

## A REVIEW OF NUCLEAR SOURCES OF NON-FOSSIL CHEMICAL FUELS

by

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### Summary

Energy derived from nuclear sources can be utilized either in the form of high energy radiation, thermal energy or electrical energy. Each of these energy forms can be employed to produce non-fossil chemical fuels by transformation of available non-fossil substances. As a general definition, available non-fossil fuel substances are all resources other than coal, petroleum, or natural gas. Thus the substances that can serve as raw materials for nuclear energy conversion to non-fossil chemical fuels, are basically the substances found in water, air, and minerals.

High energy radiation from nuclear fission can be utilized either directly as fission fragment energy in a chemonuclear reactor or indirectly as neutron, gamma, and beta energy from isotopic sources. Fission fragment energy is actually the only radiation energy source that can be generated in sufficient quantity and at low enough cost of be considered for production of fuels. The two basic fuels that can be generated are hydrogen from water and carbon dioxide, and carbon monoxide from carbon dioxide. The hydrogen and carbon monoxide can be used as fuels or can be subsequently converted to high BTU gas or other liquid hydrocarbons. The main difficulties with fission fragment chemonuclear systems are obtaining sufficiently high yields of fuel gases and demonstrating that a fuel essentially free of radioactive fission fragments can be produced.

Thermal energy from nuclear fission in the form of steam or a high temperature gas stream such as helium can, conceivably, be used to crack water to hydrogen and carbon dioxide to carbon monoxide. Carbon dioxide can be derived from thermal de-

composition of limestone or by extraction from the atmosphere. However, the temperatures are too high to allow safe operation of the nuclear reactors required for these processes with the materials of construction generally available. Nuclear thermal energy can be used to preheat streams and makeup heat balances and to gasify coal and thus, although not strictly a source of non-fossil chemical fuel serves to partially extend the supply of non-fossil fuel.

Nuclear based electrical energy derived from standard steam and gas power cycles or from more advanced cycles such as MHD can be utilized to power electrolytic cells or electric discharges. In electrolytic cells, water can be used as a primary source of fuel or converted to a number of other fuels including ammonia, methanol, methane, hydrazine, acetylene, and others. The electric discharge can also be employed to decompose water and carbon dioxide, however, this process is usually less efficient than electrolysis. Aluminum, magnesium, and other reactive metals can be electrochemically produced and used as fuels.

Probably the most practical source of nuclear based non-fossil chemical fuels is the nuclear fission reactor powered electrolytic decomposition of water to hydrogen.

Another class of non-fossil fuels are the boranes, and silanes, These can be derived from hydrogen, borax and silica.

In the longer term future it is conceivable that fusion energy will replace fission as a nuclear source. Generally fusion could be applied in similar fashion to the above processed to produce non-fossil chemical fuels.

## I. Introduction

Probably the best way to set the ground rules for this Symposium is to define what a non-fossil chemical fuel is. Very generally a fuel is a substance which when made to react releases energy in one form or another. A chemical fuel is a fuel which releases energy when the fuel is made to undergo a chemical transformation. A non-fossil chemical fuel is a chemical fuel which is derived from non-fossil substances. Non-fossil substances are generally all substances other than coal, petroleum or natural gas.

Some of the reasons for considering non-fossil chemical fuels are as follows:

1. Fossil fuels are being depleted at an increasingly rapid rate. It is estimated that by the end of this century the U.S. natural gas supplies will be largely exhausted and that less than 10% of the electrical power generating capacity will be supplied by oil and gas<sup>(10)</sup>. The major sources of fuel for electrical power will be derived from coal and nuclear. Oil and gas will be mainly used for fueling mobile engines. Alternate sources of chemical fuels would thus conserve our fossil fuel reserves.

2. Fossil fuel in the form of natural gas and oil also serve the chemical industry for non-fuel purposes. Thus non-fossil chemical fuels would aid the chemical industry in extending its reserves of raw materials.

3. Non-fossil chemical fuels would add to the supply of low pollution fuels. Natural gas and some oil reserves are presently premium sources of low pollution electrical power.

4. Non-fossil chemical fuels can act as energy storage systems.

5. It is also possible that more efficient fuels can be produced from non-fossil sources.

In order to produce a chemical fuel from non-fossil substances, energy is required in the transformation process. Adhering strictly to definition, this energy must be derived from non-fossil fuels. This restricts the energy sources to nuclear, hydroelectric, solar, geothermal, tidal, and meteorological. From the point of view of long term availability and intensity, nuclear energy will be the main viable non-fossil energy source. Nuclear energy at present is derived from fissionable fuel. In the future, nuclear fusion will also be a major energy source.

In order for non-fossil substances to be a major source of raw material for non-fossil chemical fuels the substances must be readily available and abundant in supply. The raw material sources, essentially reduce to the following:

1. Water -  $H_2O$
2. Air  $CO_2$  -  $O_2$ ,  $N_2$  and Ar
3. Minerals - limestone, dolomite, bauxite, borax, and silica.
4. Waste Materials.

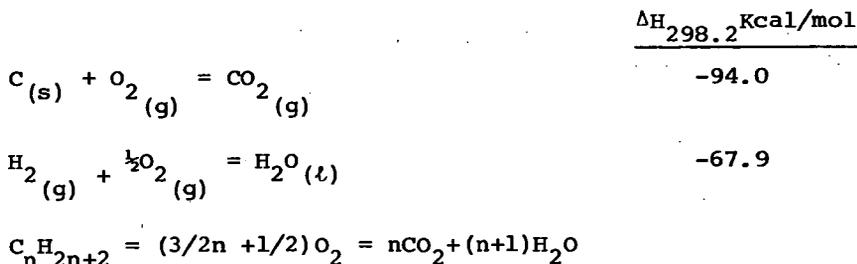
Without necessarily going into the actual quantity of  $CO_2$  existing in the atmosphere, the almost 600 million tons of coal produced and consumed in the United States annually is released to the atmosphere as carbon dioxide. There is thus no question that there is an abundant  $CO_2$  supply in the atmosphere. It is an engineering and economics problem to recover the  $CO_2$  by some process for example, either absorption or by cryogenic separation. A benefit of a  $CO_2$  recovery process might be to maintain the  $CO_2$  balance in the atmosphere and avoid the possible "greenhouse effect" of increasing the earth's temperature by infra-red absorption due to increasing  $CO_2$  concentrations.

The reason waste materials are included in the above listing is that there is a mounting supply and although much of the waste is derived from fossil fuel, the production of chemical fuel from waste is not a direct derivation from fossil fuel. For example part of the  $\text{CO}_2$  in the atmosphere is derived from fossil fuel and it becomes available as a non-fossil source of chemical fuel.

Other properties that can be ascribed to non-fossil chemical fuels are:

1. Storable
2. Transportable
3. Easily utilized in conventional and non-conventional engines.

Fossil fuels are essentially reduced chemical substances which when oxidized in the atmosphere yield exothermic reactions which is the basis of the fuel cycle. Several prime reactions and energy releases are as follows:



To produce non-fossil fuels, nuclear energy can be used to reverse this thermodynamic cycle and essentially the energy is converted and stored in the form of chemical energy in the chemical fuels. In another sense, nuclear energy is used to recycle products formed in the utilization of fossil fuels.

Energy derived from nuclear sources can be utilized either in the form of high energy radiation, thermal energy or electrical energy as discussed in the following.

#### Chemonuclear Reactors

High energy radiation from nuclear fission can be utilized either directly as fission fragment energy in a chemonuclear reactor or indirectly as neutron, gamma and beta energy from isotopic sources. Fission fragment energy containing 85% of the energy released in fission is actually the only radiation

energy source that can be generated in sufficient quantity as at low enough cost to be considered for production of fuels. The two basic chemical fuels that can be generated are hydrogen from water and carbon monoxide from carbon dioxide. The following table indicates the maximum radiation yield (G values in molecules/100 ev) and efficiency of conversion for these two systems (3).

Table 1

| Reaction                               | $\Delta H_{298.2}$<br>Kcal/mol | G values   |            | Energy E<br>Kwh(t)/lb | Thermal<br>efficiency % |
|--|--------------------------------|------------|------------|-----------------------|-------------------------|
|  |                                | $G_{\max}$ | $G_{\exp}$ |                       |                         |
| $H_2O(g) = H_2(g) + \frac{1}{2}O_2(g)$ | +57.9                          | 39.9       | 6          | 101.5                 | 15.0                    |
| $CO_2(g) = CO(g) + \frac{1}{2}O_2(g)$  | +67.6                          | 34.1       | 10         | 4.3                   | 29.4                    |

Because the fuel gases are generated together, separation from the oxygen is required. Furthermore, since the thermal efficiency is not very high, attempts are made to utilize the excess thermal energy for the generation of electrical power. However, upper temperature limits must be imposed to prevent back reactions. This could act as a restriction for generating power in multi-purpose chemonuclear reactors. The hydrogen and the CO can be converted by means of the water gas reactions to gaseous or liquid hydrocarbon fuel.

|                                       | $\Delta H_{298.2}$ Kcal/mol |
|---------------------------------------|-----------------------------|
| $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$  | -9.7                        |
| $2H_2(g) + CO(g) = CH_4(g) + H_2O(g)$ | -49.4                       |

The source of  $CO_2$  could either come from the atmosphere which has an abundant supply although it is in relatively low concentrations (0.03% by volume).  $CO_2$  can also be derived from the calcination of limestone.



$$\Delta H_{298.2} = 43.7 \text{ Kcal/mol}$$

A flow sheet of a chemonuclear process for the synthesis of CO and subsequently hydrogen is shown in Figure 1.

The main difficulties with fission fragment chemonuclear systems are obtaining sufficiently high yields of fuel gases and demonstrating that a fuel essentially free of radioactive fission fragments can be produced. The development of chemonuclear reactors progressed to the point of the installation of an in-pile research loop into the Brookhaven Graphite Research Reactor.<sup>(3)</sup> Unfortunately the development was interrupted due to a reduction in funds for maintaining operation of the research reactor. Potential economic feasibility was indicated assuming the technological problems were solved.

### Thermal Energy from Nuclear Reactors

Conventional nuclear fission reactors usually have clad fuel elements so that the fission fragments are slowed down and remain in the solid elements. The high intensity energy in the fragments is degraded to heat and the temperature of the fuel elements rise. This thermal energy can be used to carry out chemical reactions. In water type reactors, both of the pressurized or boiling water type, the fuel element cladding materials are usually stainless steel. For long life of the elements in the reactor, the temperature of the steam generated in the reactor is usually limited to  $\approx 575^{\circ}\text{F}$  and 1000 psi pressure.

In the near term future it is expected that the liquid metal fast breeder reactors will take over a large part of the nuclear power economy. These reactors are expected to operate at a higher temperature in the order of  $1200\text{--}1400^{\circ}\text{F}$ . These temperatures are too low to supply energy for producing non-fossil chemical fuels either by decomposition of water or carbon dioxide or by gasification reactions.

The thermal decomposition of water requires temperatures in the order of  $5000^{\circ}\text{F}$  or more to yield over 10% conversion to hydrogen. There are no reliable materials of construction for nuclear reactors that could achieve these thermal conditions. The highest temperature experimental reactors developed were for gas turbine conditions in the aircraft nuclear propulsion program. The materials that were being considered were of the refractory metal variety including, rhodium and tungsten. However, they were not expected to generate high temperature gas streams much above approximately  $3000^{\circ}\text{F}$ . The ultra-high temperature reactor experiment at Los Alamos (UHTREX) was a molten plutonium reactor experiment and was intended to operate below  $3000^{\circ}\text{F}$ .

It appears possible to carry out gasification reactions using nuclear heat. Although strictly not a source of non-fossil chemical fuel, because the gasification reactions are

endothermic, the nuclear heat can be considered as being converted to non-fossil chemical fuel in a hybrid system.

The coal gasification reactions are as follows:

|  | $\Delta H_{298.2}$ | Reaction Temperature |
|--|--------------------|----------------------|
| $C_{(s)} + H_2O_{(c)} = CO_{(g)} + H_{2(g)}$ | +41.5              | 1600°F               |
| $C_{(s)} + CO_{2(g)} = 2CO_{(g)}$            | 41.3               | 1800°F               |

The reactions are endothermic and require energy input to the system.

By means of the water has shift reaction and the methanation reaction, high BTU pipe line gas can be produced.

|   | $\Delta H_{298.2}$ | Reaction Temperature |
|---|--------------------|----------------------|
| $CO_{(g)} + H_2O_{(g)} = H_{2(g)} + CO_{2(g)}$  | -9.7               |                      |
| $3H_{2(g)} + CO_{(g)} = CH_{4(g)} + H_2O_{(g)}$ | -49.4              | 700°F                |
| $C_{(s)} + 2H_{2(g)} = CH_{4(g)}$               | -17.9              | 1000°F               |

These are exothermic reactions and usually do not require any external source of energy.

Normally the endothermic heat of the gasification reaction is supplied internally by combustion of additional amounts of coal. In order to prevent dilution of the gases with nitrogen from the atmosphere, pure oxygen is used to react with the coal. By using nuclear heat, oxygen would not be required. From an overall heat balance an equivalent of approximately 30% of the fuel gas would be generated from the non-fossil nuclear fuel source.

Another significant source of non-fossil chemical fuel is the solid waste generated in either urban or agricultural communities. For example, urban wastes contain up to 70% combustible material and usually have heating values ranging in the order of 4000-5000 BTU/lb. Solid waste can also act as a source of carbon and hydrogen in gasification reactions analogous to the coal reactions given above.

The high temperature gas cooled reactors (HTGR) which are cooled with helium can generate gas temperatures in the order of 1600°F. The high temperature helium stream can be used to indirectly heat the coal gasification reactor. The fuel elements are made of graphite clad uranium carbide. It was recently announced<sup>(9)</sup> that a study of this system is being initiated. The heat transfer material in the gasification reactor is a critical factor in the practicability of such a system.

Table 2 lists a summary of the temperature conditions for different power reactors.

Table 2  
Temperature Conditions for  
Different Types of Nuclear Reactors

| <u>Reactor type</u>                              | <u>Fuel element</u> | <u>Coolant</u>   | <u>Maximum Coolant Temperature</u> |
|--|---------------------|------------------|------------------------------------|
| Boiling Water BWR                                | st. st.             | H <sub>2</sub> O | 575°F                              |
| Pressurized Water PWR                            | st. st.             | H <sub>2</sub> O | 575°F                              |
| LMFBR Reactor                                    | Zirconium           | Na               | 1000°F                             |
| High Temperature Gas Cooled Reactor              | Graphite            | He               | 1700°F                             |
| Ultra High Temperature Reactor Experiment UHTREX | Molten Pu           |                  | 3000°F                             |
| Aircraft Nuclear Propulsion Reactor              | Tungsten, Rhodium   | Air              | 3000°F                             |

Nuclear heat can also be used to make up heat balances for hybrid power systems using coal gasification in conjunction with magnetohydrodynamic power generation.<sup>(5)</sup> This also can be considered from the point of view of extending the gas supply using nuclear.

Another place in the non-fossil fuel scheme where nuclear heat can be used is in the calcination of limestone for the generation of CO<sub>2</sub>, a source of carbon for hydrocarbon fuels. The reaction takes place at approximately 1500°F and the endothermic heat of reaction is as follows:

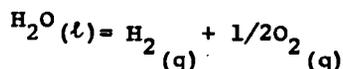


### Electrical Energy from Nuclear Reactors

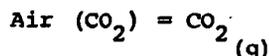
The primary purpose for developing nuclear reactors is to generate electrical power. Usually the closed steam cycle (Rankine) with a turbogenerator is used to produce A.C. electrical power. The heat is transferred from the reactor to the steam either by water, gas or liquid metal heat transfer coolants. The electrical power can be conditioned for use as D.C. power in electrochemical cells to electrolytically decompose water to hydrogen and oxygen. The hydrogen can either be used as a primary source of fuel or can be converted to a number of other fuels including ammonia, methanol, methane, hydrazine, acetylene, and other hydrocarbon fuels.

For producing high BTU pipe line gas by use of nuclear electric power the sequence of reactions are as follows.

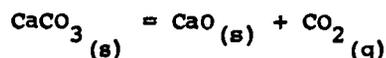
Electrolytic Decomposition



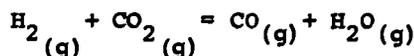
CO<sub>2</sub> Production from air or



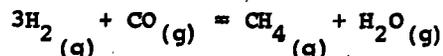
calcination



Reverse shift conversion



Methanation



The coupling of nuclear power reactors with electrochemical cells has been discussed previously under the nomenclature of electrochemonuclear systems.<sup>(3)</sup> They also form the basis for the multipurpose agro-industrial complex and the Nuplex<sup>(4,7)</sup> which have been widely discussed and recently studied in detail.

The electrochemical decomposition of water has been accomplished in well developed low pressure atmospheric cells at efficiencies of 60 to 70%. The more recently developed high pressure cells which operate at pressures of 30 atmospheres or above can develop efficiencies of 85% as listed in Table 3.

Table 3

## The Electrochemical Decomposition of Water

| <u>Cell Efficiency</u> | <u>KWH/lb H<sub>2</sub></u> | <u>KWH/MSCF H<sub>2</sub></u> |
|------------------------|-----------------------------|-------------------------------|
| 100% theoretical       | 17.8                        | 94.5                          |
| 85% hi-pressure        | 21.0                        | 112.0                         |
| 65% low-pressure       | 27.4                        | 145.5                         |

A flow sheet of the process steps for the synthesis of non-fossil high BTU methane pipeline gas is shown in Figure 2. The economics of the process depends strongly on the cost of electrical power from large nuclear reactors and on the utilization of by-product oxygen. In the scheme in Figure 2, the oxygen is used for gasification of coal in an adjoining unit to add to the production of methane fuel. A host of other uses for by-product oxygen have been suggested such as in the basic oxygen furnace for production of steel. (1)

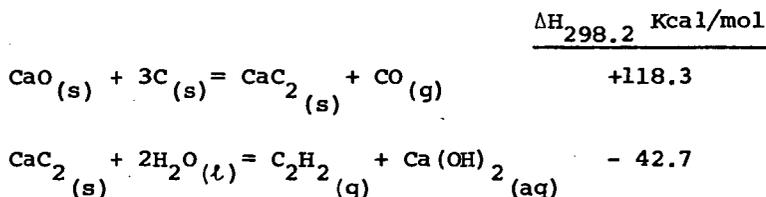
To illustrate the economics of such a process, for a very large 250 million cubic feet per day high BTU methane fuel gas plant, an electrical power consumption of 4670 MW would be required to produce the necessary hydrogen to convert the CO<sub>2</sub> to CH<sub>4</sub>. If power from nuclear units costs 3 mils/kwh, the cost of electrical power for hydrogen production is \$0.34/MSCF H<sub>2</sub>. The depreciation on the electrolytic cell plant could add another 22% to the cost, so that the electrical cost really dominates the production cost for nuclear based electrolytic hydrogen. (4) Since 4 moles of hydrogen are required to combine with 1 mole of CO<sub>2</sub> to produce CH<sub>4</sub> in the above non-fossil process scheme the cost of product methane production would be \$0.67/MSCF. If a credit of \$6/ton of oxygen can be obtained then a credit of \$0.50/MSCF methane results. Today very large scale oxygen plants might produce oxygen for as low as \$3/ton. Thus combining the lowest nuclear by-product power in the future with the lowest conventional oxygen credit could bring the major fraction of the methane production cost down to \$0.42/MSCF. This compares to natural gas today which is rising above \$0.40/MSCF. Gas from projected coal gasification plants is being estimated at \$0.50 to \$0.60 MSCF. Of course, today the above estimates are probably highly optimistic, however, the possibility of an economically competitive situation may exist in the future. This depends on a combination of factors, including the logistics of multipurpose process systems and the supply of natural gas. A continuous examination of these factors could uncover an economically viable application of nuclear based electrolytic systems.

Other fuels which can be produced from hydrogen and CO<sub>2</sub> either from the atmosphere<sup>(2)</sup> or by calcining limestone are listed in Table 4.

Table 4  
Fuels Which Can Be Produced from H<sub>2</sub> and CO<sub>2</sub>

| <u>Reaction</u>               | <u>Fuel</u>             |
|-------------------------------|-------------------------|
| $H_2O = H_2 + \frac{1}{2}O_2$ | Hydrogen                |
| $3H_2 + N_2 = 2NH_3$          | Ammonia                 |
| $CO_2 + 3H_2 = CH_3OH + H_2O$ | Methanol <sup>(2)</sup> |
| $2CH_4 = C_2H_2 + 3H_2$       | Acetylene               |
| $2NH_3 = N_2H_4 + H_2$        | Hydrazine               |

Electrical power from nuclear reactors can also be used in electric discharge processes to decompose water or carbon dioxide. Electric discharge processes are usually less efficient than electrochemical processes. An efficient process for production of acetylene from calcium carbide produced by electric furnace reaction of carbon with lime is a relatively efficient reaction.



The use of nuclear electric power for the electric furnace production of carbide and subsequently acetylene can be viewed in the same light as the use of nuclear heat in the gasification of coal. With the aid of coal, nuclear based electrical power can be converted to additional non-fossil chemical fuel.

Nuclear electric power can be used to electrochemically produce aluminum and magnesium. These reactive metals can be made to burn as solid fuel and have indeed been used as such in specially designed burners. Also hydrogen can be

made to burn with halogens such as chlorine to yield energy. Other non-fossil fuels such as the boranes which are boron-hydrogen compounds and the silanes which are silicon-hydrogen compounds can be produced from non-fossil natural resources with the aid of nuclear energy. However, all these types of fuels cannot be easily burned in conventional engines and in addition cause severe materials corrosion problems and introduce excessive pollutants into the environment.

### Nuclear Fusion Reactors

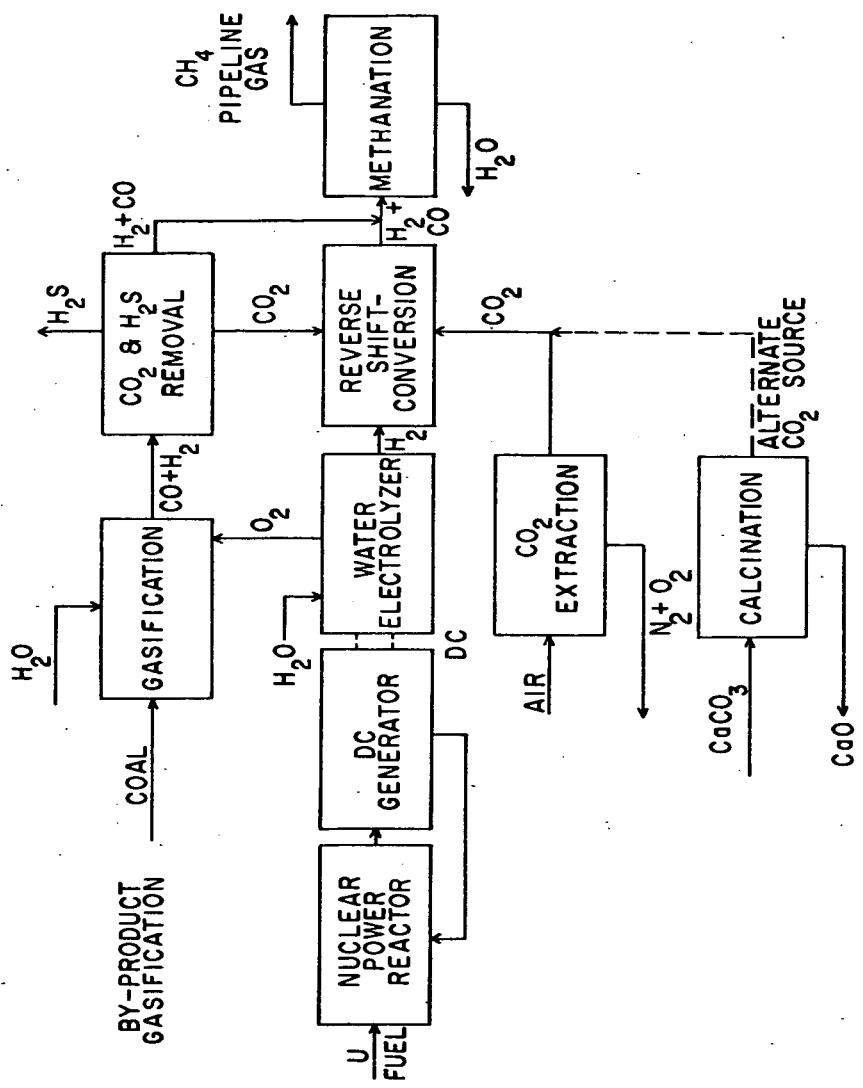
In the longer term future it is conceivable that nuclear fusion reactions utilizing deuterium as fuel will replace fission as the prime nuclear energy source. Generally speaking fusion could be applied in a fashion similar to fission as shown in the processes mentioned above for producing non-fossil chemical fuels. Probably the most practical method of utilizing nuclear fusion for production of non-fossil chemical fuel is to use the electrical energy to decompose water for hydrogen and oxygen production and these in turn can be used as such or converted to other chemical fuels.

### References

1. Meyer Steinberg, "The Impact of Integrated Multipurpose Nuclear Plants on the Chemical and Metallurgical Process Industries, I Electrochemonuclear Systems, Brookhaven National Laboratory Report No. 959 (December 1964) and *Electrochemical Technology* 3, No. 9-10, 283-293, (Sept.-Oct. 1965).
2. Morris Beller and Meyer Steinberg, "Liquid Fuel Synthesis using Nuclear Power in a Mobile Energy Depot System", Brookhaven National Laboratory Report No. 955 (Nov. 1965).
3. Meyer Steinberg, "Fission Recoil Synthesis", *Chem. Eng. Progress* 62, No. 9, 105-116 (September 1969).
4. Meyer Steinberg and J.M. Holmes "Low Cost Power and the CPI", *Chem. Eng. Progress* 63, No. 4, 35-67, (April 1968).
5. Meyer Steinberg, J.R. Powell, Morris Beller, and Bernard Manowitz, "A Pollution Free Hybrid Fossil-Nuclear Fueled MHD Power Cycle", Brookhaven National Laboratory Report No. 12319-R (May 1968).
6. Meyer Steinberg, "Chemonuclear Reactors and Chemical Processing" in "Advances in Nuclear Science and Engineering", E.J. Healey and Herbert Kouts, Ed. pp 275-333, Academic Press, New York (1962).

7. "Nuclear Energy Centers: Industrial and Agro-Industrial Complexes", Oak Ridge National Laboratory Report No. 42990 (November 1968).
8. J. P. Henry, Jr., and B. M. Louks, "An Economic Study of Pipeline Gas Production from Coal", Chem. Tech. 238-247, (April 1971).
9. Chem. Eng., p. 75 (May 17, 1971).
10. G. C. Gambs and A. A. Rauth, "The Energy Crises", Chem. Eng., 56-58 (May 31, 1971).
11. Meyer Steinberg, J. R. Powell, and Bernard Manowitz, "The Western Coal Deposits: A National Source of Power", Brookhaven National Laboratory Report No. 50187, (November 1969).





SYNTHESIS OF NON-FOSSIL PIPELINE GAS WITH NUCLEAR POWER AND BY-PRODUCT COAL GASIFICATION

Fig. 2

## SYNTHETIC FUELS FROM ATMOSPHERIC CARBON DIOXIDE

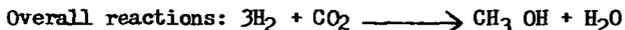
K.R. WILLIAMS AND N. VAN LOOKEREN CAMPAGNE

SHELL INTERNATIONAL PETROLEUM COMPANY LTD.,  
MKD/2, SHELL CENTRE, LONDON, S.E.1.SHELL INTERNATIONAL PETROLEUM MIJ.,  
MFD/13 CAREL VAN BYLANDTLAAN 23, THE HAGUE.Introduction

The predicted shortages of fossil fuels at some indefinite time in the future naturally gives rise to a search for alternatives. Shall we or our successors ultimately be dependent on electric power used directly or stored in electrochemical batteries? Alternatively, will there still be a role for energy stored and distributed in the form of liquid fuels? Also one wishes to know the most probable source of these synthetic fuels. Will it be best to use coal and tar sands as the source of energy or will nuclear power be more attractive?

In assessing the most probable routes which future energy distribution will take, operating and capital costs are of critical importance. Yet in dealing with the cost of a process which is not yet practised it is very difficult to be very precise in one's estimates. Nevertheless, in this paper an attempt is made to suggest the orders of magnitude of cost involved in making synthetic fuels derived essentially from carbon dioxide and water with the addition of energy from a non-fossil source. It is assumed that such a course might be desirable at some time in the future when fossil fuels are relatively scarce and nuclear power comparatively inexpensive.

For automotive use the convenience of a liquid fuel is very desirable and the most conveniently produced liquid fuel, given supplies of carbon dioxide and water, is methanol. Hydrogen may be produced by electrolysis of water and with the addition of carbon dioxide by a suitable catalytic process, methanol results:



Alternatively, it would be possible to make hydrocarbons by the Fischer-Tropsch reaction.

Thus, given the costs of making hydrogen and obtaining carbon dioxide and adding the cost of a synthetic process involved, it is possible to gain some idea of the cost of either methanol or a synthetic hydrocarbon fuel. It should be emphasised that the costs (calculated on a 1970 basis of money values) are based on figures obtained from various references and are not plant costings made by the appropriate Divisions of the Royal Dutch/Shell Group of companies.

In this paper the cost of hydrogen manufacture will be first considered followed by the cost of obtaining carbon dioxide. The synthetic processes for methanol production and Fischer-Tropsch hydrocarbon synthesis then follow.

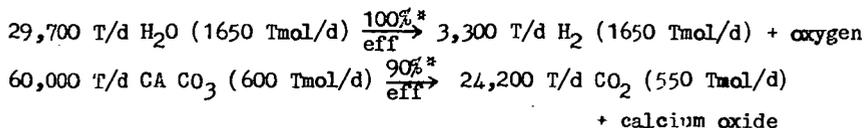
Rough estimates are made of the capital employed, the energy consumed and manufacturing costs on a stated basis. In order to put the synthetic fuel route into perspective, a comparison is made with the costs of coal based fuels. Also the overall efficiency achieved by using fuels in gasoline engines and fuel cells is compared with electricity stored in batteries and used to drive electric vehicles.

## II Processes and economics to manufacture "non fossil" methanol and Fischer-Tropsch gasoline

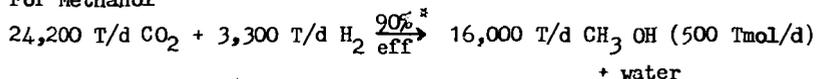
### 1. Scale of operation and overall reactions

A relatively large plant has been chosen since it is assumed that the fuel would be required for the domestic market: a methanol production of 16,000 Tonnes per day (T/d) or alternatively 9,000 T/d Fischer-Tropsch gasoline. The lower heating values (LHV) of those products is  $26.10^9$  Tcal/year; and is equivalent in LHV with  $2.8 \cdot 10^6$  T/a automotive fuel, the output of a typical modern refinery.

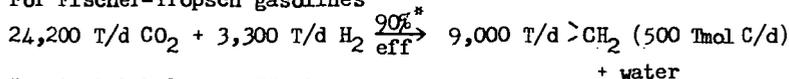
The overall reactions of the processes which will be discussed in the next section are:



For Methanol



For Fischer-Tropsch gasolines



\* material balance efficiency

### 2. Description of Processes

#### (a) Hydrogen Production

If fossil fuels are ruled out as a source of hydrogen then hydrogen by high pressure electrolysis of water is the obvious route. This subject has been considered in detail by Costa and Grimes (1) and data derived from their work are given in Table 1 which summarises process economics. In addition to hydrogen, vast quantities of oxygen are produced by electrolysis of water. If a use were available for all this oxygen then of course it would have by-product credit but it would perhaps be unwise to do this for the speculative economy for which non-fossil chemical fuels are required. In the case of Fischer-Tropsch synthesis, some oxygen would be used in the plant itself.

Reference to Table 1 will show the dominant effect of the cost of the electric power on hydrogen: 80% of the hydrogen cost being represented by cost of the electricity. It is possible that this figure might be reduced slightly by improved electro-catalysis but at this stage it would seem unwise to make any such assumptions. Similarly, electricity at less than 4.0 mils/kWh would reduce costs. Nevertheless it is felt that this particular figure is as low as can be justified.

#### (b) Carbon Dioxide Production

In their work on liquid fuel synthesis using nuclear power in a mobile energy depot system by Steinberg and Beller (2), a proposal

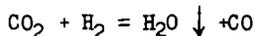
was made to extract carbon dioxide from the atmosphere directly by compressing air, condensing water from it, drying the resultant air with a molecular sieve and finally extracting the carbon dioxide by another molecular sieve. Our attempts to calculate the cost of obtaining carbon dioxide by this means were halted by the realisation that the compressor costs would be simply enormous. The pressure vessels for the molecular sieves and the molecular sieves themselves would not be negligible in cost either. At the present time obvious sources of carbon dioxide are stack gases of fossil fuel power stations and the CO<sub>2</sub> exhaust from the hydrogen units of ammonia plants, hydrocrackers etc. However it is assumed that such sources will not be available in the same region in sufficient quantities to supply wholly synthetic fuel plants. A method which would avoid the need to pressurise the atmosphere would be to scrub the carbon dioxide from air by means of sodium or potassium hydroxide solution. It is difficult however to assign cost data to this process which has not been applied on any scale.

The process finally chosen for evaluation was to obtain carbon dioxide by calcining limestone rock and spreading the resultant calcium oxide back on the land. The quicklime would subsequently hydrate and finally carbonate by natural exposure to the elements. On this basis the synthetic fuel source is thought of as being situated near to a site from which carbonate rock could be mined and which provides plenty of land on which the resultant lime could be spread to weather for re-cycle. Clearly, if ever serious consideration were given to such a process, a considerable amount of experiment would be needed to determine its feasibility. For example, rates of carbonisation and dusting problems of the quicklime would have to be evaluated. The costs given in Table 1 have been estimated from the costs of lime kilns in the U.K. Capital costs of 50% over those of a coal fired kiln were included to allow for a heat exchanger from nuclear heat. It is assumed that heat is available at half the cost of electricity i.e. 0.002/kWh. The alternative of electrical heating would increase overall costs by about 50%.

Some perspective on the amount of CO<sub>2</sub> available from the atmosphere for conversion to fuel is that the atmospheric reservoir of carbon dioxide appears to be about  $2.5 \times 10^{12}$  tons (3). As the concentration of carbon dioxide in the atmosphere is about 320 parts per million, each cubic kilometre of air contains roughly 430 tons of carbon dioxide. Because of the rapidity of air movements about the earth's surface the atmospheric system is fairly well stirred and one would not expect great difficulty due to lack of CO<sub>2</sub> in any particular area.

