieve the capital costs projected for 1977. Since these

materials have not undergone extensive testing in the actual electrolysis environment for periods in excess of three years, they have not been used to calculate the 1973 capital cost basis.

Beyond 1985, it has been assumed that an inorganic solid electrolyte, similar to the zirconia technology (13 - 14) studied in some depth in the 1967 - 1968 time period, will become available. In the 1968 time period, the energy requirements and capital costs for the zirconia technology were similar to those projected for the SPE in the 1980 - 1985 time period. This technology was severely limited by the temperature of operation (1800°F) and resulting materials problems. It has been assumed that an oxide conductor operating in a temperature range below 1800°F and above that of the  $\beta$  aluminas (650°F) could be developed within the 1985 - 2000 time frame.

Thus the projections through 1985 are based on extensions of the present SPE technology through increased temperatures of operation and lower cost materials. In the 1985 - 2000 time period the development of a  $\sim$  1000°F oxide conductor is assumed.

#### APPLICATION OF WATER ELECTROLYSIS IN FUTURE POWER SYSTEMS

In recent months, ever increasing attention is being given by industry, utilities and government agencies to the search for alternative energy sources to meet the energy crisis. The impetus behind this effort is the prospect that in the foreseeable future, if the energy demand increases at the anticipated rate, fuels such as natural gas, fuel oil and coal will either be depleted or prohibitively expensive. This concern is coupled with environmental regulations which prohibit the direct burning of high sulfur coal (which is reasonably plentiful) and restrict the amount of local thermal pollution resulting from close-by nuclear installations. The location of nuclear generating plants in remote locations, such as off-shore islands or platforms, effectively attacks the thermal pollution concern but incurs the expense of transmitting power for long distances.

As the severity and ramifications of the energy shortage become better defined, the utilization of hydrogen as a fuel and/or a means of transmitting or storing energy comes into contention. Hydrogen as a fuel is clean and its product of combustion is pure water when reacted with either oxygen or as a hydrogen-rich air mixture. It also offers the highest specific energy density (Btu/lb) of any potential fuel. Piped hydrogen as a future means of transmitting large amounts of energy for relatively long distances offers the potential advantages of:

- a) Plentiful supply since the basic requirement is water.
- b) Compatibility with remote nuclear plants located off-shore where thermal environmental effects are minimal.
- c) Lower cost, to the extent that the savings in transmission and distribution costs more than offset the cost of generating the hydrogen.
- d) Improved visual environment since hydrogen pipes are underground and can utilize existing natural gas networks.
- e) Flexibility, since hydrogen can be used directly in home and industry with minor modification to natural gas burning equipment, converted to electricity via gas turbines or fuel cells, or it can be liquified and distributed for automotive or aircraft use.

- f) Storage, either in gaseous or liquid form which allows: 1) utilization of power at the off-peak periods where desirable (nuclear or conventional fossil fuel plants); or 2) utilization of cyclic or periodic electrical power sources (such as wind power systems, solar energy systems or tidal systems).

In addition to the above advantages, the electrolysis of water produces oxygen as a byproduct along with the hydrogen. This "free" oxygen could potentially be utilized for sewage treatment, fresh water purification, or sold for industrial use.

Many studies of the economics of various aspects of the hydrogen energy cycle compared to present and predicted fossil fuel cycles have been performed by utilities, industry and government agencies (1 - 8). Most studies conclude that based on present technology, energy in the form of hydrogen could be transmitted at less cost than electrical energy and by 1985, local re-conversion of hydrogen to electric power via combustion turbines would be competitive with underground transmission of electrical energy.

All of the present studies assume electrolysis energy requirements in the area of 22 to 28 KWH/lb H<sub>2</sub> and capital costs in the range of \$785/lb H<sub>2</sub>/hr output capacity.

Based on the projected performance and cost estimates discussed previously, we see energy requirements of 18 to 20 KWH/lb H<sub>2</sub> in the 1985 - 1990 time period, dropping as low as 15 KWH/lb H<sub>2</sub> by the year 2000. A capital cost of \$785/lb H<sub>2</sub>/hr capacity is reasonable for the 1985 time period with reduction to \$250 - 350/lb H<sub>2</sub>/hr capacity by the year 2000.

#### Conceptual Hydrogen Utility System

A conceptual hydrogen utility system is depicted in Figure 8. Electricity is generated in a large-scale power plant located in a remote, unpopulated land area or an off-shore platform where environmental pollution effects are minimized and a ready supply of water (either sea, river or lake) is available. The power plant produces DC power directly (utilizing homopolar generators) for use by the electrolysis plant located at or close by the power plant. This avoids the requirement of AC-DC conversion equipment. The waste heat from the nuclear plant is utilized to desalinate the water utilized in the electrolysis process.

In the electrolysis plant the water is electrolyzed into hydrogen and oxygen. The hydrogen can be stored in sub-surface tanks, either under pressure or as liquid H<sub>2</sub>, in sufficient quantity to compensate for load fluctuations while allowing the power plant and electrolysis plants to operate at full capacity at all times. The hydrogen, which can be generated under pressure, is then transmitted through sub-surface pipe lines to local distribution points where it can be 1) distributed and used directly as fuel by domestic and industrial customers, 2) re-converted to electricity via either gas turbine generators or fuel cells, or 3) liquified and distributed in the liquid form for automotive or aircraft use.

The attractiveness of such a system is based not only on the fact that hydrogen is an alternative to the dwindling fossil fuel supply or that it has important environment advantages, but that it is potentially less expensive to transmit large amounts of energy for long distances in the form of hydrogen than as electric energy and, since hydrogen can be stored, it offers the cost advantage of steady load operation. The following discusses each of these options in more detail.

Hydrogen as a Fuel

Hydrogen as a fuel has several advantages over natural gas and other fossil fuels, such as:

- . Low pollution levels; hydrogen produces much less pollution than hydrocarbon fuels and can be used in combustion equipment with little, if any, modification.
- . High specific heat; the heat content of hydrogen is almost three times as great as gasoline on a weight basis.

Based on the predicted energy requirements and capital equipment costs discussed previously, the cost of hydrogen generated by SPE electrolysis can be expressed for the year 1985 as:

$$C_{GF} = 0.312 C_o + 0.227 \quad \$/10^6 \text{ Btu}$$

where  $C_o$ , the cost of electrical energy, is expressed in mils/KWH.

For the year 2000, the cost of generated hydrogen drops to

$$C_{GF} = 0.250 C_o + 0.090 \quad \$/10^6 \text{ Btu}$$

The above costs include the cost of desalinated water at a cost of 32 cents per 1000 gallons (9) or about 0.006  $\$/10^6$  Btu.

The fixed cost factor represents the capital equipment cost of the electrolysis cells (exclusive of ancillary pump and control cost) depreciated at 15% per year (6.67 years of continuous operation or 58,4000 hours).

An approximate total cost including ancillary costs and pumping requirements can be obtained by adding 10% to  $C_{GF}$ . This factor is small relative to the uncertainty regarding future electrical energy costs and has, therefore, been excluded. Likewise, no credit has been taken for the potential cost offset of the oxygen which is a byproduct of the electrolysis process.

Based on a DC electricity cost of 5 mils/KWH, the cost of SPE-generated hydrogen would be  $\$1.79/10^6$  Btu by 1985 and  $\$1.35/10^6$  Btu by the year 2000.

Figure 9 shows the predicted cost of SPE electrolytically generated hydrogen through the year 2000 with electrical energy costs of 5 and 10 mils/KWH. Shown also are typical costs of other gaseous fuels. It is apparent that during the 1990's, local electrolytically produced hydrogen could be competitive with foreign natural gas transported to the United States via LNG tankers, natural gas transmitted from Alaska by pipeline or locally produced synthetic natural gas generated from either oil or naphtha or the gasification of coal.

The real cost of the hydrogen, of course, will be directly influenced by the cost of electrical energy. A deciding factor in the use of hydrogen will be the relative rates of electrical energy cost increase vs. fossil fuel cost increase.

Energy Transmission by Hydrogen Pipe Line

Figure 10 is a model used for comparing the cost of energy transmission by piping hydrogen vs. both overhead and underground electric cabling. As in the model for hydrogen generation, electrical energy at cost  $C_o$  mils/KWH is fed to a water electrolysis plant and desalinated water is fed to the plant at a cost of 32 cents per 1000 gallons or about 0.02 mil/KWH. Again, for the purposes of this analysis the oxygen is assumed dumped to the atmosphere and no credit is given for potential use of the oxygen such as water purification, sewage processing, etc. The hydrogen is transmitted through sub-surface pipe lines at 750 psi to distribution points at a cost of 3.5 cents/MBtu/100 miles or 0.12 mil/KW/100 miles (7) assuming a compressor station every 65 miles.

Based on this model, the cost of energy at the distribution point can be expressed as:

$$C_{DF} = 1.064 C_o + 0.77 + 0.12 M \text{ in the year 1985, and}$$

$$C_{DF} = 0.854 C_o + 0.31 + 0.12 M \text{ in the year 2000}$$

where M is the distance in hundreds of miles between the electrolysis plant and the distribution point. The fixed cost factor represents capital equipment cost depreciated at 15% of the original capital per year (6.67 years of continuous operation).

Assuming the cost of DC electricity via homopolar generator is the same as AC electricity, the above cost at the distribution point can be compared directly to the cost of electrical transmission estimated at 21 cents/MBtu or 0.714 mil/KWH/100 miles for overhead high voltage wires (10) and 5 mils/KWH/100 miles for underground wires (1).

This comparison is shown graphically in Figure 11 based on a cost for electricity at the generating plant ( $C_o$ ) of 5 mils/KWH. This shows that in 1985, the transmission of energy in the form of hydrogen would be competitive with overhead wires for distances greater than 190 miles and with underground wires for distances greater than 20 miles. By the year 2000, hydrogen energy transmission will be less expensive than electrical transmission regardless of transmission distance.

For that portion of hydrogen energy which must be re-converted for use as electrical energy, the cost and efficiency of the conversion equipment (combustion turbine/generator or fuel cell/inverter) must be added to the hydrogen energy cost. Based on predicted gas turbine/generator costs and efficiencies of

	<u>1985</u>	<u>2000</u>
\$/KW <sub>out</sub>	\$120/KW	\$120/KW
$\eta$	55%	70%

the cost of electrical energy at the distribution substation ( $C_{DE}$ ) can be expressed as

$$C_{DE} = 1.94 C_o + 3.78 + 0.12 M \text{ in 1985 and}$$

$$C_{DE} = 1.22 C_o + 2.50 + 0.12 M \text{ by the year 2000.}$$

These relationships are shown in Figure 12, again compared against overhead and underground electrical transmission and assuming a generation cost of 5 mils/KWH. This shows that even with the cost of re-conversion to electricity factored in, energy transmission by piped hydrogen will be less expensive than by underground wires for distances of 175 miles or greater in 1985, and for distances of 75 miles or greater by the year 2000.

The above analyses show that energy transmission by hydrogen pipe line could offer significant cost advantage over electrical energy transmission in the not too distant future. It should also be recognized that a cost of generated electricity above the 5 mils/KWH assumed would make hydrogen energy transmission less attractive relative to electrical energy transmission. Thus the cost of future electrical energy remains the determining factor in the use of hydrogen for energy transmission.

#### Energy Storage - In Hydrogen Energy Transmission

One of the major advantages apparent in the use of hydrogen as a method of energy transmission is that it can be stored either as a gas or cryogenically. This storage capability makes hydrogen generation advantageous in systems where either the energy load is cyclic or periodic, or the energy source is periodic. In the case where the load is cyclic, the utilization of stored hydrogen allows the power and electrolysis plants to operate at a constant level close to full capacity at all times, with load peaks being supplied from the storage tanks which are then recharged during off-peak hours.

In the case where the energy source is periodic or cyclic such as a solar energy system, some of the hydrogen generated during the "on" period can be stored to supply the "off" period load.

Storage of hydrogen as a low pressure gas requires very large storage volumes (one lb of hydrogen requires 190 cu ft at sea level ambient pressure or 17.5 cu ft at 150 psi), but may be practical for limited storage. Such schemes as large undersea balloons have been suggested (3), as have underground cap rock aquifers similar to those used for natural gas (7).

However, by liquifying hydrogen the storage volumes are greatly reduced, to the point where large quantities of energy can be stored in very small dewars (at -423°F, one lb of hydrogen occupies only 0.225 cu ft).

Liquid hydrogen dewars as large as 0.9 million gallons have been built at costs of approximately \$2 per gallon capacity (11). This is approximately a \$55.40/10<sup>6</sup> Btu or 189 mils/KWH storage capacity. Large-size tanks have boil-off rates as low as 0.03 to 0.05% per day. Boil-off, as such, has minimal effect on storage costs since any boil-off can be returned to the main supply and does not necessarily represent waste. The heat required to reheat the liquid hydrogen for transmission as a gas would be readily available from the waste heat of the electrical generation plant.

Assuming 1% of the annual output is stored, storage dewars amortized over 35 years, and a liquification cost of \$0.70/MBtu stored, leads to an additional cost on delivered energy of \$0.023/10<sup>6</sup> Btu (or 0.08 mil/KWH). This small cost could be greatly overshadowed by the savings in capital equipment costs due to being able to size the plant for nominal load rather than peak load.

### Energy Storage - As Part of Existing Electrical Power System

At the substation level, energy storage as hydrogen may be competitive as a means of utilizing off peak power to meet peak load demands. Consider the case where the typical daily load curve has: 1) an 8-hour off peak period from midnight to 8 AM where demand is below the nominal load level; and 2), an 8-hour peak load period in the afternoon and evening when the load level is higher than the nominal load level. Off peak electricity is available at a cost of  $C_{op}$  mills/KWH.

A water electrolysis/storage/gas turbine or fuel cell-inverter system could utilize the off peak power to form hydrogen, store it in either gaseous or liquid form, and utilize it to generate electricity during the peak load period.

Such a system, shown in Figure 13, would have an overall energy efficiency of about 52% in 1985 and around 82% by the year 2000. Capital costs are estimated at approximately 7.8 (1985) to 4.9 mills/KWH daily output (2000) if gaseous storage is used, with an additional 4.3 (1985) to 3.4 (2000) mills/KWH if cryogenically stored to allow for liquification. This method of storage would be attractive if the actual cost of off peak ( $C_{op}$ ) electricity at the substation is sufficiently less than the cost of peak load electricity ( $C_p$ ). The relationships are shown at the bottom of Figure 13.

### Future Applicability

It seems apparent, due to its cleanliness as a fuel, capacity for energy storage, ease of transmission and the availability of its raw material (water), that hydrogen may become an extremely important element in tomorrow's utility power system. The degree to which it will find application largely depends on the degree to which water electrolysis hardware costs can be reduced and efficiency increased, and on the future costs of electrical energy relative to fossil fuels.

General Electric's water electrolysis technology holds the promise of both the low capital cost and high efficiency required for future power system application.

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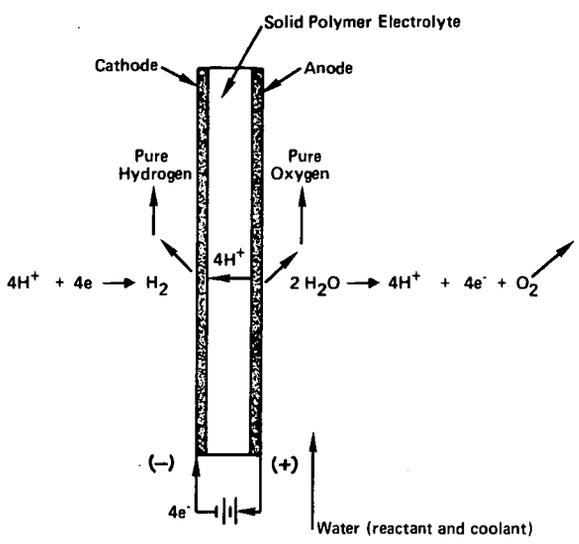