(c) Manufacture of Methanol

Methanol-synthesis is a well established industrial process. Feedstock for this process - as well as for the Fischer-Tropsch route - is a synthesis gas consisting of H<sub>2</sub> and CO in the ratio of about two, with minor amounts of CO<sub>2</sub> and H<sub>2</sub>O. The CO is obtained from CO<sub>2</sub> by the reversed shift reaction



The latest low pressure processes have improved the economics of the Methanol-synthesis. Published data have been used to provide the figures summarised in Table 1.

Since one is talking about the future, it is interesting to speculate about an alternative process for the manufacture of methanol by means of the electrolysis of potassium carbonate. The authors are not aware of any data which show whether or not this process is in fact feasible, but were it to be so the following cathodic reaction could be expected to take place.



If indeed it were possible to carry out this reaction then it would not be necessary to manufacture hydrogen and one would have a wholly electrolytic process.

Materials of construction of the electrolysis plant for methanol would be similar to those for hydrogen-oxygen production since both involve an alkaline electrolyte and in each case the most corrosive conditions would be expected at the oxygen evolving anodes. On the other hand a stripper would be needed to remove methanol from the electrolyte and catalysts would be needed for the methanol electrodes. Some tentative figures for methanol production by this hypothetical process are included in Table 1. The assumption has been made that the plant would involve a 50% increase in capital cost over that for electrolysis of water.

(d) Fischer-Tropsch Manufacture of Gasoline

Although gasoline would be the main product, other liquid fractions are obtained in the Fischer-Tropsch reaction. These are reflected in Table 1. Economics of the overall process have been described by Govaarts and Schutte (5) and their data have been used in preparing the relevant figures in Table 1.

TABLE 1  
Rough economics for synthetic fuel manufacture (1970 basis)

|  | Capital (1)<br>employed<br>10 <sup>6</sup> \$ | Energy Consumed (2)<br>(a) Electrical<br>(b) Other energy<br>MWh | Manufacturing costs in 10 <sup>6</sup> \$/a                        |   |                        |     | Total<br>Manufacturing<br>Costs |
|--|---|--|--|---|------------------------|-----|---------------------------------|
|  |   |  | All costs<br>related (3)<br>with capital<br>(20% annual<br>charge. | Energy costs<br>4\$/MWh for<br>Electricity,<br>2\$/MWh for<br>heat. | All other<br>costs (4) |     |                                 |
| Electrolysis Water<br>3,300 T/d H<br>(=1.1 10 <sup>6</sup> T <sup>2</sup> /a)                          | 250   | (a) 7,700  | 50   | 250   | 5                      | 305 |                                 |
| CaCO <sub>3</sub> dissociation <sup>a)</sup><br>24,200 T/d CO <sub>2</sub><br>(=8.10 <sup>6</sup> T/a) | 100   | (b) 2,900  | 20   | 45  | 20                     | 85  |                                 |
| Methanol synthesis <sup>b)</sup><br>16,000 T/d methanol<br>(=5.3 10 <sup>6</sup> T/a)                  | 250   | (a) 300<br>(b) 350   | 50   | 15  | 10                     | 75  |                                 |
| Total for Methanol<br>route (5.3 10 <sup>6</sup> T/a<br>product)                                       | 600   | 11,200   | 120  | 310   | 35                     | 465 |                                 |
| Fischer-Tropsch<br>synthesis c) 9,000<br>T/d F.T. gasoline<br>(3.10 <sup>6</sup> T/a)                  | 300   | (a) 200<br>(b) 800   | 60   | 20  | 15                     | 95  |                                 |
| Total for Fischer-<br>Tropsch route<br>(3.10 <sup>6</sup> T/a product)                                 | 650   | 11,600   | 130  | 315   | 40                     | 485 |                                 |
| Methanol via<br>electrolysis<br>(hypothetical)<br>(5.3 10 <sup>6</sup> T/a product)                    | 375   | (a) 7,700  | 75   | 250   | 15                     | 340 |                                 |

(1), (2), (3), (4), (a), (b), (c) see Appendix A.

### III Discussion of Results

Summarising the above results, one can state that liquid synthetic automotive fuels for present type engines can be made from  $\text{CO}_2/\text{H}_2\text{O}/\text{energy}$  at capital investments of roughly  $650 \cdot 10^6$  \$ for a plant to produce  $3 \cdot 10^6$  T/a Fischer-Tropsch gasoline (or  $5.3 \cdot 10^6$  T/a Methanol) at a thermal efficiency of 34%. The manufacturing costs for Fischer-Tropsch gasoline would be about 160 \$/ton (= 45 \$/US gallon  $\approx$  450 \$/MM BTU). For methanol it amounts to 90 \$/ton (= 30 \$/US gallon  $\approx$  450 \$/MM BTU).

Table 2 compares these results with:

- (a) the present situation in which gasoline is made with other products in a modern oil refinery,
- (b) a situation in the future, in which it is assumed that crude oil supply would be insufficient to meet the energy requirements, with consequential use of coal/tar sands/shale to fill the gap by converting these primary energy sources into synthetic methane, and crude oils (gasoline etc.).

The comparison made in Table 2 of course is only a rough one, but the data seem to be clear enough to make the conclusion that fossil primary fuels will be used preferentially for the manufacture of automotive fuels for existing engines and that the  $\text{CO}_2/\text{H}_2\text{O}/\text{energy}$  route has little chance to be competitive for a long time to come.

The above comparison is made on the basis of our present engines requiring specific fuels. The cost and efficiency aspects were discussed of manufacturing these fuels from a variety of "primary energy sources".

As indicated in Table 1, the energy-efficiency of the manufacture of methanol and FT gasoline is only 34% and these fuels are used in the engines with an efficiency around 15%; consequently, from the energy produced by the nuclear plant only about 5% is actually "used in traffic".

In Table 4 a comparison is made with the following routes, featuring "futuristic engines".

| Energy  | Engine                           |
|---|----------------------------------|
| A. Nuclear energy — methanol                        | fuel cell/battery/electric motor |
| B. Nuclear electrical energy — storage in batteries | battery/electric motor           |

For the purpose of discussion it is assumed that batteries of 100 W/lb will be available at a cost of \$20/kWh stored. Efficiency charge to discharge of 50% is assumed. This allows for electrode polarisation in a zinc-air battery or heat losses from a high temperature battery (e.g. sodium-sulphur).

In Europe it is found that gasoline service stations sell much more full at weekends in the four summer months than the mean throughput of the station. In order not to overstress the disadvantages of batteries the figure of 50% overall utilisation of facilities will be assumed. If batteries are exchanged at service stations, a day's store of energy will be needed to meet with fluctuating demands. Distribution of electricity costs about \$200/kW and a charger cost of \$200/kW will also be assumed. Bearing in mind the need for elaborate controls to ensure safety together with automatic handling of the batteries, this does not seem excessive. It is interesting to note that a service station with the relatively modest throughput of a million US gallons a year (equivalent to a mean output of 600kW allowing for

TABLE 2  
 ROUTES TO PRODUCE AUTOMOTIVE FUELS FOR EXISTING VEHICLES

| Primary energy/conversion route/<br>"energy product"   | Order of magnitude (1970)                                     |  | Manufacturing cost<br>(exchange price)<br>of product  |
|--|---|--|---|
|  | Capital for<br>conversion process 1)<br>\$/annual ton product | Thermal<br>efficiency<br>conversion<br>process |   |
| As discussed above: methanol and<br>FT-gasoline from H <sub>2</sub> O/CO <sub>2</sub> /energy<br>(Data from Table 1)                       | 220 <sup>2)</sup>   | 34   | Methanol: 90 \$/ton<br>= 36 \$/US gallon =<br>450 \$/MM BTU<br><br>FT gasoline: 160<br>\$/ton = 45 \$/US<br>gallon = 450 \$/MM<br>BTU |
| Present situation: gasoline/kero-<br>sine/gasol from crude oils in<br>modern complex refinery  | 20-30   | 94   | Gasoline 9 \$/US<br>gallon = 90 \$/MM<br>BTU<br><br>Manufacturing costs<br>SNG: 70-100 \$/MM BTU                                      |
| Projected plants to convert coal <sup>3)</sup><br>tar sands/shale into syncrudes<br>(automotive fuels) and substitute<br>natural gas (SNG) | SNG: 50-75<br>Syncrude: 60-100                                | 65-75  | Manufacturing costs<br>SNG: 70-100 \$/MM BTU<br>Syncrudes: 3.5-6<br>\$/bbl; 70-120 \$/MM<br>BTU                                       |

1. Basis lower heating value products equivalent 104 Kcal/Kg.
2. Excl. nuclear plant to produce electricity/heat.
3. Coal price in calculations: 12-17 \$/MM BTU.

15% efficiency of the gasoline engine) would require a peak output of about 2.5MW. The energy stored in the station would be of the order of 30MWh hours in batteries weighing a total of some 150 tons. Data pertaining to batteries are summarised in Table 3.

It will be noted from Table 1 that the electrolytic plant for hydrogen generation is a significant cost item. Perhaps surprisingly the total synthesis costs of gasoline is only little higher than methanol on an energy basis.

More revealing is the comparison of efficiency of energy conversion and capital cost per kW of mean throughput given in Table 4. As might be expected, the battery system has the highest overall efficiency but this factor is overshadowed by very high capital requirements. Even when the cost of nuclear power plant at an assumed \$300/kW is added, the system looks most unattractive.

Despite the reasonable conversion efficiency of electrical energy to gasoline, the low efficiency of the gasoline engine gives rise to extremely high overall capital requirements. Some perspective on these figures can be gained from the fact that a Fischer-Tropsch conversion plant costs about \$1000/kW available from a gasoline engine. This figure is so high that it makes the process unattractive. The best hope for synthetic fuels appears to lie in the use of methanol in a fuel cell (assumed efficiency with electric motor 50%). If electrolytic reduction of potassium carbonate solutions can be developed as an effective route to methanol synthesis this will clearly be more attractive than the existing chemical route.

One may conclude then that fossil fuels will be used for transport and other forms of "portable energy" for as long as they are economically available. If the methanol fuel cell is developed then fossil fuels will still remain the most attractive source of fuels for vehicles and other portable use. The high efficiency of the fuel cell will tend to prolong the life of fuel reserves. Ultimately when nuclear power is the major source of energy liquid fuels will still be available, albeit at higher prices than now.

TABLE 3

COST BREAKDOWN OF BATTERY STORAGE SYSTEM

|   |                  |
|---|------------------|
| Distribution system                             | \$200/kW         |
| Rectifier and charger system                    | \$200/kW         |
| Batteries                                       | \$20/kW          |
| Utilisation of distribution and charger         | 50%              |
| Efficiency charge to discharge                  | 50%              |
| Batteries equivalent to 1 days peak output      | 48 kW/hr/kW mean |
| Capital investment/kW distribution and charging | \$800/kW         |

TABLE 4

EFFICIENCY OF ENERGY CONVERSION AND CAPITAL INVESTMENT

| Fuel/Power Plant                              | Efficiency of conversion electrical to chemical Energy % <sup>1</sup> | Power Plant Efficiency % | Overall Efficiency % | Capital investment in plant \$ per kW delivered | Capital plant + nuclear at \$300/kW \$ per kW delivered |
|---|---|--------------------------|----------------------|---|---|
| Synthetic Methanol Table 1                    | 34  | 50 <sup>2</sup>          | 17                   | 675   | 2,175   |
| Synthetic Gasoline Table 1<br>Gasoline Engine | 34  | 15 <sup>3</sup>          | 5                    | 2,660   | 7,660   |
| High Energy Battery                           | 50  | 90 <sup>4</sup>          | 45                   | 2,950   | 4,150   |

1. To compensate for the fact that thermal energy is assumed to be used in chemical synthesis, thermal energy is available at twice the "efficiency" of electrical energy; i.e. 1 kWh of thermal energy is equated to  $\frac{1}{2}$  kWh electrical energy. Assuming electricity generation at 40% thermal efficiency, reactor heat is available at 80% efficiency.
2. Fuel Cell and Electric Motor.
3. Gasoline Engine.
4. Electric Motor.

REFERENCES

1. Costa R.L. and Grimes P.G., Chem. Eng. Progress 63 (4) 56-8 and Symposium Series.
2. Steinberg M. and Beller M., Brookhaven National Laboratory Report, October, 1964.
3. Nature 229 514.
4. Hydrocarbon Processing, September 1970, 277.
5. Govaarts J.H. and Schutte C.W., 8th World Energy Conference, Bucharest 28th June - 2nd July 1971, Paper 3.3-187.

DETAILS COST DATA TABLE 1

1. Capital employed = Total erected plant ready for start-up, including all facilities and land and interest during construction and working capital (basis USA 1970).
2. Energy consumed = All energy consumed in processes (minus minor quantity of energy produced by combustion of energy produced as by-products from synthesis routes). Electrical energy 4 Mills/kWh; heat 2 Mills/kWh.
3. All costs which for costimating can be related with capital (in % of total capital investment, average over 15 years lifetime) : total 20%. This can be split-up as follows: depreciation 6.7%; return on investment (av.) 6.3%; all costs related with maintenance (supply, labour, supervision, overheads) averaged over 15 years = 4%; plant overhead (office supplies, R/D, accounting, legal, etc.) and property taxes and insurance = 3%.
4. All other costs = Remaining fixed and variable costs such as Operating labour and supervision, chemicals and catalysts, utilities (excluding energy), royalties etc.

a)  $\text{CaCO}_3$  dissociation; 24,200 T/d  $\text{CO}_2$ 

Energy consumed is twice dissociation energy of reaction  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  (to take into account evaporation of water from  $\text{CaCO}_3$  feedstock and heat efficiency of kiln). Assumption: heat available from nuclear plant at 900°C. Capital 50% higher than U.K. lime kilns with coal firing. Operating, stone handling and return at U.K. costs.

## b) Methanol synthesis; 16,000 T/d methanol

Capital in \$/annual ton methanol

- ref. 4, complete train, incl. synthesis gas generation, scale 800 short ton/d : 62 \$/annual ton
- same, excluding synthesis gas plant : 43 \$/annual ton
- as reported in Table 1 : 48 \$/annual ton

Energy:

200 MWe for syngas compressors; 100 MWe for rest of plant, 300 MW heat.

## c) Fischer-Tropsch synthesis; 9,000 T/d gasoline

Capital in \$/annual ton product

1. As reported ref. 5 (including syngas plant), South Africa 1970: 200 \$/annual ton.
2. Same, but excluding coal handling, gasification, gas purification, part of steampower generation: 100 \$/annual ton.
3. Assumption that main product "gasoline" and by-products require same capital/annual ton product: this gives cap. requirement gasoline plant in Table 1: 100 \$/annual ton.

Energy consumed

1. As reported ref. 5: 200 MWe + 4000 MW heat for 2,510<sup>6</sup> T/a plant.
2. Assumed for our 3.10<sup>6</sup> T/a plant (excluding the high energy consumption of the syngas part): 200 MWe + 800 MW heat.

A Macro System for the Production of  
Storable, Transportable Energy  
from the Sun and the Sea

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Introduction

The purpose of this paper is to present a candidate technical concept for solar energy utilization in large scale. This concept, though offering nothing new in technical detail, does offer a singular departure from previous concepts on the overall systems engineering level. This is the idea of locating the solar energy conversion system on the open seas, as opposed to basing it on land.

The important technical benefits of sea-basing a solar energy conversion system are these: 1) Proximity to an excellent thermal sink and source of working mass (viz. the ocean, particularly the depths), 2) Mobility of rotation and translation, 3) Space availability for large solar collector areas, and 4) Logistical ease in initial construction, servicing, and in the distribution of products from the macro system on a world-wide basis.

Proceeding from the fourth point, the energy form to be produced is required to be both storable and transportable over significant duration and distance by way of delivering this energy to the ultimate consumer. It is proposed that solar energy be used to convert water (purified sea water) into cryogenic liquid hydrogen and oxygen. In this form the stored energy of the sun can be readily shipped to points-of-use on a worldwide basis via "cryo-tankers". Once unloaded at port, the cryogenic liquids can be stored and eventually transported by rail, over-the-road trailers, or by pipelines. Alternatively, the hydrogen and oxygen can be gasified and piped in the manner of natural gas. The energy form can be finally consumed in the process of heat-release or it can be converted into an electrical form by fuel cells or their shaftpower-producing equivalents.

Also, though not really assessed in the paper, a number of collateral products in addition to the cryogenic energy form may be readily produced from a sea-based solar energy converter. Possibilities are these: seafood products, mineral and chemical products, and certain finished and semi-finished goods. If these prove economically feasible, such co-production might very significantly reduce the cost of energy by spreading the capital investment and operating cost over a wider range of salable products. This surmise is, however, taken to be outside the scope of the present paper. Much more study will be required to quantify the potential of such collateral output; a multidisciplinary effort is clearly needed here.

Finally, the candidate scheme, as is characteristic of solar energy utilization systems in general, offers one extremely important advantage to our environmentally-conscious world: its operation will not degrade the environment. No fossil-fuel is combusted and no radiation conditions are produced nor are long half-life radioactive wastes created.

This unique environmental aspect of the solar energy conversion approach, together with its intrinsic non-dependence on resources in increasingly short supply, may in fact be a

decisive factor in favor of its eventual development. Unfortunately, it is not yet apparent what the economic ramifications of these characteristic benefits will be, hence these can not be assessed in the paper.

In summary, the paper introduces and discusses a new energy system concept based on the synthesis of known subsystem approaches to create a "macro system" (large scale system-of-systems). This macro system employs solar energy to convert water to the energy form: cryogenic hydrogen and oxygen. This is deemed a feasible storable and transportable commodity for a wide variety of end-consumption means. The macro system will not produce environmental degradation in its operation, nor at the point of consumption. Water is the sole "exhaust" product in reconversion as heat or electrical energy (thermal rejection will occur, however, dependent on the conversion efficiency). The approach offers distinct possibilities of cost-beneficial coproduction of other salable products, although this aspect is not further developed in the paper.

#### Description of the Technical Concept

A general overview of the problems addressed, the general technical approach to be taken, and the technologies which might contribute to feasibility, for the subject macro system approach has been published (1, 2)\* and will not be repeated here. Rather, this paper concentrates on a specific formulation of the technical approach, sizing calculations, and a rough cost estimate applicable to the macro system. Necessary to this scope, a brief analysis of the solar energy input to be received is included, including cloud-cover considerations.

Production of cryogenic hydrogen and oxygen from sea water using solar energy takes place by integrating five of the six systems (blocks) in the manner shown in Figure 1. The sixth system, "Marine Farming System", is representative of a potential collateral production unit (seafood), which uses ocean resources and solar energy (via photosynthesis). Also, the "sea water concentrates" output of the Water Purifier System (top) is suggestive of chemical and mineral production. Figure 2 is a pictorial schematic of the macro system reflecting an overall geometric relationship of the constituent systems. Note that items are located both on the surface and in the ocean depth for reasons to be discussed.

The macro system is sized on the basis of an equivalent production of 1000 Mw of cryogenic energy form continuously. The energy-content reference is the higher heating value of hydrogen at 61,030 Btu/lb. This equates to a daily production of 670 tons of liquid hydrogen and 5360 tons of liquid oxygen (609 and 4890 metric tons, respectively).

Macro system operation is conducted in basically two modes: 1) During periods of solar energy collection for 8 hours of day (when there is no cloud cover), and 2) Around-the-clock during which product liquefaction takes place. The consideration governing the continuous liquefaction process lies in the problem of the characteristic extended start-up and shut-down time involved with industrial liquefier train operation. This need (and it should be more closely examined) assumes a supply of "service power" which is provided by reconversion of some of the hydrogen and oxygen electrolyzed from water to create an electrical supply at all times. The remainder of the macro system is operated only during periods of sunlight. This entails the Solar/Electric Conversion System, the Water Purifier System, and the Electrolytic Cells System as "off-on"-capable units. It is noted that the specific characterization of Figures 1 and 2 represent a "first look" with regard to macro system formulation. It is by no means optimized; a number of improvements are forseen.

\* Numbers enclosed in parentheses denote references listed at the end of the paper.

### Cryogenic Hydrogen and Oxygen

Central to the theme of the macro system is cryogenic hydrogen and oxygen, the "energy form" to be produced. Hydrogen, in combusting with oxygen in the air or with pure oxygen (the approach emphasized), provides greater heat-release per unit mass than any other chemical fuel. On a volumetric basis, however, hydrogen has about one-third the energy content of natural gas (principally methane), and less than one-fourth of that contained in the conventional liquid hydrocarbon fuels, gasoline, kerosene, and fuel oil. The characteristic problem of hydrogen's very low density is evident here.

Technology deriving from the aerospace sector over the past several decades, and particularly that from the Apollo effort, has made consideration of the cryogenic form of hydrogen (liquid oxygen development and mass-use came much earlier) eminently practicable for large-scale system applications. Liquid hydrogen, despite its extreme physical characteristics (viz. 0.07 specific gravity, 21°K boiling point) has been demonstrated to be a tractable, desirable chemical fuel and working fluid (See Scott's volume on liquid hydrogen technology (3) for cases in point).

The potential of hydrogen as a fuel has been frequently discussed. Apollo represents a pinnacle of experience in actual usage in ground-testing of engines and stages, as well as in the actual mission flights. A recent review with emphasis on the cryogenic form is that of Jones in Science (4). The clean combustion characteristics of hydrogen (water only with oxygen, whereas a nitrogen oxide problem remains with combustion in air) has caused increased attention to be given this fuel in recent times. A number of prime move types have been operated on hydrogen-air and hydrogen-oxygen. Still others have been proposed (viz. 5) for a number of technical advantages gained over hydrocarbon fuels. Fuel cells operating on hydrogen-oxygen are well developed as demonstrated in the Gemini and Apollo programs.

A second, longer-term incentive for considering hydrogen as an "emerging" energy form is reflected in a study recently undertaken by the Institute of Gas Technology for the American Gas Association. This is the consideration of hydrogen as a distant-term replacement for natural, and synthetic "natural" gas (via coal gasification, for example). The consideration here is that of natural resource exhaustion of fossil-fuel reserves, and a conversion to a nuclear-electric energy base. A basic approach here is the use of nuclear power to extract hydrogen (and oxygen) from water; hydrogen is very significantly cheaper to transmit over long distances via pipelines than electrical power, particularly so if the electrical conduits must be placed underground. Since this study effort was only recently announced (6), no published results are yet available. Gregory's review of this area (7) provides a worthwhile overview.

The "arrival" of cryogenic hydrogen and oxygen as a viable energy form capable of long-term storage and long-distance transportation -- characteristics crucial to the concept of the paper -- is indicated in the equipment shown in Figures 3 - 5.\* Figures 3 and 4 show the largest liquid oxygen and hydrogen tanks in existence as located at the Kennedy Space Center, Florida. These vacuum-jacketed spherical tanks approach one million gallons in capacity. Figure 5 shows liquid hydrogen (foreground) and liquid oxygen (background) barges used to transport the cryogenics from their point of production to the test facility of NASA near Gainesville, Mississippi. The liquid capacities are over 300,000 and 100,000 gallons, respectively. Hydrogen and oxygen are also shipped routinely across country in rail tankers and over-the-road trailers. Although hydrogen and oxygen "cryo-

\* Photographs courtesy of Chicago Bridge & Iron Company, the equipment suppliers

tankers", as envisioned to supply the macro system's product to the mainland, do not presently exist, the commercial success of LNG (a "mild cryogenic" at  $-258^{\circ}\text{F}$ ) tankers presages success. A dozen LNG tankers are currently in service, and by 1980 there are projected to be one-hundred (8). Actually, hydrogen cryogenic vessels have been considered in some engineering detail in Air Products & Chemicals' comprehensive study of liquid hydrogen production for global hypersonic aircraft fueling (9).

### Solar Energy Available in a Practical Large-scale Array

The rate of energy radiated by the sun is  $3.805 \times 10^{26}$  watts which corresponds to a continuous loss of solar mass of  $4.234 \times 10^{12}$  g/sec, or 4.67 million tons per second via nuclear fusion conversion. Of this amount of radiant energy, the Earth-atmosphere system receives each year  $5.445 \times 10^{12}$  joules ( $1.301 \times 10^{24}$  cal). This corresponds to an energy density as expressed by the Solar Constant of  $135.3 \text{ w/m}^2$  ( $1.353 \text{ kw/m}^2$ ). (The Solar Constant is the amount of total radiant energy received from the sun per unit time per unit area exposed normal to the sun's rays at the mean Earth-sun distance in the absence of the Earth's atmosphere.) (The data given in this paragraph were taken from (10).)

In principle, a solar collector located in near-Earth space and oriented continuously toward the sun would receive energy perpetually at the Solar Constant rate. This "ideal" condition has, in fact, been proposed by Glaser in several papers (e. g. 11) as one which we should seriously consider exploiting.

Unfortunately, but invariably, Earth-bound collectors will receive considerably less energy than such a space-borne system. Of that potentially available, large-scale collectors at sea level may receive 6 to 10 percent of the maximum value. This is because of the following essentially uncontrollable factors: 1) Rotation of the Earth occluding the sun for much of the time, 2) Seasonal variations in the mean sun-angle for a fixed latitude, 3) Clear-day atmospheric attenuation, and 4) Cloud-cover and adverse weather conditions (fog, humidity, etc.). Further, though perhaps easy enough for a space-borne collector, it is usually not practical to orient large Earth arrays normal to the sun as it moves across the sky. Instead, the array is layed out in the horizontal datum plane of the Earth's surface. This results in a loss in incident radiation over that potentially available proportional to the cosine of the total sun-angle.

A typical observed solar radiation pattern over a (clear) day's observation period is presented in Figure 6 (the upper right hand note calls out this curve), as adapted from Daniels (12). The integrated radiation intensity (Langleys\*/min) for that day was reported as 678 Langleys\*. Returning for the moment to the case of an ideal collector located in Earth-space, a maximum of 1.937 Langleys/min times the number of minutes in a 24-hour period would be received. This is approximately 2790 Langleys. The observational data of Figure 6 accordingly represents about 24 percent of that potentially available. As will now be shown, a practical large-scale collector will not achieve this effectiveness.

Returning to Figure 6, the dashed curve has been estimated as a "maximum solar radiation characteristic" for an Earth collector. At noon the peak intensity of this estimated reference curve is about 1.4 Langleys/min, or 72 percent of the potential 1.937 (Solar Constant). Over a 24 hour period, however, only the order of 25 percent can be realized. Also, the sunrise/sunset "tails" of the baseline data curve were clipped to accord to the "sudden" nature of the sun's appearance and disappearance in the tropics.

\* See Figure 6 for a definition of the Langley unit and its equivalent in  $\text{kw/m}^2$

Unless the collector's constituent areas are rotated normal to the sun's rays at all times during the collection-day (and do not shield one another from the sun) this 25 percent effectiveness cannot be achieved in practice. This results in the cosine loss factor mentioned previously as denoted in the third curve of Figure 6, that of least area. Also the length of the nominal day has been reduced to the 12 hours experienced near the equator (for it is the quasi-equatorial region which appears most desirable for locating the macro system). This time-scale forms the basis of the nominal sun-angle scale established below it. The quite-evident narrowing of the daily intensity characteristic due to applying the cosine loss factor (array non-normal to the sun, except nearly so around noon) significantly reduces the area under the curve, the integrated solar energy quantity received.

One more penalty is observed as the deletion of the shaded areas on each side of the curve. This corresponds to non-operation of the solar collector at sun-angles greater than 60 degrees (as can be noted on the lower scale). This somewhat arbitrary cut-off is for practical design considerations as will become evident when the collector geometry envisioned for the macro system is introduced in a later section.

The last two reductions in effectiveness (non-normal collector and cut-off beyond 60 degrees) account for a reduction of the 25 percent effectiveness to approximately 18 percent. Over 8.0 hours the net result is that the net energy collected is  $5.86 \text{ kwh/m}^2$  for a horizontal, quasi-equatorial, concentrator type solar collector. The mean daily (clear skies) input of  $0.732 \text{ kw/m}^2$  for 8.00 hours was entered into the macro system sizing calculations. This will be reduced by the "clear skies" factor next to be developed.

#### Cloud Cover Considerations

Since the solar energy collector type selected is of the concentrator (i. e. focused) configuration (the arguments for this are cost and available technology), operation can take place only in direct sunlight. Therefore cloud cover must be minimal commensurate with restraints applied to the macro system, e. g. sea-basing. It is for this reason that desert locations are typically suggested in solar energy conversion proposals. For example, Meinel cites 330 clear days per year for Yuma, Arizona (13) in connection with his recent proposals.

As it turns out, an ocean-borne solar converter such as the subject macro system will not fare nearly this well as becomes evident in examining a marine climatic atlas (14). Such an atlas can be used to develop a "clear skies factor" to be applied to the solar energy characteristics developed in the preceding discussion. Representative results are shown in Figure 7, where the selection of a favorable locale is indicated for the macro system in the mid-Pacific as determined by cloud-cover minimization tactics. The hatched area was found to be contained by the maximum monthly clear skies isopleth over the year, as read from the "total cloud cover" charts of (14). (An exception was the month of June, for which the 60 percent isopleth was displaced to the east, as can be noted on the figure.)

The indicated area was then selected as the model for quantifying the clear skies factor whose value was estimated as 0.497, or approximately 50 percent. Geographically, this region is centered at  $8^{\circ}\text{S}$ ,  $138^{\circ}\text{W}$  and is about 250 km northeast of the Marquesas Islands. A depth of over 14,000 ft is noted with a mean surface water temperature of about  $82^{\circ}\text{F}$ . The clear skies factor of 0.497 was entered into the sizing calculations.

### Macro System Sizing Calculations

The energy and mass-flow characteristics of the macro system were determined on the basis of the foregoing findings (solar energy characteristic, clear skies factor) and the physical characteristics of the constituent systems. This required an estimate of individual system efficiencies, process variables, and associated physical and chemical data for the process fluids and their transformations. These assumptions derived from information made available to the writer in communication with a number of workers in the various fields involved, as well as that from the open literature. However, in the end-analysis the values listed represent only opinion -- hopefully, a reasonably informed one. Two estimates are made, a "current" and a "projected" technology basis.

The scope of the paper does not allow for the details of these assumptions or the calculations to be included here, unfortunately. However Table 1 provides a summary of results. These provide a basis for physically characterizing the macro system, which in turn will provide a baseline for a rough cost assessment.

### Conceptualizing the Macro System

Physically, as would be expected for any solar energy converter, the overall macro system layout is dominated by considerations of collector area. The required active collector area for 1000 Mw continuous equivalent liquid hydrogen and oxygen production is  $47.3 \text{ km}^2$  (6.88 km square) and  $26.9 \text{ km}^2$  (5.19 km square) for the "current" and "projected" bases, respectively (Table 1). The latter is 57 percent of the former. However, the larger "current" technology version will be used as the baseline for conceptualization and costing in the paper in order to bias the results toward a more conservative estimate.

Rounding the 6.88 km on the sides to an even 7.0 km, an obvious geometric arrangement of 49 square modules, each 1.0 km on the side is arrived at. If the central one of these is removed to provide for a "central operations" zone for the macro system, as shown in Figure 8, the total active area is  $48 \text{ km}^2$ , slightly more than the indicated  $47.3 \text{ km}^2$  requirement.

Figure 8 reflects a spacing-out of the modules by a separation of 414 m, enlarging the overall area required by a factor of 2. The reason for this is to provide complete rotational freedom for the individual square modules. Somewhat closer spacing is possible for other than square modules, the limit being reached with circular shaped units whereupon the expansion experienced (Figure 8) can be reduced by about 64 percent. The need for rotational freedom is associated with the characteristic of the solar collector geometry assumed, viz. a two-dimensional reflector.

An individual 1-km square module (designated L-3, for a third level of modular build-up) is conceptualized in Figure 10. This unit is equipped with twenty  $100 \times 500 \text{ m}$  solar collector modules, referred to as L-1 units, the basic building block of the macro system solar array. Each symmetrical corner of the L-3 module consists of 5 solar collectors and is designated L-2. The overall macro system is thus composed of 48 L-3s, 192 L-2s and 960 L-1s (Figures 8-11).

A five-flotation-point suspension is shown supporting the frame of the basic L-3  $1 \text{ km}^2$  module. This places the support points a maximum of 600 m apart which, in view of the much larger spans achieved by bridge builders, seems reasonable. With lightweight

structural elements and the use of tension rigging, a minimal-mass structure should be achievable. Any concentrated loads such as machinery, tanks and personnel accommodations can be separately floated below the array or located within the flotation units. The solar collector surface is elevated considerably above the ocean surface to minimize adversities of the ocean-atmosphere interface, such as salt-spray.

On the other hand, the center of mass and wetted volume of the flotation units (spar buoy configuration) is sufficiently deep to be virtually uninfluenced by surface and near-surface wave action. A number of spar-buoy type vessels such as FLIP (15) and MOSES (16), have demonstrated the intrinsic stability afforded by this configuration. Each flotation unit, towed into its assembly point in a horizontal attitude, and erected by ballast control, is equipped with its own propulsion system. Electrical or hydrogen-oxygen (5) powered thrusters will be used to position and stabilize the flotation units, and also to provide azimuthal rotation of the L-3 modules as well as translatory capability (e. g. to counter currents).

An overall "macro-servomechanism" is envisioned to maintain the geometric integrity of the entire macro system without "hard" structural connections. This includes the rotation for sun-tracking (Figure 9), translation of the total array with respect to the ocean body, and maintaining proper inter-modular spacing.

The essential features of the 50,000 m<sup>2</sup> solar collector module (L-1), which is a two-dimensional "trough" paraboloid-of-translation, are represented in Figure 11. Instead of a point-focus, this configuration provides a line-focus of considerably lower intensity. In this application, the focal boiler being of linear design, the geometry is quite compatible with the working fluid flow path as energy is absorbed. It can be seen that, since the module is free only to rotate and translate on a horizontal datum, viz. the ocean, it must be oriented such that the vertical plane containing the sun must also contain the focal line. Hence, continuous rotation of the module to "track" the sun is required. (An exception to this would occur for an equatorial site on the equinoxes). Figure 11 reflects the need for overhanging the focal boiler for full-mirror utilization up to the cut-off angle of 60 degrees. The problem of tracking the sun effectively beyond this angle is apparent in that the amount of overhang becomes quickly impractical, and/or only partial utilization of the mirror can be made. Hence, the "cut-off ruling".

The focal boiler is viewed as basically a linear receiver of focused solar radiation for transferring this energy to the working fluid (provisionally, water). A transparent casing surrounding the metallic or refractory receiver/working-fluid passage may be applicable, in which case a vacuum or inert gas atmosphere can surround the receiver element. An objective is to minimize thermal losses due to reradiation and convection, and to protect the high temperature element from oxidation.