Figure 1. SPE Electrolysis Cell Schematic

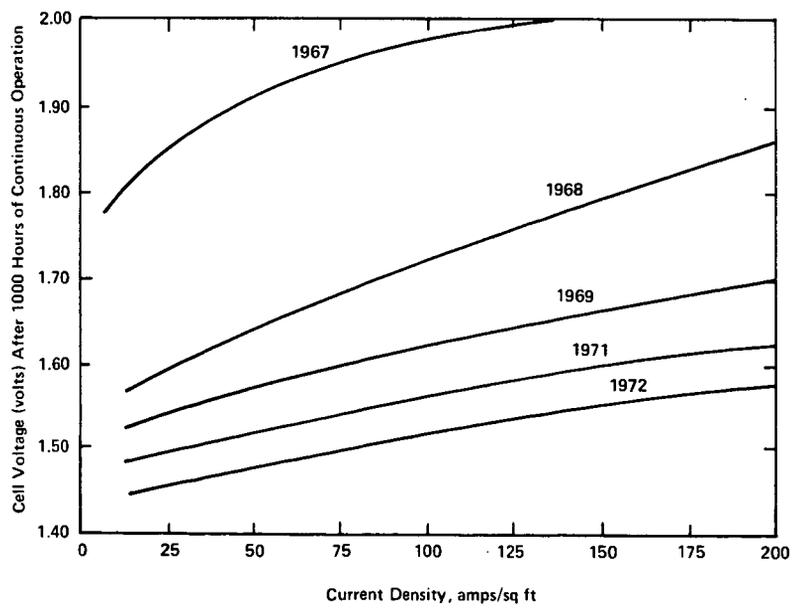


Figure 2. SPE Electrolysis Performance at 120°F and Ambient Pressure

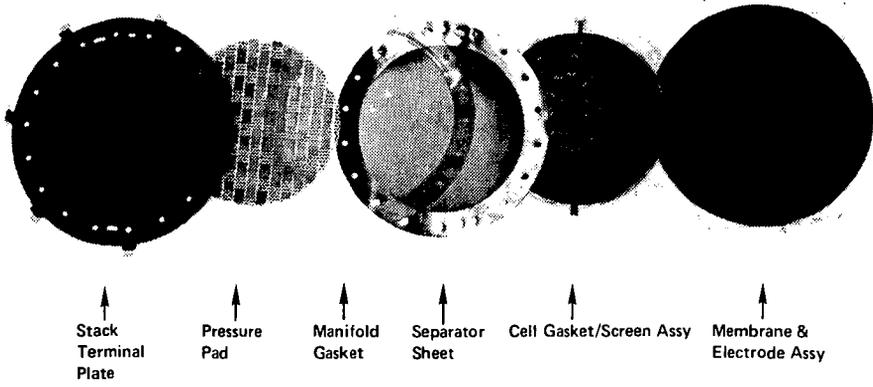


Figure 3. Electrolysis Cell Component Parts

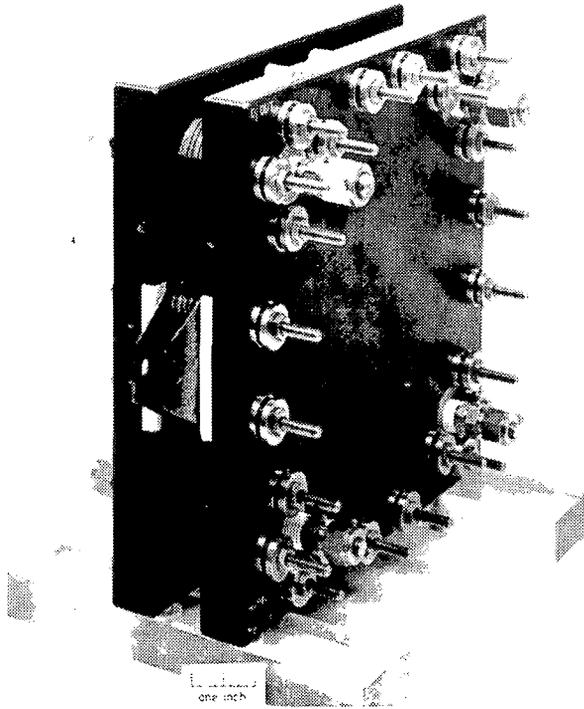


Figure 4. Seven-Cell NASA/LRC Electrolysis Stack

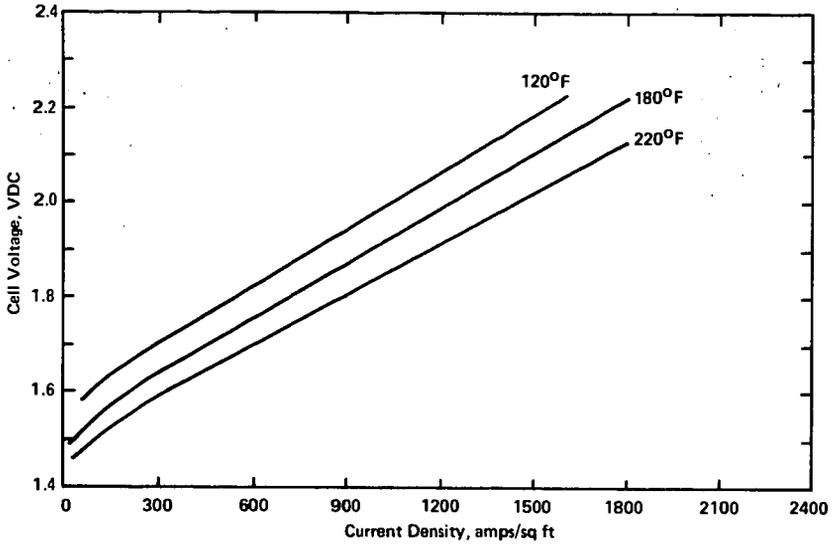


Figure 5. 1972 SPE Water Electrolysis Capability

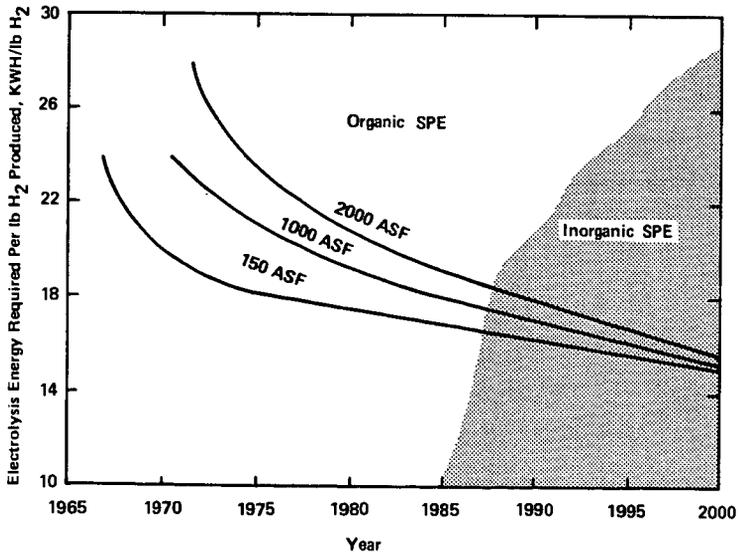


Figure 6. Energy Requirements for SPE Electrolysis

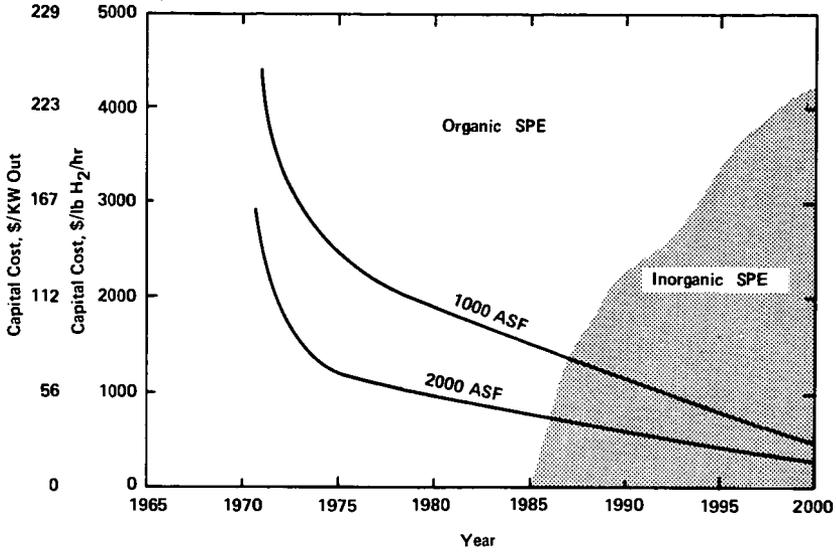


Figure 7. Capital Cost Requirements for SPE Electrolysis

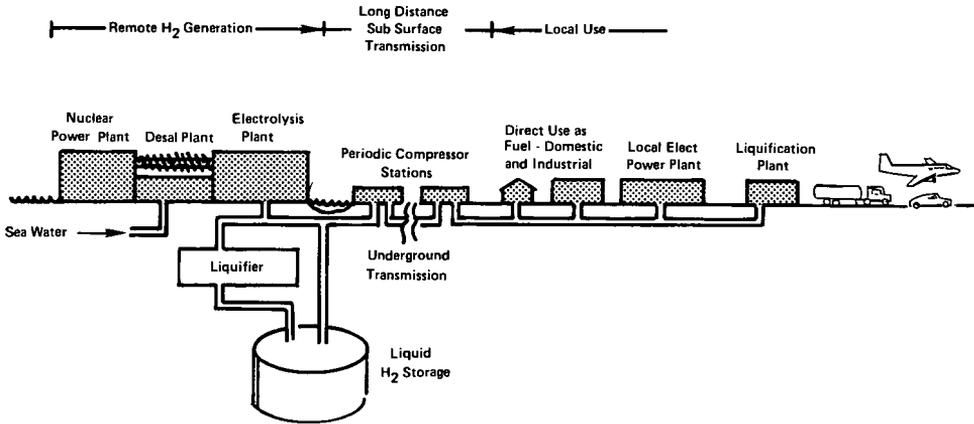


Figure 8. Conceptual Hydrogen Utility System

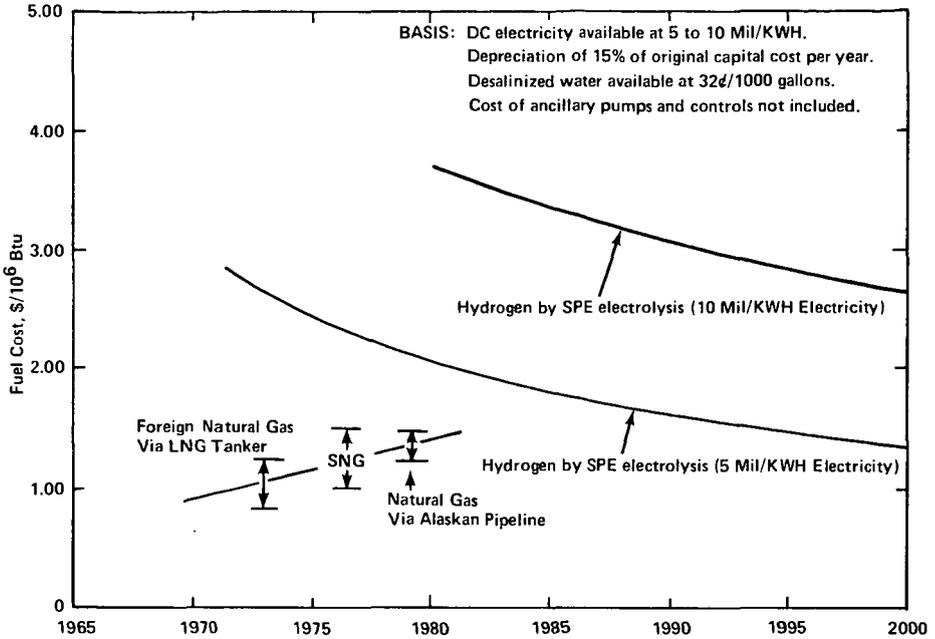


Figure 9. Projected Cost of Hydrogen Production by SPE Electrolysis

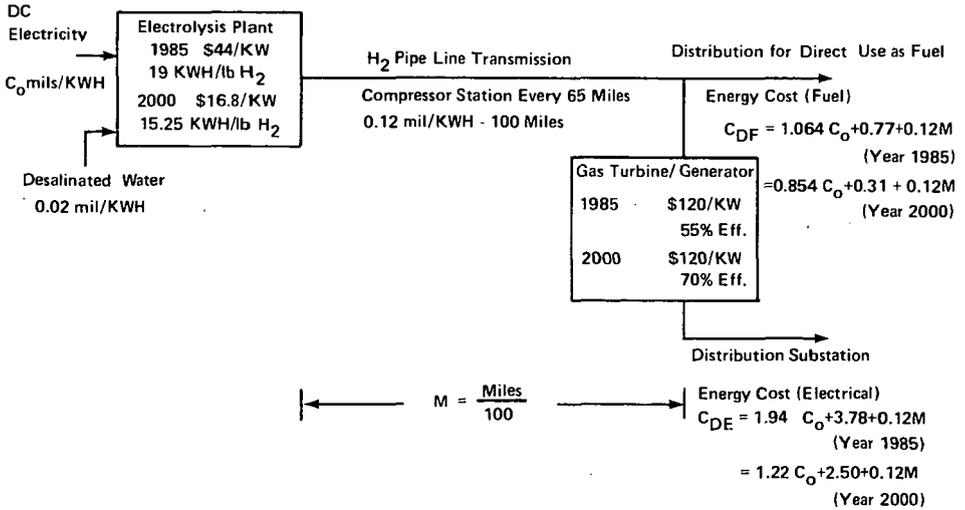


Figure 10. Model of Hydrogen Pipe Line Energy Transmission

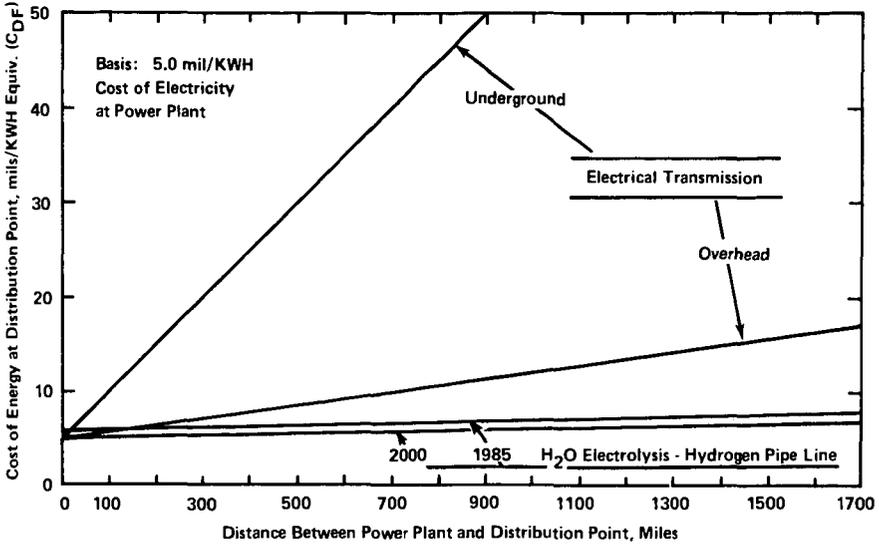


Figure 11. Comparison of Cost of Energy at Distribution Point for Electrical vs. Hydrogen Pipe Line Transmission

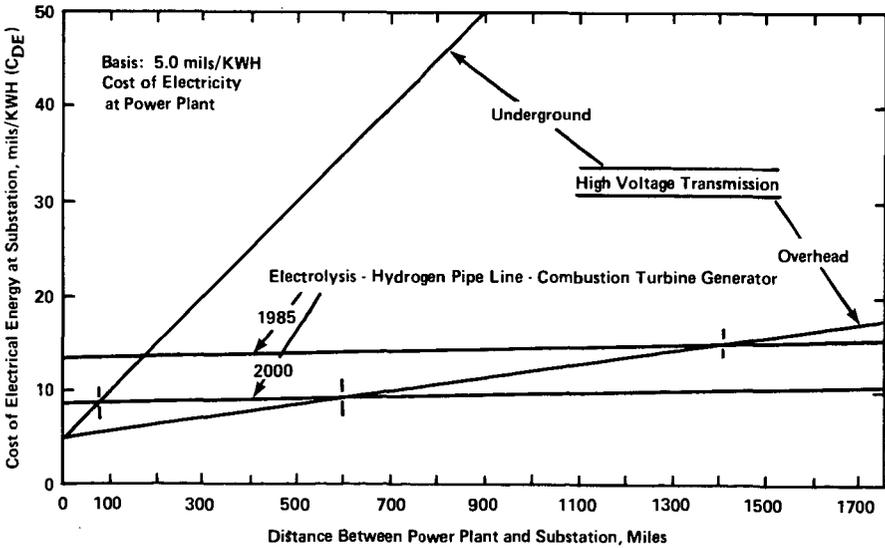
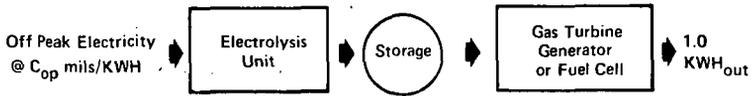
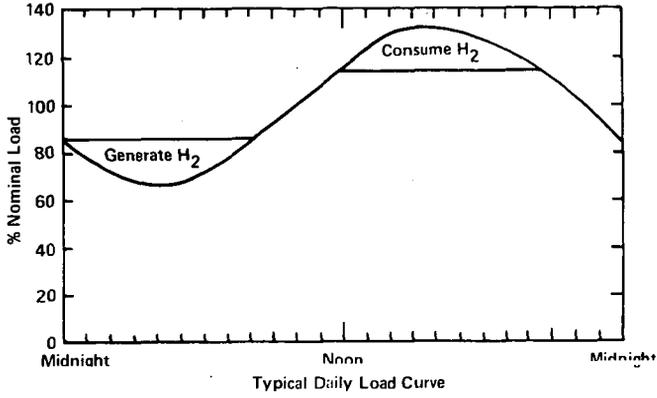


Figure 12. Comparison of Cost of Electrical Energy at Distribution Substation for Electrical Transmission vs. Hydrogen Pipe Line



1985	\$44/KW <sub>out</sub> 19 KWH/lb H <sub>2</sub>	Tankage Cost 0.02 mil/KWH	1985	\$120/KW <sub>out</sub> 9.8 KWH/lb H <sub>2</sub>
2000	\$17/KW <sub>out</sub> 15.25 KWH/lb H <sub>2</sub>	Liquification 4.3 mils/KWH (1985) 3.4 mils/KWH (2000)	2000	\$120/KW <sub>out</sub> 12.5 KWH/lb H <sub>2</sub>

COST RELATIONSHIPS

Gaseous H <sub>2</sub> storage $C_{op} \leq 0.52 C_p - 7.8$ mils/KWH	$C_{op} \leq 0.82 C_p - 4.9$ mils/KWH
Liquid H <sub>2</sub> storage $C_{op} \leq 0.52 C_p - 11.3$ mils/KWH	$C_{op} \leq 0.82 C_p - 8.3$ mils/KWH

Figure 13. Typical Bulk Storage System

THERMOCHEMICAL SYSTEMS FOR HYDROGEN GENERATION. R. E. Hanneman and R. H. Wentorf, Jr.  
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Closed-cycle thermochemical hydrogen production, using water and heat as input ingredients and yielding hydrogen, oxygen and degraded heat as products, through multi-step reactions with cycled chemical intermediates will be treated. The approaches, criteria and limitations for identification of potentially viable closed-cycle methods of water splitting will be described. Key features of a new closed-cycle process developed in our laboratory will be presented in terms of the above factors. Practical overall thermal efficiencies based on hydrogen combustion energy produced relative to endothermic nuclear heat supplied can range from less than 20 percent to more than 60 percent with maximum input temperatures of 750°C for the various systems analyzed in our study. Limitations due to corrosion, reaction kinetics, system complexity, ecological and economic factors will be briefly outlined. Closed-cycle approaches will be compared to evolving open-cycle methods of hydrogen production with a fossil fuel, such as coal, wherein water and heat are input ingredients and hydrogen, CO<sub>2</sub> and degraded heat are the idealized exit products. Other methods of hydrogen generation including electrolysis, mixed-cycle, photolysis, and biological means will be briefly discussed.

NUCLEAR REACTORS FOR HIGH TEMPERATURE PROCESS HEAT;  
A SURVEY OF REACTOR TYPES AND TEMPERATURE REGIMES

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INTRODUCTION

The annual energy consumption of the US in 1970 was about  $72 \times 10^{15}$  Btu, and of this about 20% was used to furnish process heat. The term "Process Heat" is very commonly used in a narrow sense, referring to heat obtained from steam boilers at temperatures up to perhaps 230°C. In the following discussion, process heat will be taken to include heat supplied for process purposes up to the highest temperatures which material properties will permit.

The comparative economic attractiveness of nuclear energy as a source of process heat is likely to be subject to substantial alteration in coming years as the balance of energy sources changes in response to cost and availability. Indeed, it is clear from the large volume of literature published that interest in supplying process heat from nuclear sources is intense. However, the great bulk of this interest has to do with low temperature heat and in particular with desalination, usually combined in some way with electric power production. Another concept that has received considerable attention is typified by the Agro-Industrial Complex suggested by workers at ORNL. In such a complex, the nuclear reactor is used as a source of energy for chemical processing, but generally as electricity and not directly as thermal energy from the reactor.

It is evident, especially in the last few years, that there is growing interest in direct use of high temperature thermal energy from nuclear reactors as a source of process heat. This is especially true in Germany and Japan, and it is the opinion of some that we are at the threshold of economic feasibility of applications of nuclear energy as evidenced by the increasing consideration being given to solution of design and material problems.

The growing shortage of gas and oil in the US clearly points to the need for major emphasis to be placed on the gasification and liquefaction of coal. Most of the heat requirements of oil refineries for operations such as cracking and distillation are in the range of 300 to 550°C and could be met by adaptation of existing nuclear reactors although this will not be economically attractive until the price of petroleum products is higher. However, the use of nuclear heat to reduce consumption of coal as a source of energy in the gasification process has attracted interest. A key reaction in many of the processes being considered for that purpose is the endothermic reaction between C and H<sub>2</sub>O to produce CO and H<sub>2</sub>. The temperature required for this reaction is in the range of 1050-1150°C and the required heat is produced at the expense of coal. If the energy requirements for gasification were met by nuclear energy, the consumption of coal could be limited to supplying the carbon atoms required for the hydrocarbon synthesis. In view of the limitations of the world's coal and the huge rate of hydrocarbon consumption that exists, the saving could be very significant.

The distribution of manufacturing process heat among industry groups is shown qualitatively in Table 1. The four largest users account for about three fourths of the demand. The primary metals industry group is by far the greatest consumer

\*Work done under the auspices of the U. S. Atomic Energy Commission.

TABLE 1

PROJECTED HEAT CONSUMPTION BY  
U.S. MANUFACTURING INDUSTRIES IN 1967<sup>a</sup>

Industry Group	Btu x 10 <sup>15</sup>	% of Total
Primary Metals	4.678	32
Petroleum and Coal Products	3.522	24
Chemical and Allied Products	1.614	11
Stone, Clay, and Glass Products	1.256	9
Food and Kindred Products	0.907	6
Paper and Allied Products	0.656	5
Textile and Mill Products	0.227	2
All Other Industrial Groups	<u>1.692</u>	<u>11</u>
Total	14.552	100

<sup>a</sup>After Tarrice (1)

of energy and the iron and steel industry dominates by using about 85% of the energy of the group. The technical problems of supplying nuclear heat directly in the iron and steel industry are typical of the problems of utilizing nuclear heat for chemical processing. The energy derived from the coke used in the blast furnace is about equally divided between that used to heat the ore, limestone and air blast, and that which acts as a reducing agent. Thus, supplying the needed heat from a nuclear source would decrease the coke requirement by up to a factor of two. This can be a consideration of growing importance because reserves of coal suitable for making high quality coke are becoming scarce and the price is bound to reflect the growing scarcity. The temperature required depends somewhat on the character of the feed materials but is about 900°C. As will be seen, this is well above the temperature that is available from power reactors in use today but is within reach of some reactor concepts that are under development.

A consideration of the greatest importance today in any use of nuclear energy is that little or no radioactivity be released into the environment. This rules out processes in which one or more of the reactants pass through a nuclear reactor. The most practicable design for process heat reactors therefore employs a heat transfer fluid contained in a closed loop, circulating through the reactor and passing heat to the process materials by a heat exchanger external to the reactor. In addition to confining fission products to the reactor, this approach has the added advantages of avoiding some chemical compatibility problems of reactor fuel elements and core materials with the process material to which heat is being delivered, and of keeping the processed material free of induced radioactivity. The addition of a second heat transfer system, however, does impose the penalty of increased differential between

fuel temperature and the temperature imparted to the process materials.

Not surprisingly, the feasibility of using low temperature process heat is dominated more by cost considerations than technical problems, while technical problems mount as the upper limits of reactor temperature are approached.

### Water-Cooled Reactors

The major focus of power reactor development in the US has been on water-cooled reactors which rely almost entirely on slow neutron induced fission of  $^{235}\text{U}$ . These may be divided into two main categories, the Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR). Numerous variations of these reactors have been made but, because the output temperature of all of them lies in a rather narrow range, the two main classes will be dealt with in general terms.

Following development of the PWR for submarine propulsion, the first commercial electric power plant was put in operation at Shippingport in 1957. This reactor was followed by many others which have incorporated improvements, mostly notably an increase in burn-up from about 8000 to about 33000 MWd/t. The fuel material is usually slightly enriched  $\text{UO}_2$  ( $\sim 3\%$   $^{235}\text{U}$ ) clad in zircalloy or stainless steel which presents a barrier to escape of fission products. Problems which tend to limit the performance of PWR fuel include fuel swelling and fission gas pressure, irradiation effects on fuel and cladding, stress corrosion of stainless steel cladding and oxidation and hydriding of zircalloy cladding. The output temperature is modest, falling in the range  $260^\circ$  to  $350^\circ\text{C}$ , though pressures are high, up to 2500 psia to prevent boiling. Useful heat is extracted from the primary hot water coolant loop through a heat exchanger located inside the reactor containment vessel. In the usual case where electricity is desired, steam is generated in the heat exchanger and supplied to a turbine. If process heat were desired, the steam, usually at  $\sim 260^\circ\text{C}$  and  $\sim 720$  psi could be used to transport heat to the desired process. Alternatively, in some instances, it might be desirable to transfer heat directly from the primary pressurized water core coolant loop through a heat exchanger to one or more of the materials to be processed. Safety considerations would probably determine whether such direct heat transfer was acceptable or whether instead a secondary heat transfer loop between the primary heat exchanger and the desired heat sink was preferable.

The BWR power reactor prototype was built at Vallecitos and put in operation in 1957. The fuel material of reactors of this type is usually  $\text{UO}_2$  with zircalloy cladding. The output saturated steam temperature is  $250^\circ$  to  $300^\circ\text{C}$  at steam pressure of about 1000 psia and burnup is of the order of 30,000 MWd/t.

For electric power generation, the steam produced in the reactor core goes to a turbine. If steam were desired for process purposes it might be used directly or, for greater safety against escape of fission products from the core, a heat exchanger could be interposed between the primary steam loop and the process heat sink.

There has been substantial interest in the possibility of superheating the steam produced by BWR reactors in order to increase the efficiency of turbine power generation. These efforts have resulted in output temperatures in the range  $440^\circ$  to  $580^\circ\text{C}$ , a very significant increase. However, the corrosion conditions to which the fuel cladding is subjected are more severe than in the basic PWR and BWR. Radiation damage, attack by oxygen from radiolysis and deposit of chlorides on the cladding occur, with the result that no fully satisfactory cladding has been adopted.

A variant of the water cooled reactor which has been the object of several experimental reactors is that of using an organic coolant. The principal compound used has been terphenyl, a cyclic hydrocarbon whose boiling point is  $213^\circ\text{C}$  at atmospheric pressure. The boiling point being greater than that of water, the possibility of significant superheating of steam is offered. Organic compounds

inevitably decompose under heat and irradiation, and though terphenyl decomposes slowly, provision for removal of decomposition products must be made. In addition, the thermal conductivity and heat transfer characteristics of coolants of this type are poor. The relatively non-corrosive character of the organic coolants has permitted more latitude in choice of fuel and cladding than in water cooled reactors, although magnesium and alloys undergo intergranular attack and iron is not satisfactory. The hydride forming metals, i.e., Zr, Nb and Ta, are contraindicated, but aluminum and stainless steels are not attacked. Both  $UO_2$  and a uranium metal alloy have been used as fuels. Output temperatures have ranged from 250° to 375°C and 400°C is regarded as an upper limit set by coolant decomposition.

### CO<sub>2</sub> Cooled Reactors

The British and French nuclear power reactor programs are based on CO<sub>2</sub> cooled, graphite moderated reactors using metallic natural uranium fuel with a magnesium alloy cladding, Magnox. This is a Mg alloy containing 0.8% Al, 0.008% Ca, 0.002%–0.05% Be, and 0.006% Fe. The British Calder Hall reactors began operation in 1956 and a total of about 35 such reactors have been built. Reactors of this type are conservative in design and have operated with very low fuel element failure rate. An inherent and important limitation is that the practical limit of reactor output temperature is about 500°C, because of oxidation of the cladding by CO<sub>2</sub>. The core output temperatures of this and other types of reactor are compared<sup>(2)</sup> in Fig. 1. Indeed, the melting point of the cladding is about 645°C and, in addition, uranium undergoes a phase change from  $\alpha$  to the lower density  $\beta$  at about 665°C. Problems with the fuel have been mainly;

- a) irradiation induced creep of the uranium fuel at low temperature and thermal creep at higher temperature.
- b) Swelling of the uranium at high temperature because of agglomeration of fission gas bubbles.
- c) Deformation of high temperature parts by mechanical load because of proximity to melting temperature.

In 1963 the British Advanced Gas Reactor (AGR) at Windscale began operation. This is a higher temperature modification of the CO<sub>2</sub> gas cooled reactor leading to more efficient power generation. The fuel element temperature limitations of the Calder Hall reactor were significantly relieved by the substitution of UO<sub>2</sub> for uranium metal and of stainless steel cladding for the magnesium alloy. The stainless steel alloy, containing 20% Cr, 25% Ni, resists oxidation by CO<sub>2</sub>. However, stainless steels and nickel alloys undergo loss of ductility as a result of neutron irradiation. The output gas temperature of this type of reactor has been in the range 500° to 575°C and burnup typically 10000 MWd/t. For electric power generation, heat is transferred through a heat exchanger to steam for turbine operation. If it were desired to use the output heat for process purposes, the considerations would resemble those applying to the PWR.

### Na Cooled Moderated Reactors

The concept of a sodium-cooled graphite moderated reactor was explored in two reactors, the SRE being a reactor experiment and the Hallam reactor which was built to demonstrate feasibility of the concept for electric power generation. The output temperatures achieved were in the range 500° to 650°C.

The fuel elements tested were of several types all using 304 stainless steel cladding. The Hallam reactor used a fuel alloy consisting of somewhat enriched U and 10 wt% Mo with Na thermal bond to the cladding. This type of reactor has not been pursued further.

### Breeder Reactors

Consideration of the need for and feasibility of supplying high temperature process heat in the years ahead must take into account what appear to be emerging as the important factors in the energy supply situation that we are moving into. In the relatively short term the decreasing availability and accompanying increase in price of oil and natural gas suggest looking to coal and nuclear energy. Two important factors not always clearly appreciated are: a) the limitations of coal supply if the burden of substituting for oil and gas is thrown on coal, and b) the limitations of the US' and the world's supplies of low cost uranium. The first factor suggests that a shift from oil and gas to coal should not be looked upon as a long term solution to the energy supply problem and that even with our best efforts the development of large scale nuclear and other energy sources is unlikely to occur before it is badly needed.

Let us consider the limitations of uranium supply, Table 2. The nuclear power reactors so far put into operation all derive roughly 2/3 of their energy from fission of  $^{235}\text{U}$ , leaving nearly unused the 99.3% of the energy potential of uranium supplied by nature in the more abundant  $^{238}\text{U}$  which does not fission significantly in moderated reactors. Figure 2 shows a projection of the consumption rate for  $^{235}\text{U}$  in the US and the consequent rising price. Clearly, the depletion of cheaper uranium ores leads to rapidly rising cost of uranium even in the relatively near term. This problem has led to the large amount of effort expended over many years in the US and the world on development of breeder reactors to convert  $^{238}\text{U}$  into the fissionable  $^{239}\text{Pu}$  while delivering useful energy. The anticipated shift of the burden of power production from thermal reactors using  $^{235}\text{U}$  to reactors of the breeder type is expected to reduce the price rise of uranium with time as shown in Fig. 2. Furthermore, the small amount of uranium used relative to the amount of energy released will render the cost of energy quite insensitive to the cost of uranium ore. Although fission of thorium does not occur easily, thorium can be converted in nuclear reactors into the readily fissionable  $^{233}\text{U}$  as shown in Table 3. It is therefore important that the world's supply of thorium, although not accurately known, appears to be at least commensurate with the uranium supply. The conversion of  $^{232}\text{Th}$  into  $^{233}\text{U}$  takes place best with a neutron flux of thermal velocities and the high temperature gas cooled reactors (HTGR's) belong to this class of reactors. In reactors of this type, the partial conversion of  $^{232}\text{Th}$  to  $^{232}\text{U}$  results in high burn-up and reduces fuel cost.

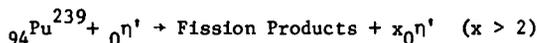
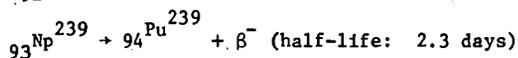
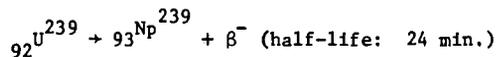
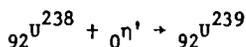
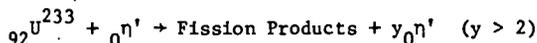
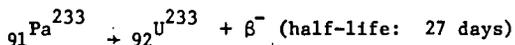
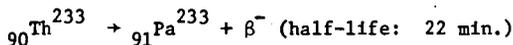
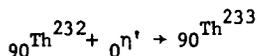
TABLE 2

<u>Price of Uranium Concentrates</u> <u>\$/pound <math>\text{U}_3\text{O}_8</math></u>	<u>Tons of Uranium Resources</u> <u>at this or Lower Price<sup>a</sup></u>
8	594,000
10	940,000
15	1,450,000
30	2,240,000
50	10,000,000
100	25,000,000

<sup>a</sup>AEC Report WASH 1098 (3)

The conversion of  $^{238}\text{U}$  to  $^{239}\text{Pu}$  does not take place to a large degree with thermal neutrons in highly moderated reactors such as are used for power production today but requires a fast neutron population, i.e., a fast reactor. Several types of breeder reactors are believed to be possible but all must have high burn-up, of the order of  $10^5$  MWd/t, in order to achieve low fuel cost. The most important types of breeder reactor are the liquid-metal cooled fast breeder reactor (LMFBR), the gas-cooled fast breeder reactor (GCFR), and the molten salt breeder reactor (MSBR).

TABLE 3

THE PRINCIPAL FUEL BREEDING REACTIONSUranium Breeding CycleThorium Breeding Cycle

The first two are Pu breeders and the last is a moderated reactor using the thorium breeding cycle. The first type is favored in the US and several experimental reactors have been built in this country and other countries, notably Russia, England, and France.

The breeder fuel generally contains initially about 85 wt% U and 15 wt% plutonium to provide a fissionable fuel for startup. A variety of fuel compositions has been considered, including metal alloys of U and Pu, as well as  $\text{UO}_2\text{-PuO}_2$ , UC-PuC and UN-PuN. Of these,  $\text{UO}_2\text{-PuO}_2$  has been the principal choice, in part because of its high melting point and good compatibility with cladding and coolants, good fission product retention and relative tolerance of irradiation. Several cladding materials have been considered including mainly stainless steels as well as nickel alloys and zirconium alloys. If the reactor is operated at a useful power density, the low thermal conductivity of  $\text{UO}_2$  results in approach to the melting point of  $\text{UO}_2$  at the fuel element centerline and this limits reactor operating temperature. Carbide fuels have higher thermal conductivity and greater metal atom density and reactors using them would be expected to have shorter Pu doubling time. There is, however, less experience with high irradiation of carbide fuels than with oxide fuels.

Several experimental breeder reactors have been tested with output temperatures ranging from 320°C in the case of the EBR-1 to typically 400° to 600°C, Fig. 1. Some studies have been made which would lead to a somewhat higher output temperature of 650°C. The output temperature of Na cooled LMFBR's of the kind that are expected to come into use for power generation in the 80's is likely to be limited to this range. Presumably a later generation of breeder reactors might be adapted for the production of process heat. The Na coolant of the LMFBR is so strongly activated by neutrons that it would probably prove necessary to interpose a secondary Na loop between the

primary loop and the process heat sink. In fast reactors of the gas cooled type, the helium core coolant itself does not become radioactive from neutron bombardment. The radioactivity level of the coolant resulting from fission products leaking from the fuel and from activation of impurities in the gas might be kept low enough to permit transfer of heat directly to steam or to some material to be processed.

#### Gas Cooled Moderated Reactors

The high temperature gas-cooled type of reactor, HTGR, cooled by helium is pre-eminent by a wide margin as a potential source of high temperature process heat. The output temperature achieved extends upward from 750°C, for Peach Bottom and 785°C for Ft. St. Vrain, both intended for electric power generation, to 1300°C for the ultra high temperature reactor experiment (UHTREX), Fig. 1. Hot helium at ~ 750°C, passing through a heat exchanger, will generate steam at the highest temperature and pressure that a modern steam turbine-electric generating plant can use. If it is desired to use the heat from the HTGR for process purposes, then a choice exists between a) interposing a secondary heat transfer loop between the primary heat exchanger and the desired heat sink and b) circulating one or more of the process materials directly through the primary heat exchanger. In general, the higher the operating temperature level the more stringent the limitations on choice of materials of construction and for temperatures in excess of ~ 750°C the cost of these materials becomes of increasing importance. The potential for process heat applications in this regime are just beginning to be explored.

This type of thermal neutron reactor employs graphite as moderator and a graphite fuel element with fissionable fuel particles dispersed in it. Use of the chemically inert helium as coolant avoids problems of chemical reaction of coolant with fuel and to a large extent with structural materials in the core. The comparative absence of neutron absorbers in the core, which essentially contains only fuel and moderator, permits high specific power and very high burnup. The burnup in reactors of this class, 10<sup>5</sup> MWD/t in the case of Ft. St. Vrain, promises fuel economy.

The fuel elements are based on the thorium to <sup>233</sup>U conversion cycle, with <sup>235</sup>U present as the start-up fuel. Substantial conversion helps to achieve the highest degree of fuel utilization and lowest power cost of any thermal neutron reactor system.

With variations of detailed structure, the fuel elements of HTGR's are based on the use of coated fuel particles contained in graphite. A great deal of effort has been expended in developing particle coatings and measuring their performance. The basic reason for coating the fuel is to impede the release of fission products to the coolant gas stream. Although at the highest operating temperatures it is not possible to completely retain fission products, the ratio of fission product atoms released to those born has been improved a great deal. The particles used in the Ft. St. Vrain reactor are called TRISO particles.<sup>(4)</sup> The core of a fissile particle is about 200 μm in diameter and consists of (Th,U)C<sub>2</sub> in an atom ratio of 4.25 Th to 1 U. It is covered first with a low density layer of pyrocarbon about 50 μm thick which provides void volume to accommodate gaseous fission products, furnishes a cushion to allow for thermal expansion mismatch of core and coating, and protects the outer layers of coating substantially from damage by recoiling fission fragments. A 20 μm layer of higher density isotropic pyrocarbon greatly slows the release of iodine, tellurium and noble gas fission products. A third layer of pyrolytically deposited SiC about 20 μm thick acts as a very effective diffusion barrier, greatly improving the retention of metal fission products, notably Cs, Ba and Sr. The coating is completed by an outer layer of isotropic pyrocarbon about 20 μm in thickness. Fertile particles for this reactor contain 400 μm diameter cores of ThC<sub>2</sub> with the same coatings as fuel particles.