If water is used as the Rankine cycle working fluid, then conventional steam turbine and associated equipment can be employed. There will be an incentive to raise the steam temperature well over the conventional utility-plant levels of 1000-1100 °F, however. This will be set by the focal boiler and turbine temperature capability, with an actively-cooled turbine a distinct possibility at temperatures above 1500 °F or thereabout. The incentive is, of course, increased system efficiency which permits a reduction in hardware size, and hence, costs -- assuming that this is not countered by the more expensive "advanced technology" equipment. In the interest of maximizing efficiency, the use of cold depth water for condenser cooling (41 °F vs. 82 °F for the surface water) is very likely, since the gain far outweighs the cost of pumping the water up (favorable implications for marine farming).

Since dc power is required for the water electrolyzers (located in the depths to achieve high pressure gases and cell advantages, without the need for thick wall, expensive structures), generation of dc power by the turbine-generator is highly attractive. The alternative (conventionally done) of rectification of ac power is costly in terms of equipment and some loss of power. Fortunately, the acyclic (homopolar, unipolar) dc generator has this potential in the size range of interest (17).

With regard to the electrolyzers, it would appear that both unipolar (tank type) and bipolar (filter-press configuration) configurations should be examined for applicability; each has characteristic advantages and disadvantages. Applicable references are (18, 19). Depth storage of the hydrogen and oxygen at ambient generation pressure offers economic advantages as discussed for natural gas storage in (20).

The high-pressure (nominally 1500 psi) accumulator is essentially to smooth the flow of gas to the liquefiers and service power unit, and would be minimized for this function, since expensive heavy-walled containers will be required. The liquefaction plants would be of conventional design very likely, but would be so engineered to gain any synergistic benefits from the co-production of hydrogen and oxygen. Cryogenic storage at the surface of the type described in (20) would be located near the docking facility for convenient loading into the cryotankers (Ref. 8).

#### Macro System Cost Estimate

The macro system was broken down into 17 items of capital cost as listed in Table 2. Based on the anticipated distribution of these components within the macro system (i. e. whether associated with the 1 km modules, or with "central operations"), the number of items and the size were determined and listed. Cost factors, based on communications with specialists as well as open literature assessment were developed. Occasionally these were merely intuitive estimates. Using the "current" technology baseline, a total capital cost estimate was arrived at. To this was added ten percent for installation and testing services. The resulting rough estimate for the macro system was approximately \$ 1.5 billion. (See Table 2).

At this level of cost associated with 1000 Mw continuous production of energy, it is of interest to compare the macro system with both present and alternative projected sources of energy. These three bases of comparison were examined, although none expressly matched the macro system's input/output: 1) Conventional electric energy generation systems, 2) Conventional hydrogen and oxygen production plants, and 3) Alternative solar energy utilization schemes which are of the same general scale as the subject one (11, 21, 22).

Summarizing the results of these three comparisons, the cost of energy produced by the macro system is indicated to be significantly higher than those conventional sources of electrical power and cryogenics, a factor of 4 to 5 being observed. On the other hand, the macro system's energy cost fell into the range estimated for representative solar energy alternative approaches, being at the lower or higher end, dependent on whether the end product desired was cryogenic or electrical.

It should be noted that considerable reductions in the macro system's energy costs would

seem possible, however, through these principal avenues: 1) Optimized system design, 2) Technology advancements, and 3) Collateral production of salable products to spread costs over a broader revenue base. Further improvements in each of these areas will be complementary, that is, gains will compound one another. Based on the writer's judgement in assessing these potentials, a gross reduction of the cited factor of 4 to 5 is achievable if a number of the potential gains identified qualitatively could be brought to fruition. If so, the macro system would be quite competitive with conventional sources of energy, and considerably better than the alternative solar energy proposals. However, the depth of the investigation to date is not sufficient to make this other than a surmise.

### Concluding Remarks

This paper has introduced and discussed yet another approach for harnessing solar energy directly (Ref. 11, 21, 22). Its novel approach of open-seas basing may offer substantial advantages over land-basing as in previous proposals. Sea-basing also embraces problems peculiar to the nautical environment, with a significantly lower clear skies factor than can be had in a desert location. Other concerns with forseen difficulties in locating a large solar array on the ocean may be countered through judicious marine engineering approaches, particularly that of oceanographic stable platforms (14, 15). It does appear that the concept of locating a stabilized, reasonably long-lived solar collector and attendant component systems of the subject macro system on the open sea is supportable.

But in at least an emotional way, the single most distracting characteristic of a solar utilization scheme of the magnitude presented is the enormous proportions of the solar collector. This is a reflection of the innate nature of the solar energy intensity at the Earth and it cannot be altered. At best, we can move the array into near-Earth space as proposed by Glaser (11) to maximize exposure duration and to eliminate atmospheric attenuation.

The approach taken here in view of the intrinsic collector area problem is straightforward: 1) Select the largest practical solar collector deemed "reasonable", and 2) Incorporate sufficient numbers of these as modules to make up the overall requirement. The objective of minimizing the cost of the collector goes without saying.

If the technical feasibility of the subject concept is accepted, the singular issue is that of energy cost. Although "fuel" cost and the required investment in property are zero, the overall capital cost appear very high by today's utility and chemical industry standards. As a result, energy cost is very high based on the rough assessment performed. But as noted above, there are avenues for cost reductions which are definitely promising. These should be evaluated quantitatively.

What will be perhaps more difficult to evaluate is the dollar-worth of the macro system's "benevolent environmental interaction" characteristic. This, with the fact that no natural resources potentially in short supply are consumed. These two areas of national and global concern must enter into the decision-making process in future energy systems.

## REFERENCES

1. Escher, W. J. D., "Helios-Poseidon, A Macro System for the Production of Storable, Transportable Energy and Foodstuffs from the Sun and the Sea", Escher Technology Associates Publication PM-3, July 1971
2. Congressional Record, Volume 117, No. 164, 2 November 1971, PP. S17386-8
3. Scott, R. B., et al (ed.), Technology and Uses of Liquid Hydrogen, Pergamon Press, 1964
4. Jones, L. W., "Liquid Hydrogen as a Fuel for the Future", Science, 22 October 1971
5. Reese, R.A. and Carmichael, A.D., "A Proposed Hydrogen-Oxygen Fueled Steam Cycle for the Propulsion of Deep Submersibles", Paper No. 719079, Intersociety Energy Conversion Engineering Conference, 3-5 August 1971, Boston
6. American Gas Association, Research and Development -1971, p. 21, Arlington, Va.
7. Gregory, D. P., "A New Concept in Energy Transmission", Public Utility Fortnightly, 3 February 1972
8. Conch LNG Tankers, Conch Methane Services Limited, London, England
9. Hallett, N. C., "Cost and System Analysis of Liquid Hydrogen Production", Air Products and Chemicals, Inc., NASA CR 73,226, June 1968
10. Solar Electromagnetic Radiation, NASA Report SP-8005, Revised May 1971
11. Glaser, P. E., "The Environmental Crisis in Power Generation and Possible Future Directions", presented at the 39th national meeting of the Operational Research Society of America, 7 May 1971, Dallas, Texas
12. Daniels, Farrington, "Direct Use of the Sun's Energy", American Scientist Volume 55, No. 1, March 1967 (revised as communicated by the author, 1970)
13. Meinel, A. B., "A Proposal for a Joint Industry-University-Utility Task Group on Thermal Conversion of Solar Energy for Electrical Power Production", for Presentation to the Arizona Power Authority, 27 April 1971, Phoenix, Arizona
14. Crutcher, H. L. and Davis, O. M., "U.S. Navy Marine Climatic Atlas of the World, Volume VIII, The World", Report Navair 50-1C-54, 1 March 1969
15. Spiess, F.N., "Oceanographic and Experimental Platforms", Systems Design-The Technology (Chapter 15), available separately from the Scripps Marine Physical Laboratory, La Jolla, California

16. Norris, K.S. and Hanson, J.A., "Manned Open Sea Experimentation Station", (MOSES), A feasibility study, Oceanic Institute Report No. OI-70-28-1, The Oceanic Foundation, Waimanalo, Hawaii, 30 June 1971
17. Burnett, J.R. and Kaestle, F.L., "Acyclic Generator - A New D. C. Power Generation Tool for Industry", Direct Current, July 1963
18. "Stuart Electrolytic Hydrogen Plants", Technical Marketing data from The Electrolyser Corporation Limited, Toronto, Canada
19. Costa, R.L. and Grimes, P.G., "Electrolysis as a Source of Hydrogen and Oxygen", Chemical Engineering Progress, Vol. 63, April 1967, pp. 55-58
20. Tek, M.R. and Wilkes, J.O., with Katz, D.L. et al, "New Concepts in Underground Storage of Natural Gas", Monograph by the University of Michigan for American Gas Association Project PO-50, Published by the American Gas Association, New York, March 1966
21. Rink, J.E. and Hewitt, J.G., Jr., "Large Terrestrial Solar Arrays", Paper No. 719005, Intersociety Energy Conversion Engineering Conference, 3-5 August 1971, Boston
22. Ralph, E.L., "Large Scale Solar Electric Power Generation", Presented at the Solar Energy Conference, Greenbelt, Maryland, 10 May 1971

TABLE 1

## Results of Macro System Sizing Calculations

Rated Production of Macro System (Daily Basis) (1000 Mw, continuous equivalent)

|                  |                                       |  |
|------------------|---------------------------------------|--|
| Liquid Hydrogen  | 1.34x10 <sup>6</sup> lb<br>670 Tons   | 0.609x10 <sup>6</sup> kg<br>609 Tons-metric  |
| Liquid Oxygen    | 10.72x10 <sup>6</sup> lb<br>5360 Tons | 4.89x10 <sup>6</sup> kg<br>4890 Tons-metric  |
| Total Cryogenics | 12.06x10 <sup>6</sup> lb<br>6030 Tons | 5.499x10 <sup>6</sup> kg<br>5499 Tons-metric |

Results of Sizing Calculations (Daily Basis)Technology Bases

"Current"

"Projected"

|   |   |   |
|---|---|---|
| Hydrogen liquefaction energy            | 6.03x10 <sup>6</sup> kwh  | 5.36x10 <sup>6</sup> kwh  |
| Oxygen liquefaction energy              | 2.68x10 <sup>6</sup> kwh  | 2.14x10 <sup>6</sup> kwh  |
| Hydrogen required for service power     | 0.405x10 <sup>6</sup> kg  | 0.298x10 <sup>6</sup> kg  |
| Oxygen required for service power       | 3.24x10 <sup>6</sup> kg   | 2.39x10 <sup>6</sup> kg   |
| Service power level, continuous         | 400 Mw  | 343 Mw  |
| Water to be electrolyzed                | 9.10x10 <sup>6</sup> kg   | 8.15x10 <sup>6</sup> kg   |
| Solar still effective area              | 2.68x10 <sup>6</sup> m <sup>2</sup>   | 1.79x10 <sup>6</sup> m <sup>2</sup>   |
| Electrolysis energy input               | 50.0x10 <sup>6</sup> kwh  | 35.8x10 <sup>6</sup> kwh  |
| Average power level, 4 hours duty cycle | 12.5x10 <sup>3</sup> Mw   | 8.95x10 <sup>3</sup> Mw   |
| Peak power level, at local noon         | 16.6x10 <sup>3</sup> Mw   | 11.9x10 <sup>3</sup> Mw   |
| Thermal energy to turbine               | 105.4x10 <sup>6</sup> kwh   | 67.0x10 <sup>6</sup> kwh  |
| Incident solar energy required          | 137.8x10 <sup>6</sup> kwh   | 78.3x10 <sup>6</sup> kwh  |
| Solar collector area required           | 47.3x10 <sup>6</sup> m <sup>2</sup><br>47.3 km <sup>2</sup><br>(6.88 km square) | 26.9x10 <sup>6</sup> m <sup>2</sup><br>26.9 km <sup>2</sup><br>(5.19 km square) |

TABLE 2

| Item  | Requirement                                       | Rough Cost Assessment of Macro System |                                    |                                       | Item Cos<br>Million \$ |
|---|---|---------------------------------------|------------------------------------|---------------------------------------|------------------------|
|   |   | No.<br>Units                          | Unit Size                          | Cost Factor                           |                        |
| Solar Collector                                   | 48 km <sup>2</sup>                                | 960                                   | 100x500m                           | \$5/m <sup>2</sup>                    | 240                    |
| Focal Boiler                                      | 500 km  | 960                                   | 500 m                              | \$100/m                               | 50                     |
| Turbine & Condenser                               | 16,600 Mw (peak)                                  | 48                                    | 345 Mw                             | \$20/kw                               | 335                    |
| Generator, dc                                     | 16,600 Mw (peak)                                  | 48                                    | 345 Mw                             | \$7/kw                                | 115                    |
| Electrical Conduits                               | 990,000 Mva-mi                                    | 96                                    | 0.62 mi                            | \$20/kw                               | 20                     |
| Depth water System                                | 7x10 <sup>6</sup> T/day H <sub>2</sub> O          | 48                                    | 36,000 gpm ?                       |                                       | 5                      |
| Solar Still                                       | 2.7x10 <sup>6</sup> gal/day                       | --                                    | --                                 | \$1.00/ft <sup>2</sup>                | 30                     |
| Water Electrolyzer                                | 560x10 <sup>3</sup> lb/hr, H <sub>2</sub>         | 48                                    | 12,000 lb/hr                       | \$150/lb/hr                           | 85                     |
| Gas Storage (depth)                               | 40x10 <sup>6</sup> ft <sup>3</sup> (actual vol.)* | 48                                    | 1x10 <sup>6</sup> ft <sup>3</sup>  | \$1.00/gal                            | 50                     |
| Gas Accumulator                                   | 40x10 <sup>3</sup> ft <sup>3</sup> (actual vol.)* | 1                                     | 40x10 <sup>3</sup> ft <sup>3</sup> | ?                                     | 15                     |
| Service Power Unit                                | 400 Mw  | 1                                     | 400 Mw                             | \$100/kw                              | 40                     |
| Hydrogen Liquefier                                | 670 T/day   | 1                                     | 670 T/day                          | \$25x10 <sup>6</sup> for<br>250 T/day | 55                     |
| Oxygen Liquefier                                  | 5360 T/day  | 1                                     | 5360 T/day                         | \$8/T/day                             | 45                     |
| Cryogenic Storage                                 | 18x10 <sup>6</sup> gal*                           | 1                                     | 18x10 <sup>6</sup> gal             | \$1.5/gal                             | 30                     |
| Flotation Units                                   | 5 per L-3 module                                  | 240                                   | --                                 | @ \$1x10 <sup>6</sup>                 | 240                    |
| Platform Structure                                | Forms L-3 module                                  | 48                                    | 1 km <sup>2</sup>                  | @ \$1x10 <sup>6</sup>                 | 50                     |
| Docking Facility                                  | "Descartes" class cryo-<br>tanker capability      | 1                                     | --                                 | @ \$10x10 <sup>6</sup>                | 10                     |
| Delivered hardware subtotal                       |   |                                       |                                    |                                       | 1415                   |
| Integration, installation & test services (@ 10%) |   |                                       |                                    |                                       | 142                    |
| Total rough cost estimate                         |   |                                       |                                    |                                       | \$ 1557                |

Summary: Macro system sized for 1000 Mw continuous equivalent production of the cryogenic hydrogen and oxygen energy form is estimated to cost in the vicinity of \$ 1.5 billion. This is for the "current" technology version without system optimization or refinements. No credit is taken for collateral product potentialities. Dollars are "today's".

\* Total volumes for both hydrogen and oxygen; storage would be in separate containers.

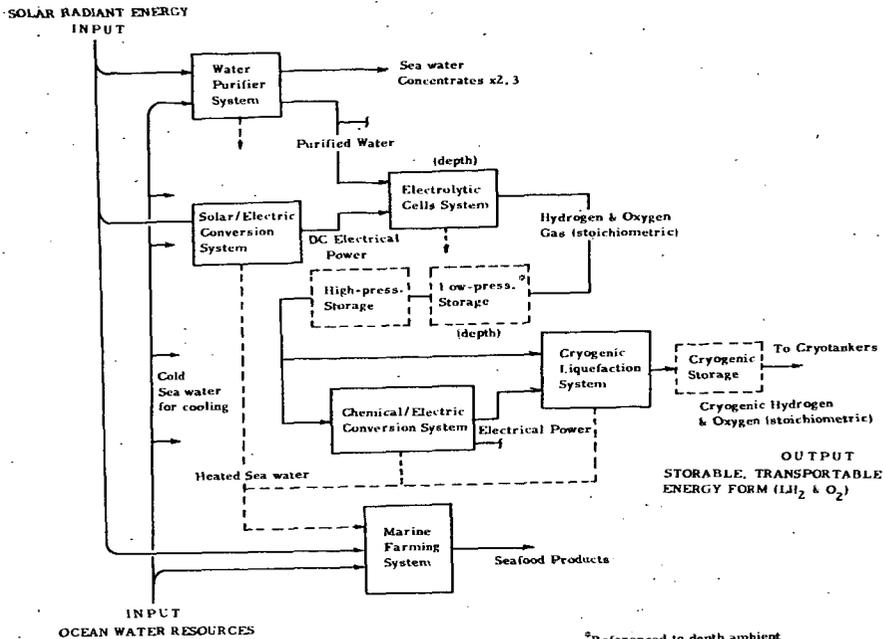


Figure 1 - Block Diagram of Macro System

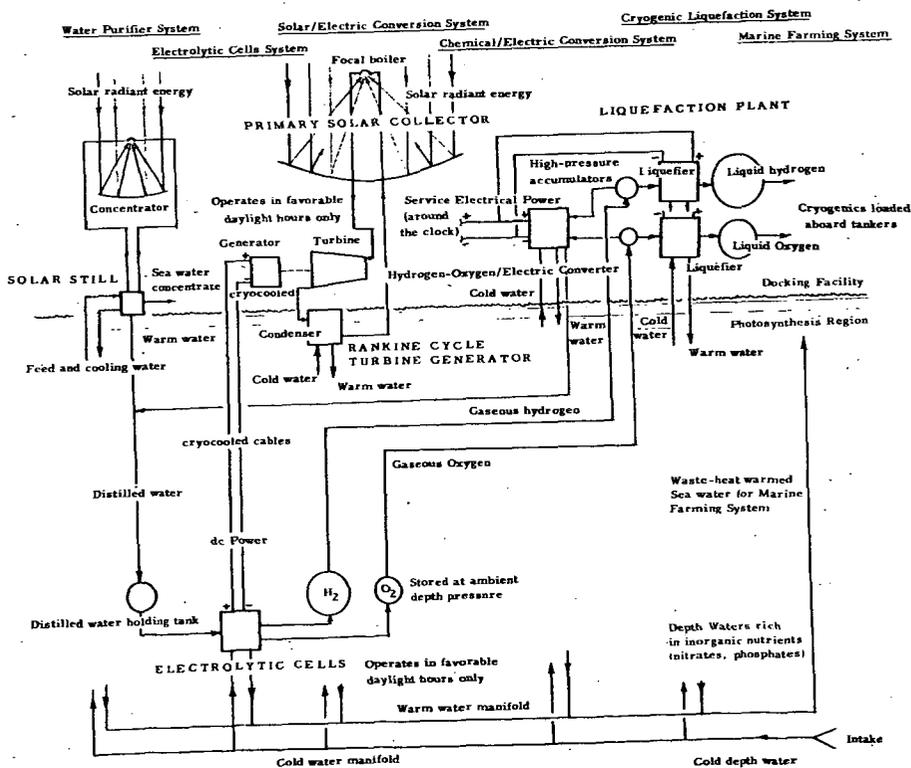


Figure 2 - Pictorial Schematic of Macro System

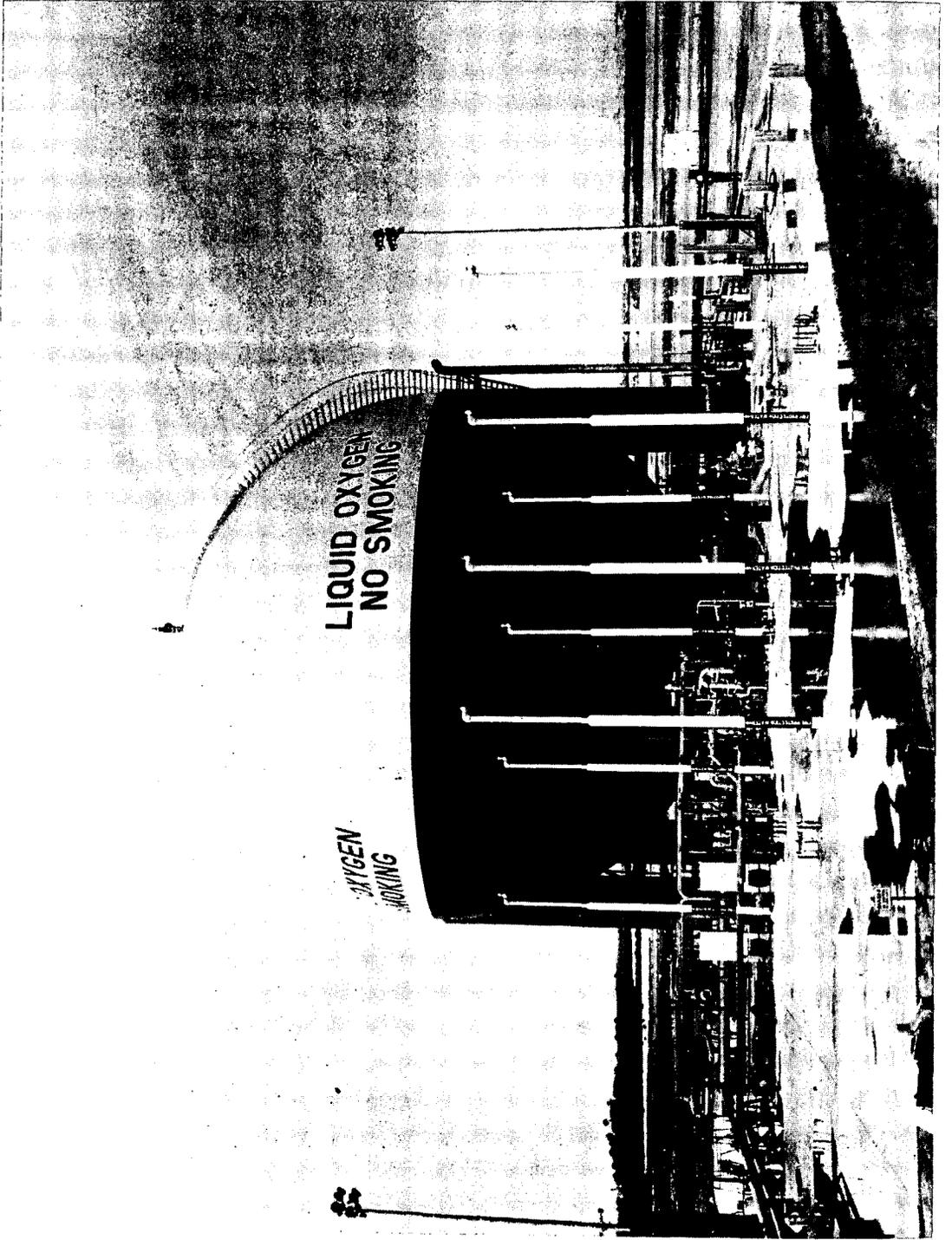


Figure 3 - Large Liquid Oxygen Storage Container

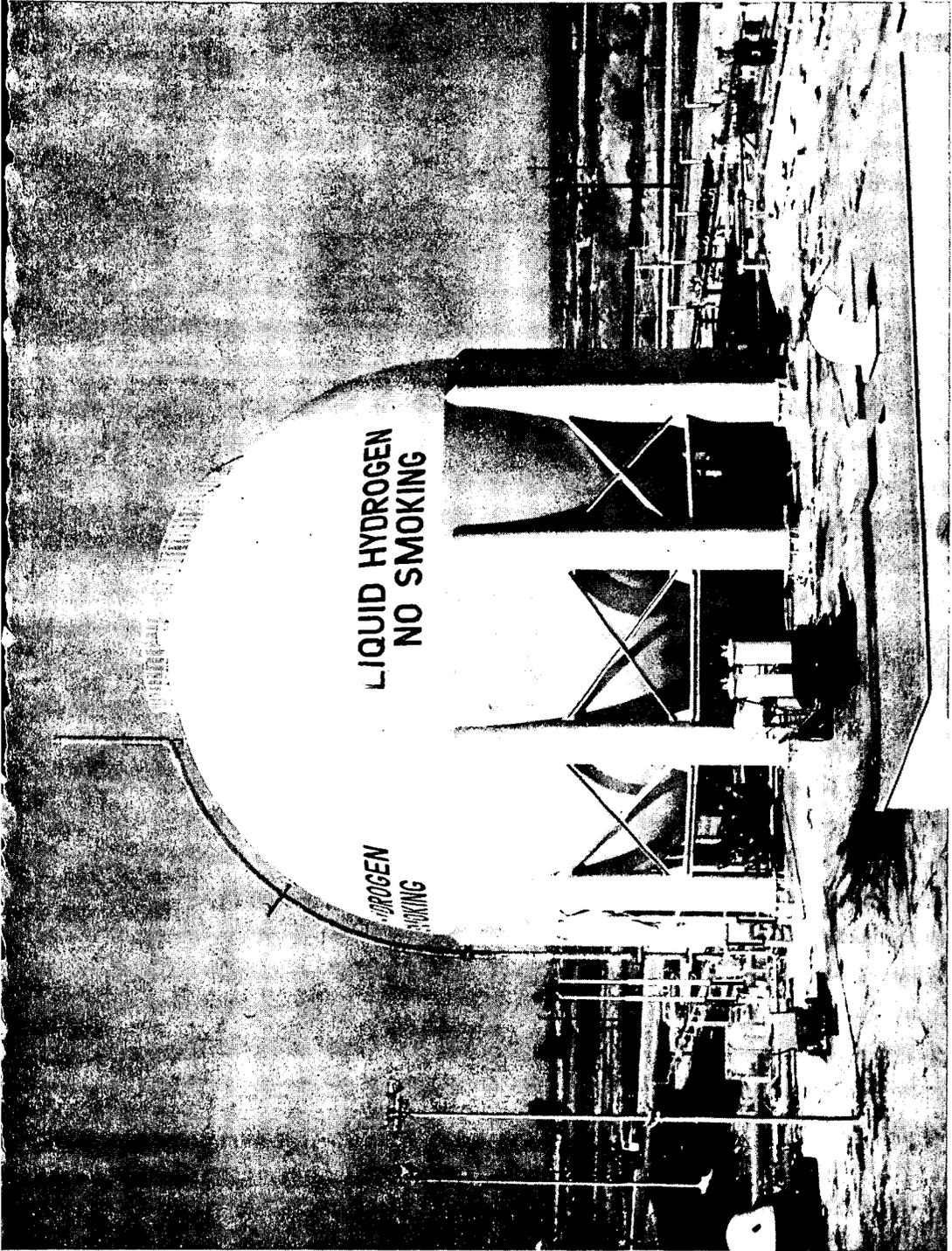


Figure 4 - Large Liquid Hydrogen Storage Container

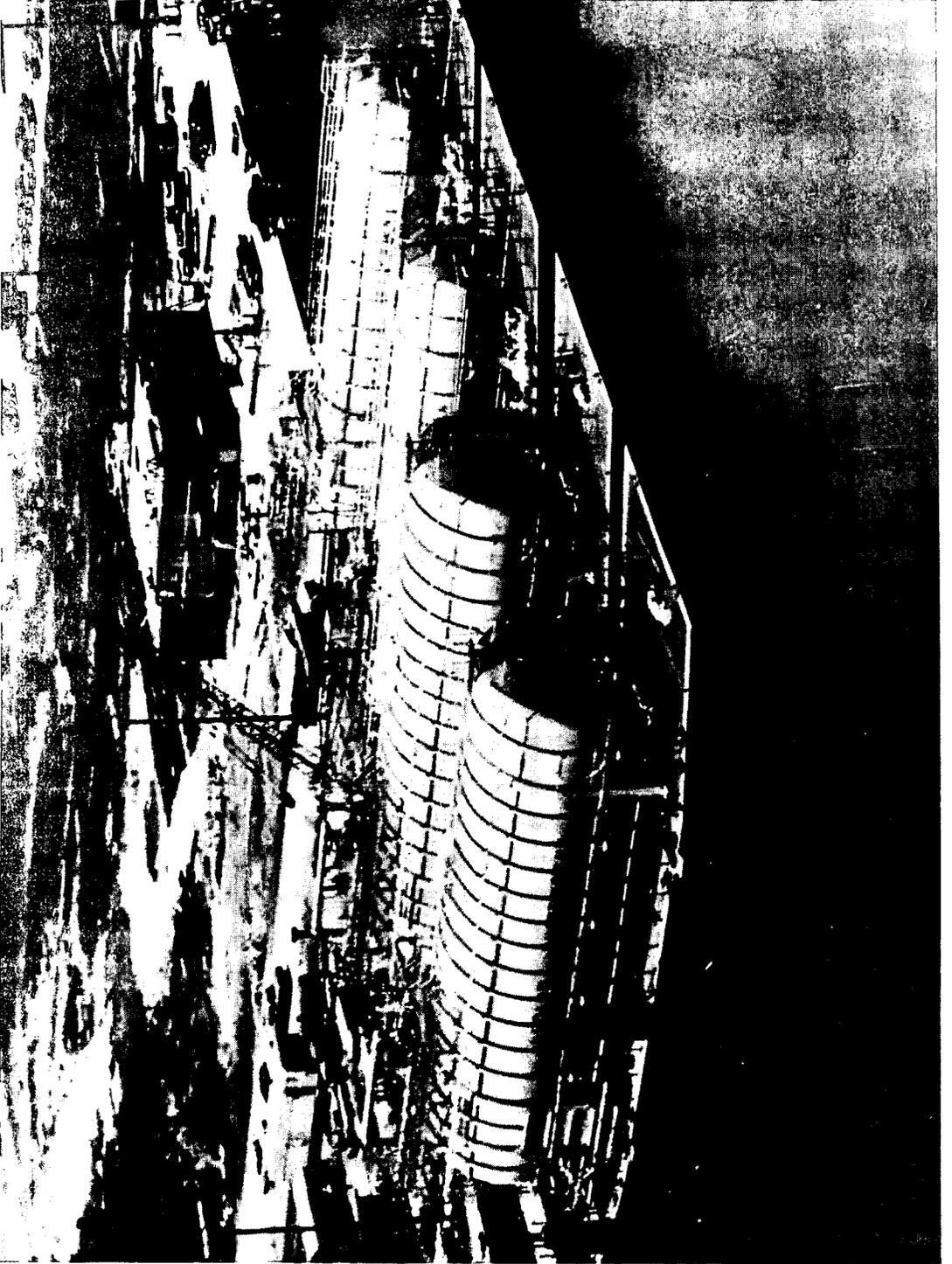


Figure 5 - Liquid Hydrogen (foreground) and Liquid Oxygen (background) Barges

Note: Langley is equivalent to 1 cal g(mean) cm<sup>-2</sup>

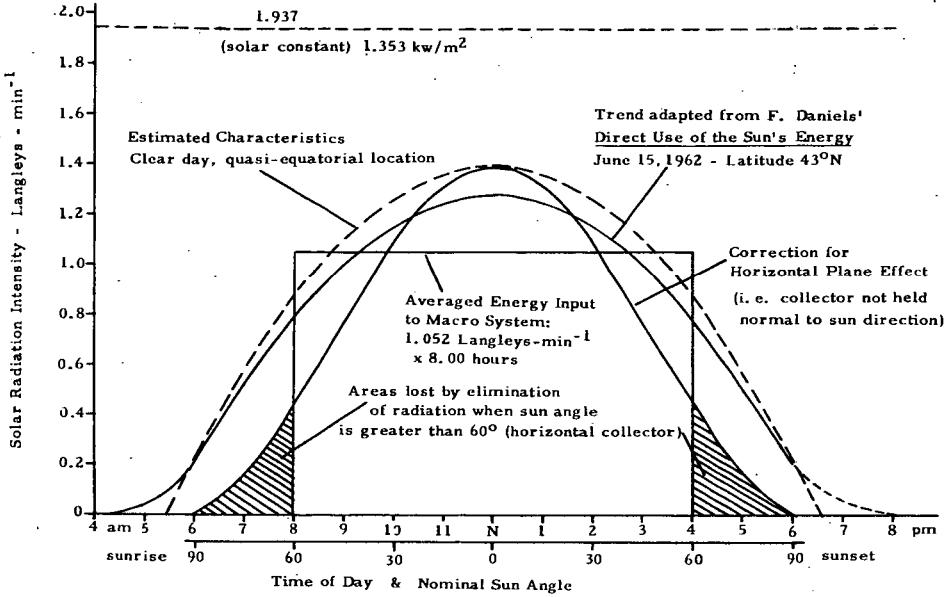


Figure 6 - Solar Energy Diurnal Characteristics

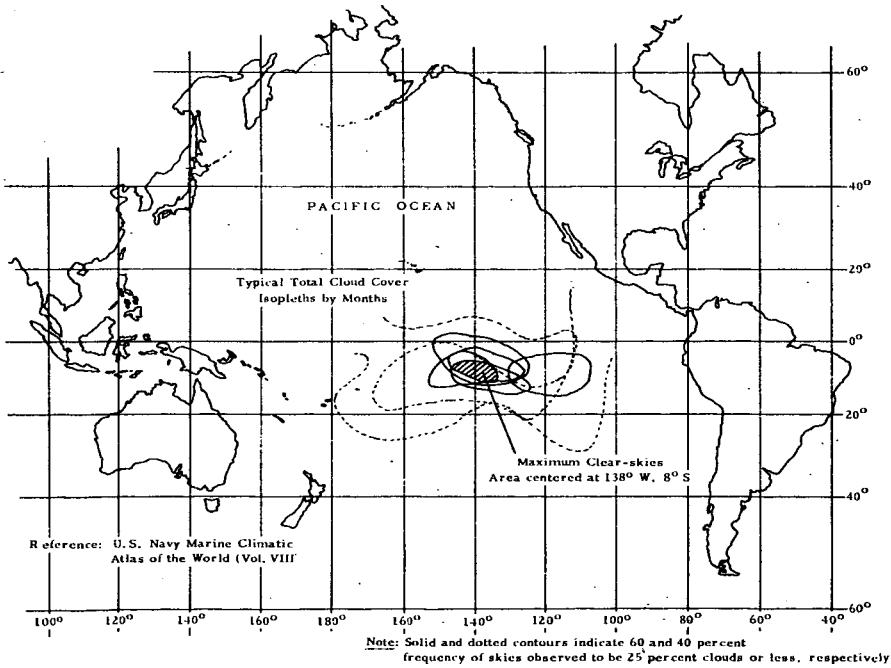


Figure 7 - Cloud Cover Minimization Trends for Mid-Pacific Region

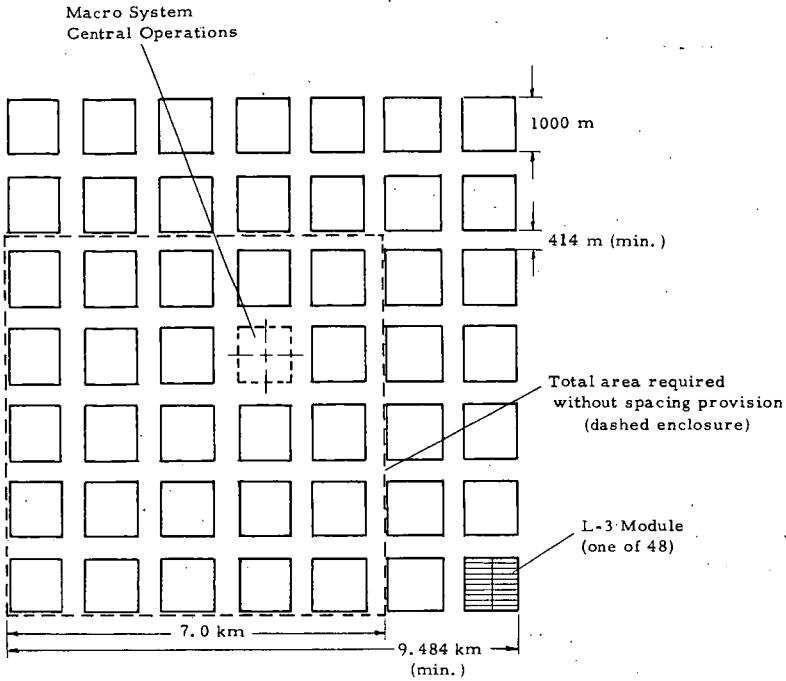


Figure 8 - Representative Overall Layout of Macro System

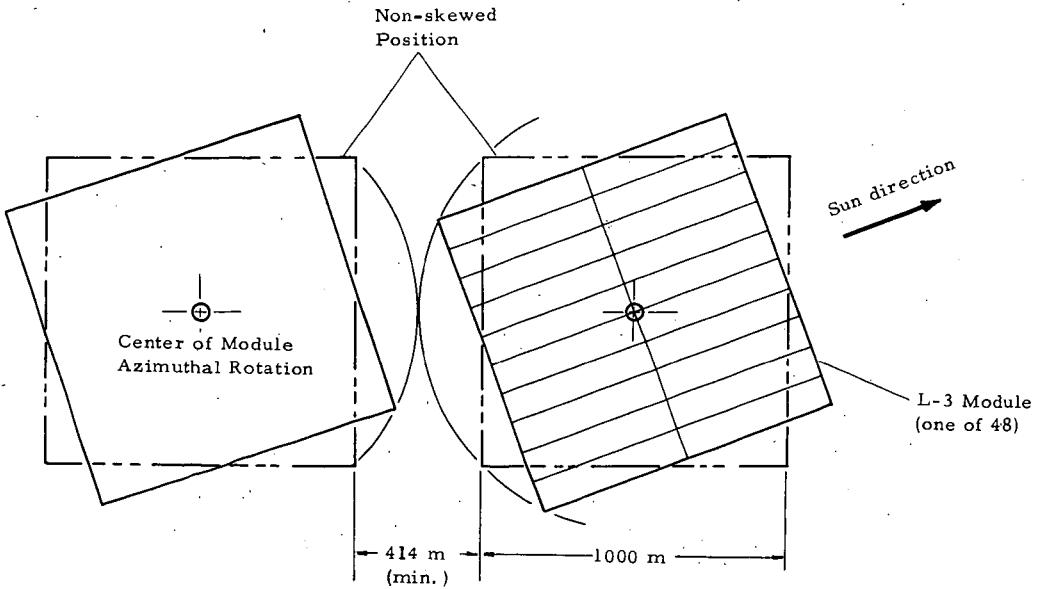


Figure 9 - Spacing Requirements Due to Azimuthal Rotation Capability

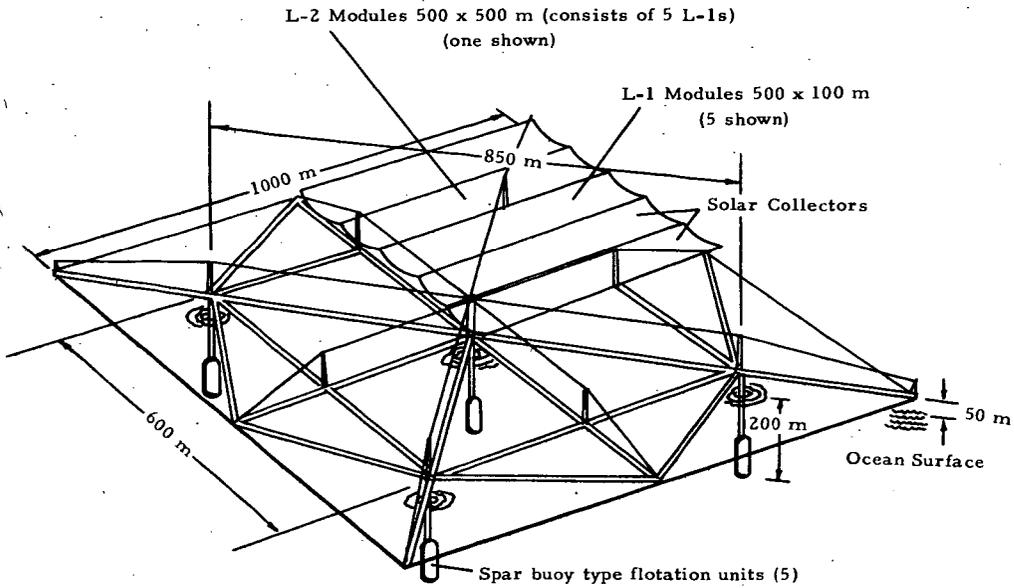


Figure 10 - Conceptual Configuration for Basic Macro System Module ( 1 of 48 )

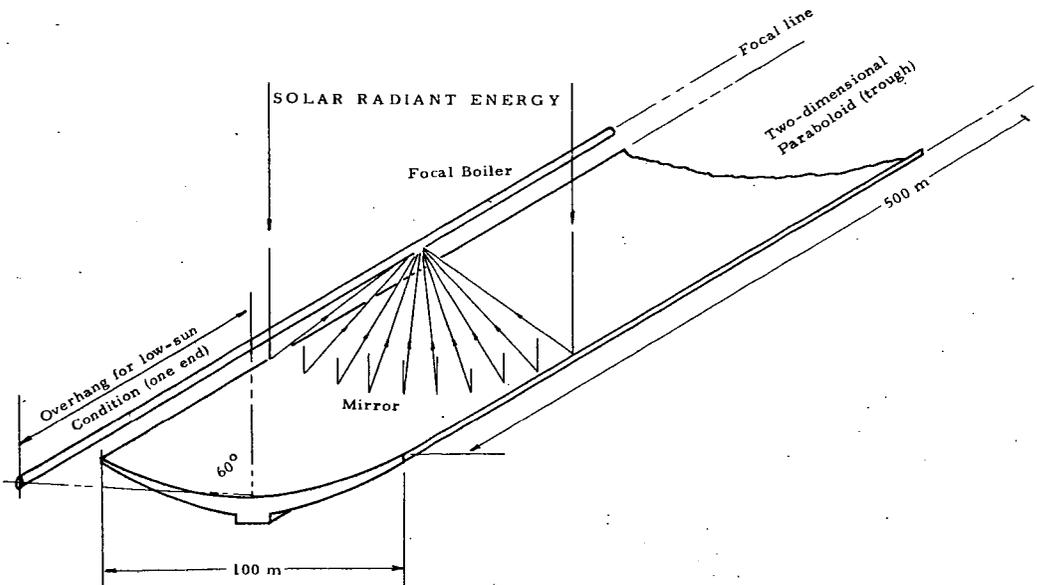


Figure 11 - Basic Geometry of Solar Collector Scheme

## REFUELABLE BATTERIES

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In the non-fossil fuel society, it is proposed (1) that electricity will be generated by nuclear power stations which will be situated in underpopulated areas for environmental and safety reasons. Since gas transmission is cheaper than electricity transmission and since the demand for power is not constant, it is suggested (1) that hydrogen will be produced at these nuclear power stations and transported via pipeline to the consumer where it will be used for heating, cooking etc. and for the local production of electricity via fuel cells.

In this hydrogen fueled society, electrochemical power sources will replace the hydrocarbon fueled equipment which is presently used for many mobile and portable applications. The high power applications (e. g., automobiles, trucks) may be served by fuel cells. However fuel cells are only practical in situations where 1) the total energy requirement of the system is high and the weight of hydrogen is a large percentage of the total system weight and 2) the required power is sufficiently high to justify the weight of the ancillary controls. They are not suitable either for low power applications since the fuel cell has a minimum weight which is determined by the weight of the ancillary equipment, or for portable applications since the hydrogen tanks cannot be readily carried.

Thus there are many medium power (1/2 KW - 5 KW) devices (e. g., outboard motors for boats, lawnmowers, motor bikes, camping equipment) which use hydrocarbon fueled engines at present but which will require low cost, high energy and power density batteries in the non-fossil fuel society.

Lead acid, nickel/cadmium, nickel/iron secondary batteries will probably continue to provide rechargeable energy sources for applications where their low energy density and cost/KW are relatively unimportant. However for reasonable cycle life (e. g., > 200) all of these storage batteries have energy densities less than 20 watt-hours/pound and this is a major deterrent to their use in many lightweight portable devices or traction vehicles where cost, weight and operating range are important.

The limitations of the present storage batteries have stimulated research in high energy density systems such as 1) secondary zinc/air cells, 2) organic electrolyte cells and 3) molten salt cells. However these internally rechargeable batteries (i. e., charged by applying a direct current to the electrodes while they are contained in the battery) suffer from the following limitations:

- 1) They have limited cycle life at high depths of discharge,
- 2) For long cycle life (hence low depths of discharge) storage batteries have significantly lower energy densities than primary batteries,
- 3) Charging at low rates (i. e., overnight) limits the type and extent of use of the device,
- 4) The charging efficiency at high rates of charge is low.

Thus a new battery system is required for the medium power applications in the hydrogen fueled society and refuelable batteries are one possibility.

In this paper we will review the present technology of refuelable metal/air batteries and discuss the future research required on these systems. We have not set out to make a clear cut case for these batteries over other electrochemical power sources (such as fuel cells and molten salt batteries) but rather our aim is to point out the advantages and disadvantages of the metal/air system in the hydrogen

fueled society. In particular we will describe novel methods of recharging the anodes which will be applicable due to the availability of hydrogen.

### 1. Refuelable Batteries

In principle a refuelable battery is one in which the discharged plates can be easily replaced. In practice it is simpler to replace only the anode and mechanically rechargeable metal/air batteries are the only refuelable batteries which have been developed.

In metal/air batteries, the oxidant (air) reacts with an electropositive metal to form a metal oxide (or hydroxide) and electrical energy. Mechanically rechargeable metal/air cells are refueled by withdrawing only the discharged anodes and replacing them with new ones. The advantages of these batteries are:

- 1) The discharge efficiency of the anodes is 80% or greater and this allows high energy densities to be obtained,
- 2) They are capable of giving high power densities,
- 3) They can be refueled (recharged) rapidly since the anodes can be readily removed and replaced,
- 4) The charging efficiency is high since the spent anodes may be recharged externally at a low rate,
- 5) There is flexibility in anode regeneration (Section 6),
- 6) The oxygen cathode is used only during discharge and then it is capable of many cycles.

Thus it can be seen that refuelable batteries could be recharged rapidly and still use off-peak power for anode regeneration so that extra fuel cell capacity would not be required for battery charging (low capital cost).

By reviewing the present technology of mechanically rechargeable metal/air batteries, we can define some of the limitations of such batteries and then describe the improvements that are required and the likelihood of their being achieved.

We will restrict this review to the following cells: zinc/air, aluminum/air, magnesium/air, iron/air and cadmium/air. These systems have been included since: 1) they have high theoretical energy densities and 2) several studies have been made with them so that their problems are well-defined. Other cells with high theoretical energy densities (e. g., lithium/air and sodium amalgam/air) have not been included since their state of the art is not far advanced (2).

Lead/air batteries have not been included (although the anode is well-developed and carbonate formation in the acid electrolyte is not a problem) since: 1) they have a low theoretical energy density (183 Wh/lb), 2) the cost per watt-hour of lead is high (.77¢/KWh), 3) only expensive, noble metal cathode catalysts are stable in the acid electrolyte, 4) the cathode polarization is significantly higher in acid than in alkaline electrolyte (3) and 5) Pt dissolves in the electrolyte and is transported to the anode (i. e., lowers its  $H_2$  overvoltage), thus decreasing the anode shelf life and preventing efficient recharge.

### 2. Design of Refuelable Batteries

Mechanically rechargeable zinc/air batteries have been used by the military for communications equipment (2, 4-6) and similar designs have been used for Al/air (2, 7), Mg/air (8-11), Fe/air (12) and Cd/air (2, 13) cells.

The basic cell consists of two cathodes (0.200 - 0.250 inches apart) connected in parallel and separated by a porous zinc anode inserted between them.

With this design it is simple to remove a discharged anode from the bicell and replace with a new one. Figure 1 shows the arrangement of anode and cathode, Figure 2 shows the bicell design and Figures 3 and 4 show 2 battery designs.

The present zinc anodes are made from zinc powder which is impregnated with dry potassium hydroxide and then pressed to the required dimensions. The electrodes are wrapped in a separator (a few thousandths of an inch thick) and stored in aluminum/mylar envelopes to retard water pick-up and zinc oxidation.

The air electrodes (Figure 1) must be held flat and parallel to the negative plate to minimize  $iR$  losses in the cell and to prevent electrode shorting but the lightweight air cathodes are not sufficiently rigid to be dimensionally stable. Thus non-compressible, porous spacers are placed in the air chambers between bicells and then subjecting the whole cell stack to an external pressure which is applied by a screw adjustment (Figure 4). Pressure is released to allow refueling (replacement of zinc plates) and reapplied before the next discharge. Obviously this requires that the tolerances on the dimensions of the zinc electrodes must be within a few thousandths of an inch.

Air flow is generally achieved by natural convection and the space between the bicells is therefore a critical design factor. The air spacing is a compromise between the need to provide sufficient air for high discharge rates and the need to minimize the volume of the battery. Forced air convection is used to increase the battery power density. However this results in a lower energy density due to the extra weight of the fan and to the parasitic current drawn from the battery and in faster carbonation of the electrolyte (Section 5).

### 3. Technology of Metal/Air Cells

Table 1 gives values of the E.M.F.'s ( $E$ ), the theoretical energy densities, the thermoneutral voltages ( $E_T$ ) (2) and the anode cost per theoretical KWh of metal/oxygen cells. The theoretical energy densities were calculated from the electrochemical equivalent of the anode and the cell E.M.F.

Table 1 lists the thermoneutral voltages of the metal/oxygen couples. This parameter is defined as  $-\Delta H/RT$ , where  $\Delta H$  is the enthalpy of the cell reaction. It is an abstract quantity and it represents an unachievable voltage at which no heat would be generated by the cell.

The thermoneutral voltage permits simple calculations of heat generation in metal/air cells. For example, the ratio of the heat generation to electrical power is given by  $(E_T - E_C)/E_C$ , where  $E_C$  is the cell operating voltage, and this ratio is useful in comparing the heat generation of the metal/air cells.

Figure 5 shows the polarization curves for metal/air cells. Clearly these polarization curves will depend on many parameters (e.g., anode and cathode manufacturing technique, anode porosity, cathode catalyst etc.) which will vary from manufacturer to manufacturer. However the curves in Figure 5 do give an indication of the expected initial performance of the metal/air cells.

The polarization curves for Al/ and Mg/air cells were obtained with a chloride electrolyte (NaCl or KCl) while those for the other metal/air batteries were obtained with an alkaline electrolyte (31% KOH). The curve for Zn/air cells

TABLE 1

Energy Densities of Selected Metal/Oxygen Couples

| Reaction                            | E. M. F. (1)<br>(V) | Energy Density<br>(Wh/lb) | Thermoneutral<br>Voltage (V)(3) | Cost(4)<br>(\$/theoretical KWh) |
|-------------------------------------|---------------------|---------------------------|---------------------------------|---------------------------------|
| $2Al + 3/2 O_2 \rightarrow Al_2O_3$ | 2.71                | 3665                      | 2.93                            | 0.07                            |
| $2Mg + O_2 \rightarrow 2MgO$        | 3.09                | 3090                      | 3.11                            | 0.12                            |
| $2Fe + 3/2 O_2 \rightarrow Fe_2O_3$ | 1.28                | 836(5)                    | 1.42                            | 0.10                            |
| $2Zn + O_2 \rightarrow 2ZnO$        | 1.62                | 603                       | 1.80                            | 0.25                            |
| $2Cd + O_2 \rightarrow 2CdO$        | 1.20                | 260                       | 1.35                            | 9.14                            |

1. For air ( $P_{O_2} = 0.21 \text{ atm.}$ ), 11mV should be subtracted from these potentials
2. Calculated from the electrochemical equivalents of the metals and the cell E. M. F. 'B'
3. Thermoneutral Voltage =  $-\Delta H/nF$
4. Based on the cost of metal ingot
5. This value is for the oxidation of the metal to the 3 valent state. The energy density for the oxidation of Fe to the 2 valent state is 557 Wh/lb.

is the best literature value (14) and it was presumably obtained with thin electrodes since the cell voltage depends on the anode thickness (15). For example, the voltage at  $100\text{A}/\text{ft}^2$  for a zinc/air battery with a 0.200 inch thick anode was 0.1V less than the value given in Figure 5 (4). The polarization curve for the Cd/air cell was obtained (2) with a 0.030 inch thick commercial Cd anode and those for the Al/ and Mg/air cells were obtained with alloy sheet anodes. No polarization curves have been reported for alkaline electrolyte Fe/air cells in the literature and the data given in Figure 1 was calculated on the assumption that the Fe/air cells voltage would be 0.4V less than that of Zn/air cells. This assumption agrees with the cell voltages calculated from half cell data of iron electrodes (16) and of air cathodes (Figure 6).

Table 2 gives values of the ratio of the heat generation to electrical power at a discharge rate of  $40\text{mA}/\text{cm}^2$ . This data was calculated using the value of the operating voltage at  $40\text{mA}/\text{cm}^2$  from Figure 1 and the cell thermoneutral voltage (Table 1). Dissipation of this heat is important even in zinc/air batteries (Table 2).

TABLE 2

Heat Generation by Metal/Air Cells

| Couple | $\left( \frac{\text{Heat Generation}}{\text{Electrical Power}} \right)^{(1)}$ at $40\text{mA}/\text{cm}^2$ |
|--------|--|
| Al/air | 1.15   |
| Mg/air | 1.78   |
| Fe/air | 0.61   |
| Zn/air | 0.46   |
| Cd/air | 0.55   |

(1) Calculated from the thermoneutral voltages (Table 1) and the operating voltages at  $40\text{mA}/\text{cm}^2$  (Figure 5).

## a) Zinc/Air

Zinc anodes offer a compromise between Al and Mg anodes on one hand which have high theoretical energy density but poor use-life and polarization characteristics, and Cd anodes which have low theoretical energy density but good shelf-life and polarization characteristics. The anodic behaviour of zinc is determined by its relatively high hydrogen overvoltage and the solubility of zinc oxide in alkaline solution. The former means that Zn has a relatively long shelf-life and this can be further increased by amalgamation while the high solubility of zinc oxide prevents zinc passivation and allows high discharge rates to be obtained.

The anode thickness and porosity are determined by the required energy and power densities and typical values of these parameters are 0.05" - 0.250" and 75% - 85% respectively. The energy density of the cell is increased by increasing the cell capacity per unit area of cell (i. e., increase anode thickness and decrease anode porosity). However high power densities are only obtained by increasing the electrode porosity but this results in a lower weight of zinc in the electrode and hence in a lower energy density. Thus there is a trade-off between energy and power density.

A major limitation of the present zinc/air batteries is the heat genera-

tion at high rates of discharge. From the value of the thermoneutral voltage of this cell (Table 1) it can be seen that a zinc/air cell delivering electrical power at 0.9V must dissipate an equivalent amount of energy as heat. This is undesirable since it results in an increase in cell temperature which consequently: 1) increases the rate of zinc anode self-discharge and 2) causes water loss from the cells by evaporation.

It is difficult to compare values of energy density and power density from the literature since these two parameters are dependent on operating temperature, duty cycle of the battery and the cathode catalyst. Energy densities of 80 Wh/lb with power densities of 45 W/lb have been reported (5) for a 1/3 KW battery. A larger system (1 KW), which is closer to the system required in the hydrogen fueled society, demonstrated a maximum power-density of 26 W/lb at an energy density of 30 Wh/lb (14). The author (14) projected that further improvements might be possible up to limits of 80 W/lb and 80 Wh/lb but these goals have not been achieved at present. Neither of these batteries used forced air convection and therefore cannot be used to project power and energy densities for larger (5 KW) batteries.

The 1/3 KW battery mentioned above is used for military communications equipment. The cost of the batteries and of the replacement anodes is \$400/KWh and \$40/KWh, respectively. Thus with 100 discharge cycles, the operating cost is \$44/KWh. This is too expensive for non-military applications and it is necessary to decrease both the anode manufacturing cost and the cathode catalyst cost.

In summary the problems which limit the use of zinc/air batteries at present are:

- 1) The use-life of the Zn anode is limited and it is preferable to use these cells continuously rather than in intermittent operation,
- 2) The lower discharge efficiency of thick Zn anodes at high rates of discharge,
- 3) The heat generation at high discharge rates,
- 4) Since the oxidized state is soluble, the zinc oxide in the discharged anodes slumps to the bottom of the current collector and thus the shape of the electrode must be reformed during anode regeneration,
- 5) The cost and stability of the cathode catalyst.

#### b) Aluminum/Air

The high cell E.M.F., the high theoretical energy density, its low cost per watt-hour and the ease of manufacture of anodes makes aluminum an attractive anode for metal/air cells. However the aluminum/air cell has two major problems: 1) the discharge of aluminum anodes is irreversible and 2) the self-discharge of aluminum anodes is very rapid.

Aluminum electrodes dissolve rapidly on open circuit in alkaline solution with the evolution of hydrogen and consequently Al/air cells generally use either a neutral (KCl) or acidic ( $\text{AlCl}_3$ ) electrolyte (2). However even in this electrolyte, pure aluminum dissolves rapidly on open circuit and polarizes excessively. More reversible behaviour is exhibited by aluminum/tin alloys. Optimum performance (2) was obtained with the aluminum/tin alloy A6 (Olin Mathieson Chemical Corp.) and Figure 5 (2) shows the polarization curve of an Al/air cell with this alloy in a 2.5 MKCl solution.

As a consequence of the high self-discharge rate of Al alloy anodes and of the cell irreversibility, a major limitation of Al/air cells is the heat generation and Table 2 shows that for cells operating at the same power, Al/air cells generate approximately three times more heat than zinc/air cells. This heat generation results in a high rate of water loss, it creates hazardous and runaway conditions

and it severely decreases the anode shelf-life. It may be alleviated by using a large electrolyte reservoir or by forced air convection, but neither approach permits high energy density designs.

The advantages of Al/air cells are that the anodes can be made from sheets of the metal alloy which are simple and cheap to manufacture and they use a cheap, CO<sub>2</sub> rejecting, safe electrolyte which can be easily handled by the consumer.

No work has been reported on operable, mechanically rechargeable battery systems. Single cell data in alkaline electrolyte (7), have been used to project an energy density of 200 Wh/lb and a power density of 76 W/lb. However these values were calculated on the basis of the weight of the reactants only and the electrolyte and Al were separated while the cell was on open circuit. It is vital that the system includes adequate provision for cooling, since the experimental design data is based on cell voltages of 0.9 - 1.25 volts which indicates heat generation at 2 to 3 times the rate of power generation. Thus the total battery weight will markedly decrease the values of energy and power density and the energy and power density data quoted above (7) is considerably greater than would be obtained in an operable system.

#### c) Magnesium/Air

Magnesium anodes exhibit the same disadvantages as aluminum anodes, i. e., irreversible polarization characteristics and high self-discharge rates. In addition, the discharge product of Mg anodes is a solid sludge which masks the bottom portion of the Mg anode and makes anode removal difficult (8, 9, 11).

In alkaline electrolyte magnesium anodes passivate and Mg/air cells utilize a sodium chloride solution (11). Even in this electrolyte pure magnesium anodes polarize excessively and this has resulted in the use of magnesium alloys which are often ternary alloys of magnesium, aluminum and zinc. Figure 5 shows the polarization curve for a Mg/air battery using the Mg alloy AZ61 (Olin Mathieson Chemical Corp.) in 18% NaCl solution (11). As with Al alloys, low Mg alloy polarization is associated with a high rate of self-discharge and the alloy AZ61 gave the optimum performance.

The product of Mg anode discharge in a Mg/air cell is magnesium hydroxide (or hydroxylchloride) (11). This product remains in the cell as a sludge and the volume of the cell must be sufficiently large to contain this product and to allow easy removal of the anode after discharge.

Heat generation due to anode self-discharge and cell irreversibility is an even greater problem with Mg/air cells than with Al/air cells (Table 2). Thus Mg/air requires a water reservoir and/or forced air convection to aid in cell cooling and it has been shown that these cells operate more efficiently at low temperatures (10).

A 23 cell Mg/air battery of similar design to that in Figure 3 has been reported (11). From data given in the paper (11) and assuming the battery weight (4) is the same as that of zinc/air batteries (Figure 3), the battery energy density was approximately 65 Wh/lb and the maximum power density was 50 W/lb. Water evaporation during battery operation was a major problem and water had to be added to the cell, otherwise the Mg was not consumed uniformly and the cell voltage decayed (11).

#### d) Iron/Air

Iron anodes have been used for over fifty years in Ni/Fe batteries. The

advantage of this material is its availability, abundance and basically low cost.

The theoretical energy density for iron/air cells (Table 1) was calculated assuming the oxidation of iron to the 3 valent state. However the anodic discharge of an iron electrode in alkaline electrolyte occurs at two discrete voltage levels. The first at  $-0.8\text{V}$  vs Hg/HgO corresponds to the conversion of iron to ferrous hydroxide while the second at  $-0.65\text{V}$  vs Hg. HgO corresponds to the conversion of iron to the three valent state (16, 17). The iron electrode is normally operated only to the first discharge voltage plateau (i. e., 2 valent state) and the theoretical energy density for the iron/air cell is then 557 Wh/lb.

Sintered iron electrodes have the ability to be deeply discharged and hence make lightweight, low cost iron electrodes a possibility. Low electrode cost, however, is dependent on developing an inexpensive means of increasing the  $\text{H}_2$  over-voltage of iron. This is presently achieved by refining the iron oxide powder to a high degree of purity before reducing it to powdered iron particles but this adds considerably to the electrode cost.

The advantages of iron/air cells compared with zinc/air cells are:

1. The lower cost of iron/KWh (Table 1),
2. Iron oxide is cation conductive and hence less prone to passivation,
3. There is no material slumping in the discharged anode since the oxidized state of the iron electrode is relatively insoluble.

No mechanically rechargeable Fe/air batteries have been reported although it has been claimed (12) that energy densities of 65 Wh/lb are achievable.

#### e) Cadmium/Air

The cadmium/air couple has the lowest theoretical energy density of the couples considered in this paper (Table 1) but thin (0.030 inches) cadmium electrodes are readily available and hence development costs for this cell should be relatively low. The cadmium/air cell (2) has a lower voltage at all current densities than the zinc/air cell (Figure 5) and the practical energy density is lower.

Refuelable cadmium/air batteries could be manufactured with today's technology but would probably not provide high enough energy or power densities to justify their high cost. Thus the lower cell voltage and the lower electrochemical equivalents probably (2) restrict the maximum achievable energy density for refuelable Cd/air cells to 20 Wh/lb.

The advantages of cadmium/air cells compared with the zinc/air systems are: 1) Cd anodes have good shelf-life, 2) Cd anodes have long cycle life and 3) the anode could be recharged without using d. c. power (18) which may be particularly advantageous in the hydrogen fueled society (Section 6).

#### f) Air Cathode

The cathode structure used in most metal/air systems (2) consists of a mixture of catalyst and Teflon (19) supported on a hydrophobic film with the current collected by an expanded metal mesh embedded in the catalyst/Teflon matrix. The Teflon aids in the formation of an air/electrolyte/catalyst three phase boundary which ensures that the maximum catalyst area is used efficiently in the electrochemical reaction. The hydrophobic film prevents electrolyte seepage from the cell and acts as the outer case of the bicell (Figure 2). The advantages of these electrodes are: 1) they are lightweight and the oxidant does not contribute to the cell weight, 2) they exhibit high limiting currents, 3) they exhibit a stable voltage

during discharge and 4) they exhibit a flat polarization curve which permits operation of the electrode over a wide current density without large voltage variations.

Figure 6 (2) shows the polarization curves for oxygen reduction on a Teflon bonded Pt electrode (Pt loading  $5\text{g}/\text{ft}^2$ ) in air saturated 31% KOH solution and in air saturated 2.5 M KCl solution. The cathode overvoltage (i. e.,  $E - E_C$ ) was plotted versus the current density (Figure 6), in order to compare the cathode polarization in alkaline and chloride electrolyte.

Comparison of the cathode polarization in alkaline electrolyte (Figure 6) with the Zn/, Fe/ and Cd/air cell polarization (Figure 5) indicates that the cathode polarization is the major fraction of total cell polarization up to  $100\text{A}/\text{ft}^2$ . Thus most of the heat is generated at the cathode in these cells and a decrease in the cathode polarization will markedly decrease the heat generated as well as increase the battery power density. A decrease in cathode polarization may be achieved either by increasing the catalyst activity (i. e., decrease the activation polarization) or by improving the electrode structure (i. e., decrease the concentration polarization).

Platinum has been used as the cathode catalyst in those applications (military) where high energy density is more vital than battery cost, but Pt cathodes are a major cost limitation of commercial Zn/, Fe/ and Cd/air batteries. For example, a zinc/air battery with a Pt catalyzed cathode ( $5\text{gms}/\text{ft}^2$  of Pt) gave  $100\text{ W}/\text{ft}^2$  ( $100\text{A}/\text{ft}^2$  @  $1.0\text{V}$  (4)) and the platinum cost was then approximately  $\$300/\text{KW}$ . Clearly such costs limit the commercial usefulness of present, refuelable zinc/air batteries and require far more than the 100 discharge cycles, which is obtainable at present (4), to be economically attractive.

Another reason why Pt cannot be considered as a practical catalyst is the gradual transfer of Pt from the diffusion electrode to the negative plate (20). This will clearly limit the number of cycles obtainable with the cathode and the presence of Pt on the anode will increase its rate of self-discharge and will lower the coulombic efficiency of anodes which are recharged electrochemically.

Carbon, on which a hydrogen peroxide decomposition catalyst was supported, has been used to decrease the cathode catalyst cost. For example, a zinc/air battery with a carbon catalyzed cathode containing  $1/4\text{ g}/\text{ft}^2$  of a noble metal gave (15)  $65\text{ W}/\text{ft}^2$  ( $65\text{A}/\text{ft}^2$  at  $1\text{V}$ ) and the catalyst cost was then approximately  $\$25/\text{KW}$ . However this lower weight of noble metal catalyst resulted in a greater cathode polarization, a low cell power density and greater heat generation.

The polarization of Pt catalyzed air cathodes is much greater in KCl solution than in KOH solution (Figure 6). This may be due both to the lower buffer capacity of KCl solution (concentration polarization) and to the influence of chloride ions on the catalytic activity of Pt (activation polarization). Comparison of the cathode polarization curves (Figure 6) with those for Al/ and Mg/air cells (Figure 5) indicate that in these cells approximately 50% of the heat evolution is due to cathode irreversibility.

There are no efficient catalysts for oxygen reduction in chloride electrolyte and the exchange current density for oxygen reduction on platinum was found to be a minimum at pH 7 (21). However polymeric cobalt phthalocyanine (22) has been shown to exhibit a lower polarization for oxygen reduction in neutral than in acid electrolyte and it may prove worthwhile to investigate the activity of these cathode catalysts in chloride electrolyte.

#### 4. Heat Generation and Dissipation

Heat is generated during the discharge of all metal/air cells. As a

result of the heat generation, the cell temperature must be controlled to minimize the anode self discharge rate and water evaporation rate. This is of particular importance in Al/ and Mg/air cells (Table 2) but cell temperature control is also very important with the other metal/air cells.

The provisions for heat dissipation are dependent on the discharge rate of the cell. Thus the higher the rate of discharge the greater the cell polarization and the greater the ratio of heat generation to electrical power.

Very little heat can be dissipated by conduction from the cells to the battery case since the lightweight current collectors are the only metal connection between cell and case. Therefore the major heat transfer path has to be to the air and hence the heat is dissipated by convective heating of the air and by water evaporation (2, 23). The relative contributions of these heat transfer modes depends on the cell temperature, water vapor pressure, air flow rate, inlet and outlet temperature, and the relative humidity of the air stream. The interdependence of these parameters is quite complex and the relationships have been derived for a 10 KWh zinc/air battery (2, 23).

Battery cooling is achieved either by the use of forced air convection or by using an excess of electrolyte. However both these solutions limit the cell energy density since they increase the battery weight and, in addition, the air circulation rates must be kept low to minimize the parasitic power drain and electrolyte carbonation.

## 5. Carbon Dioxide Removal

Adsorption of  $\text{CO}_2$  in the electrolyte occurs with all the alkaline electrolyte metal/air batteries. Carbonation of the electrolyte affects the metal/air cell performance by changing the electrolyte pH in the vicinity of the cathode, by precipitating carbonate in the cathode pores and by causing anode passivation.

With the present military zinc/air batteries the electrolyte is discarded after discharge of the anode, but this is an expensive maintenance procedure, it is hazardous and it presents disposal problems. It can only be tolerated for small batteries where the application permits the high operating cost and where weight and volume are at a premium. The carbonate concentration in larger alkaline electrolyte metal/air batteries must be controlled by scrubbing the  $\text{CO}_2$  from the atmosphere.

The removal of  $\text{CO}_2$  from the atmosphere has been studied for alkaline electrolyte fuel cells and has been reviewed in detail (24). Table 3 lists the expendable and regenerable carbon dioxide scrubbing systems which have been studied.