Several ways of exploiting the improved retention of fission products are open. In reactors designed to operate at temperatures below  $\sim 1300^{\circ}\text{C}$  where fission product leakage is very small, fission product cleanup in the circulating coolant may be minimized. Alternatively, advantage may be taken of the good fission product retention to facilitate operation at higher temperature without incurring the need for an extensive gas cleanup system.

The Ultra High Temperature Reactor Experiment (UHTREX) yielded an output gas temperature of  $1300^{\circ}\text{C}$  which is several hundred degrees higher than any other reactor of the HTGR type, Fig. 1. The purpose of the reactor was to demonstrate the capability of this type of reactor for producing power and high temperature process heat. The fuel elements were unclad graphite containing coated  $\text{UC}_2$  particles. This reactor had the unique capability of permitting refueling without interruption of full power operation. There was some fission product escape from the fuel and this was continuously removed by a coolant gas purification system. The UHTREX project was terminated in 1970 because of stringent budget limitations.

The Rover project for developing a nuclear powered rocket engine pointed a way toward a type of very high powered density gas-cooled reactor capable of still higher output temperature. These reactors were intended to heat high pressure hydrogen to as high temperature as feasible before allowing it to expand through a de Laval nozzle to produce thrust. Operating temperatures of  $2300$  to  $2500^{\circ}\text{C}$  were achieved in reactor tests. The operating duration required was from 1 to 10 h depending upon the choice of mission. The funding of this project was terminated in early 1973. Reactor lifetime increases extremely fast with decrease in temperature and this suggests the capability of such a reactor to operate for a year or more at substantially higher temperatures than HTGR's. The fuel used in the last Rover reactor tested was a composite of graphite and uranium-zirconium carbide solid-solution with thin zirconium carbide coating to restrain corrosion by the hydrogen but no attempt was made to contain fission products and in fact substantial release occurred. Some experimental fuel elements consisting solely of uranium zirconium carbide, substoichiometric in carbon, were also evaluated for possible use at higher temperatures and longer life. If fission product retention in the fuel is a requirement, these carbide and carbide-graphite composite fuels are not well suited for use in a process heat reactor. Coated fuel particle loaded graphite fuels, such as would be suitable for a process heat reactor, were also successfully tested in Rover reactors up to temperatures of  $2300^{\circ}\text{C}$  for a duration of one hour. As in the case of UHTREX, there was substantial fission product escape from the fuel.

#### Economic Considerations

The large growth of the nuclear reactor industry, which has taken place despite the problems and delays of licensing, siting, construction, and financing, is due to the highly favorable economic position of nuclear power today. Nuclear fuel costs are very low (roughly the same as coal in the Four Corners area of New Mexico on an equal Btu basis) and this is the primary justification for the nuclear industry. Furthermore, current projections of fuel costs suggest that the advantage of nuclear power will increase in the future. Nuclear plants are somewhat more costly to build than other central station electrical generating stations, but not enough so to overcome their advantageous economic position. Since the annual fixed charge for capital is held constant, once a plant is built, the economic position of a nuclear reactor improves with time (in a climate of escalating fuel costs) relative to other systems with a lower fractional capitalization.

Since nuclear reactors have only been built for central station electrical power use, we can only meaningfully compare their cost with that of similar fossil fueled plants. This is done in the following table which lists capital costs (exclusive of escalation, allowance for funds during construction, contingency, taxes and utility adders) for various plants assuming startup in 1981:

	<u>Nuclear (LWR)</u>	<u>Oil</u>	<u>Coal*</u>
Capital cost, \$/kw <sub>e</sub>	305	177	270
Capital cost, \$/kw <sub>t</sub>	99	71	108

\*with SO<sub>2</sub> scrubbers.

It is difficult to separate the fraction of the cost of these plants which can be charged to the nuclear reactor and its associated shielding, building, refueling equipment, electrical equipment, piping and mechanical systems (the "nuclear island"). One detailed estimate studied indicates that the fraction of the total cost attributable to this is roughly 40%. On this basis, a rough estimate of the cost of nuclear heat would be 40 dollars/kw (thermal). Addition of escalation (5% for equipment, 3% for materials, 8% for labor), allowance for funds during construction (AFDC, 8%/year), use and sales taxes, and utility cost adders (startup, licensing, training, property taxes, administration, consultants, insurance, general plant and spares, engineering, land, relocation and utilities) will bring this total up to roughly 80 dollars/kw (thermal) for a typical 8.6 year phased construction schedule. If one assumes a 16% annual fixed charge rate and a 0.85 utilization factor, the net cost of energy attributable only to the cost of capital, is roughly 50 cents/million Btu for a nuclear plant.

The projected cost of fuel in the future is as follows: (cents/million Btu).

	<u>Nuclear (LWR)</u>	<u>Oil</u>	<u>Coal (Northeast U.S.)</u>
(1973)	17	75	45
1985	27	163	91
1995	38	272	140
15 year levelized (1981-1996)	30	189	99

These comparisons indicate that nuclear heat will be an increasingly good buy in the future. The values listed for nuclear heat are based on light water reactors (PWR's and BWR's) which are the only types of reactors for which experience is available. Projections for HTGR capital plant costs are slightly higher (20%) than for LWR's, on an equal Btu basis, although the higher temperature may make the heat more valuable for some applications. The projected HTGR fuel cycle costs are roughly equal, on an equal Btu basis, to those of the LWR. Lack of experience in fuel fabrication and reprocessing creates some uncertainty in the estimates.

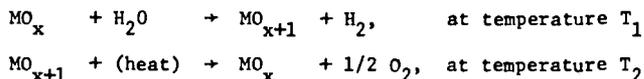
#### The Question of Plant Size

The foregoing economic values are based on a plant that generates ~ 3600 Mwt. While fuel cycle costs are roughly independent of plant size, the capital cost varies roughly as the plant size to the 0.42 power. Thus one is led to very large reactor sizes because of economic considerations. The AEC currently limits the size to 3600 Mwt until more experience is gained, however even larger sizes may come in the future. Few process heat applications lend themselves to such large size units and smaller units will certainly incur a cost penalty.

#### Hydrogen as an Energy Distribution Medium

One approach to the problem of reactor plant size which seems attractive is to convert the nuclear energy to a more suitable, transportable and convenient form and

then distribute this go-between energy to its multitudinous end users. Hydrogen is a very attractive medium to consider for this distribution system. It has a high heat content, is readily available (in H<sub>2</sub>O), easily transportable, and ecologically attractive. It can readily be used in various industries such as ammonia synthesis, plywood drying, glass making, coal hydrogasification, metal ore reduction, petroleum refining, as well as for primary heating. The central problem is how best to make use of heat energy from a nuclear reactor for the decomposition of water. Although the indirect electrical generation/electrolysis route is technically feasible it is inefficient (28% presently, 40% ultimately may be possible). A more attractive approach from the thermodynamic viewpoint is the use of a dual temperature thermochemical cycle shown schematically by: (M stands for metal or compound and, in fact, four or more actual reactions may be necessary.)



The maximum cyclic efficiency of this process, from H<sub>2</sub>O back to H<sub>2</sub>O, is given simply by the Carnot relation,  $(T_2 - T_1)/T_2$ . The advantage of a process using a high temperature heat source is evident. If suitable reactants can be found in the temperature range of 1000°C to 1300°C, and if 80% of Carnot efficiency can be realized, then an efficiency of 60 to 65% will be achievable. These are two big ifs, but the incentive is sufficient to warrant a thorough search.

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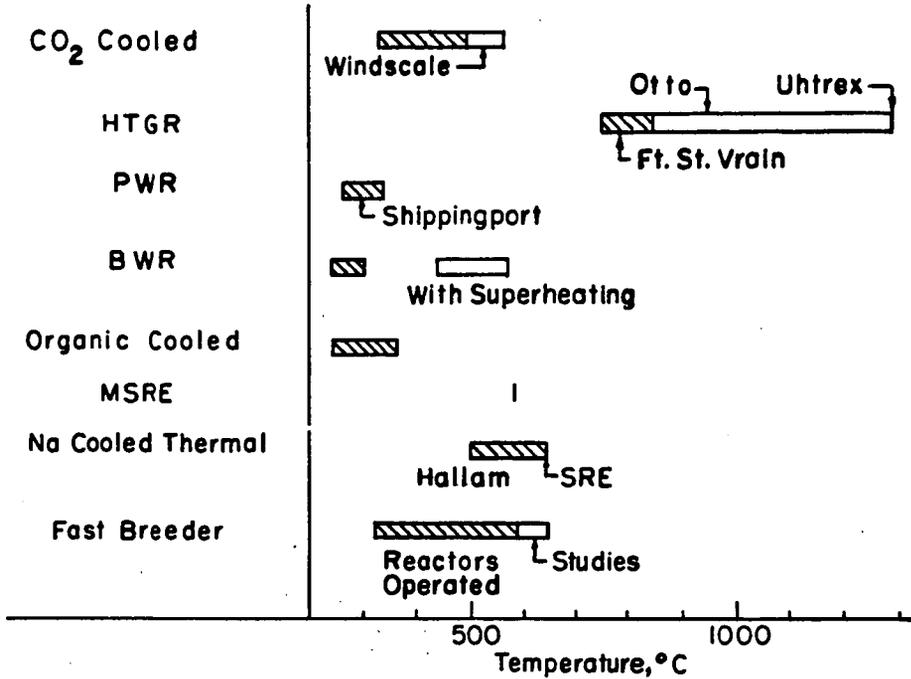


Fig.1 Output Temperature From Core of Various Types of Reactor

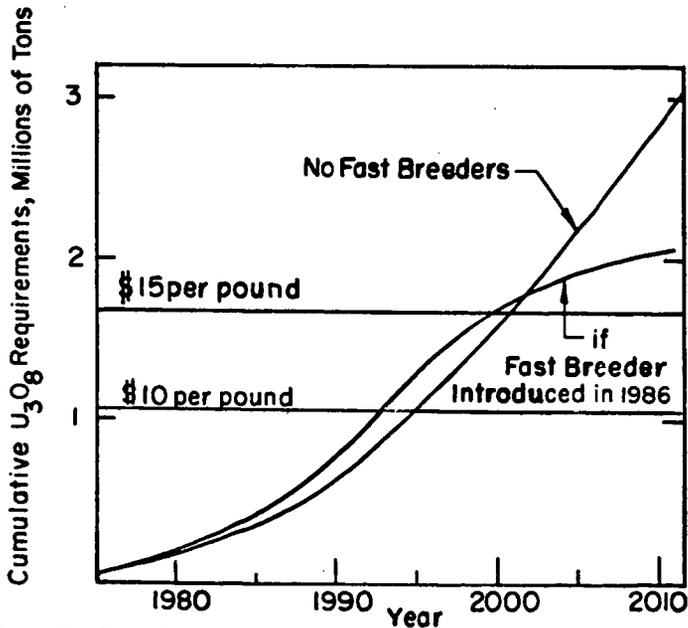


Fig.2 U.S. Cumulative Uranium Requirements

IRON TITANIUM HYDRIDE: ITS FORMATION,  
PROPERTIES, AND APPLICATION

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Iron and titanium form two known stable intermetallic compounds, FeTi and Fe<sub>2</sub>Ti.<sup>1</sup> It is also generally accepted that a third compound, FeTi<sub>2</sub>,<sup>2</sup> exists above 1000°C, decomposing to FeTi and Ti below that temperature. We have briefly noted previously<sup>3,4</sup> that one of these compounds, FeTi, will react directly with hydrogen to form an easily decomposed hydride which may be useful as a hydrogen storage medium. Our primary purpose here is to discuss the Fe-Ti-H system in some detail with particular emphasis on the reaction of FeTi with hydrogen and the formation and properties of two ternary hydrides, FeTiH<sub>~1</sub> and FeTiH<sub>~2</sub>. A further, though secondary, purpose is to discuss the application of iron titanium hydride as a storage medium for hydrogen fuel.

## I. FORMATION AND PROPERTIES

### Experimental

The Fe-Ti alloys were prepared from zone-refined Fe and Ti in an arc furnace under an argon atmosphere, although it should be noted that no significant differences were observed when commercial grade Fe and Ti were substituted for the zone-refined starting material. Initially we had prepared the alloys in an induction furnace; however, it appeared that the resulting products were contaminated by the alumina crucible material, which had an inhibiting effect upon their reaction with hydrogen. Contamination of iron titanium alloys by alumina crucibles has been noted previously.<sup>1</sup> All the alloys were

quite brittle and could be easily crushed to pass through a 10-mesh screen. It was not necessary to carry out the crushing step in an inert atmosphere. The samples, weighing ~10 g, were introduced into a high pressure hydriding reactor, the construction of which has been previously discussed in detail.<sup>5</sup>

Our procedure for hydriding metals which form unstable hydrides, as in this instance, has also been described,<sup>6</sup> and only a brief synopsis will be given here. The reactor was loaded with the granular alloy samples, sealed, evacuated and then heated to 400-450°C while outgassing continuously. Upon reaching the cited temperature range, hydrogen was admitted to the reactor until the pressure was ~100 psia. After ~30 minutes the reactor was evacuated and cooled to room temperature and H<sub>2</sub> was admitted to the reactor until the pressure was ~950 psia. Usually the metal-hydrogen reaction proceeded immediately with the evolution of heat. If no reaction took place over a course of ~15 minutes the above procedure was repeated. It should be noted that if the alloy is in ingot form, rather than granular, the initiation of the reaction is somewhat more difficult and may require several such treatments. In order to obtain a highly active metal substrate, the sample was hydrided and dehydrided several times. Dehydriding was accomplished by outgassing and heating to ~200°C.

The procedure for obtaining the pressure-composition isotherms presented here is essentially the same as that described previously.<sup>5,6</sup> Briefly, it consisted of equilibrating the metal hydride with hydrogen at >900 psia at a pre-determined temperature. Hydrogen was then withdrawn in a measured amount from the system by venting to an evacuated reservoir of known volume, after which equilibrium was allowed to become re-established. This step was repeated until the equilibrium pressure was below 1 atmosphere, at which point the sample

was heated to  $>400^{\circ}\text{C}$  and any further hydrogen that evolved was measured. Finally, the sample was cooled to room temperature, removed from the reactor and analyzed for Fe, Ti and residual hydrogen. Occasionally, the reverse procedure was followed in order to determine hysteresis effects. In these runs, the starting material was an alloy sample that had been activated by previous hydriding and dehydriding; and the points on the pressure vs. composition curve were obtained by adding successive small increments of hydrogen.

All the x-ray data were obtained using a 114.59 mm dia. Norelco powder camera (Debye-Scherrer type) and with Cu K  $\alpha$  radiation.

### Results and Discussion

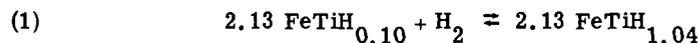
The Fe-Ti-H system was explored between the approximate limits, by weight, of 70% Fe-30% Ti and 37% Fe-63% Ti, corresponding to the atomic proportions  $\text{Fe}_2\text{Ti}$  and  $\text{FeTi}_2$ . At the iron-rich end of this range no hydrogen was absorbed, but all compositions richer in Ti than  $\text{Fe}_2\text{Ti}$  did take up hydrogen to some extent. The stable intermetallic compound, FeTi, reacted readily, and a series of pressure-composition isotherms for the FeTi-H system is shown in Figure 1. The composition of the starting alloy was 53.6% Fe and 46.7% Ti. The metal phase present should be only that of FeTi, which was confirmed by an x-ray diffraction pattern taken of the sample. In the graphs the equilibrium dissociation pressure of the hydride is plotted against the hydrogen content of the alloy expressed as the ratio of hydrogen atoms to that of the total number of metal atoms ( $\text{H}/(\text{Fe} + \text{Ti})$  or simply  $\text{H}/\text{M}$ ). The shape of the isotherms can be interpreted as follows: on the left, where the isotherms rise steeply as the hydrogen content of solid increases, is the region of solid solution of hydrogen in the FeTi metal lattice. This solid solubility region may be designated as the  $\alpha$  phase of the FeTi-H system. As the hydrogen

content of the solid is further increased the equilibrium pressure remains constant and forms, so to speak, a plateau. The composition at which the plateau begins marks the point at which a new phase appears and also marks the maximum solubility of hydrogen in the  $\alpha$  phase. At room temperature that composition corresponds to  $\text{FeTiH}_{0.10}$  ( $\text{H}/\text{M} = 0.05$ ). The new phase is the monohydride or  $\beta$  phase of the FeTi-H system. Both the  $\alpha$  and  $\beta$  phases coexist until the solid composition corresponds to  $\text{FeTiH}_{1.04}$  where the isotherms begin a steep ascent. At this point the  $\alpha$  phase has disappeared. (For the present we shall ignore the dip shown in the lower temperature isotherms just below this composition.) As the hydrogen content of the  $\beta$  phase is increased a new phase appears, the  $\gamma$  or dihydride phase. Its exact point of inception is temperature dependent and is somewhat difficult to determine since the upper plateaus are narrow and the breaks in the isotherms quite gradual. The  $55^\circ$  isotherm shows only a vestigial plateau structure and it appears that this temperature is quite close to the critical temperature, above which two discrete solid hydride phases cannot coexist and the monohydride is transformed continuously into the dihydride phase. The  $70^\circ$  isotherm shows no evidence of a plateau in this region. These data and observations are summarized in the phase diagram of the FeTi-H system shown in Figure 2.

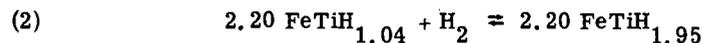
The effect of hysteresis in the FeTi-H system is illustrated in Figure 3. It is worth noting that the system almost forms two loops, the reason being that in the region of the pure  $\beta$  phase hysteresis is reduced substantially, which is the usual case in single phase regions. The loops are not closed since the composition range over which only the  $\beta$  phase is present is quite narrow. As the  $\gamma$  phase appears hysteresis again increases. It is also of interest to point out that the dip occurring in the lower temperature desorption

isotherms at H/M 0.5 does not occur in the absorption isotherm. This situation appears to be analogous to that occurring in the uranium-hydrogen system below 400°C, where a similar dip in the desorption isotherm was noted by Spedding et al.<sup>7</sup> and by Wicke and Otto.<sup>8</sup> Our results indicate that at higher temperatures the dip is less pronounced and finally disappears altogether in the 70° isotherm. This behavior is, again, similar to that of the uranium-hydrogen system, where Libowitz and Gibb<sup>9</sup> found no dips in isotherms determined at high temperatures (450°+). Wicke and Otto have suggested that the phenomenon is due to the supersaturation of hydrogen vacancies in the hydride phase, while Flotow et al.<sup>10</sup> have proposed that it is an effect caused by the state of subdivision of the solid.

The reaction taking place in the lower plateau region (H/M 0.10 to H/M = 0.52) may be written as follows



which is followed by



The variation of the log of the equilibrium dissociation pressure with the reciprocal temperature for several solid compositions is shown in Figure 4. The relationship is linear and obeys the van't Hoff equation in the form of  $\ln P = \frac{A}{T} + B$  where A and B are constants and T is the absolute temperature. Thermodynamic values for the iron titanium-hydrogen system were derived from these data and are shown in Table 1. They are given as relative partial molal quantities,  $(\bar{X}_H - \frac{1}{2}X_{H_2}^O)$  where  $\bar{X}_H$  is the partial molal enthalpy (entropy or free energy) of hydrogen (as atoms) in the solid relative to hydrogen in its standard state as a pure diatomic ideal gas at a pressure of 1 atm.

The products of reactions 1 and 2 are gray metal-like solids, essentially not different in appearance from the granular starting alloy. They are very brittle but are not pyrophoric in air; on the contrary, exposure of these materials to air tends to deactivate them. Even though both hydrides have dissociation pressures appreciably above one atmosphere at 25°, they will decompose relatively slowly in air. Once exposed to air they may be reactivated by repeating the procedure described in the experimental section, but a precautionary note should be added here; the remaining hydrided material, though apparently inert, will decompose quite rapidly as elevated temperatures are reached (200°-300°) and should not be heated to such temperatures in closed systems unless the free volume is sufficient to accommodate the evolved hydrogen without the buildup of excessive pressure.

The existence of the ternary compound  $\text{TiFeH}_1$  is strongly supported by evidence gathered from x-ray diffraction patterns of material whose composition lies in the lower plateau region of the P-C isotherm. In order to obtain a suitable sample for x-ray analysis, an amount of  $\text{FeTiH}_{\sim 1}$  was cooled to -70° and the hydrogen remaining in the gas phase was quickly evacuated; the sample was then contacted with air and allowed to warm to room temperature. This, in effect, "froze" the hydrogen content of the solid at a high level since such a procedure deactivates the hydride by air contact, thus preventing its rapid decomposition even at relatively high temperatures under conditions far removed from equilibrium. A portion of this material was taken and its x-ray diffraction pattern determined. The remaining material was analyzed for hydrogen by heating and decomposing it. While it is quite possible that the x-ray sample was not of the same composition as the bulk of material, or suffered some subsequent decomposition after sampling, as long as its composition

was within the lower plateau region, the pattern due to the  $\beta$  hydride phase should be discernible. We have followed this technique with material of a composition corresponding to  $\text{FeTiH}_{0.89}$ . Upon subtracting the lines due to  $\text{FeTi}$  ( $\alpha$  phase), the ternary hydride phase  $\text{FeTiH}_1$  was indexed as having tetragonal symmetry with  $a = 3.18^\circ\text{A}$  and  $c = 8.73^\circ\text{A}$ , giving a  $c/a$  ratio of 2.74. The observed and calculated d lines are given in Table II.

In addition, the density of another sample having composition corresponding to  $\text{TiFeH}_{0.80}$  was measured under benzene and found to be 6.003. Since this is a mixture of two phases, hydrogen saturated  $\text{TiFe}$  and  $\text{TiFeH}_1$ , and the density of  $\text{TiFe}$  is known (6.50), the density of  $\text{TiFeH}_1$  was calculated to be 5.88. Knowing the density and using the lattice parameters given above, the number of molecules in a unit cell were calculated to be 2.99 or 3. That the calculated value is so very close to an integral number is substantial evidence that the indexing treatment is correct.

The situation with solids of higher hydrogen contents, i.e. in the  $\beta$ - $\gamma$  region is more complex and has not been resolved. A sample of the higher hydride was treated the same as outlined above; however, this material is more unstable than the lower hydride and decomposes more rapidly. We have taken an x-ray pattern at room temperature of material whose bulk composition was  $\text{FeTiH}_{1.75}$ , but it is quite possible that some decomposition took place in the process of obtaining the diffraction pattern. Only 5 lines were observed, which are listed in Table III. Three of these (2, 3, 4) are lines which are also observed with  $\text{FeTiH}_1$  and one (5) is a line observed with unhydrided  $\text{FeTi}$ . On this basis no identification can be made. However, it does appear that the crystal structure is quite similar to that of the monohydride phase; a presumption which is supported by the low critical temperature of  $\beta$ - $\gamma$  two phase region.

For unequivocal results low temperature diffraction studies would have to be carried out.

The FeTi phase is homogeneous in the composition region extending from 45.9% Ti to 48.2% Ti. The equiatomic composition is 46.17% Ti; thus an appreciable amount of Ti can be dissolved in the intermetallic phase. This fact may be responsible for the behavior illustrated in Figure 5, in which the starting alloy was enriched in Ti to the extent that its initial composition, 49.3 wt/% Ti and 50.7 wt/% Fe, was slightly above that corresponding to the single phase region. The isotherm (B) has been significantly distorted, the equilibrium dissociation pressure markedly decreased and the boundary between the lower and higher hydride almost indistinguishable. Such a situation is not without precedent and a somewhat similar effect occurs in the  $\text{LaNi}_5$ -hydrogen system when excess nickel is added to the starting alloy,<sup>11</sup> i.e. the dissociation pressure of the hydride is increased by a factor of over three upon increasing the nickel content of the alloy from  $\text{LaNi}_{4.90}$  to  $\text{LaNi}_{5.5}$ . Thus, in order to obtain reproducible behavior it is advisable to control the intermetallic composition as closely as possible. Upon increasing the Ti content to 63.2 wt/%, the pressure-composition isotherm (C) is greatly distorted as also shown in Figure 5. This alloy was annealed at 1000° for 12 hours, and then quenched in an unsuccessful attempt to prepare metastable  $\text{FeTi}_2$ ; but only FeTi and Ti were produced. After hydriding, an x-ray diffraction pattern of the product indicated the presence of  $\text{FeTiH}_{\sim 2}$ ,  $\text{TiH}_{\sim 2}$ , TiFe and Ti. The increased amount of residual hydrogen in the solid is undoubtedly due to the presence of the stable titanium hydride.

Upon departing from the single phase region in the opposite direction, i.e. that of higher iron content, there appears to be no significant effect other than

a reduction in the amount of hydrogen sorbed as shown in Figure 5. The starting alloy was a two-phase mixture,  $\text{Fe}_2\text{Ti}$  and  $\text{FeTi}$ , having an overall composition of 60.5 wt/% Fe and 39.5% Ti. The isotherm (A) is essentially congruent with that obtained with  $\text{FeTi}$ , indicating little interaction between the two phases or solid solubility of Fe in  $\text{TiFe}$ ; an observation which is in accord with the known homogeneity range of  $\text{FeTi}$ . The amount of hydrogen actually sorbed is somewhat less than that expected from the proportionate amount of  $\text{FeTi}$  present in the alloy, which may be due to the mere physical presence of  $\text{Fe}_2\text{Ti}$ .

## II. APPLICATION TO HYDROGEN STORAGE

We have noted previously the advantage of using certain metal hydrides as a storage medium for hydrogen fuel.<sup>3, 4, 12</sup> Iron titanium hydride was included in this group and, as we became more familiar with its properties, it appeared to be an outstanding candidate as a hydrogen storage medium when measured against the following criteria: cost, hydrogen content and availability, and safety.

A simplified diagram in Fig. 6 shows a hydrogen storage reservoir of  $\text{FeTiH}_{\sim 2}$  integrated with a hydrogen burning energy converter. The heat of decomposition is supplied from the waste heat of the energy converter by circulating its coolant through a heat exchanger in contact with the metal hydride. The heat, of course, must be supplied at a rate consistent with the fuel demand of the converter. For example, if the reservoir temperature can be maintained at  $\sim 25^\circ\text{C}$  by the waste heat, the hydride is readily capable of delivering  $\text{H}_2$  fuel continuously, at high flow rates and at pressures in excess of one atmosphere. If the heat supply is insufficient the bed will progressively cool and the  $\text{H}_2$  flow will decrease until a balance is struck between the decomposition rate and the available heat. When the bed is exhausted it can be regenerated by following the opposite procedure, i. e., the bed is contacted with hydrogen at

a pressure substantially above the dissociation pressure, making due allowance for hysteresis (Fig. 3) and a coolant is circulated through the bed to remove the heat of reaction. In practice, the composition limits may be expected to range from  $\text{FeTiH}_{\sim 0.10}$  to  $\text{FeTiH}_{\sim 1.85}$  to give a total of 1.67 wt % available hydrogen.

We have demonstrated in the laboratory the feasibility of the scheme outlined above using a small Wankel engine and two metal hydride reservoirs each containing 1.5 Kg of  $\text{FeTiH}_{\sim 2}$ . The engine was a Sachs type KM48 with a maximum output of 8 H. P.; it was purchased from Sachs Motors Ltd., Pointe-Claire Dorval 700, Quebec, Canada. The alloy, FeTi, was part of a 73 Kg heat supplied by Cannon-Muskegon Corporation of Muskegon, Michigan. In lots of  $\sim 100$  Kg the price was \$5.15/Kg. The material contained about 7000 ppm oxygen which apparently affected the properties of the hydride in two important respects, i.e. the maximum hydrogen content was reduced and its equilibrium dissociation pressure was increased. However, for our specific purpose these changes were not of a critical nature. The reservoirs (Fig. 7) were constructed of stainless steel and had an i.d. of 1-3/4 in. and an overall length of 14 $\frac{1}{4}$  in. They were made from two 500 ml gas sampling cylinders (Hoke #4HS500) by fitting each cylinder with an outlet connection and sintered metal filter disk to prevent particle entrainment in the gas stream. Other ancillary equipment included a pressure regulator and rotometer, throttling valve, several pressure gauges and a dynamometer.