TABLE 3

Carbon Dioxide Removal Systems

| Expendable Adsorbers | Regenerable Adsorbers  |
|----------------------|------------------------|
| Soda Asbestos        | Molecular Sieves       |
| Lithium Hydroxide    | Monoethanolamine       |
| Soda Lime            | Aqueous Caustic Alkali |

### a) Expendable Adsorbers

Of the three expendable carbon dioxide adsorbers which have been studied

(Table 3), soda lime is generally preferred. Thus although LiOH has a 20% greater capacity for CO<sub>2</sub> adsorption, it is more expensive while soda asbestos tends to block if the air has a high humidity.

Soda lime was used as the air scrubber in a demonstration of an alkaline electrolyte fuel cell/lead acid battery power source for a small car (25). It was found that 20 lbs. of soda lime lasted for 500 miles of driving and from the data given it can be shown that this is equivalent to 1/4 lb of soda lime/KWh.

#### b) Regenerable Adsorbers

The required CO<sub>2</sub> levels can be achieved with molecular sieves but they can only be used in dry air and they require considerable power for regeneration.

The CO<sub>2</sub> concentration cannot be reduced below 30 ppm with a mono-ethanolamine scrubber and this is rather high for continuous use of the electrolyte. In addition there is a constant loss of ethanolamine due to vaporization and the material requires considerable heat for regeneration.

Aqueous caustic solutions have been investigated for scrubbing air for alkaline electrolyte fuel cells (24) and these solutions may be regenerated electrochemically. In the regeneration technique, hydrogen and oxygen are evolved at two electrodes and the regenerating cell is operated under mass transfer conditions so that the acid generated in the vicinity of the anode results in the evolution of carbon dioxide from the electrolyte. The major disadvantage of this system is the inefficiencies which result from the high overvoltage for oxygen evolution and from the concentration polarization required to reach a pH in the range 11-14. Polarization losses can be reduced if the anode and cathode are depolarized with H<sub>2</sub> and air respectively. Clearly this regenerative technique would mean a large parasitic power loss and it is necessary to have more details on the scrubbing efficiency of alkaline electrolyte and on the regeneration efficiency before it is known whether this system is competitive with soda-lime for small power levels.

### 6. Battery Refueling

Two processes are involved in the refueling of mechanically rechargeable metal/air batteries:

- a) Removing the discharged anodes and replacing them with new electrodes,
- b) Anode regeneration.

The battery system must be designed so that the former process can be carried out rapidly by unskilled personnel since speed of recharging is one of the major advantages of refuelable batteries. However the anode regeneration could be carried out slowly and use off-peak power (H<sub>2</sub>). Except for the reduction of cadmium oxide (Section 6(b)), reduction of the metal oxide is probably too complex to be carried out by the consumer and will have to be performed at service stations.

#### a) Anode Replacement

Practical experience has been gained recharging zinc/air batteries and a description of the recharging of these batteries serves to identify the problems in charging all metal/air batteries.

After discharge and removal from the bicell (Figure 2), the zinc electrode is little more than a conductor surrounded by a mass of zinc oxide particles in a separator bag which is wet with KOH solution. Because of the lack of cohesion between zinc oxide particles, anode shape change occurs during the battery discharge

(i. e., the zinc oxide slumps to the bottom of the plate) and the spent plate is no longer uniform. Thus these discharged anodes must be first pressed into approximate dimensions and then be restrained to these dimensions while they are cathodically reduced to zinc in alkaline electrolyte. They must then be removed from the reduction bath, washed free of KOH, dried and pressed to the exact cell dimension.

The disadvantages of using this type of zinc electrode are: 1) they have poor rigidity and adherence in the discharged state, 2) the regeneration process is complex and expensive, 3) porous zinc anodes impregnated with KOH are potentially hazardous and could not be handled safely by unskilled personnel, 4) re-generated zinc anodes of this form have a limited life before capacity degenerates to an unacceptable level because of particle size growth during each discharge/charge cycle.

These problems have led to the development of a zinc/air battery which utilizes a zinc powder (26). In this system (26), which is being developed as a power source for electric automobiles, the zinc powder fuel was stored as a suspension in water and distributed intermittently with electrolyte to the bicell. The bicell was similar to that in Figure 2 and the air cathodes were catalyzed by silver (loading 60 g/KW). After discharge the spent fuel and electrolyte was drawn from the battery and regenerated independently of the battery operation.

The major disadvantage of the cell was that a large volume of electrolyte was required for efficient discharge of the zinc powder (i. e., 4l of 10N KOH solution for 1 KWh), otherwise the zinc powder passivated. Thus a typical small electric car would need approximately 10 gallons of tank storage for a day's operation (10 KWh). On this basis, daily refueling would be desirable and would probably best be met by storing zinc powder and electrolyte in the car owner's garage. The authors did not indicate time needed for refueling. However this would probably require about 5 minutes since the battery has to be drained of electrolyte and ZnO and the tanks have to be replenished with a Zn/H<sub>2</sub>O slurry and with fresh electrolyte.

The battery had an energy density of 42 Wh/lb and a 10 hour operating capacity. Capital costs for the battery were quoted as \$100/KW, but this did not cover the fuel regeneration equipment and no data was provided to indicate this cost.

The work so far looks promising for the intermediate electric vehicle, but vast improvements would be needed for it to serve the hydrogen fueled society efficiently.

Magnesium/air and aluminum/air batteries offer greater flexibility for refueling since they use regular alloy sheet. The simplicity of this type of anode and the need for only minimal protection against bending during shipment and storage means that manufacturing costs would not be much higher than the cost of commercial alloy sheet. These anodes are also non-adherent after discharge but, since Al/ and Mg/air batteries use a chloride electrolyte, the spent anodes could be safely handled by the consumer. These discharged anodes could not be reprocessed by the consumer but they would be discarded and new ones would be purchased from a store. Thus the ease of refueling, reinforced by the fact that they use a cheap, CO<sub>2</sub> rejecting, safe electrolyte, provides an incentive for further research to develop a commercial Al/air or Mg/air battery.

Discharged cadmium and iron electrodes are rigid and adherent in the discharged state and thus many of the processes used in recharging Zn anodes would not have to be used in recharging Fe and Cd anodes. In addition the discharged anodes could be readily recharged in the hydrogen fueled society and hence the high initial electrode cost would be countered by the low regeneration cost.

## b) Metal Oxide Reduction

In the non-fossil fuel society, internally rechargeable batteries would be recharged by using the d. c. power from the fuel cell. However the electrochemical efficiency of the fuel cell is only 70% and the watt-hour efficiency of charging is at best (i. e., with slow charging rates) only 60-80%. Thus the volume of hydrogen used to recharge storage batteries would be two to three times greater than the theoretical value.

In this section we will describe methods of recharging discharged Fe, Zn and Cd anodes in the H<sub>2</sub> fueled society. Since the discharged anode is removed from the bicell and the metal oxide is reduced in a separate apparatus, hydrogen can be used directly for anode regeneration and this gives a particularly high charging efficiency. Discharged Al and Mg anodes cannot be reduced in aqueous electrolyte and it would be more convenient and economical to reclaim these metals by recycling.

There are three ways of recharging the discharged anode:

1. Reduction of the metal oxide by d. c. power using an inert counter electrode (oxygen evolution),
2. Reduction of the metal oxide by d. c. power using a hydrogen depolarized electrode as the counter electrode,
3. Thermal reduction of the metal oxide with hydrogen.

In Table 4 the operating costs (expressed as a volume of hydrogen) of each method are compared. The data in columns 1 and 2 (Table 4) were calculated assuming a fuel cell electrochemical efficiency of 70%.

In method 1 the discharged anode is cathodically reduced in an alkaline electrolyte bath using an inert counter electrode. Thus the applied voltage during charge is equal to the sum of the E. M. F. of the metal/oxygen couple and the total overvoltage for the electrode reactions. The data in Table 4 (column 2) was calculated by assuming that the total cell overvoltage during charge would be 0.6V.

The procedure in method 2 is similar to that in method 1 except that a hydrogen depolarized electrode is used as the counter electrode. Thus the applied voltage during charge is equal to the sum of the E. M. F. of the metal/hydrogen couple and the total overvoltage of the electrode reaction. The data in Table 4 (column 3) was calculated by assuming that the hydrogen overvoltage is 0.05V, and that the volume of H<sub>2</sub> required for the H<sub>2</sub> depolarized electrode is equal to the theoretical coulombic value.

Table 4 shows that it is significantly more expensive (larger volume of H<sub>2</sub>) to reduce the metal oxide by method 1 than by method 2. This is because the applied voltage during charge is less in the latter method since: 1) the E. M. F. of the metal/hydrogen cell is approximately 1.2V lower than that of the metal/oxygen cell and 2) the overpotential for H<sub>2</sub> oxidation is significantly less than that for oxygen evolution. For example, the Zn/ZnO electrode potential is only 0.4V more negative than that of hydrogen and thus, with a hydrogen depolarized counter electrode, the applied voltage for oxide reduction is only 0.45V, whereas the applied voltage is 2.2V with an inert counter electrode.

In the third method the metal oxide is reduced by heating in hydrogen. The data for this method (Table 4, column 4) was calculated by using the stoichiometric volume of hydrogen and no allowance was made for the hydrogen required to heat the oxide to the required temperature (i. e., these values are the theoretical volume of hydrogen required for anode regeneration).

Table 4 (column 5) also shows the minimum temperature required for the

TABLE 4

Energy Required (expressed as the volume of H<sub>2</sub>) to Recharge the Anodes

| Anode             | Volume of Hydrogen to Recharge Anode (SCF/KWh) (1) |                | Temperature of Oxide Reduction (°C) |
|-------------------|--|----------------|-------------------------------------|
|                   | Electrical(2)                                      | Thermal(3)     |                                     |
|                   | O <sub>2</sub> Evolved at Counter Electrode        | Hydrogen Anode |                                     |
| Fe <sup>(4)</sup> | 21   | 12             | 500°C                               |
| Zn                | 22   | 13             | > 1000°C                            |
| Cd                | 23   | 12             | 25°C                                |

1. Volume of H<sub>2</sub> required to form 1 KWh of energy in the form of metal from the metal oxide based on the theoretical energy densities of the metal/oxygen couples.

2. Assuming the electrochemical efficiency of the fuel cell is 70%.

3. Calculated from the volume of H<sub>2</sub> required to reduce the oxide; No allowance is made for heating Zn and Fe to the required temperature.

4. Calculated for Fe (II).

thermal reduction of the metal oxide with hydrogen. These values were calculated using literature values of the free energy of formation of the oxides (27) and of the elements (28).

Direct reduction of ZnO occurs at too high a temperature (Table 4) for this method to be economical and thus zinc electrodes would be recharged by the cathodic reduction of the metal oxide utilizing a hydrogen depolarized anode.

Since the Fe/Fe(OH)<sub>2</sub> electrode is only slightly less noble than the H<sub>2</sub> electrode (0.05V), iron oxide can be reduced in a similar way but the external voltage would now only be 0.10V. However iron oxide may also be reduced by heating the oxide in a hydrogen atmosphere to a temperature of approximately 500°C (Table 4). This temperature was calculated by assuming that the anode discharge product was FeO since there was no information in the literature on the variation of the free energy of formation of Fe(OH)<sub>2</sub> with temperature. If little heat is needed, direct reduction of the discharged iron anode may be as economical as the electrochemical reduction and it is probably more convenient.

Reduction of CdO with hydrogen is possible at room temperature (Table 4) but the reaction is very slow. However cadmium oxide can be reduced by externally connecting the cadmium oxide to a hydrogen depolarized anode (18) and no external power need be applied for this process since the Cd/CdO electrode is more noble than the hydrogen electrode.

Clearly this technique for recharging Cd electrodes can also be carried out in the battery without removing the anodes from the bicells and this may possibly be carried out by the consumer. This would be done by sweeping air from the system with nitrogen and bleeding H<sub>2</sub> into the gas space behind the diffusion electrode. Each cell is then shorted out (positive to negative) until H<sub>2</sub> consumption ceases. The short-circuit is then broken and the N<sub>2</sub> - H<sub>2</sub> mixture replaced by N<sub>2</sub> again and then air. Thus this battery system needs only a H<sub>2</sub> supply and adequate gas-manifolding for recharging. The simplicity of the system however must be weighed against its initial cost and low energy density. Careful control of alkalinity is also necessary to avoid carbonate build-up and consequent short-cycle life of the cadmium electrode.

In this section we have only compared the operating costs (Table 4) of anode regeneration but the cost of the recharging equipment (capital cost) would partially determine the total battery recharging cost. At present there is no information on this cost but, if extra fuel cell capacity had to be added for battery recharging the capital cost would be markedly increased. However, in contrast to rapid charging of conventional storage batteries, refuelable batteries can be recharged rapidly and yet use off-peak power for anode regeneration.

## 7. Summary

This review has necessarily been restricted to mechanically rechargeable metal/air cells since these are the only refuelable batteries which have been developed. These refuelable batteries have many possible advantages over internally rechargeable systems but these advantages are counterbalanced by the problems with each metal/air cell.

Table 5 summarizes the cell energy densities and the present and possible future capabilities of the metal/air batteries. The first value of energy density (Table 5) was calculated from the electrochemical equivalents of the metals and the metal/air cell voltage at 40A/ft<sup>2</sup> (Figure 5). Comparison with the theoretical energy density values given in Table 1 indicate the influence of cell polarization on energy density. The second value of energy density given in Table 5 takes into account the total battery weight. These values were either obtained from the literature (Zn), or calcu-

TABLE 5

Capabilities of Metal/Air Batteries

| Anode | Energy Density<br>(Wh/lb) |            | Capabilities of Batteries                 |   |
|-------|---------------------------|------------|---|---|
|       | Wt. of Metal(1)           | Battery(2) | Present                                   | Future  |
| Al    | 1894                      | No data    | Low power density due to heat generation. | High energy and power density; cheap electrode manufacture.           |
| Mg    | 1150                      | 65         | Low power density due to heat generation. | High energy and power density; cheap electrode manufacture.           |
| Fe    | 607                       | 65         | Moderate power density.                   | Low operating cost; Moderate energy density.                          |
| Zn    | 457                       | 80         | Relatively high power density.            | Low anode replacement and regeneration cost; Moderate energy density. |
| Cd    | 186                       | 20         | Low energy and power density.             | Low operating cost.   |

1. Calculated from the electrochemical equivalents of the metals and the cell voltage at 40 A/ft<sup>2</sup> (Figure 5).

2. Values based on the total battery weight which have been reported in the literature or extrapolated from literature data.

lated from data given in the literature.

Clearly none of the existing metal/air cells meet the requirements of the hydrogen fueled society (Table 5) but neither do the present storage batteries (e. g., lead acid and nickel/cadmium). The improvements which must be made in order to improve the metal/air systems to the point where they will provide energy densities of 100 Wh/lb and power densities of 75-100 W/lb at acceptable costs/KW and /KWh are:

1. Cost of cathode catalyst,
2. Irreversibility of the cathode,
3. Heat generation by the battery,
4. Removal of discharged anodes from the bicell,
5. Adsorption of CO<sub>2</sub> by the electrolyte (alkaline electrolyte cells only).

In addition improvements must be made in each anode to achieve the goals listed in Table 5. Thus in order to make zinc/air batteries more viable the manufacturing cost and the recharging cost of zinc anodes must be decreased. To provide the basis for low cost, high energy density aluminum/ and magnesium/air batteries, Al and Mg alloys giving more reversible potentials and having a lower rate of self-discharge are required. The energy and power density of iron/air cells is limited by the electronegativity of iron but the intrinsically low cost of iron would allow low cost iron/air cells to be made providing the self discharge rate of non-purified iron can be decreased.

#### Acknowledgements

The authors thank Electric Storage Battery Inc. and Energy Conversion Ltd. for permission to publish the zinc/air battery photographs.

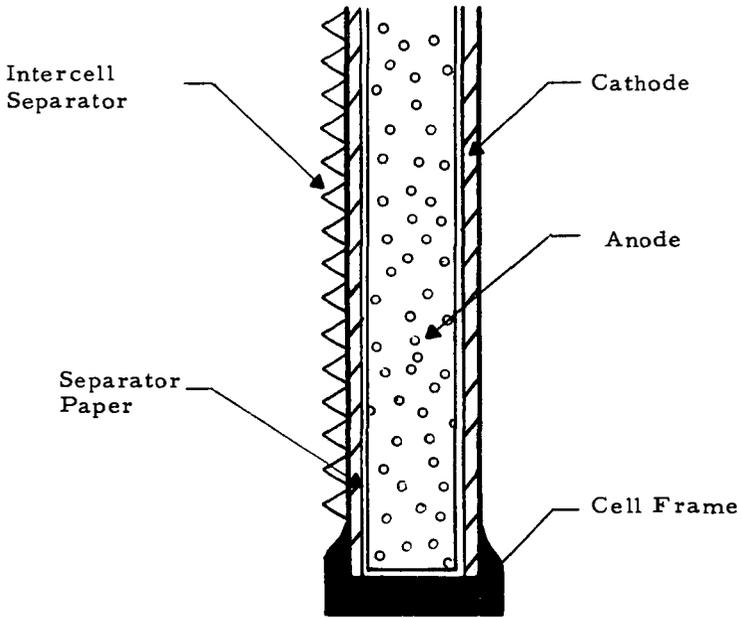


FIGURE 1 Diagram of Zinc/Air Bicell

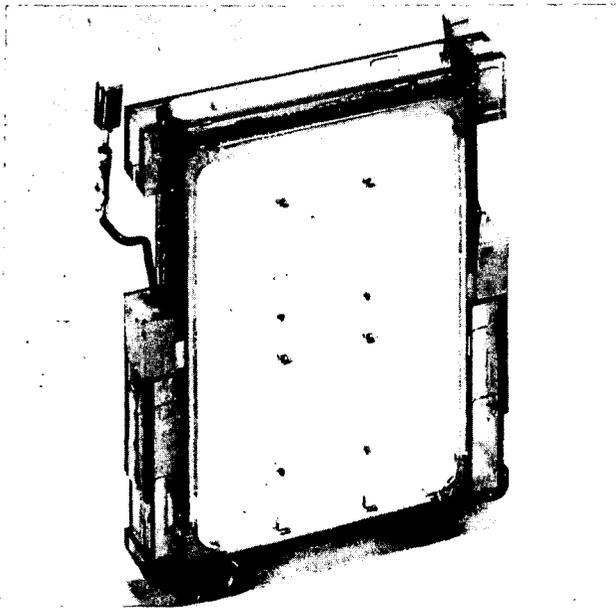


FIGURE 2 The Bicell



FIGURE 3 ESB INC. Zinc/Air Battery

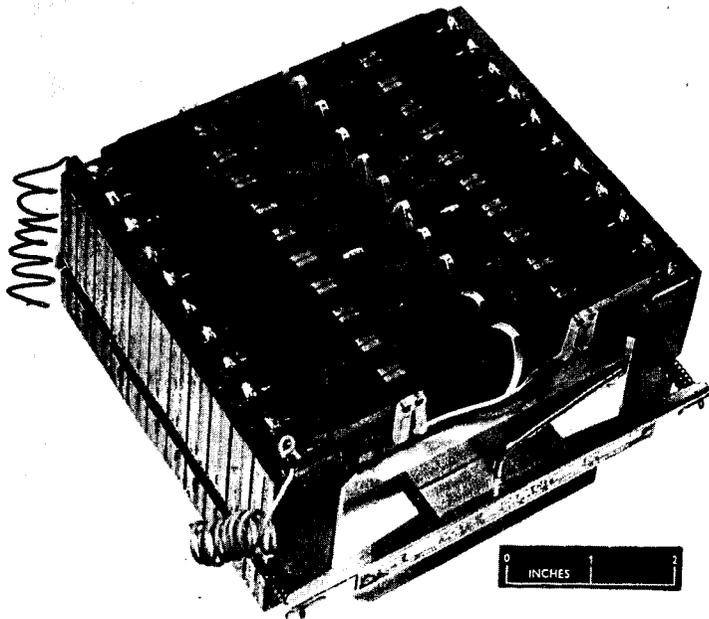


FIGURE 4 ECL LTD. Zinc/Air Battery

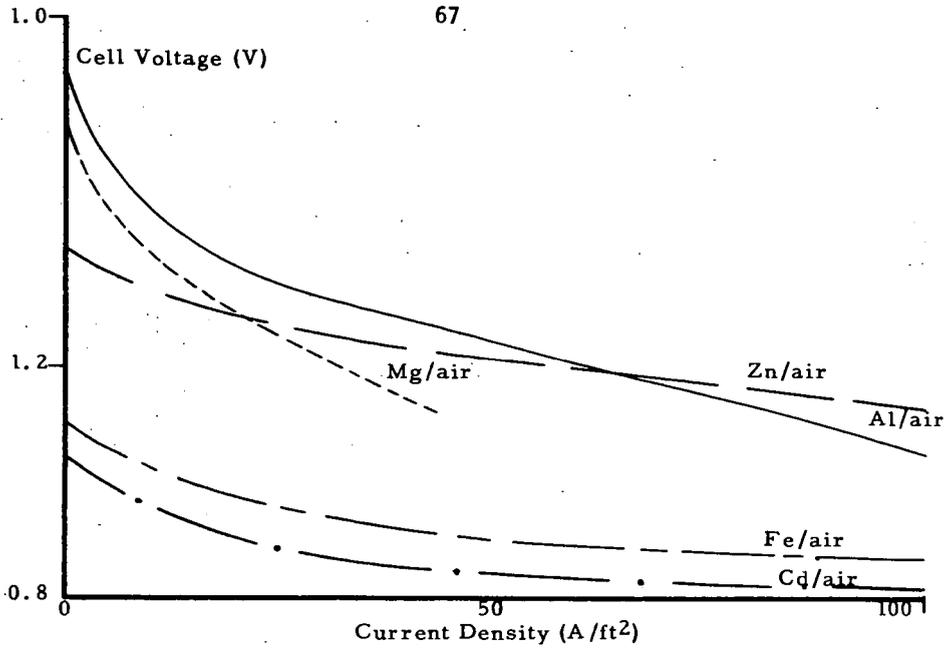


FIGURE 5 Polarization Curves of Zinc/Air Cells

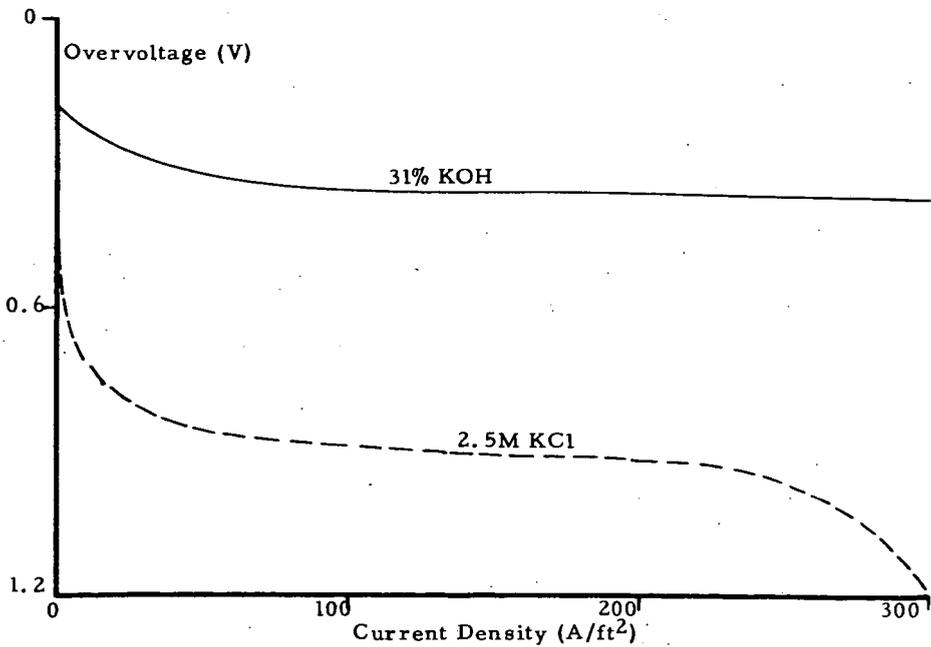


FIGURE 6 Cathode Polarization Curves in Alkaline and in Chloride Electrolyte

## REFERENCES

1. D. P. Gregory, D. Y. C. Ng and G. M. Long, "The Hydrogen Economy" in *The Electrochemistry of Cleaner Environments*, Edited by J. O'M. Bockris, Plenum Press, 1971
2. H. G. Oswin, Paper presented to the 29th Meeting of Agard Propulsion and Energetics Panel, Liege, Belgium, June 1967, p. 397
3. K. F. Blurton and E. McMullin, *Energy Conversion*, 9, 141 (1969)
4. D. Linden and H. R. Knapp, Proc. 21st Annual Power Sources Conference, Atlantic City, May 1967, p. 109
5. D. Linden, USAECOM Technical Report ECOM 3159, Fort Monmouth, August 1969
6. S. M. Chodosh, B. Jagid and E. Katsoulis, *Power Sources 2*, Edited by D. H. Collins Pergamon Press(1970), p. 423
7. S. Zaromb, *Power Systems for Electric Vehicles Symposium*, Sponsored by U. S. Department of HEW, April 1967, p. 255
8. C. E. Kent and W. N. Carson, Proc. 20th Annual Power Sources Conference, Atlantic City, May 1966, p. 76
9. W. N. Carson and C. E. Kent, *Power Sources*, Ed. by D. H. Collins, Pergamon Press (1967), p. 119
10. A. Charkey, Report to USAECOM, Fort Monmouth, Contract No. DA-28-043-AMC-01614 (E), July 1966
11. R. P. Hamlen, E. C. Jerabek, J. C. Ruzzo and E. G. Siwek, *J. Electrochem. Soc.*, 116, 1588 (1969)
12. F. P. Kober and M. Yarish, Paper presented to the Electrochemical Society Meeting, Chicago, October 1967
13. O. C. Wagner, *J. Electrochem. Soc.*, 116, 693 (1969)
14. R. R. Witherspoon, Paper presented to the International Automotive Engineering Congress, Detroit, January 1969
15. R. A. Powers, R. J. Bennett, W. G. Darland and R. J. Brodd, *Power Sources 2*, Edited by D. H. Collins, Pergamon Press(1970), p. 461
16. J. Labat, J. C. Jarrousseau and J. F. Laurent, *Power Sources 3*, Edited by D. H. Collins, Oriel Press(1971), p. 283
17. H. G. Silver and E. Lekas, *J. Electrochem. Soc.*, 117, 5 (1970)
18. H. G. Oswin, U. S. Patent No. 3,479,226, November 1969
19. L. W. Niedrach and H. R. Alford, *J. Electrochem. Soc.*, 112, 117 (1965)
20. R. Thacker, *Electrochim. Acta*, 14, 433 (1969)
21. K. H. Hamann, *Ber. Bunsenges. Physik Chem.*, 71, 612 (1967)
22. P. Andro, C. Bernard and M. Savy, *C. R. Acad. Sci., Paris*, 272, 366 (1971)

23. M. Vertes, J. Oxley, E. Katsoulis and K. Alfredson, Report to USAERDL, Fort Belvoir, Contract No. DA44-009-AMC-1469(T), December 1966
24. D.K. Ross and A.A. Law, Power Sources 2, Edited by D.H. Collins, Pergamon Press (1970), p. 583
25. K.V. Kordesch, J. Electrochem. Soc., 118, 812 (1971)
26. H. Baba, Paper presented to Automotive Engineering Congress, Detroit, January 1971
27. Handbook of Chemistry and Physics, 43rd Edition, The Chemical Rubber Publishing Co., 1961
28. D.R. Stull, Advances in Chemistry Series, Vol. 18, (1956)

THE PRODUCTION OF METHANE BY THE ANAEROBIC DECOMPOSITION  
OF GARBAGE AND WASTE MATERIALS

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### Introduction

The natural gas reserves of this country are dwindling, and this resource will some day in the not too distant future have to be augmented or replaced by synthetic gaseous or other types of fuel. At the same time, waste materials of all types are ever increasing so that waste disposal is one of the largest problems facing an ecology-minded society of today.

The magnitude of the problem is shown by the fact that about 3 billion tons of solid organic wastes are generated yearly in the United States. (3)<sup>1/</sup>

Agricultural wastes generated total 2.5 billion tons per year, of which about 2 billion tons are manure. Total urban wastes generated including domestic, commercial, municipal, and industrial, are 400 million tons per year. Solid waste discards collected by private and municipal agencies currently total about 200 million tons per year and average about 6 lb per day per person (1). Predictions call for doubling this rate long before the end of the 20th century.

The objective of this work was to study the production of methane by the anaerobic digestion of garbage and waste materials. Other methods of utilizing waste materials have been proposed and investigated. At the U.S. Bureau of Mines Energy Research Center at Pittsburgh, Pa., garbage and waste materials have been pyrolyzed and hydrogenated to convert them to useful products (2, 2). Both of these processes, however, require special equipment, and the processes are complex. Hydrogenation, for example, is done at high pressures (2000 to 6000 psi) and high temperatures (250° to 400° C), and the waste must be reacted with a gas (hydrogen or carbon monoxide). Pyrolysis of wastes is accomplished at atmospheric pressures, but elevated temperatures of 200° to 900° C are required as are special furnaces and auxiliary equipment. Anaerobic digestion, however, would not require special high-temperature or high-pressure equipment, because it is done at atmospheric pressure and about 100° F, and would utilize conventional equipment used in the liquid waste-treatment industry today.

### Description of Equipment and Test Methods

Figure 1 illustrates the glass equipment used in batch tests for the anaerobic digestion of waste materials. The procedure of testing was as follows: The side-arm flasks used as digestion vessels were first purged with helium to exclude air since the methane-forming organisms cannot survive in an oxygen atmosphere. Weighed amounts of garbage or waste material to be tested were placed in individual flasks. Measured quantities (usually 2 liters) of digester sludge from a nearby activated sludge-type sewage-treatment plant<sup>2/</sup> treating essentially domestic wastes were

<sup>1/</sup> Numbers in parentheses refer to literature cited at end of paper.

<sup>2/</sup> Pleasant Hills Sewage Treatment Plant, 1222 Cochran Mill Road, Pittsburgh, Pa., 15236

transferred to the helium-filled flasks. The flasks were then stoppered and placed in a water bath controlled at 95° to 100° F where digestion began. One of the flasks of each series of tests contained no solid wastes but only the digester sludge and served as a control for the other flasks.

The gaseous products of digestion were collected in a rubber balloon contained in a water-filled jar, which prevented contact between the gas and the water. Measurement of the water displaced as the balloon inflated gave a direct measurement of the gas produced. Gas samples were periodically removed for chromatographic analysis by deflating the balloons. The only circulation of the contents of the flasks, besides occasional manual shaking of the flasks, was the natural circulation provided by the heated liquor and passage of gas bubbles through the mixture.

#### Tests With Various Waste Materials and Discussion

Table I illustrates data from a batch test with garbage. One flask contained 2 liters of digester sewage sludge, and the other contained 2 liters of digester sludge and 25 grams (dry weight) of processed, shredded garbage. The processed garbage was obtained at Altoona, Pa., where residents separate bottles and cans from their refuse so that the destructible wastes can be shredded and ground prior to undergoing an aerobic mulching treatment.

After 24 hours of digestion, the sludge (SG-55) had produced 945 ml of gas (50% methane), while the sludge-garbage mixture (SG-56) produced 2080 ml of gas (63% methane). In a total of 336 hours of digestion, the sludge generated 2735 ml of gas (1748 ml of CH<sub>4</sub>), and the garbage-sludge mixture generated 6620 ml of gas (4048 ml of CH<sub>4</sub>). At the end of 336 hours, gas generation had ceased in both flasks. Assuming that the sludge would produce the same amount of gas in each flask, the difference in gas production is attributable to the garbage; or, in this test, 1.50 ft<sup>3</sup> of methane was produced per lb of garbage.

Table II illustrates a test with sewage sludge, cow manure, and dried grass clippings. The control (sewage sludge alone) produced only 422 ml of methane, the cow manure produced 6949 ml, and the grass clippings produced 7483 ml. Correcting for the methane produced by the control, the cow manure produced 1.11 ft<sup>3</sup> of methane/lb of dry waste, and the grass clippings yielded 1.20 ft<sup>3</sup> of methane/lb.

Other materials tested for the production of methane by anaerobic digestion, with sewage sludge as the source of the methane-producing bacteria, are listed in table III. As in previously discussed tests, the gas produced by the control (sewage sludge alone) was deducted from the gas produced by the mixture of sewage sludge-waste material, and the total methane produced by the waste material is listed in cu ft/lb (dry weight) of solid waste material.

Numerous coals were tested for methane production by anaerobic digestion, but only two results are listed: LVB coal produced 1.04 ft<sup>3</sup> methane/lb coal; the HVAB coal produced 0.44 ft<sup>3</sup> methane/lb coal. Since this symposium is concerned with fuels from nonfossil sources, the coals are mentioned merely to show that they too are amenable to bacteriological degradation.

The garbage char of test SG-38 (table III) was the residue from pyrolysis at 500° C of a processed garbage. Processed garbage is a raw garbage that has been shredded after the removal of glass and metal materials. The fresh garbage of test SG-41 was a hand-picked, blended mixture of the following: apple, orange, silicone rubber, waxed milk carton, potato, newspaper, onion, aluminum foil, eggshell, lemon, and plum. As noted, both of these garbages produced about 1.3 ft<sup>3</sup> of methane/lb of waste. The processed garbages (SG-43 and SG-44) were the best methane producers generating 3 to 4 ft<sup>3</sup>/lb of garbage. Other materials tested were shredded brown paper hand towels, shredded newspaper, wood excelsior, and

cow manure. Apparently, any organic material is susceptible to some degree of degradation by anaerobic digestion, which makes the process attractive for the disposal of urban solid wastes since they are a conglomeration of discarded materials.

#### Process Improvements Needed

Although the methods used in our tests gave results that were comparable and reproducible, it is felt that digestion would have been more complete and higher yields of methane could have been obtained if changes in test operation were made to more nearly simulate conventional sewage treatment practice. For example, continuous circulation of the solid-liquid mixture would provide better contact between the methane-producing organisms and materials on which they feed. This would also provide more consistent temperature control. Likewise, periodic feed of waste material and withdrawal of digested solids would aid digestion by providing the proper balance between organisms and food material.

One of the drawbacks of this system is the length of time required to obtain complete digestion. As shown by the data in tables I and II, digestion times of 300 to 900 hours may be required. In today's sewage treatment practice, a 1-month minimum detention time is usually required for providing well-digested sludge. Any methods of reducing these long digestion times would add greatly to the attractiveness of the process.

#### Combined Sewage-Garbage Treatment

To operate a combined sewage-garbage treatment plant, tin cans, glass, and undigestible solids would have to be removed from the garbage. The digestible garbage should then be shredded or otherwise comminuted before addition to the sewage system. The ideal location for addition of the comminuted garbage would be at the sewage treatment plant. However, it could just as easily be added anywhere along the sewage collection system, and the sewers would transport it to the treatment plant. In large cities there could be numerous garbage collection centers strategically located to reduce haulage costs. A disadvantage of this type of system could be that the additional water added to the garbage to render it transportable might tend to overload the treatment plant. Wherever the garbage or waste is added in the system, when it gets to the treatment plant it would undergo conventional treatment.