We have previously noted the performance of the Wankel engine using hydrogen fuel<sup>4</sup>; our purpose here is merely to demonstrate the application of iron titanium hydride as the hydrogen storage medium. We did not optimize the storage system in any way or quantitatively weigh such factors as kinetics,

heat transfer or thermal conductivity of the bed material, but merely chose a configuration which we qualitatively judged would be adequate to prove our thesis. The system, a photograph of which is shown in Fig. 8, differs from the ideal in one respect. For the sake of simplicity the waste heat of the engine was not extracted to provide the heat of decomposition of the hydride; rather it was supplied by immersing the hydride reservoirs in hot water.

The FeTi alloy was activated by the procedure outlined in Section 1. Following activation and several hydriding-dehydriding cycles, a composition corresponding to  $\text{FeTiH}_{\sim 1.8}$  could readily be attained. During the hydriding step, the reservoirs were exposed to hydrogen at a pressure of 60 atm and were cooled by immersion in an ice bath. After hydriding, the ice bath was replaced with hot water ( $\sim 50^\circ\text{C}$ ) and the reservoirs were connected to the engine intake manifold through the intermediate  $\text{H}_2$  flow control and monitoring devices. The hydrogen delivery pressure was regulated at about 25 psia which insured good throttling capability. The pressure at the engine intake manifold was slightly below atmospheric and no air regulation or supercharging was required. Lubricating oil, normally mixed with the gasoline fuel, was aspirated into the engine by the gaseous fuel mixture.

The total amount of hydrogen in the reservoir was about 54 g of which about 50 g were readily and continuously available. At a delivery pressure of 25 psia the maximum sustainable flow rate of hydrogen was  $\sim 40$  lSTP/min. Higher flow rates were possible but could only be maintained for short periods; this is attributed to a limitation to the rate of heat transferred to the reservoirs. It may be pointed out in this regard that the hydrogen evolution rate, per unit weight of alloy, is undoubtedly much higher than it would be in practice for a large, working hydrogen storage system. Nevertheless, if desired, an

increased decomposition rate could easily be realized through the adoption of a more efficient heat exchanger and/or a higher temperature heat source. Engine speed, which ranged from 1000-4000 RPM, was regulated by throttling the  $H_2$  flow. The dynamometer load was varied from 0 to 2 H. P.

Although the work described above is of a qualitative nature, there is no doubt that its essential purpose was successfully realized. Indeed, the results have given an added impetus to a program of a more ambitious scope, which has recently been initiated as a cooperative effort by Public Service Electric and Gas of New Jersey and Brookhaven National Laboratory. Its objective is to design and build a hydride storage reservoir capable of storing and delivering a minimum of 4.5 Kg of hydrogen. The reservoir will be part of a pilot unit designed to examine the feasibility of storing electrical energy via the production, storage and reversion of hydrogen. This will be accomplished by producing hydrogen electrolytically using off-peak power, storing the hydrogen in iron titanium hydride and finally decomposing the hydride to supply hydrogen to a fuel cell which will supply power for on-peak loads. The reservoir will have an internal diameter of 12 in. and will be ~6 ft long and will contain ~409 Kg of FeTi to give a maximum available hydrogen content of about 6.8 Kg. The unit will have an internal heat exchanger through which hot (~45°C) and cold (~17°C) water will circulate. The hydride will go through a complete sorption-desorption cycle once a day. Sorption will be carried out at a pressure of approximately 40 atm at a rate of 141 l STP/min. During the desorption portion of the cycle hydrogen will be delivered to the fuel cell at ~141 l STP/min regulated at a pressure of 3 atm.

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Table 1

Relative Partial Molal Quantities Per Gram Atom of Hydrogen

<u>Composition</u>	$(\bar{H}_{\text{H}-\frac{1}{2}\text{H}_2^0})$ <u>Kcal</u>	$(\bar{S}_{\text{H}-\frac{1}{2}\text{H}_2^0})$ <u>e. u.</u>	$(\bar{F}_{\text{H}-\frac{1}{2}\text{H}_2^0})$ <u>Kcal</u>
FeTiH <sub>0.1</sub> -FeTiH <sub>1.04</sub>	-3.36	-12.7	+0.42
FeTiH <sub>1.20</sub>	-3.70	-14.4	+0.57
FeTiH <sub>1.40</sub>	-3.98	-15.6	+0.65
FeTiH <sub>1.60</sub>	-4.03	-15.8	+0.68

Table II

d Spacings for  $\text{FeTiH}_1$ 

<u>Relative Intensity*</u>	<u>d obs.</u>	<u>d calc.</u>	<u>hkl</u>
40	2.2488	2.2488	110
20	2.1931	2.1931	004
100	2.1454	2.1472	103
10	1.9950	1.9990	112
50	1.5676	1.5644	201
20	1.2840	1.2840	204
20	1.2553	1.2474	007

\* by visual inspection

Table III

d Spacings Observed with  $\text{FeTiH}_{>1.04}$ 

<u>Line No.</u>	<u>Intensity*</u>	<u>Observed d Spacing, Å</u>
1	10	2.391
2	50	2.320
3	20	2.243
4	100	2.186
5	20	2.090

\* by visual inspection

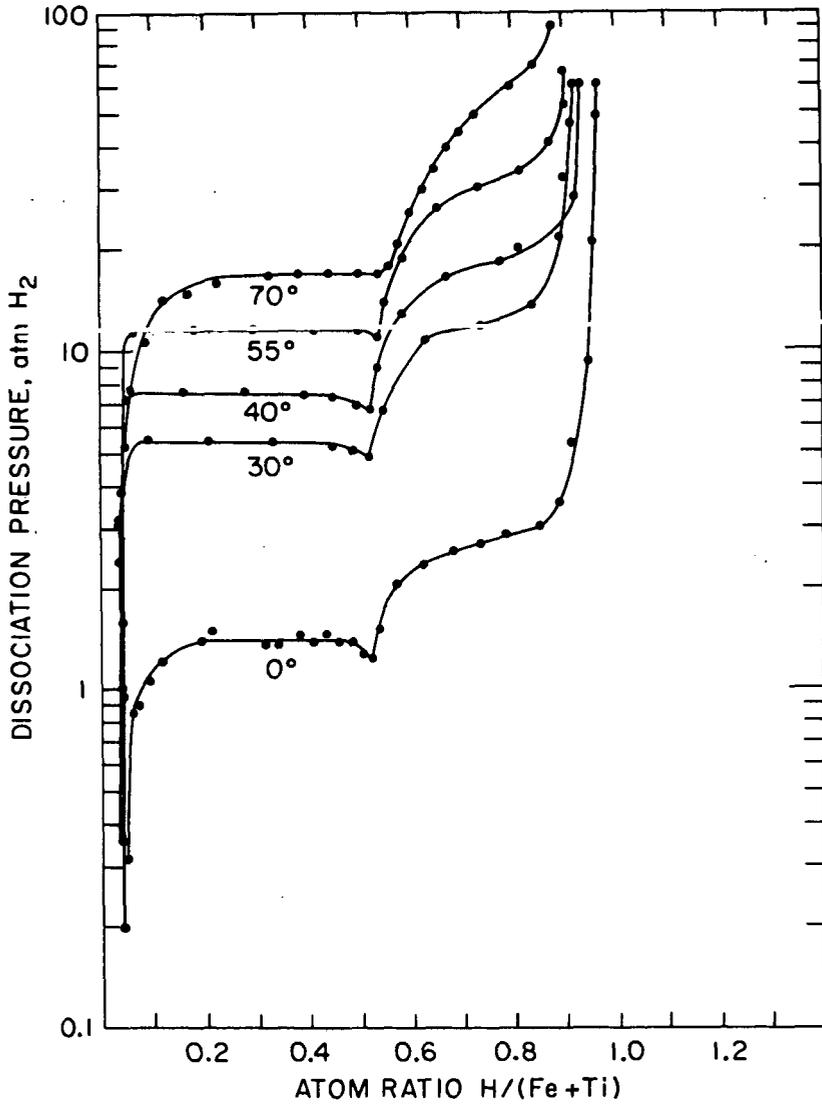


Figure 1 - Pressure-composition isotherm for the FeTi-H system. The initial alloy composition was 53.6% Fe and 46.7% Ti.

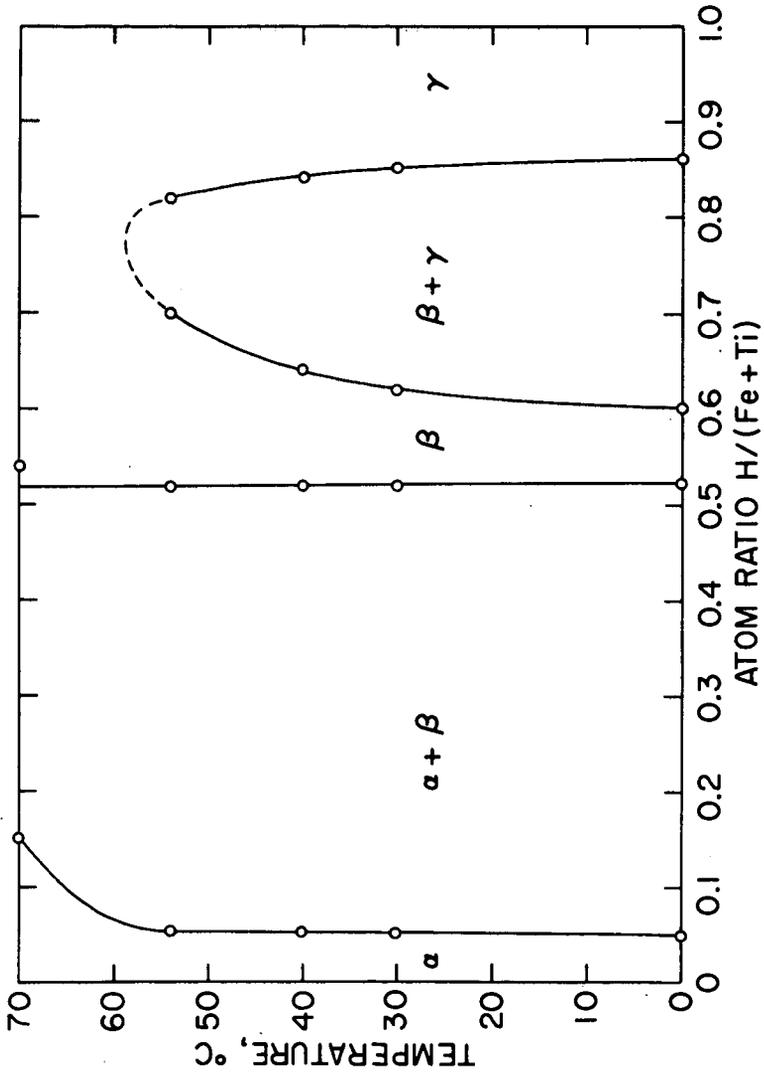


Figure 2 - Phase diagram of the FeTi-H system.

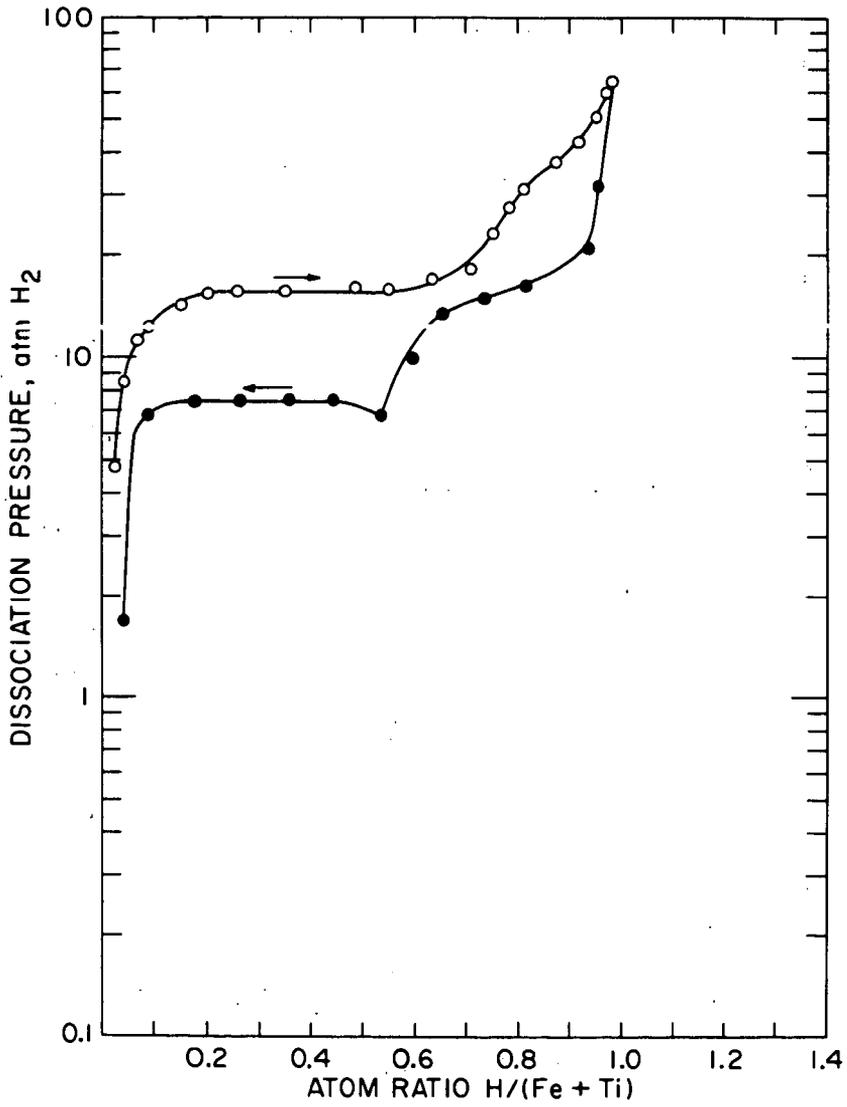


Figure 3 - Hysteresis in the FeTi-H system.

40°C

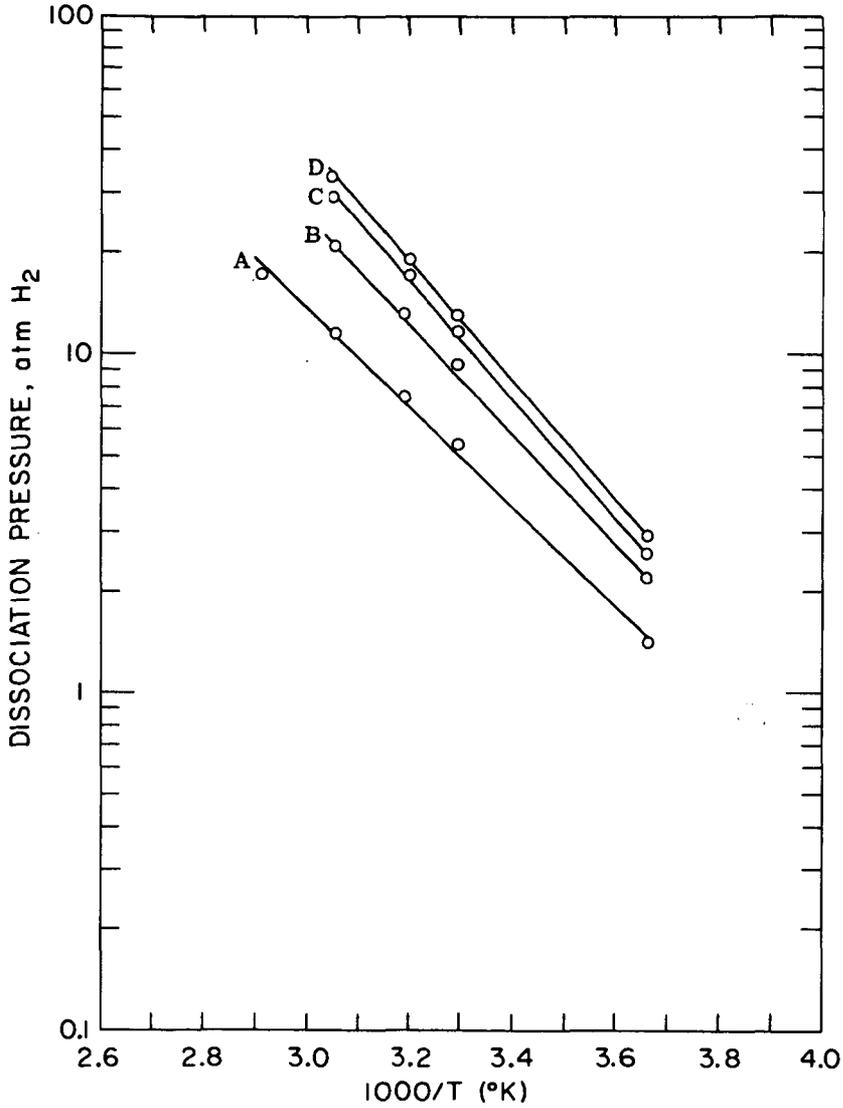


Figure 4 - Equilibrium dissociation pressure vs. reciprocal temperature for  $\text{FeTiH}_x$ .  
 A)  $\text{FeTiH}_{0.1}$ - $\text{FeTiH}_1$ ; B)  $\text{FeTiH}_{1.2}$ ;  
 C)  $\text{FeTiH}_{1.4}$ ; D)  $\text{FeTiH}_{1.6}$ .

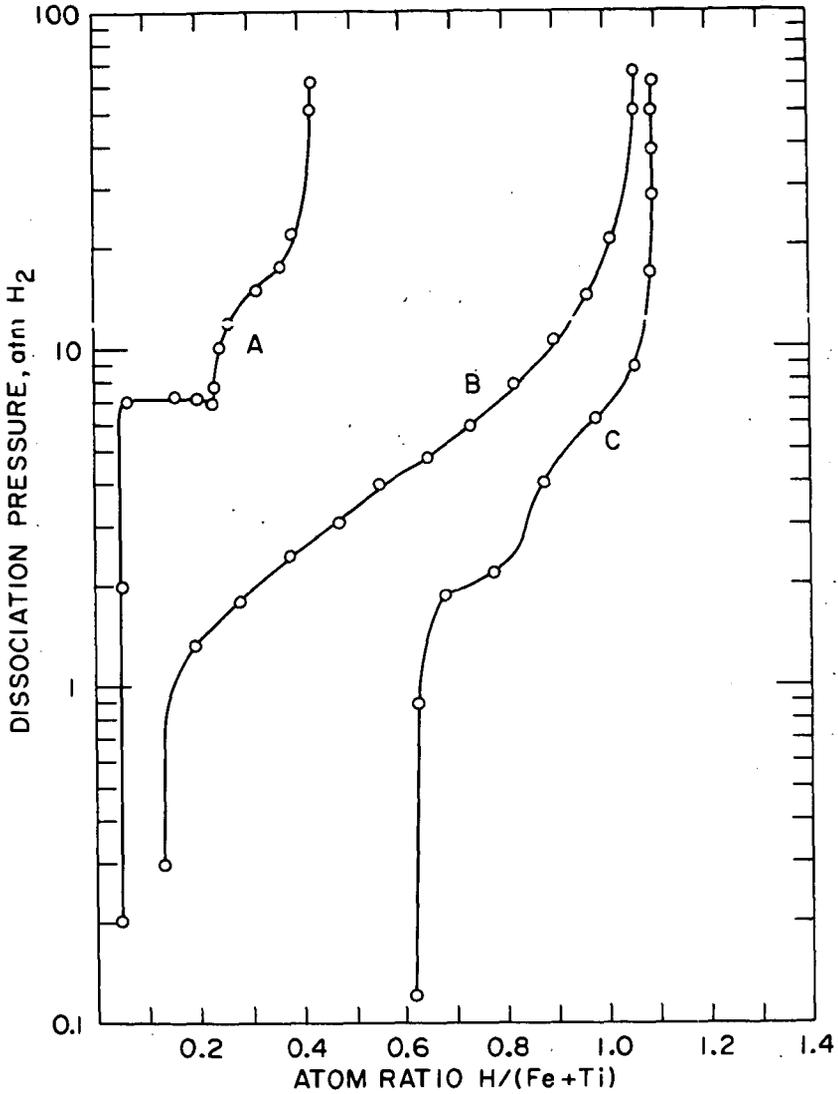


Figure 5 - Pressure-composition isotherms for alloys of various Fe/Ti ratios at 40°C. A) 60.5 wt % Fe, 39.5 wt % Ti; B) 50.5 wt % Fe, 49.2 wt % Ti; C) 36.7 wt % Fe, 63.2 wt % Ti.

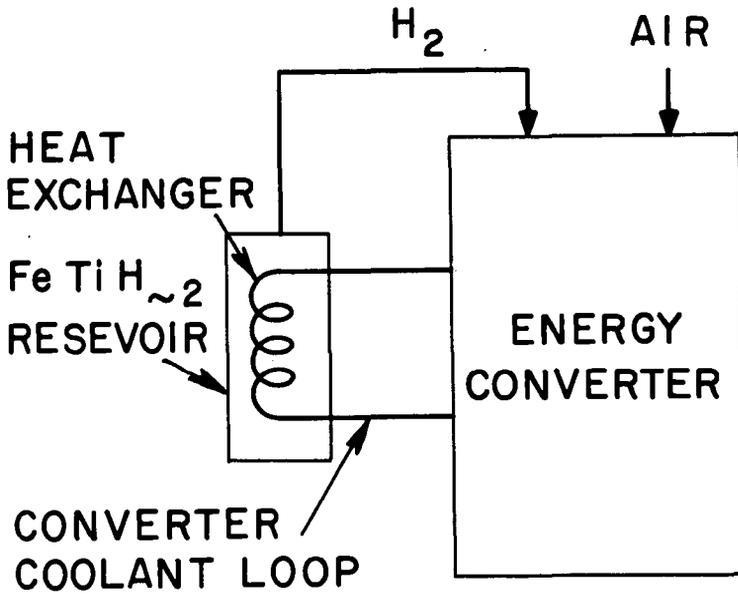
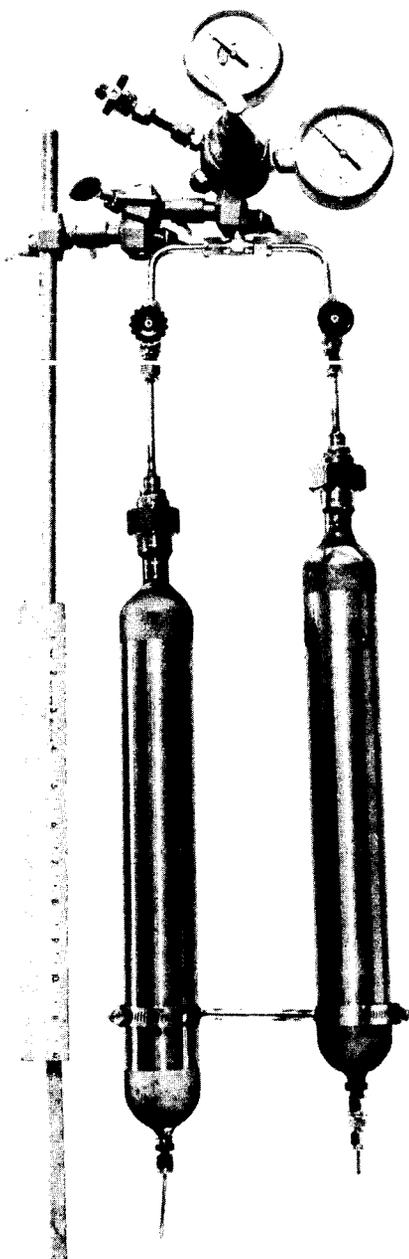


Figure 6 - Schematic of an Integrated Metal Hydride-Energy Converter System.



**Figure 7 - Metal Hydride Reservoirs - Each Reservoir Contains 1.5 Kg of  $\text{FeTiH}_{\sim 1.8}$**

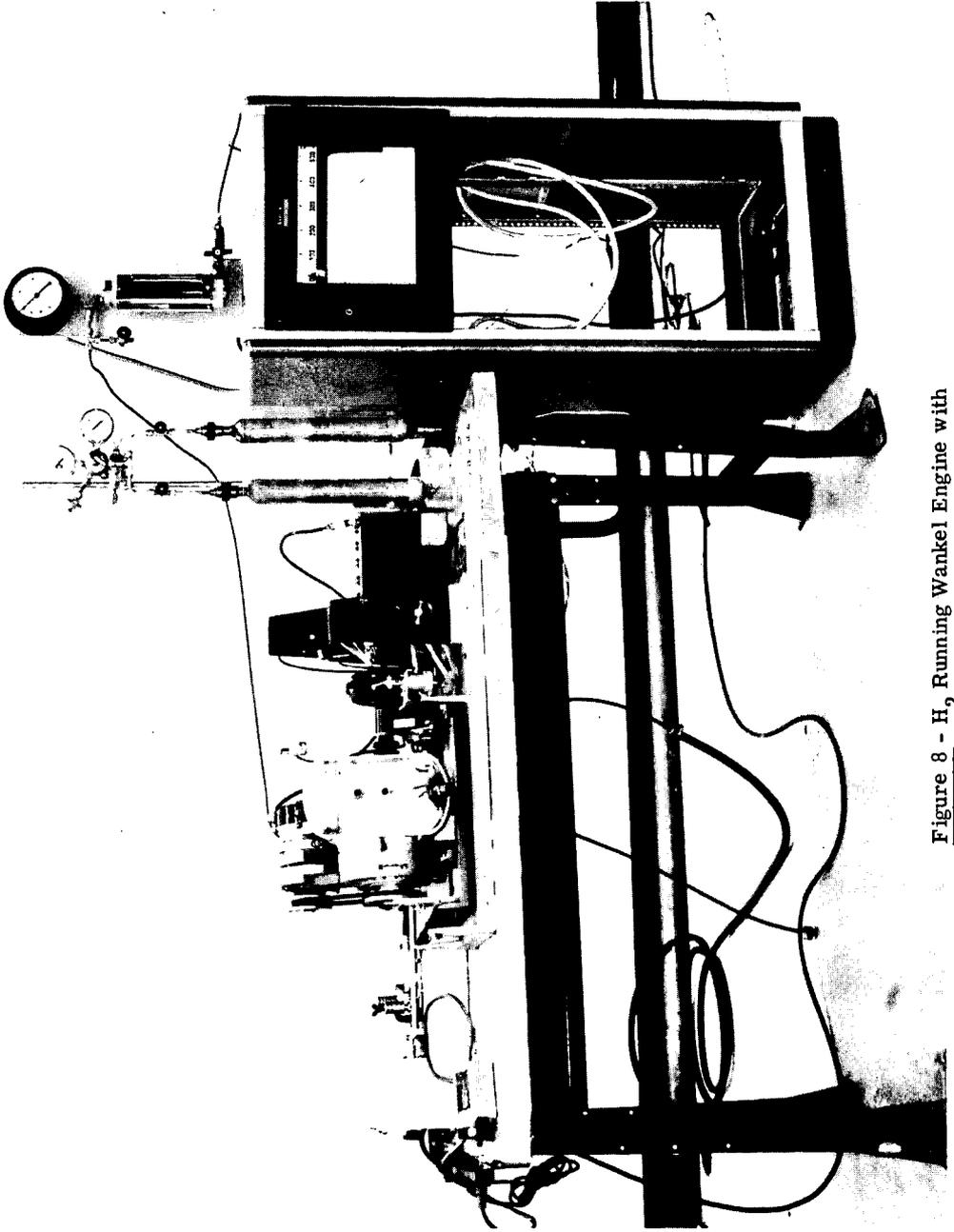


Figure 8 - H<sub>2</sub> Running Wankel Engine with Hydride Reservoirs.