The block diagram of figure 2 is an illustration of an activated sludge plant. The solids removed by the primary sedimentation step (generally about 50% of the total solids) are pumped to the anaerobic digesters, which are maintained at about 95° to 100° F. In figure 2, the garbage is shown as being added before the inlet to the treatment plant; it could also be added to the raw sludge from the primary sedimentation step, thus subjecting all the garbage to anaerobic digestion rather than only 50% of the garbage solids. Pumps provide recirculation of the digester contents. As the solids become digested, they settle to the bottoms of the digestion tanks. The supernatant liquor, which includes excess water and nonsettling solids, is drained to the secondary treatment system where it undergoes aerobic digestion, final clarification, and chlorine treatment before being released to the receiving stream.

Digested solids from the digestion tank bottoms are drained to sand-drying beds or vacuum-filter presses for drying. The dry digested solids, which have been reduced in mass at least 50%, are useful as low-grade fertilizers and soil conditioners. As practically sterile digested solids, they are much more acceptable aesthetically and much less offensive than the original raw garbage.

The gaseous products of digestion consist essentially of methane (about 65%) and carbon dioxide (about 35%). Many sewage treatment plants today utilize the 650-Btu gases that they generate in their digesters to operate internal-combustion engines to drive blowers, pumps, and other plant auxiliary equipment. One such plant<sup>3/</sup> treating about 2 million gallons per day, produced 606,300 ft<sup>3</sup> of methane during a recent 1-month period. This amount of methane was produced from about 80 tons of solids contained in the raw sludge pumped to the digesters, or 3.8 ft<sup>3</sup> of methane was produced/lb of sewage solids.

If all the solid waste discards that are collected annually in this country by collection agencies (200 million tons) were subjected to treatment by anaerobic digestion, potentially some 1.2 trillion ft<sup>3</sup> of methane would be produced based on yields obtained in our batch tests. Likewise, if all the animal wastes (manure--2 billion tons) were also to receive this treatment, an additional 4.4 trillion ft<sup>3</sup> of methane could be produced annually. These amounts together are about one-fourth the annual U.S. consumption of natural gas (4). The value of gas from this potential source would amount to millions of dollars, and this is a renewable energy source that is today being wasted.

#### Conclusions

The urban and agricultural solid wastes being generated in the United States are a potential source of more than 5 trillion ft<sup>3</sup> of methane per year--about one-fourth our annual consumption. Methane could be produced from these wastes by the process of anaerobic digestion, the same process utilized in the operation of household septic tanks. The digestion process would not require exotic or expensive equipment since it would take place at 95° to 100° F and at atmospheric pressure. In addition to a gaseous product consisting of 65% to 70% methane and 30% to 35% carbon dioxide, a solid product remains (reduced more than 50% in mass from the original waste) that is useful as a fertilizer or soil conditioner. One of the biggest advantages of this scheme is that waste materials are a renewable energy source that will not diminish like our fossil fuels but will continue to increase.

#### Literature Cited

1. American Chemical Society Report, "Cleaning Our Environment, The Chemical Basis for Action," Washington, D.C., 1969, pp. 165-191.
2. Appell, H. R., Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender, "Converting Organic Wastes to Oil," BuMines Report of Inv. 7560, 1971, 20 pp.
3. Kenahan, C. B., "Solid Waste Resources Out of Place," Environmental Science and Technology, vol. 5, July 1971, pp. 594-600.
4. Mills, G. A., H. R. Johnson, H. Perry, "Fuels Management in an Environmental Age," Environmental Science and Technology, vol. 5, No. 1, Jan. 1971, pp. 30-38.
5. Sanner, W. S., C. Ortuglio, J. G. Walters, and D. E. Wolfson, "Conversion of Municipal and Industrial Refuse Into Useful Materials by Pyrolysis," BuMines Report of Inv. 7428, 1970, 14 pp.

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<sup>3/</sup> Work cited in footnote 2.

Table I. Gas Production by Anaerobic Digestion of Garbage and Sewage Sludge

|  | Digestion<br>time, hr | Gas produced, ml |                 | Gas analysis, % |                 |                |
|--|-----------------------|------------------|-----------------|-----------------|-----------------|----------------|
|  |                       | Total            | CH <sub>4</sub> | CH <sub>4</sub> | CO <sub>2</sub> | N <sub>2</sub> |
| SG-55                                    | 24                    | 945              | 473             | 50.0            | 39.1            | 10.9           |
| 2 liters digester }<br>sewage sludge }   | 72                    | 1690             | 974             | 67.2            | 23.6            | 9.2            |
|  | 264                   | 2495             | 1570            | 74.0            | 19.7            | 6.3            |
|  | 336                   | 2735             | 1748            | -----           | -----           | -----          |
| SG-56                                    | 24                    | 2080             | 1310            | 63.0            | 35.1            | 1.9            |
| 2 liters digester }<br>sewage sludge + } | 72                    | 4375             | 3017            | 74.4            | 24.0            | 1.6            |
| 25 grams proc-<br>essed garbage }        | 264                   | 6230             | 3724            | 82.7            | 16.9            | 0.4            |
|  | 336                   | 6620             | 4048            | -----           | -----           | ---            |

Methane produced by sludge-garbage mixture (SG-56) 4048 ml  
 Minus methane produced by sludge (SG-55) - 1748 ml

Methane produced from garbage: 2300 ml

$\frac{2300 \text{ ml CH}_4}{25 \text{ g garbage}} = 1.50 \text{ ft}^3 \text{ CH}_4/\text{lb garbage}$

Table II. Gas Production by Anaerobic Digestion of Bovine Waste, Grass Clippings, and Sewage Sludge

|                     | Digestion time, hr    | Gas produced, ml |                 | Gas analysis, % |                 |                |
|---------------------|-----------------------|------------------|-----------------|-----------------|-----------------|----------------|
|                     |                       | Total            | CH <sub>4</sub> | CH <sub>4</sub> | CO <sub>2</sub> | N <sub>2</sub> |
| SG-60               | 82                    | 1175             | 227             | 19.3            | 14.8            | 65.9           |
| 2 liters digester)  | 286                   | 1425             | 336             | 43.5            | 13.8            | 42.7           |
| sewage sludge )     | 310                   | 1625             | 422             | ----            | ----            | ----           |
|                     | Gas production ceased |                  |                 |                 |                 |                |
| SG-61               | 46                    | 1930             | 867             | 44.9            | 34.2            | 20.9           |
| 2 liters digester ) | 82                    | 2870             | 1480            | 64.2            | 27.0            | 8.8            |
| sewage sludge + )   | 160                   | 4035             | 2248            | 65.9            | 27.4            | 6.7            |
| 100 g cow manure )  | 286                   | 5095             | 2966            | 67.7            | 27.6            | 5.3            |
|                     | 502                   | 7475             | 4592            | 68.3            | 28.1            | 1.7            |
|                     | 957                   | 10700            | 6949            | 73.1            | 25.2            | 1.7            |

$$\frac{6949 \text{ ml CH}_4}{100 \text{ g manure}} = 1.11 \text{ ft}^3 \text{ CH}_4/\text{lb manure}$$

|                    |     |       |      |      |      |      |
|--------------------|-----|-------|------|------|------|------|
| SG-62              | 82  | 1395  | 239  | 17.1 | 29.6 | 53.3 |
| 2 liters digester) | 160 | 3220  | 1093 | 46.8 | 37.1 | 16.1 |
| sewage sludge + )  | 238 | 4605  | 2072 | 70.7 | 25.3 | 4.0  |
| 100 g dried )      | 286 | 5550  | 2778 | 74.7 | 23.3 | 2.0  |
| grass clippings)   | 502 | 8940  | 5409 | 77.6 | 22.4 | 0    |
|                    | 957 | 12190 | 7905 | 76.8 | 19.4 | 3.8  |

$$\frac{7483 \text{ ml CH}_4}{100 \text{ g grass}} = 1.20 \text{ ft}^3 \text{ CH}_4/\text{lb grass clippings}$$

Table III. - Methane Yields from Waste Materials and Coals  
by Anaerobic Digestion

| Test No. | Material                      | Dry wt, g | Duration of test, hr | Gas production, ml  |                  | Ft <sup>3</sup> methane produced/lb waste material |
|----------|-------------------------------|-----------|----------------------|---------------------|------------------|--|
|          |                               |           |                      | Total <sup>1/</sup> | Methane          |  |
| SG-19    | LVB coal minus 325 mesh ....  | 100       | 1330                 | 7600                | 6460             | 1.04   |
| SG-20    | HVAB coal minus 325 mesh .... | 100       | 1330                 | 4015                | 2770             | 0.44   |
| SG-38    | Garbage char...               | 100       | 840                  | 9850                | 8195             | 1.31   |
| SG-41    | Fresh garbage..               | 50        | 360                  | 8980                | 4215             | 1.35   |
| SG-43    | Processed garbage.....        | 50        | 864                  | 18735               | 12571            | 4.03   |
| SG-44    | Processed garbage.....        | 25        | 864                  | 7895                | 5282             | 3.39   |
| SG-47    | Shredded brown paper towels   | 25        | 816                  | 865                 | 692              | 0.44   |
| SG-49    | Shredded news-papers.....     | 25        | 734                  | 1500                | Gas not analyzed | 0.67 <sup>2/</sup>                                 |
| SG-50    | Wood excelsior                | 25        | 734                  | 770                 |                  | 0.34 <sup>2/</sup>                                 |
| SG-58    | Cow manure.....               | 100       | 234                  | 7800                | 4402             | 0.71   |

<sup>1/</sup> Deduction from total production has been made for gas produced by control.

<sup>2/</sup> Estimated.

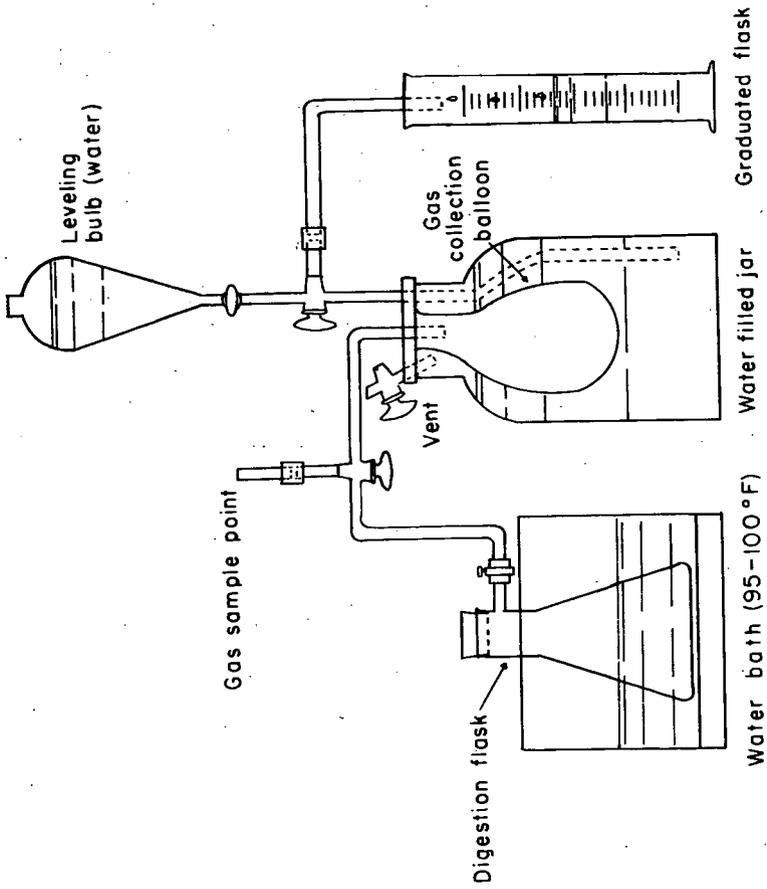


Figure 1. Apparatus for Production-Collection of Gases from Anaerobic Digestion of Wastes.

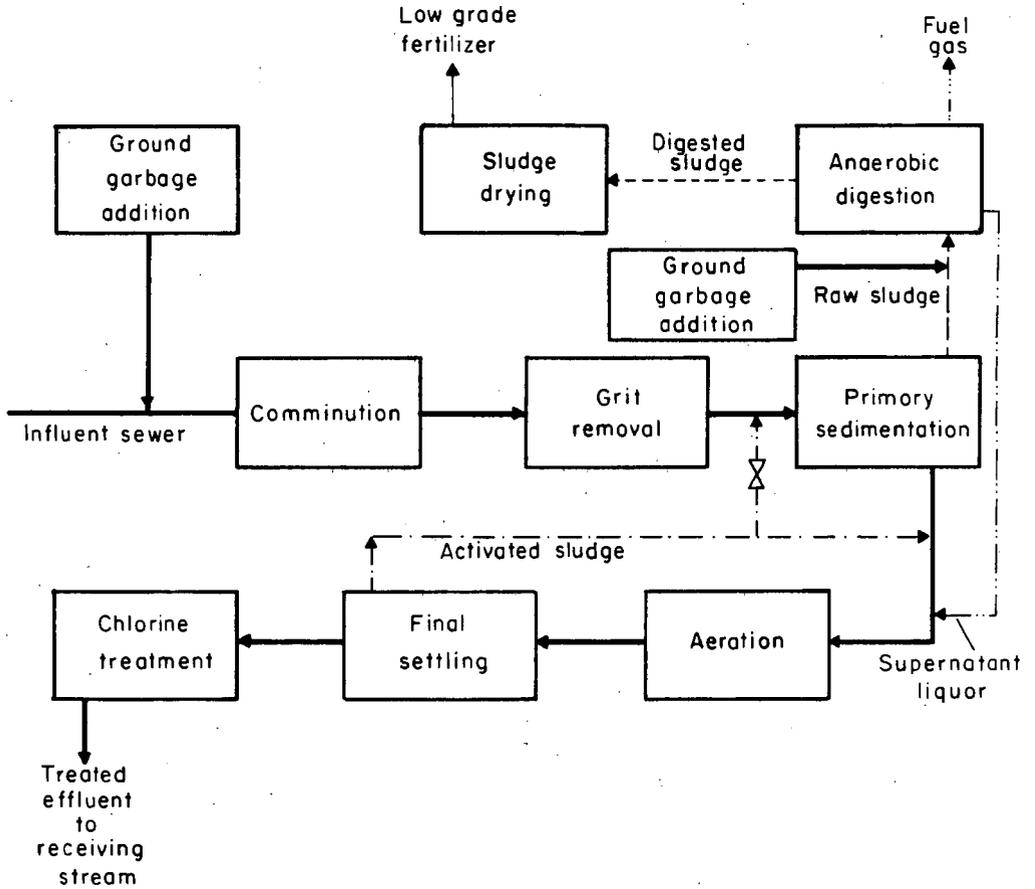


Figure 2. Flow Diagram of Garbage-Sewage Treatment Process.

## Thermodynamics of Multi - Step Water Decomposition Processes

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Processes which convert water into hydrogen and oxygen are of interest for many reasons, including the many advantages accruing to the transport of energy as hydrogen. Hydrogen may be used as a source of thermal or electrical energy, depending on whether it is burned or used in an electrochemical device such as a fuel cell.

Hydrogen is also a key raw material in the chemical process industries and in petroleum refining. It is estimated that by 1975 the total consumption of hydrogen in the U.S. will be at the rate of four trillion cubic feet per year and growing. Gaseous and liquid hydrocarbons are now the principal raw materials for producing large quantities of hydrogen by means of either catalytic steam reforming or partial oxidation. The pressure for inexpensive and plentiful pipeline gas, artificial natural gas, will increase the demand for hydrogen even more. It would clearly be in the interest of conservation of natural resources to develop an economical process to produce hydrogen from water.

A comprehensive study of thermal processes to produce hydrogen from water was performed and reported by General Motors (1,2). A three step process involving either tantalum chloride or bismuth chloride and a four step process using either mercury chloride or vanadium chloride were described. A general discussion of energy requirements for the decomposition of water was published by Funk and Reinstrom (3) and, more recently, a four step thermal process was described by deBeni and Marchetti (4). A review of the current status of electrolytic hydrogen as a fuel has been published by Gregory, et.al. (5).

### Second Law Limitations

If one gram mole of water of liquid water at 25°C and 1 atm is converted into one gram mole of hydrogen and one half gram mole of oxygen at 25°C and 1 atm the gibbs function for the system increases by 56.7 kcal, the enthalpy increases by 68.3 kcal and the entropy increases by 39 cal/°K. If the decomposition is done reversibly at 25°C and 1 atm--say in an electrolysis cell--56.7 kcal, the change in the gibbs function, must be supplied as useful work and 11.6 kcal, the difference between the enthalpy change and gibbs function change, must be supplied as heat.

The amount of useful work required may be decreased by operating the single step decomposition at some higher temperature. The amount of energy required as heat will increase by the same amount that the work required is decreased under the best case assumptions of equal specific heats and perfect thermal regeneration of products and reactants.

If the process is depicted on a temperature entropy diagram, the work reduction is equal to the area enclosed when the process loop is closed by allowing the cooler hydrogen and oxygen to form water

reversibly, say in a fuel cell. From this viewpoint the process is a heat engine and is, therefore, limited in efficiency to the "Carnot" efficiency. This second law limitation has been discussed in more detail elsewhere (1,2,3).

It is desirable, of course, to reduce the amount of useful work required to decompose water since such work must be produced from heat in an engine of some sort. A figure of merit,  $\eta$ , may be defined such that

$$\eta = \frac{\Delta H_0}{Q_t} \quad (1)$$

where  $\Delta H_0 = 68.3$  kcal

$Q_t$  = total amount of heat required by process which accepts 1 gram mole of liquid water at 25°C and 1 atm and delivers 1 gram mole of hydrogen and 1/2 gram mole of oxygen at 25°C and 1 atm.

Limitations on  $\eta$  resulting from the first and second laws of thermodynamics have already been derived and discussed (3).

The quantity  $Q_t$  comprises two terms,

$$Q_t = \left( \frac{W}{\xi} \right) + Q \quad (2)$$

where  $W$  = energy as useful work required

$\xi$  = efficiency of converting heat to work

$Q$  = thermal energy required

A 100% efficient electrolyzer operating with a power plant with a  $\xi$  of 30% would yield a value for  $\eta$  of 34%. If the electrolyzer had a voltage efficiency of 60%  $\eta$  would drop to 22%.

### Multi-Step Processes

If one supposes that water is to be decomposed by heating it and separating the components (i.e., a single step process) the rate of reduction of the change in gibbs function with temperature is approximately equal to the reaction entropy change. As will be shown later, the theoretical work of separation is equal to or greater than the change in the gibbs function.

For a single step process the work requirement simply does not decrease fast enough as the temperature is increased because the entropy change for the reaction is more or less constant and not large. In a multi-step process the reaction entropy change is not fixed and may vary according to the reaction.

Consider the  $i$ th reaction in a multi-step process. The work and heat requirements are

$$w(i) = w_0(i) - \Delta s(i) [T(i) - T_0] \quad (3)$$

$$q(i) = q_0(i) + \Delta s(i) [T(i) - T_0] \quad (4)$$

It has been assumed that  $\Delta s(i)$ , the reaction entropy change, is independent of temperature. The subscript zero refers to conditions at the reference temperature,  $T_0$ , (assumed to be 25°C).

The total work and heat requirements are obtained by summing (3) and (4) over the I reactions to obtain

$$W = \Delta G_o - \sum_{i=1}^{i=I} \Delta s(i) [T(i) - T_o] \quad (5)$$

$$Q = \sum_{i=1}^{i=I} \Delta s(i) T(i) \quad (6)$$

Another important feature becomes apparent if the process is divided into J reactions which have positive entropy changes and L reactions which have negative entropy changes. To minimize the required work, the first group of reactions should be operated at some high temperature,  $T_H$ , and the second group operated at  $T_o$ . In this case,

$$W = \Delta G_o - \sum_{j=1}^{j=J} \Delta s(j) [T_H - T_o] \quad (7)$$

As is evident from Eqn. (7), the required work is zero when

$$\sum_{j=1}^{j=J} \Delta s(j) = \frac{\Delta G_o}{T_H - T_o} \quad (8)$$

There is no reason why (8) cannot be satisfied along with

$$\sum_{i=1}^{i=I} \Delta s(i) = \sum_{j=1}^{j=J} \Delta s(j) + \sum_{l=1}^{l=L} \Delta s(l) = \Delta S_o = 39 \frac{\text{cal}}{\text{g mole H}_2\text{-}^\circ\text{K}} \quad (9)$$

This result cannot be obtained for a single step process, in which case the zero work requirement must be accomplished by a temperature manipulation rather than the selection of a suitable sequence of reactions.

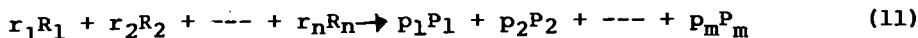
#### Work of Separation

The theoretical work of separation,  $\Delta G_s$ , required to separate a mixture of ideal gases into its components is given by

$$\Delta G_s = -RT \sum_k n_k \ln x_k \quad (10)$$

where  $n_k$  is the number of moles of the kth component and  $x_k$  is the mole fraction of that component.

Fig. 1 shows a reaction process which accomplishes the reaction



The amount of material entering the separator depends on  $\epsilon$ , the fractional molar conversion of  $R_1$ , which in turn depends on the standard free energy change for the reaction,  $\Delta G_R$ . Combining the definition of the standard free energy change for a reacting mixture of ideal gases with Eqn. (10) yields

$$\Delta G_s = \Delta G_R - RT \left[ \frac{r_1}{\epsilon} \ln x_{R_1} + \frac{r_2}{\epsilon} \ln x_{R_2} + \dots - (\Sigma p - \Sigma r) \ln p^* \right] \quad (12)$$

where 
$$x_{R_1} = \frac{r_1(1-\epsilon)}{\Sigma r + \epsilon(\Sigma p - \Sigma r)}, \text{ etc.}$$

and  $p^*$  is the operating pressure

Eqn. (12) shows that the theoretical work of separation is greater than standard free energy change for the reaction.

An example of the theoretical work of separation for the vanadium chloride process is shown in Figs. 2 and 3. Fig. 2 is a schematic of the first stage in which there is a gas phase reaction of chlorine with water at 1000°K at 1 atm. Fig. 3 shows the theoretical work of separation and it may be noted that the separation work is increased if the mixture leaves the reaction chamber at less than equilibrium conditions. Fig. 3 is for the separation of all four components and the minimum work requirement is 9.2 kcal per gram mole of hydrogen produced. A similar calculation for the separation of only the HCl and  $O_2$  yields a work requirement of 7.1 kcal.

#### The Vanadium Chloride Process

The entire vanadium chloride process is shown in Fig. 4. The sums of the enthalpy, entropy, and free energy changes do not exactly equal those for water composition because of questionable thermochemical data.

This process was studied in considerable detail. A plant layout was made assuming a helium cooled nuclear reactor as the heat source. Estimates were made for pumping, heat regeneration, etc. The results are shown in Table 1 and, as can be seen, this process is not as efficient as a water electrolysis plant.

The object here is not to describe an inefficient process - any number of such processes can be easily devised. It is, rather, an attempt to indicate that processes which may be initially attractive can quite quickly lose their appeal when subjected to somewhat more practical considerations of work of separation, thermal regeneration, pumping power, etc. Such a result is not especially surprising in view of the objective, which, in its most fundamental terms, is an attempt to convert heat to useful work more efficiently than in a state of the art power plant.

#### References

1. Final Technical Report - Ammonia Production Feasibility Study, Allison Division of General Motors, EDR 4200, November, 1965.
2. System Study of Hydrogen Generation by Thermal Energy, Allison Division of General Motors, EDR 3714, vol. 11, Supplement A, 1964.

3. Funk, J. E., and Reinstrom, R. M., "Energy Requirements in the Production of Hydrogen From Water", I & EC Proc. Des. & Dev., vol. 5, No. 3, pp 366-342, July 1966.
4. deBeni, G. and Marchetti, C., "Hydrogen, Key to the Energy Market", Euro Spectra, 9, 46-50, June, 1970.
5. Gregory, D. P., Ng D.Y.C., and Long, G. M., to be published in The Electrochemistry of Cleaner Environments, J.O'M. Bockris, Ed., New York, Plenum Press, 1971.

#### Acknowledgment

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Table 1  
Vanadium Chloride Process Data Tabulation

| Parameter                                 | Units                                  | Systems |      |      |      | Remarks  |
|---|--|---------|------|------|------|--|
|   |  | 2000    | 2000 | 1500 | 1500 |  |
| Maximum helium temperature                | F                                      | 2000    | 2000 | 1500 | 1500 |  |
| Minimum helium temperature                | F                                      | 37      | 37   | 67   | 67   |  |
| Helium system pressure                    | atm                                    | 10      | 1    | 10   | 1    | He pressure drop equals 10 psi in all cases          |
| Process heat input                        | kcal                                   | 155     | 155  | 475  | 475  |  |
| Total heat rejected                       | kcal                                   | 312     | 382  | 698  | 998  | Includes unrecovered shaft work                      |
| Total heat regenerated                    | kcal                                   | 262     | 262  | 872  | 872  |  |
| Helium flow                               | $\frac{\text{moles}}{\text{mole H}_2}$ | 113     | 113  | 383  | 383  |  |
| Helium pumping power                      | kcal                                   | 3       | 24   | 14   | 105  | 100% efficiency                                      |
| Separation work (VCl <sub>4</sub> and He) | kcal                                   | 18      | 18   | 23   | 23   |  |
| Total separation work                     | kcal                                   | 33      | 33   | 38   | 38   | 4 stages plus VCl <sub>4</sub> and He separations    |
| Shaft work input                          | kcal                                   | 69      | 90   | 90   | 18   | Separation work at 50%; pump work at 100% efficiency |
| Thermal power                             | kcal                                   | 230     | 300  | 296  | 600  | 30% efficient (Heat to work)                         |
| Total reactor thermal power               | $\frac{\text{kcal}}{\text{mole H}_2}$  | 385     | 455  | 770  | 1075 | Process heat plus shaft work                         |
| Figure of Merit, $\eta$                   | %                                      | 18      | 15   | 9    | 6    | $\frac{\Delta H_o}{Q_t}$                             |

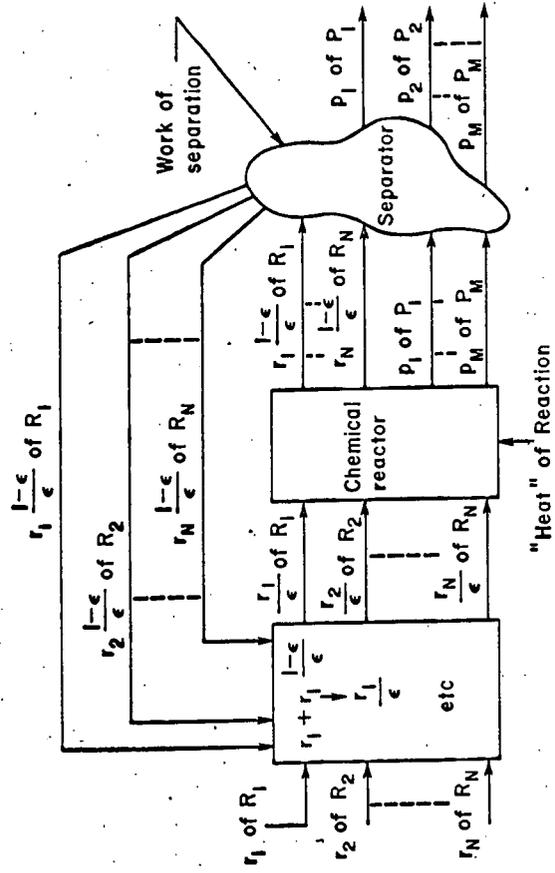


Fig. 1 Overall Reaction Process

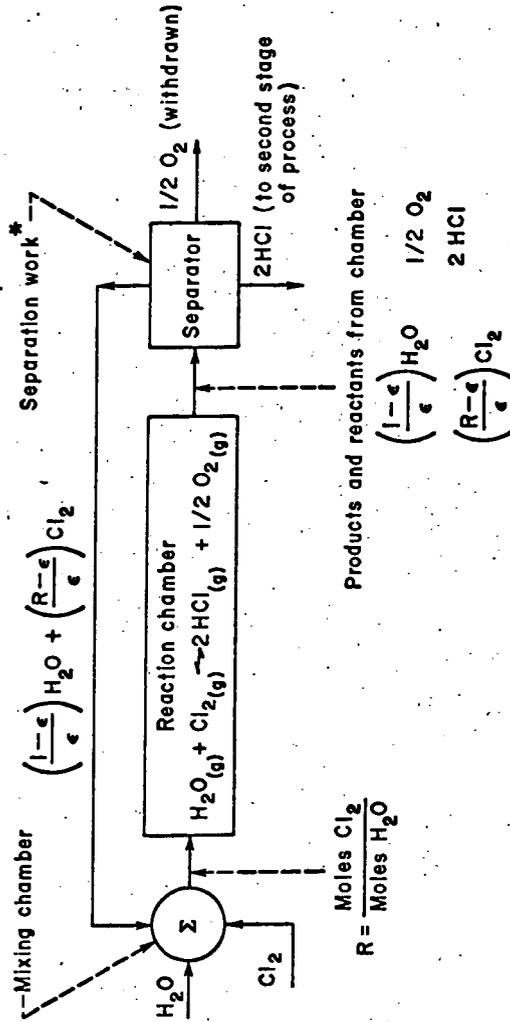


Fig. 2 First Stage of the Vanadium Chloride Process

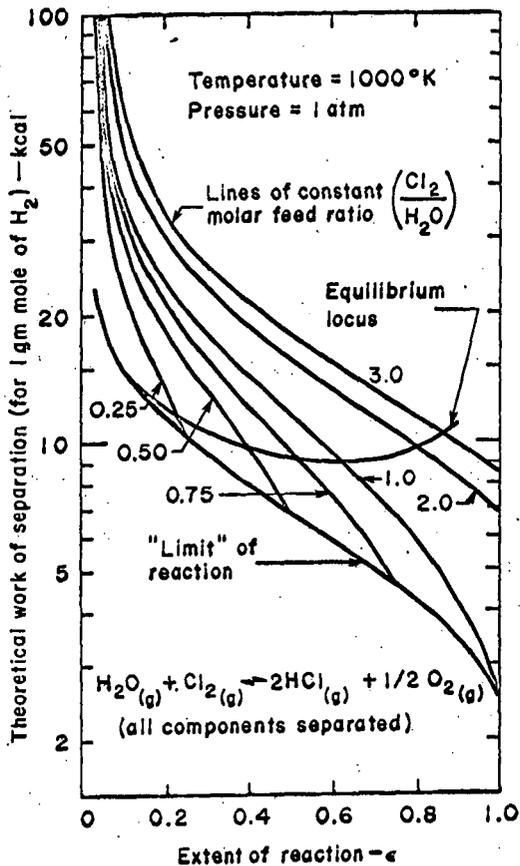
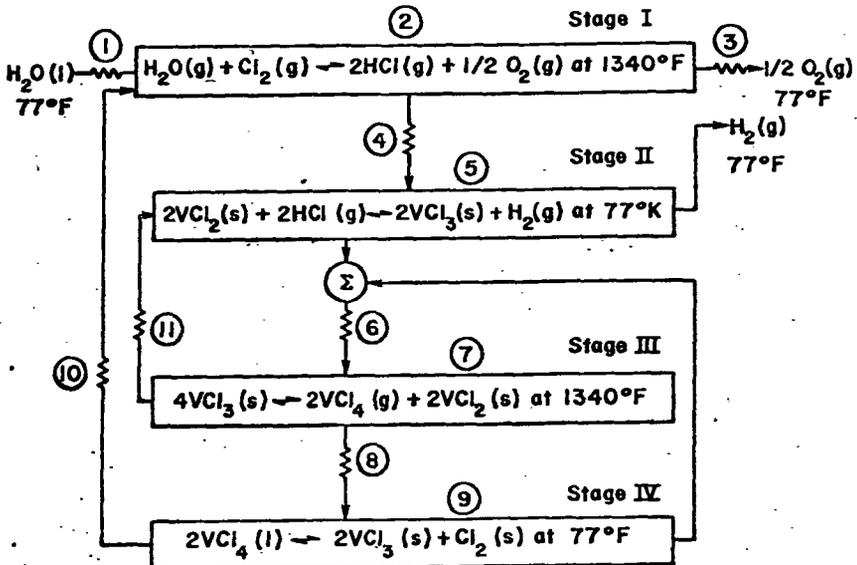


Fig. 3 Theoretical Work of Separation



Enthalpy, entropy, and free energy tabulation  
(values in kilocalories)

| Step | ①     | ②    | ③    | ④     | ⑤     | ⑥     | ⑦    | ⑧      | ⑨   | ⑩     | ⑪     | Σ    |
|------|-------|------|------|-------|-------|-------|------|--------|-----|-------|-------|------|
| ΔH   | 16.7  | 15.8 | -2.7 | -10.1 | -18.0 | 72.5  | 83.0 | -65.2  | 2.0 | 6.1   | -26.7 | 73.4 |
| ΔS   | 45.7  | 18.5 | -4.6 | -17.4 | -45.4 | 123.6 | 77.8 | -119.0 | 4.7 | 10.4  | -46.0 | 48.3 |
| ΔG   | -36.0 | -2.7 | 19.1 | 69.9  | -0.5  | 138.9 | 5.2  | 139.0  | 0.6 | -41.7 | 53.9  | 59.9 |

Fig. 4 Vanadium Chloride Process

## A HYDROGEN-ENERGY SYSTEM

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### INTRODUCTION

For some years now, interest has been growing in the use of hydrogen as a universal fuel — hydrogen that is produced from unlimited seawater by nuclear energy to provide a clean, universally useful fuel and chemical raw material. Early interest in the concept dates back before the availability of nuclear power and was stimulated by the fact that hydrogen could be manufactured by the electrolysis of water using off-peak electricity. Rudolf Erren,<sup>6</sup> working in Germany and later in England in the early 1930's, foresaw the need to utilize off-peak power to reduce oil imports into Britain and to reduce pollution from vehicle emissions. In 1933, he published a paper in which he outlined the use of hydrogen as a fuel for automobiles and steam locomotives.

Among others who have since given their attention to the hydrogen fuel concept are Weinberg,<sup>16</sup> Steinberg,<sup>12</sup> and others at Brookhaven National Laboratory, who considered hydrogen as an essential part of the nuclear-agricultural complex concept; Winsche *et al.*<sup>17</sup> of Brookhaven, who looked at hydrogen as an urban fuel; Murray and Schoepfel<sup>9</sup> at Oklahoma State University, who stimulated work on the use of hydrogen as an internal combustion engine fuel; Bacon<sup>2</sup> at Cambridge, England, who saw in the reversible hydrogen fuel cell a simple way of storing off-peak electricity; Rosenberg<sup>11</sup> at the Institute of Gas Technology, who saw the uniquely favorable qualities of hydrogen as a fuel for domestic appliances; and Marchetti<sup>4</sup> at Euratom, Italy, who realized the inherent inefficiencies of producing hydrogen from nuclear energy via an electrolytic process. These are but few of the many who have proposed or studied various aspects of what we shall call "The Hydrogen Economy." Today reasons why an overview of the whole concept of hydrogen as a fuel should be made are even more pressing.

### ENERGY SUPPLY

The economy of the civilized world today is geared to the use of energy. Many studies show that the usual measure of prosperity, the gross national product per capita, has grown in almost every country of the world at a rate directly related to the growth rate of the per-capita use of energy. Almost all of this energy comes from combustion of fossil fuels, fuels which, although they have taken millions of years to form, are being consumed in a few hundred. The signs are already here that we are approaching the end of our fossil fuel supply: In the U.S., we are now consuming natural gas at a rate faster than the rate at which new reserves are being discovered. The U.S. is importing an ever-increasing portion of its oil requirements, and the cost of coal is rising rapidly as we bite into less readily worked deposits.

Elliott<sup>5</sup> has shown that patterns of producibility of the fossil fuel resources of the U.S. and Canada can be used to predict that the maximum rate of production of fossil fuels will occur early in the next century. After that time, the amount of available fossil fuel energy will fall year by year, although our overall energy demands are expected to continue to rise. It is therefore vital to develop nuclear or solar energy sources.

## NUCLEAR ELECTRIC POWER

The development of nuclear power stations has been described by the Federal Power Commission as a "race for our lives" to meet our energy needs. Let us hope that we win the race, but let us also observe that almost the whole research and development effort in nuclear energy today is directed toward the conversion of nuclear energy to electrical energy. This same observation can also be made about the relatively smaller efforts going on to harness solar energy and geothermal energy: The goal is to produce electricity.

Electrical energy is a convenient, clean, and universal energy source in its end use, but it suffers from a number of technical disadvantages that prevent it from having already become the universal "fuel." First, it cannot be stored without conversion to another form. Storage batteries are relatively expensive and heavy, and sites for pumped storage systems are limited. This limitation requires that the generation rate match, almost exactly, the consumption rate, responding instantaneously to fluctuations in demand. The result is an expensive and necessarily "overdesigned" supply system. Second, it is incredibly expensive to transmit electric power over long distances without the use of unsightly overhead cables and towers. Underground power lines of similar capacity to those more familiar overhead cross-country systems cost 10-40 times as much as overhead lines.<sup>14</sup>

## NUCLEAR CHEMICAL POWER

Since we use a very large proportion of our energy directly as heat, perhaps it makes more sense to satisfy this portion of our needs by burning fuel directly rather than using the intermediate and inefficient conversion to electricity. We should look, then, for a synthetic fuel that can be used to store and transport the energy produced by nuclear power stations.

It is possible to conceive of a number of synthetic chemical fuels that could be produced from a nuclear heat source. The choice is severely limited, however, if we consider the use of the atmosphere as a carrier to return the "spent" fuel to the synthesis station. We certainly cannot consider any synthetic high-energy chemical that produces a noxious or voluminous combustion or oxidation product, and, except for specific applications, we cannot afford to collect and transport the spent fuel back to its point of origin.

To obtain compatibility with the atmosphere, therefore, we must limit the combustion products to water, nitrogen, and carbon dioxide, from which the fuel itself must also be synthesized. Although alcohols, hydrazine, and ammonia fall into this category, their combustion raises the possibility of production of noxious carbon or nitrogen compounds, including carbon monoxide and the oxides of nitrogen. Hydrogen has the unique combination of being readily synthesized from water, being readily auto-ignited and undergoing low-temperature combustion on a catalytic burner, and, in doing so, forming a completely clean combustion product - water.

## HYDROGEN FUEL

Two major criticisms can be leveled at the use of hydrogen as a fuel: 1) It is too expensive to produce, and 2) its transportation to the point of use is costly because it requires heavy compressed-gas cylinders. Neither of these criticisms is valid if an imaginative approach is taken to the problem. Very large electrolysis plants running off the entire output of a large nuclear power station are technically feasible. Since we are accustomed to moving huge quantities of natural gas across the country in pipelines, the same approach can be applied to hydrogen. We will show that even today, the concept

of making hydrogen on a large scale and delivering it to a nationwide transmission and distribution system should be able to provide delivered energy more cheaply than the average selling price of electricity.

### Hydrogen Production

Today, most of the enormous quantity of hydrogen produced in the United States — over 2500 billion cubic feet per year and growing fast — comes from the reaction of natural gas with steam. Smaller quantities are made by electrolysis of water where cheap electricity is available, or where extreme reliability is needed. These are the key words of the future: Nuclear power will provide "cheap electricity" — perhaps not cheaper than today, but cheap in comparison with the future cost of fossil fuel energy — and any energy supply system must be endowed with "extreme reliability." Electrolysis therefore appears to be one logical choice of process. Studies carried out in 1965-66 by Allis-Chalmers for the Atomic Energy Commission<sup>3</sup> and subsequent cost analyses published by Oak Ridge National Laboratory<sup>8</sup> are the most reliable and recently published sources of predictions on the cost and availability of large-scale electrolyzers. These studies investigated two sizes of plants intended to produce hydrogen for ammonia production in an agricultural-nuclear complex. Table 1 gives the estimated costs of the larger of the plant sizes studied and other relevant details of the plant's characteristics.

Table 1. INSTALLED COST OF  
ELECTROLYTIC HYDROGEN PLANT\*

|  | <u>\$</u>         | <u>% of Total</u> |
|--|-------------------|-------------------|
| Mechanical Instrumentation, Processing,<br>Piping and Structures | 5,413,000         | 14.1              |
| Electrical   | 21,018,000        | 56.0              |
| Electrolysis Cell Modules  | <u>11,109,000</u> | <u>29.6</u>       |
| Total  | 37,540,000        | 100.0             |

\* Hydrogen production rate: 44,000 lb/hr, or 7.8 million SCF/hr.  
Electrical input: approximately 1000 MW.  
Source: Reference 3.

In calculating the hydrogen production cost, we have to assign an operating efficiency for the electrolyzer, which leads in turn to an interesting observation: When hydrogen is burned, the energy released is equal to the whole of the combustion energy, or enthalpy change. However, only a portion of this, the free energy, is interchangeable with electricity, either in a fuel cell or its reverse, the electrolysis cell. The remainder, the entropy change, must be supplied or released as heat. An ideal electrolyzer cell absorbs the free energy change as electricity and requires the input of a further 20% of heat energy to maintain an overall balance. In other words, a perfect electrolysis cell would absorb heat, and the heating value of the hydrogen produced would be 120% of the electrical energy put in.

Although modern electrolyzer cells are only about 60% efficient, it seems reasonable a) to aim at a figure close to 100% in electrical efficiency as a target and b) to suppose that this could be achieved if considerable research and development is applied to electrolyzer technology in the next 2 or 3 decades. In fact, some of the Allis-Chalmers published data on its laboratory cells indicate that they were operated at electrical efficiencies exceeding 100% at elevated temperature and pressure.

Because of uncertainty over future electricity generating costs, we choose to subtract the electric power costs from all the other costs of building and operating the electrolyzer. This gives us an incremental cost for the conversion of electricity to hydrogen, which is a useful figure independent of power costs. As far as cost is concerned, we make two observations. One is that the cost of the whole electrolyzer plant is about \$35/kW input, which is small - almost insignificant - in comparison with today's estimates of \$400/kW or more for 1980 nuclear power plants. The other is that the extra cost of producing energy at the power station as hydrogen rather than as electricity is likely to be about \$0.29-\$0.57/million Btu - the higher figure being based on a 70% and the lower figure on a 100% electrical efficiency.

### Hydrogen Transmission

Over 86% of the households in the U.S. are at present supplied with natural gas fuel. This ubiquitous natural gas may arrive in our homes after a transcontinental journey from a well in Texas or Louisiana, and after a temporary sojourn through the summer months of light demand in a natural underground storage system in another part of the country. This country already has an efficient and highly developed network of transmission pipelines, storage systems, and distribution pipes which are capable of moving energy around the country in enormous quantities at relatively low cost. But because the system is buried underground, most of us are unaware of its existence, or we simply take it for granted. In contrast, complaints about the obvious growth of the aboveground electricity network have presented the electricity industry with an incredibly difficult problem, both in public relations and in the sheer economics of burying the cables.

Nobody has yet constructed a 1000-mile pipeline to carry hydrogen at high pressure; however, many shorter pipelines are in use in industry<sup>10</sup> to carry bulk hydrogen from the production plant to the consumer. The technology exists, but the need for long-distance applications has not yet arisen.

Because of hydrogen's lower heating value (325 Btu/SCF compared to 1000+ Btu/SCF for natural gas), it might appear to require significantly larger pipelines to carry the same amount of energy. However, although we have to move about 3 times the volume of gas, the lower specific gravity of hydrogen produces a nearly compensating increase of 2.5 times the flow capacity of a given pipeline.<sup>15</sup> The greater volume of gas to be handled results in an increase of 3 times the pumping power needed for transmission. Experience in moving large volumes of hydrogen within chemical plants and refineries makes it appear that we can use pipelines of similar size and materials to those used for natural gas. The combination of these factors suggests that an increased capital and operating cost of about 60% will result from the long-distance transmission of hydrogen rather than natural gas, based on equivalent amounts of energy. Because the safety precautions in a hydrogen distribution system will be more demanding, we will assume a 100% increase in capital and operating costs for a local hydrogen distribution system.

### Hydrogen Cost

Using statistical data published by the American Gas Association<sup>1</sup> and the Federal Power Commission,<sup>13</sup> it is possible to break down the average selling prices of gas and electricity into their production, transmission, and distribution components. Using the average production price of electric power, the cost of electrolysis referred to earlier, and the assumptions previously outlined for the increased cost of transmitting and distributing hydrogen, we arrive at the figures shown in Table 2, based on the latest available (1969) statistical information.

Table 2. RELATIVE PRICES OF DELIVERED ENERGY

|                               | <u>Electricity</u>     | <u>Natural Gas</u> | <u>Hydrogen</u> |
|-------------------------------|------------------------|--------------------|-----------------|
|                               | <u>\$/million. Btu</u> |                    |                 |
| Production                    | 2.52*                  | 0.16               | 2.81-3.09*      |
| Transmission                  | 0.62                   | 0.18               | 0.22            |
| Distribution                  | <u>1.61</u>            | <u>0.27</u>        | <u>0.34</u>     |
| Total (average selling price) | 4.75                   | 0.61               | 3.37-3.65       |

\* Power purchased at 8.6 mills/kWhr.

Table 2 illustrates clearly the already recognized facts that transmission and distribution of energy in underground natural gas pipelines cost only about 20% as much as transmission and distribution of electrical energy (largely by overhead lines) and that purchase of delivered energy as natural gas is nearly 8 times cheaper than electricity. What is also apparent from these figures is that if we could build and operate an Allis-Chalmers electrolyzer today at the predicted costs, we should be able to deliver hydrogen energy to the average user more cheaply than electrical energy.

As time progresses, we expect the costs of natural gas and electricity to rise, but at different rates. Nuclear electricity costs are predicted to rise only slowly because the breeder reactor will provide energy with very little limitation in the fuel supply. In contrast, all fossil fuel prices, including natural gas, will rise more rapidly because the resources are being depleted, and future production becomes correspondingly more expensive. Ultimately, the cost of natural gas will exceed that for hydrogen. At that point, the "hydrogen economy" will be truly justified economically. Before that time, conservation of fossil fuel supplies and of a clean environment could accelerate the justification of a hydrogen system.

### CONCLUSIONS

This paper has not dealt with the opportunities and the problems that would be raised by the universal availability of hydrogen as a fuel. Some of these will be obvious, and others are dealt with elsewhere.<sup>7</sup> The sheer magnitude of a conversion operation would be so great as to require years of planning. The benefits of such a conversion would be immense to the gas industry, which would thus have an active role in the "nuclear age"; to the electric industry, which would benefit from the improved load factors, lower transmission costs, and greater freedom in power station siting; to the waste disposal industry, which would find an abundance of by-product oxygen available at a very low price; to the chemical and metallurgical industries, which would both find expanding uses for commodity hydrogen; and to the general population, which would benefit from the almost complete elimination of atmospheric pollution. Perhaps most important of all, such a change-over does not appear to present any technical "roadblocks." Although the problems are immense, they appear to be straightforward technological problems which do not require the "technological breakthrough" that appears to be the stumbling block of so many otherwise sound concepts.

REFERENCES CITED

1. American Gas Association, 1970 Gas Facts. Arlington, Va., 1971.
2. Bacon, F. T., "The High Pressure Hydrogen-Oxygen Fuel Cell," Ind. Eng. Chem. 52, 301-03 (1960) April.
3. Costa, R. L. and Grimes, P. G., "Electrolysis as a Source of Hydrogen and Oxygen," Chem. Eng. Prog. 63, 56-58 (1967) April.
4. De Beni, G. and Marchetti, C., "Hydrogen, Key to the Energy Market," Euro Spectra 9, 46-50 (1970) June.
5. Elliott, M. A., "Energy Conversion and Fuel Reserves." Paper presented at the ASME North American Fuel Technology Conference, Ottawa, May 31-June 3, 1970.
6. Erren, R. A. and Hastings-Campbell, W., "Hydrogen From Off-Peak Power," Chem. Trade J. 92, 238-39 (1933).
7. Gregory, D. P., Ng, D. Y. C. and Long, G. M., "Electrolytic Hydrogen as a Fuel," in Bockris, J. O'M., Ed., The Electrochemistry of Cleaner Environments. New York: Plenum Press, in press.
8. Mrochek, J. E., "The Economics of Hydrogen and Oxygen Production by Water Electrolysis and Competitive Processes," in Grigorieff, W. W., Ed., Abundant Nuclear Energy, 107-22. Washington, D.C.: U.S. Atomic Energy Commission, 1969.
9. Murray, R. G. and Schoepfel, R. J., "Emission and Performance Characteristics of an Air Breathing Hydrogen-Fueled Internal Combustion Engine." Paper 719009 presented at the 1971 Intersociety Energy Conversion Engineering Conference, Boston, August 1971.
10. "Pipeline Distribution for Carbon Monoxide and Hydrogen Is Expanding," Chem. Week 108, 49 (1971) May 19.
11. Rosenberg, R. B. and Kweller, E., "Catalytic Combustion of Reformed Natural Gas," Appliance Eng. 4, 32-36 (1970) August.
12. Steinberg, M. and Holmes, J. M., "Low Cost Power and the Chemical Process Industry," Chem. Eng. Prog. 63, 35-67 (1967) April.
13. U.S. Federal Power Commission, Statistics of Privately Owned Electric Utilities in the United States, 1969. Washington, D.C.: U.S. Government Printing Office, 1970.
14. U.S. National Power Survey Transmission Technical Advisory Committee, The Transmission of Electric Power. Washington, D.C.: U.S. Federal Power Commission, 1971.
15. Von Fredersdorff, C. G., "Relative Costs of Transmission of Pipeline Gas," in American Gas Association Operating Section Proceedings - 1959, CEP-59-18.
16. Weinberg, A. M. and Young, G., "The Nuclear Energy Revolution and Chemical Processing," in Eringen, A. C., Ed., Recent Advances in Engineering Science, Vol. 2, 1-19. New York: Gordon and Breach, 1965.

17. Winsche, W. E., Sheehan, T. V. and Hoffmann, K. C., "Hydrogen - A Clean Fuel for Urban Areas." Paper 719006 presented at the 1971 Inter-society Energy Conversion Engineering Conference, Boston, August 1971.

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## Fluid Flow Aspects of Water Electrolyzers

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In considering possible processes for producing fuels as alternatives to fossil fuels, the Water Electrolysis Process is a feasible one. For example, the Water Electrolysis Process is being considered on a large scale in connection with Industrial Complexes which can desalt water, produce power and other products such as hydrogen, oxygen, ammonia, ammonia nitrate, and nitric acid (1). The energy source could be a large nuclear reactor coupled to a large electrolyzer system.

Water electrolysis is a process in which hydrogen and oxygen gases are produced from water by the application of electric energy. Perhaps the simplest method for controlling the production of these gases is to use an electrolyzer consisting of a number of electrolysis cells, using a liquid water solution as electrolyte, and connecting them hydraulically in parallel. Electrically the cells may be connected either in series or parallel.

Each cell is made up of a cathode (on which hydrogen is produced), an anode (on which oxygen is produced), and the electrolyte which flows through the cell. The anode and cathode are separated by a membrane which may be porous to liquid electrolyte but not to the gases being generated, so that the gases will not mix. A cross section of such a cell is shown in Fig. 1.

To develop a modern electrolyzer technology will require much more basic engineering information concerning two-phase flow, electrolytes, electrodes, and control than is available at present. The purpose of this paper is to present an analytical basis developed by the authors for investigating the two-phase flow occurring in an electrolysis cell along with a review of related experimental data.

The electrolysis process is complicated because of the simultaneous occurrence of coupled, non-linear, transport of mass, momentum, energy, and charge in the presence of electrochemical reactions in the electrolyte and on the electrodes. The precise definition of these processes is virtually impossible and in this paper one dimensional (or hydraulic) equations will be used to define the flow in an electrolysis cell configuration such as is shown in Fig. 1.

Tobias (2) seems to have been the first to contribute significant work on this problem. He assumed, however, that there was no membrane in the cell; that the inlet velocity was zero; and that the gas velocity was independent of void fraction. Funk and Thorpe (3) presented a more general analysis of the void fraction and current density distributions in an electrolysis cell subject only to the assumption that the gases are incompressible. Then later, Thorpe and Funk (4) presented a theoretical and experimental investigation of the pressure drop occurring in an electrolysis cell. There are also several papers on Electrochemical Machining (5,6) in which an allied problem is discussed.

## TRANSPORT EQUATIONS

The equations to be derived will be based on the assumption that the flows can be considered as one-dimensional, two-phase, flows. There will be, then, only one independent space variable  $s$ .

The electrolyte flow is from the bottom toward the top in a cell of width  $H$  and length  $L$ . The cell consists of two parallel channels separated by a membrane. Flow in the hydrogen side consists of a two-phase mixture of hydrogen gas and electrolyte in a thin rectangular channel ( $H$  by  $y_2$ ) formed between the membrane and the cathode. Flow in the oxygen side is similar in a channel ( $H$  by  $y_1$ ). The membrane is assumed to be porous to  $\text{OH}^-$  ions and possibly to liquid electrolyte. Subscript 1 denotes the flow properties on the oxygen side while subscript 2 denotes similar properties on the hydrogen side. Various species within a channel are identified by the subscripts  $g$  for gas,  $v$  for mixture of gas and vapor,  $f$  for liquid electrolyte, and  $h$  for the hydroxyl ion. Since only an alkaline electrolyte is considered, the hydrogen ion is neglected.

The transverse current density (current flux)  $i$  in the cell is a function of position  $s$ . If the cell is vertical the coordinate  $s$  is identical with vertical coordinate  $z$ . The current flux  $i$  generates hydrogen gas on the cathode at the local mass flux rate  $m_{g2}$ . Water may evaporate into the hydrogen gas bubbles so that instead of a dry gas, a mixture of water vapor and hydrogen gas will flow upward with average velocity  $V_{v2}$  in some equivalent area proportional to the dimension  $y_{v2}$ . The gas bubbles, or voids, are contained within an electrolyte layer near the cathode surface which is called the hydrogen bubble layer of thickness  $\delta_2$ .

The liquid electrolyte flow on the hydrogen side occurs with average velocity  $V_{f2}$  in an equivalent area proportional to  $y_{f2}$  where

$$y_2 = y_{v2} + y_{f2}. \quad [1]$$

A similar flow configuration exists on the oxygen side where oxygen gas is liberated on the anode at mass flux rate  $m_{g1}$ . Then

$$y_1 = y_{v1} + y_{f1}. \quad [2]$$

A hydroxyl ion flux occurs through the membrane which has the net effect of transporting  $\text{H}_2\text{O}$  from the cathode side to the anode side of the cell. In addition to the ion flux, the membrane may be porous to liquid electrolyte. These fluxes through the membrane are denoted by  $m_h$ ,  $m_f$ .

The definitions and derivations which follow will apply to either hydrogen or oxygen sides of the cell so that, in the interest of simplifying the notation, the numerical subscript will be omitted.

The vapor quality  $X$ , consisting of the mixture of gas and water vapor, is defined by the equations

$$X = \frac{W_v}{W}; \quad (1-X) = \frac{W_f}{W}, \quad [3]$$

where

$$W_v = \rho_v A_v V_v, \quad [4]$$

$$W_f = \rho_f A_f V_f, \quad [5]$$

$$W = W_v + W_f, \quad [6]$$

and  $\rho_f$  = liquid density,  $\rho_v$  = vapor density,  $A_f = Hy_f$  is the area occupied by liquid,  $A_v = Hy_v$  is the area occupied by vapor,  $V_f$  = average liquid velocity,  $V_v$  = average vapor velocity.

The vapor volume fraction  $\alpha$ , sometimes called the void fraction, and the liquid holdup  $(1-\alpha)$  are defined by

$$\alpha = \frac{A_v}{A} ; (1-\alpha) = \frac{A_f}{A}, \quad [7]$$

where

$$A = A_v + A_f = Hy. \quad [8]$$

If equations [3] to [7] are combined, the following important equation is obtained

$$\frac{1-\alpha}{\alpha} = \sigma \left( \frac{1-X}{X} \right) \left( \frac{\rho_v}{\rho_f} \right), \quad [9]$$

where  $\sigma$  is the slip ratio (also called the phase velocity ratio) defined by

$$\sigma = \frac{V_v}{V_f}. \quad [10]$$

In general the slip ratio depends on pressure  $p$ , void fraction  $\alpha$ , mass flow rate  $W$ , channel area  $A$ , density ratio  $\rho_v/\rho_f$  and channel orientation.

Most of the engineering quantities of interest in an electrolysis cell, such as electrolyte ohmic resistance or pressure drop, are functions of the void fraction  $\alpha$ ; the void fraction, in turn, depends on the slip ratio  $\sigma$  which in general is unknown. There are several models which express the void fraction, slip ratio relationship. The simplest model is the homogeneous model in which  $\sigma$  is assumed unity.

#### Continuity Equations (Mass Transport)

At some position  $s$  along the electrolysis cell shown in Fig. 1, consider an elemental control volume for the gas phase. Gas is considered to be generated at the interface between liquid electrolyte and gas phases. This gas enters the gas phase control volume and is represented as a source of strength  $m_g$ . The quantity  $m_g$  is a transverse flux having units of  $\text{gm cm}^{-1} \text{sec}^{-1}$ .

The law of conservation of mass as applied to the gas phase control volume is

$$\frac{d W_g}{ds} = m_g, \quad [11]$$

where  $W_g$  is the mass flow rate of gas in the channel.

In a similar way, the continuity equation for the liquid electrolyte phase is derived as

$$\frac{d W_f}{ds} = -m_g + (\pm)m_h + (\pm)m_f, \quad [12]$$

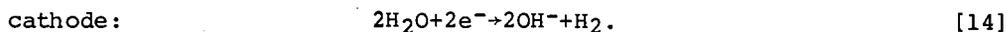
where the mass flux rate  $m_g$  is given by

$$m_g = \lambda_g i, \quad \lambda_g = \frac{N_g}{\epsilon_g}. \quad [13]$$

The atomic weight of the gas is  $N_g$  while its valence upon electrolytic decomposition is  $e_g$ . The proportionality constant  $\lambda_g$  is the electrochemical equivalent.

The mass flux  $m_f$  is non-zero only if the membrane is porous to liquid electrolyte; if the membrane does have this property, then both the magnitude and sign of the term  $m_f$  depend on the pressure distributions along the two sides of the membrane.

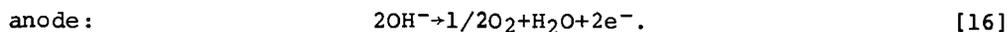
The hydroxyl ion flux  $m_h$  can be related to the flux  $m_g$  from the equation of the electrochemical reaction occurring in the channel. On the cathode side, for example, the equation is



For every gram of hydrogen generated on the cathode side, there are 17 g of hydroxyl ions passing through the membrane; this ion flow is provided by the liquid electrolyte phase. Thus on the cathode side, the minus (-) sign is selected for  $m_h$  and

$$\text{cathode:} \quad m_h = -17m_g. \quad [15]$$

On the anode side, the electrochemical reaction is



Thus for every gram of oxygen generated, there are 2.125 g of hydroxyl ions flowing through the membrane into the oxygen channel. In this instance, the plus (+) sign is selected for  $m_h$  and

$$\text{anode:} \quad m_h = 2.125m_g. \quad [17]$$

The foregoing development has not considered the mass transport due to water evaporation into the hydrogen or oxygen bubbles. However, it can readily be shown that if the gases are assumed to be saturated with water vapor, the mass fraction of the hydrogen or oxygen gas in the vapor mixture is

$$f_g = \frac{1}{1 + \frac{M_w}{M_g} \left( \frac{P_w}{P_t - P_w} \right)}, \quad [18]$$

where  $P_w$  is the water vapor pressure and  $P_t$  is the total bubble pressure;  $M_w$ ,  $M_g$  are molecular weights of water and gas respectively.

Rewriting equations [11], [12] to account for water vapor transfer, along with definitions made previously, the continuity equations become

$$\frac{d}{ds} w_v = \left[ 1 + \frac{M_w}{M_g} \left( \frac{P_w}{P_t - P_w} \right) \right] \lambda_g i, \quad [19]$$

$$\frac{d}{ds} w_f = \left[ (\gamma - 1) - \frac{M_w}{M_g} \left( \frac{P_w}{P_t - P_w} \right) \right] \lambda_g i + (\pm) m_f, \quad [20]$$

where

$$\begin{aligned} \lambda_g &= 0.228 \times 10^{-7}; \gamma = -17 \text{ (cathode side)}, \\ \lambda_g &= 1.824 \times 10^{-7}; \gamma = 2.125 \text{ (anode side)}. \end{aligned} \quad [21]$$

## Energy Equation(Energy Transport)

The energy transport of the gas phase will be neglected due to the low thermal conductivity and heat capacity of the gas compared to that of the electrolyte. Then only the liquid phase needs to be considered.

In applying the first law of Thermodynamics as it applies to a representative control volume, it will be assumed that the transport of kinetic and gravitational specific energies are negligible compared to the specific thermal energies. Also, the energy transport due to liquid conversion to vapor is neglected. Then, an energy balance gives

$$W_f \frac{dh_f}{ds} = H(q'' + iE), \quad [22]$$

where  $h_f$  is the electrolyte enthalpy,  $q''$  is the heat flux transferred to or from the electrolyte, and  $E$  is the ohmic voltage drop across the electrolyte. Note that

$$h_f = CT_f ; q'' = h(T_s - T_f), \quad [23]$$

where  $T_f$  is electrolyte temperature,  $T_s$  is electrode surface temperature,  $h$  is the heat transfer coefficient, and  $C$  is specific heat.

## Equations of Motion(Momentum Transport)

In making the momentum balance, both vapor and liquid phases are included at the same time. Then upon applying the momentum theorem to a representative control volume, it can be shown that

$$W_f \frac{dv_f}{ds} + W_v \frac{dv_v}{ds} = -A \frac{dp}{ds} - 2H\tau - \rho_m \frac{dz}{ds}, \quad [24]$$

where  $\tau$  is the average shear stress,  $\rho_m$  is the density of the two phase mixture, and  $p$  is the static pressure. In deriving this equation, the momentum transfer due to liquid conversion to vapor has been neglected.

## Electrical Relations(Charge Transport)

Consistent with the one dimensional transport equations of continuity, energy, and momentum is a one dimensional transport equation of charge within the electrode gap. However, such an equation will involve ion mobilities, electrochemical reactions, and other complicated processes which will not be presented here. Instead, the electrical phenomena will be represented by a simple form of Ohm's law.

Let the sum of the electrode polarization and decomposition potentials be denoted by  $\Delta E$  while the applied voltage is  $E_a$ . Then the voltage  $E$  available for overcoming ohmic resistance of the two-phase electrolyte is given by

$$E = E_a - \Delta E, \quad [25]$$

and

$$E = iR_C, \quad [26]$$

where  $R_C$  is the ohmic resistance of the cell. This resistance consists of a membrane resistance  $R_m$  in series with resistances  $R_1, R_2$  of the

electrolyte-bubble mixtures in the oxygen and hydrogen channels of the cell. That is

$$R_C = R_1 + R_m + R_2. \quad [27]$$

The resistances  $R_1$ ,  $R_2$  are functions of the properties of pure liquid electrolyte, the void fraction  $\alpha$ , and the temperature  $T_f$ .

The cross section of the channel occupied by vapor at position  $s$  is proportional to  $Y_g$ . This void is distributed within some bubble layer of thickness  $\delta$ . The void fraction  $\alpha'$  based on bubble layer thickness (that is, the void fraction within the bubble layer) is defined by

$$\alpha' = \frac{Y_g}{\delta}. \quad [28]$$

The resistance within the bubble layer is some function of  $\alpha'$  rather than  $\alpha$ .

The total transverse resistance, per unit cross sectional area perpendicular to  $y$  is

$$R = r_{tp}\delta + r_f(y-\delta), \quad [29]$$

where  $r_{tp}$  is the two-phase resistivity in the bubble layer and  $r_f$  is the liquid electrolyte resistivity. The quantity  $r_f$  is, in general, temperature dependent, say

$$\frac{1}{r_f} = \frac{1}{r_0} [1 + \beta(T_f - T_0)], \quad [30]$$

where  $\beta$  represents a temperature coefficient and subscript 0 denotes conditions at the cell entrance.

The two-phase resistivity, in the bubble layer, is a function of  $\alpha'$  assumed to be of the form

$$r_{tp} = r_f f(\alpha'). \quad [31]$$

The function  $f$  is determined from some void fraction-resistivity model which assumes a homogeneous distribution of bubbles within an electrolyte matrix. A generalization of such heterogeneous condition mechanisms is

$$f(\alpha') = (1 - \alpha')^{-n}. \quad [32]$$

Tobias (2) proposed that  $n = 1.5$  while Thorpe and Zerkle (5) found that  $n = 2$  gave better results in the allied problem of electrochemical machining.

It can be noted that

$$\alpha' = \frac{Y_g}{\delta} \alpha, \quad [33]$$

so that equation [29] can be written as

$$R = r_f [(y-\delta) + \delta f(\frac{Y_g}{\delta} \alpha)]. \quad [34]$$

The electrode polarization over voltages are generally assumed to obey Tafel equations of the form

$$\Delta E_p = a + b \ln i, \quad [35]$$

where  $a$ ,  $b$  are constants depending on electrode material, electrolyte, temperature, and pressure. Denoting the decomposition potential by  $\Delta E_d$ , then

$$\Delta E = \Delta E_{p1} + \Delta E_{p2} + \Delta E_d. \quad [36]$$

Equations [25], [26], [27], [34], [35], [36] can be combined to give an implicit relation between the applied voltage  $E_a$ , current density  $i$ , vapor void fractions  $\alpha_1, \alpha_2$ , bubble layers  $\delta_1, \delta_2$ , and temperatures  $T_1, T_2$ . That is

$$i = i(E_a, i, \alpha_1, \alpha_2, \delta_1, \delta_2, T_1, T_2). \quad [37]$$

As a first approximation, the quantity  $E$  could be regarded as known independent of  $i$  which greatly simplifies the problem.

#### Recapitulation

The equations above represent a one-dimensional approximation of the processes occurring within the electrolysis cell. As they stand, they involve more unknowns than there are equations so that additional relations are required. Additional equations will be the equations of state of oxygen and hydrogen gases, empirical relations for the shear stresses, and either empirical or theoretical expressions for the slip ratios. Furthermore, these equations are strongly coupled together through pressure and temperature. Although this is a complicated system of non-linear, coupled, differential equations the programming of them for computer solution is not an insurmountable task.

#### ANALYTICAL STUDIES

It is surprisingly simple to obtain algebraic equations for the vapor quality  $X$  and void fraction  $\alpha$  in terms of the slip ratio  $\sigma$  and integrals of the current density  $i$ . This is done by integrating equations [19], [20] from the inlet ( $s = 0$ ) to some point  $s$  in the cell and substituting into equations [3], [6] to obtain

$$X = \frac{\left[1 + \frac{M_w}{M_g} \left(\frac{p_w}{p_t - p_w}\right)\right] \lambda_g H_f^s \int_0^s i ds}{W_f(0) + \gamma \lambda_g H_f^s \int_0^s i ds}. \quad [38]$$

Substitution of equation [38] into [9] then gives the void fraction  $\alpha$  as a function of slip ratio  $\sigma$ , the vapor density  $\rho_v$ , and integral of the current density  $i$ .

In carrying out parametric studies of the current density distributions in electrolysis cells, Funk and Thorpe (3) used the resulting equation [9], as described above, along with the following further assumptions:

- (1) Both gas and liquid flows are assumed incompressible and isothermal. This permits a great analytical simplification in that it decouples the continuity and resistivity equations from the momentum and energy equations.
- (2) The bubble layers are assumed to extend completely across the

channels. This assumption seems to be justified from visual observations which show the bubble layer to fill the channel except in a short entrance region.

- (3) The membrane is assumed to be permeable only to the hydroxyl flux and not to liquid electrolyte.
- (4) Water vapor in the gas is assumed negligible.

With these assumptions, the system of equations reduces to a set in which there are only three more unknowns than equations; these unknowns are the applied voltage  $E_a$  and the slip ratios  $\sigma_1, \sigma_2$ . If  $E_a, \sigma_1, \sigma_2$  are regarded as parameters then the system can be solved simultaneously for the void fraction  $\alpha$  and current density  $i$ . Since integration of the equations brings the cell inlet velocity into the problem as a boundary condition, it is also a parameter.

The electrical requirement is expressed by combining equations [25], [26], [27], [34], [35], [36] to obtain

$$E_a - [(a_1 + a_2) + (b_1 + b_2) \ln i + \Delta E_d] = i \{ R_m + r_f [y_1 f(\alpha_1) + y_2 f(\alpha_2)] \}. \quad [39]$$

Equation [39] along with the two equations [9] for the void fractions  $\alpha_1, \alpha_2$  are a set of three equations in three unknowns  $\alpha_1, \alpha_2, i$  and four parameters  $E_a, \sigma_1, \sigma_2, V_0$ . These equations were programmed for numerical solution and solved for a specific cell geometry as defined in reference (3). By examining the resulting current density distributions it was concluded that:

- (1) The effect of slip ratio is pronounced particularly at the higher cell voltages.
- (2) The effect of cell inlet velocity is very important and particularly so at the higher cell voltages.
- (3) The void fraction distributions will be practically identical in the two sides of the cell if the hydrogen side cross section is twice that of the oxygen side and both are subject to the same inlet velocity.

These results are not entirely unexpected based on an intuitive understanding of what is occurring in the electrolysis cell. They did, however, point out the importance of making experimental studies to determine what the actual slip ratios will be in a real electrolysis cell.

Before describing these experiments, it is appropriate to mention some of the analytical results obtained by Thorpe and Zerkle (5,6) for electrochemical machining. There are two major conclusions which may be pertinent to electrolyzer design:

- (1) If the current density distribution is assumed to be constant along the cell as a first approximation, it is possible to integrate both the continuity and energy equations to obtain a remarkably simple set of algebraic equations. This makes possible the idea of fitting theoretical curves to experimental data in order to determine the heterogeneous conduction exponent  $n$  in a very simple and convenient manner.
- (2) Under certain conditions (say, of high electrolyzer output) it is possible to experience a choking phenomenon similar to that which is well known in the field of compressible flow. This is due to the presence of gas in the electrolyzer and this effect should be considered in the design of electrolyzers.

For further information, references (5,6) should be studied.

## EXPERIMENTAL STUDIES

Several experimental investigations of void fraction and pressure drop occurring in water electrolysis cells have been conducted at the University of Kentucky. Instead of discussing the experimental apparatus and procedures in detail, only a summary will be presented here. References (3, 4, 7) can be consulted for detailed information.

The experimental apparatus consisted basically of a flow loop, positive displacement pump, a current source, instrumentation, and a gamma ray attenuation system for measuring void fractions. The electrolyte used was one normal KOH while the electrodes were stainless steel. The test section was made from plexiglas and stainless steel with oxygen side cross section 1" by 0.18" and hydrogen side cross section 1" by 0.18". This test section was 36" in length preceded by an entrance length of 21". The membrane consisted of a polystyrene coated nylon cloth sandwiched between two slotted plexiglas holders.

Studies of the flow pattern indicated that a bubble boundary layer existed at the test section inlet but that after a short distance (6"-8") downstream, bubbles occupied the complete cross sections dispersed as small spherical bubbles in essentially a froth flow. The flow velocities were of order of magnitude  $0.5 \text{ ft sec}^{-1}$  and the current density was of order of magnitude  $250 \text{ amp ft}^{-2}$ . This resulted in oxygen bubbles having an average diameter of about  $4.5 \times 10^{-3}$  inches and hydrogen bubbles having an average diameter of  $3.5 \times 10^{-3}$  inches. For such small bubbles, the assumption that the gas is saturated with water vapor is justified and this was assumed in calculating the vapor densities.

The slip ratio was determined in the following way. First, the void fraction was determined experimentally using a 20 mc Cesium-137 gamma source, a scintillation probe as detector, collimator, and associated electronic equipment as discussed in reference (8). Next, the vapor quality  $X$  was determined by measuring the current density distribution  $i$ , the inlet flow rate  $W_f(0)$ , and substituting into equation [38].

With  $\alpha$  and  $X$  known, the only remaining unknown in equation [9] is the slip ratio  $\sigma$ . If the ratio  $(1-\alpha)/\alpha$  is plotted against the ratio  $\rho_v(1-X)/\rho_f X$ , the slope of a line through the data is the slip ratio  $\sigma$ . Such plots indicated that the slip ratio is essentially unity.

Another way of plotting the data is to plot the void fraction  $\alpha$  against the vapor volumetric flow fraction  $\phi$  defined by

$$\phi = \frac{1}{1 + \left(\frac{1-X}{X}\right) \left(\frac{\rho_v}{\rho_f}\right)} \quad [40]$$

The data is plotted in this manner in Fig. 2. Also plotted in Fig. 2 are the homogeneous model ( $\sigma = 1$ ) and Bankoff's model (9) which gives essentially the same results as those of Martinelli and Nelson (10). The figure indicates that the slip ratio is close to unity for both oxygen and hydrogen sides of the electrolysis cell. It should be remembered, though, that this conclusion is drawn for a single cell geometry and rather low throughput conditions.

The determination of the slip ratio is prerequisite to a determination of pressure drop correlations because the pressure drop

depends on the void fraction. In other words, the conclusion that the slip ratio is unity permits the pressure drop equations to be written in terms of the vapor quality  $X$  through equation [9] which, in turn, depends only on the (measured) current density distribution  $i$  and (measured) inlet flow rate  $W_f(o)$ .

Data reduction was carried out by evaluating the acceleration and elevation pressure drop components of equation [24] and subtracting them from the (measured) total pressure drop. In this way the frictional pressure drop component is isolated. The actual data reduction was programmed for digital computation and involved a determination of the void fraction  $\alpha$  at the same time.

Each test run involved a determination of both the single phase pressure drop in the absence of electrolysis (which is entirely frictional) and the two phase pressure drop with electrolysis occurring. In this way, it is possible to compute a frictional pressure drop multiplier  $\Psi$  defined by

$$\Psi = \frac{(\Delta p)_{tpf}}{(\Delta p)_{spf}} \quad [41]$$

Attempts were made to correlate  $\Psi$  against several parameters including the void fraction  $\alpha$ . These attempts led to the formulation of a variable  $\Omega$  defined by

$$\Omega = \alpha \left( \frac{\lambda g i}{\rho_v V_o} \right) \left( \frac{\rho_v}{\rho_f} \right)^{1/3} \quad [42]$$

The factor  $\lambda g i$  which has units and dimensions of a mass velocity is a measure of the lateral vapor mass flux away from the wall. Superficially, this factor can be viewed as an increased roughness of the electrode surface. When it is divided by the gas density  $\rho_v$ , a superficial transverse velocity is obtained. The ratio of this transverse velocity to the axial velocity at inlet  $V_o$  is a dimensionless similarity variable and a measure of dissipation in the flow. Attempts to correlate  $\Psi$  in terms of this ratio and also in terms of void fraction  $\alpha$  indicate that  $\Psi$  should be correlated in terms of the product of the two. However, two distinct correlations were obtained in this way for the oxygen and hydrogen sides.

It was found that the two correlations for oxygen and hydrogen could be brought together by introducing the density ratio  $(\rho_v/\rho_f)^{1/3}$ . Thus the correlation parameter  $\Omega$  was synthesized and the frictional pressure drop multiplier  $\Psi$  was correlated for both oxygen and hydrogen as shown in Fig. 3. Except for points near  $\Psi = 1$  where the experimental errors can be rather large, this correlation is accurate to within  $\pm 20$  per cent.

#### SUMMARY

In this paper, a summary of some of the fluid flow aspects of water electrolyzers has been presented along with research which has been already published in the literature. Admittedly, the approach has been restricted to a single type of electrolyzer and to data applying only to a very restricted range of geometries and flow variables. This should, however, provide a convenient basis or point of departure for future work in the event water electrolysis becomes an important mechanism for producing fuel.

Much work remains to be done in order to advance the state of electrolyzer technology. For example, further studies should be conducted over a wider range of ambient operating pressures, tempera-

tures, flows, and current densities. Also, complete system studies should be conducted which include the problems of optimization and control.

#### REFERENCES

1. Nuclear Energy Center - Industrial and Agro-Industrial complexes Summary Report, ORNL-4291, VC-80, July 1968.
2. Tobias, C. W., "Effect of Gas Evolution on Current Distribution and Ohmic Resistance in Electrolyzers", J. Electrochemical Soc., V. 106, Sept. 1959, p. 833.
3. Funk, J. E., and Thorpe, J. F., "Void Fraction and Current Density Distributions in a Water Electrolysis Cell", J. Electrochemical Soc. v. 116, Jan 1969, Pp. 48-54.
4. Thorpe, J. F., Funk, J. E., and Bong, T. Y., "Void Fraction and Pressure Drop in a Water Electrolysis Cell", J. Basic Engineering, Trans. ASME, v. 92, 1970, Pp. 173-182.
5. Thorpe, J. F., and Zerkle, R. D., "Analytic Determination of the Equilibrium Electrode Gap in Electrochemical Machining", Int. J. Mach. Tool Des. and Res., v. 9, June 1969, Pp. 131-144.
6. Thorpe, J. F., and Zerkle, R. D., "A Theoretical Analysis of the Equilibrium Sinking of Shallow, Axially Symmetric, cavities by Electrochemical Machining", Fund. of Electrochem. Mach., Symposium Volume of the Electrochemical Society, 1971.
7. Narasimhan, N. D., "Effect of Wall Flux on Frictional Pressure Drop in a Water Electrolysis Cell," MSME Thesis, University of Kentucky, 1969.
8. Bong, T. Y., Funk, J. E., and Thorpe, J. F., "Two-Phase Flow in a Water Electrolysis Cell, Void Fraction and Pressure Drop", Report TR5-68ME2, Mechanical Engineering Department, University of Kentucky, 1968.
9. Bankoff, S. G., "A Variable Density Single-Fluid Model for Two-Phase Flow with Particular Reference to Steam-Water Flow", J. Heat Transfer, Trans. ASME, v. 82, 1960, p. 265.
10. Martinelli, R. C., and Nelson, D. B., "Prediction of Pressure Drop during Forced Convection Boiling Water", Trans. ASME, v.70, 1948, p. 695.

## NOMENCLATURE (Consistent Units)

|              |   |
|--------------|---|
| a, b,        | constants in the equation describing polarization over voltage (Eq. [35]) |
| A            | channel flow area   |
| C            | specific heat of the electrolyte  |
| $E_a$        | voltage applied to the cell   |
| E            | voltage drop in the two phase electrolyte                                 |
| $\Delta E_d$ | water decomposition potential   |
| $\Delta E_p$ | electrode polarization overvoltage  |
| $\Delta E$   | sum of $\Delta E_d$ and $\Delta E_p$                                      |
| H            | channel width   |
| i            | current density   |
| L            | electrolyzer cell length  |
| m            | local mass flux   |
| M            | molecular weight  |
| N            | atomic weight   |
| p            | pressure  |
| $r_f$        | liquid electrolyte resistivity  |
| $r_{tp}$     | resistivity of the two-phase bubble layer                                 |
| R            | total cell transverse resistance  |
| $R_c$        | ohmic resistance of the cell  |
| $R_m$        | membrane resistance   |
| T            | temperature   |
| V            | fluid velocity  |
| w            | mass flow rate  |
| x            | gas quality or gas mass fraction  |
| y            | channel thickness   |
| z            | vertical coordinate   |

## Greek Letters

|              |   |
|--------------|---|
| $\alpha$     | void fraction based on channel thickness      |
| $\alpha'$    | void fraction based on bubble layer thickness |
| $\beta$      | temperature coefficient                       |
| $\gamma$     | defined by equation [21]                      |
| $\delta$     | bubble layer thickness                        |
| $\epsilon_g$ | valence upon electrolytic decomposition       |
| $\lambda_g$  | constant defined by equation [13]             |
| $\rho$       | density                                       |
| $\sigma$     | slip ratio or phase velocity ratio            |
| $\tau$       | wall shear stress                             |
| $\Phi$       | gas volume flow fraction                      |
| $\Psi$       | two-phase flow frictional multiplier          |
| $\Omega$     | correlation parameter                         |

## Subscripts

|   |                          |
|---|--------------------------|
| o | channel inlet conditions |
| l | anode side               |
| 2 | cathode side             |
| g | gas                      |
| f | liquid                   |
| h | hydroxyl ion             |
| v | vapor                    |

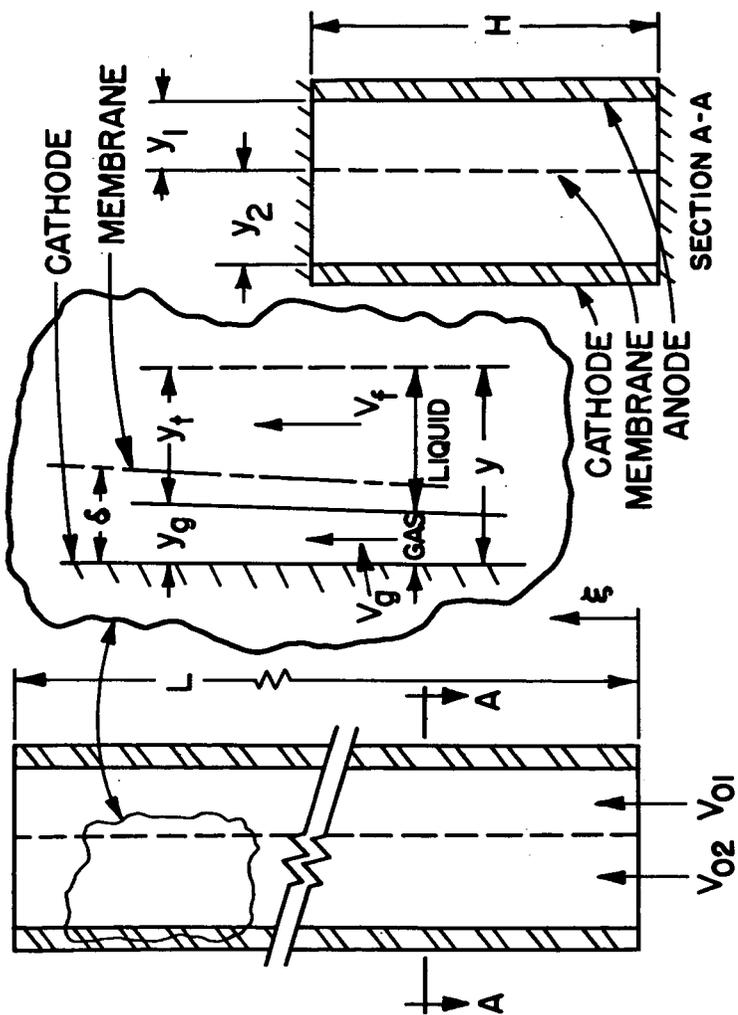


Figure 1. Electrolysis Cell Nomenclature

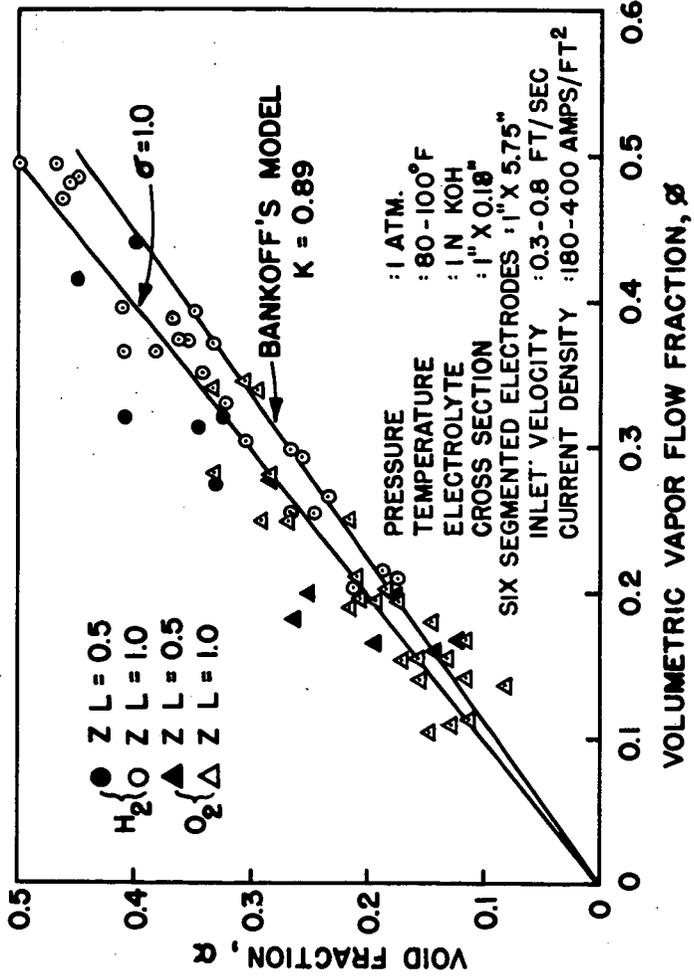


Figure 2. Void Fraction Versus Volumetric Flow Fraction

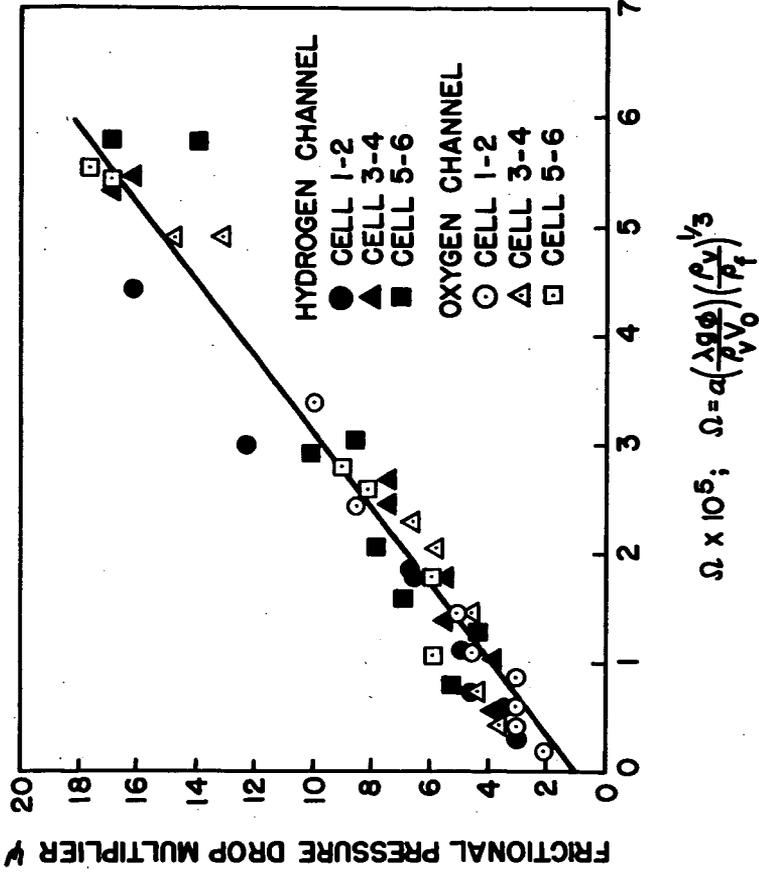


Figure 3. Correlation of Frictional Pressure Drop Multiplier

## MARK -1 , A CHEMICAL PROCESS TO DECOMPOSE WATER USING NUCLEAR HEAT

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C.C.R. EURATOM - ISPRA - VARESE (ITALY)

INTRODUCTION

The evolution of nuclear reactors has followed mainly two trends:

- 1) The increase of the maximum coolant temperature
- 2) The decrease in the heat cost due to the progress in technology and to the increase in reactor size.

The demand for higher outlet temperatures, in view of higher efficiencies in the electric energy production, led to development of reactors capable of those high temperatures, e.g. the Advanced Gas Cooled Reactors, the Molten Salt Reactors, the High Temperature Gas Reactors. HTGR's have the advantage over the other two reactor concepts that their output coolant temperature is higher and that the properties of their core materials could tolerate additional increases in temperature.

Also from the commercial point of view the HTGR's won a round against the other two with the order of Philadelphia Electric for a station equipped with two such reactors, with a total net electrical capacity of 2,320 Mwe. (1)

Electricity, the usual form for marketing nuclear energy, meets only about 20% of the energy needs for a technologically developed society. This fact limits the role nuclear energy can play in the total energy supply.

Looking for a mean to penetrate the remaining 80% of the energy market we considered that hydrogen could be the ideal carrier; so, a few years ago we started looking for a process to produce  $H_2$  using nuclear heat.

The temperature level at which heat is available from the present family of HTGR's is such that it can be used in hydrogen production processes like coal gasification or natural gas reforming. In fact, there is a strong incentive for implementing those endothermic processes with nuclear heat because the difference in price between the fossil fuel calorie and the nuclear calorie is not negligible and tends to increase. But their thermodynamics is such that only 20-25% of the energy in the product comes from the nuclear reactor. The impact of such applications on the penetration of nuclear energy into the energy market will then be necessarily small. For this reason our research was oriented towards a process for hydrogen production in which the only energy input was from a nuclear reactor. In a sense water electrolysis (2, 3) works this way, but the necessary transformations through various stages of all the primary energy from heat to electricity and then, via electrolytic cells, to hydrogen, lead to low total efficiency and high investment cost.

We thought that a more direct use of heat could lead to higher conversion efficiencies and lower capital cost and we did set our goal at decomposing water using the nuclear heat for operating some endothermic chemical reactions in a closed cycle, i.e. with nominal consumption of chemicals.

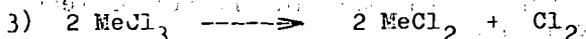
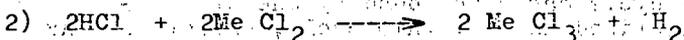
THE CHEMICAL CYCLES

Thermodynamically it is not possible to crack water, with a reasonable yield, at temperatures lower than 2500°-3000°C. If we had to run

a process with only one endothermic reaction at a lower temperature we should compensate the lower entropical level of the heat by a corresponding amount of useful work. A multistep chemical process operating at different temperatures behaves as a thermal engine(4); as a consequence the useful work requirement can be obtained through extra heat entering the system at high temperature and given off as degraded heat at low temperature in accordance with the Carnot rule.

By a two-step process it is possible theoretically to split water even with a limit of 300°C for the upper temperature, but the thermodynamic properties of the chemical substances that could be used in such a cycle are very far from the thermodynamic properties of all known substances and following (4) even at 1000°C very probably such substances do not exist nor can they be synthesized.

Three-step processes appear more feasible and in fact they have been already proposed (5). They are based on the reaction of chlorine with steam at high temperature to produce oxygen and hydrochloric acid; the last one being dissociated into hydrogen and chlorine by a reaction at low temperature with a low-valence metal chloride (metals being Ta, Bi, Hg, V) and the subsequent dissociation of the so formed high-valence chloride at high temperature. The reactions for this type of a cycle are :

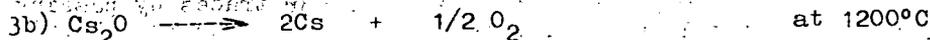
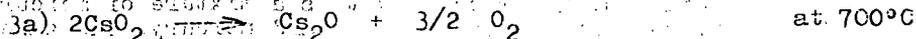
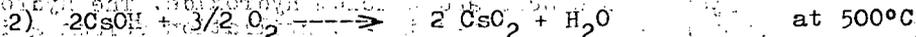
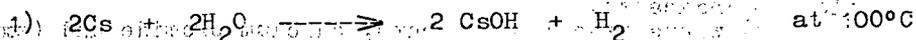


the reactions 1) and 3) run at high temperature and reaction 2) at low temperature.

Some experimental work has been done on the most promising cycle: the one employing Vanadium (6). The reaction between chlorine and steam has been tried to find the reaction rate as a function of temperature; reagents feed rate and ratio and reactor's surface-to-volume. The conditions for a practical application have been found.

Some exploratory tests have been done about the reaction between vanadium dichloride and hydrochloric acid in a static-type apparatus at atmospheric pressure and at room temperature. In spite of the favourable reaction thermodynamics essentially no reaction between  $\text{VCl}_2$  and  $\text{HCl}$  was observed in those conditions.

Another three-step process is described in U.S. Patent (1970)(7) in which Cesium metal reacts with water, then Cesium hydroxide is transformed into Cesium peroxide and finally Cesium peroxide is dissociated at high temperature. The reactions of this cycle are :

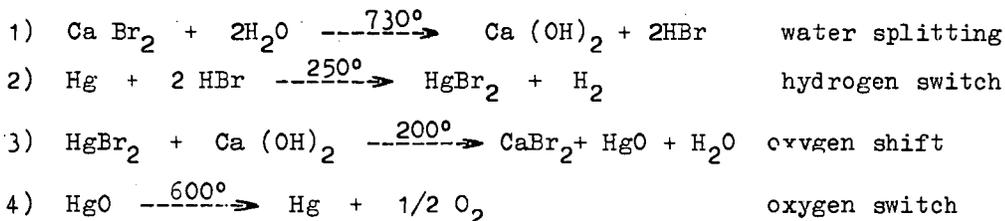


No experimental work is reported in the patent description. With the available thermodynamic data we calculate for the reaction 2) quite an unfavourable equilibrium constant:  $\text{H}_2\text{O}$  partial pressure reaches only about one thousandth of the oxygen pressure. As a consequence, apart from the high upper temperature (about 1250°C), this process

requires quite an amount of separation work.

### MARK-1 CYCLE

A four-step chemical cycle has been found by one of us (G.D.) (9) and it is briefly described in (8). This cycle, christened MARK-1, uses compounds of mercury, bromine and calcium. The set of reaction in the cycle is the following :



Whose sum is :



A block diagram of the cycle is shown in fig. 1 where only materials flow is indicated.

In block 1) where reaction 1 occurs, calcium bromide and (excess) steam reacts to hydrobromic acid and calcium hydroxide. The hydrobromic acid solution is concentrated in a distillation column and fed to the step 2 (reaction n. 2). The product is a mixture of mercury bromides, hydrogen, hydrobromic acid, water and mercury. The gases are separated and hydrogen is cleaned from HBr traces by passing it through a bed of calcium hydroxide. Mercury and mercurous bromide, which is quite insoluble, are separated from the residual solution. Their mixture is fed back to step 2); the remaining solution is stripped to separate most of the hydrobromic acid and fed back into the distillation column at the proper level; the mercuric bromide solution is fed into step 3) with water and calcium hydroxide coming from step 1). The product of reaction 3 is a solution of calcium bromide easily separated from the mercuric oxide precipitate. The solution is concentrated and recycled to step 1). Mercury oxide is fed to step 4) where is dissociated. The products can be separated by quenching in an heat exchanger or by expanding them through a turbine. Mercury is recycled to step 2).

At this point the cycle is completed; the global result is an input of water and an output of hydrogen and oxygen. In fig. 2 a schematic flow-sheet for the Mark-1 process is given with reference

- c) all by-products formed during the reactions can be reinjected at some points in the cycle, permitting a virtual 100% recuperation of the chemicals.

There are also some drawbacks :

- a) the use of mercury with the related problems of high inventory cost and the possibility of pollution in case of leakages,  
 b) the use of highly corrosive chemicals, especially hydrobromic acid, and the consequent problems for construction materials.

#### CHEMICAL STUDIES (10)

Very little information on the reactions involved in the Mark-1 cycle was found in the literature. We then started a program of experimental tests in order to determine equilibria and kinetics.

- 1) On the hydrolysis reaction there is a paper (11) which describes a series of experiments in which various salts, like halides, sulfates, phosphates and carbonates of alkaline earth were hydrolyzed. The tests were performed in such a way that they did not allow the determination of equilibrium values for the hydrolysis; however they show that in the halide's family the most hydrolyzable salt is calcium bromide. Our experiments on the hydrolysis of calcium bromide were done using water vapor at 1 atm. In order to have a preliminary idea of the equilibrium concentrations, thermodynamic calculations were made for the following reactions:



Working with steam at 1 atm. we can expect the formation of calcium hydroxide for temperature up to 550°C and the formation of calcium oxide at higher temperatures. Using for calculations the data of Brewer (12) and of Bulletin of Bureau of Mines (13) the values for the equilibrium constant range from  $8 \cdot 10^{-10}$  at 500°K to  $1.07 \cdot 10^{-4}$  at 1000°K; taking more recent data from Kubaschewski (14) these values are still lower, ranging from  $1.2 \cdot 10^{-12}$  at 500°K to  $3.5 \cdot 10^{-6}$  at 1000°K.

From our tests we find for the equilibrium constant values ranging from  $2.9 \cdot 10^{-7}$  at 573°K to  $1.12 \cdot 10^{-2}$  at 1000°K.

In fig. 3 there is a plot of calculated and experimental values for hydrolysis equilibrium constant at atmospheric pressure. Other tests are in progress to determine the equilibrium and the kinetics under pressure. A first test with 20 atm. steam led to an equilibrium constant of  $1.9 \cdot 10^{-2}$  at 727°C (1000°K).

The minimum working pressure necessary to have  $\text{Ca (OH)}_2$  as product has been determined measuring the decomposition pressure of calcium hydroxide up to 800°C (fig. 4).

- 2) Also for the reaction between mercury and hydrobromic acid there is no valuable information in the literature. We did run a series of tests to determine how the reaction rate is influenced by the volume of hydrobromic acid, the surface of mercury, the tempera-

ture, the concentration of the acid.

Reacting a mercury drop of 550 mg (2.75 milli-atoms) in a glass vessel of about 35 ml volume with an excess of concentrate hydrobromic acid (48%, 8,9 milli-moles) at 250°C the initial rate of H<sub>2</sub> formation is 218 cc (NTP)/h.cm<sup>2</sup> of mercury. The initial vapor pressure of the hydrobromic acid has been evaluated to be 20 atm. From the reaction rates at temperatures between 197°C and 250°C the activation energy for the reaction has been calculated to be about 15 Kcal/mole. The temperature dependence of rate constant is shown in fig. 5. Extrapolating the reaction rate at 300°C we can expect a hydrogen formation rate of about 700 cc (NTP)/h.cm<sup>2</sup>.

The influence of hydrobromic acid concentration on hydrogen formation rate at 200°C is given in fig. 6. It is quite evident the strong effect of the hydrobromic acid concentration.

Due to the overpotential for hydrogen evolution over mercury surfaces we have tested the effectiveness of some metals as depolarisers. At 200°C the best results have been obtained with addition of iridium black on tungsten powder: hydrogen evolution rate did increase by a factor 2,3. At 250°C the effect of the catalyst is less important.

We are doing also some research on a different way to react mercury and hydrobromic acid. By the new procedure the reaction could be realized at lower temperatures (100 + 120°C) with an acceptable rate. The lower temperature allows lower grade heat coming from other steps of the process to be used, and this permits a higher total efficiency. Analytical problems that did arise in the determination of the reaction products have been solved and the analytical procedure is described by Serrini (15).

- 3) About the reaction of mercury bromide with calcium hydroxide no information is available in the literature. Preliminary tests have shown that with calcium hydroxide, a brown colored precipitate is obtained. After boiling the solution for some minutes this brown precipitate is transformed in the usual red mercuric oxide. Nevertheless, a certain amount of mercuric bromide is held in solution by the calcium bromide formed. For this reason we began to study the influence of temperature, initial concentration of mercuric bromide and the excess of calcium hydroxide.
- 4) The dissociation of mercuric oxide is the only step of the Mark-1 cycle for which data are available in the literature. Dissociation pressures have been measured (16) and are known with a precision sufficient for our needs. In fig. 7 HgO dissociation pressure versus temperature is given. Between 450°C and 600°C the dissociation pressure varies from 1 to 20 atm, that is in a range well suitable for practical applications. From the literature (17) it is also known that the rate of dissociation can be accelerated by the presence of a proper catalyst in the form of finely divided platinum, ferric oxide, etc. As we need to know also the rate of recombination of oxygen and mercury vapors in order to define how fast the vapors must be cooled to avoid excessive back-reaction we are also studying the kinetic of HgO formation. In a very simple test, conducted by heating the mercuric oxide to 480°C at room pressure in a glass apparatus without any particular feature to cool the vapors, we did not observe any recombination. We are now assembling an apparatus

to study the recombination at temperatures up to 650°C and pressures up to 30 atm.

A list of other chemical and physical problems are under scrutiny e.g. we are measuring the vapor pressure of concentrated calcium bromide solutions, the heat of dehydration of calcium bromide and the pressures and phase composition for the liquid-vapor equilibrium in the ternary system  $H_2O-HBr-HgBr_2$ .

We are also testing the reliability of specific ion-electrodes for continuous concentration measurements.

### STRUCTURAL MATERIALS

The chemicals circulating in the various steps of the process are hydrobromic acid (vapors and solution), mercury (salts and vapor), calcium bromide and calcium hydroxide as solids and in solution, oxygen, hydrogen and water. For most of them compatible materials are known.

Problems arise with hydrobromic acid. For this product little information is available, and indication of its ability to attack material is derived from the behaviour of hydrochloric acid. Corrosion conditions can be divided in two groups :

- a) hydrobromic acid in solution
- b) hydrobromic acid as gas mixed with steam.

Solutions of hydrobromic acid are formed :

- a) where the steam and HBr mixture leaving the hydrolysis step is condensed; concentration will be about 33% by weight and at a temperature around 280°C;
- b) in the concentration and stripping columns : temperature from 250°C down to 130°C and concentrations up to 48% by weight (azeotropic);
- c) where mercury is reacted, (concentration 48% by weight, temperature 200°C).

The presence of mercury salts in the solution must be taken in account. Hydrobromic acid as a gas phase is present, mixed with steam, at a maximum concentration of 10% in volume (corresponding to a 33% in weight) in the hydrolysis step and during the cooling of the mixture; a vapor phase is also present over the acid solution.

Exploratory corrosion tests (for metallic and refractory materials) have again begun in hydrobromic acid solutions (48%). After some screening at the boiling point of the azeotropic mixture (126°C) medium term tests with the most resisting materials have been done at 200°C and 250°C. The materials eliminated in the preliminary screening are : Chlorimet-2, Hastelloy B, Durichlor, Titanium, Vanadium, Nimonic 90, Stainless Steel AISI 304, Nickel, Chromium, Iron. We have retained : Tantalum, Molybdenum, Zirconium-Niobium alloy, Zircaloy-2 and Niobium. All tests have been done in glass capsules, with an external compensating pressure when necessary. The results are summarized in the following tables :

Test temperature 200°C

| Material         | Depth of attack in $\mu$ |           |            |
|------------------|--------------------------|-----------|------------|
|                  | 100 hours                | 500 hours | 1000 hours |
| Tantalum         | nil                      | nil       | nil        |
| Molibdenum       | <1                       | <1        | ~1         |
| Zr 2,5% Nb alloy | <1                       | <1        | ~1         |
| Zircaloy 2       | <1                       | <1        | ~1         |
| Niobium          | 100                      | ---       | ---        |

Test temperature 250°C

| Material         | Depth of attack in $\mu$ |           |            |            |
|------------------|--------------------------|-----------|------------|------------|
|                  | 100 hours                | 500 hours | 1000 hours | 1500 hours |
| Tantalum         | nil                      | <1        | <1         | <1         |
| Molibdenum       | <1                       | ~2        | ~5         | ~6         |
| Zr 2,5% Nb alloy | ~3                       | ~3        | ~4         | ~7         |
| Zircaloy 2       | ~3                       | ~9        | ~12        | ~14        |

COUPLING WITH THE HTGR

The cycle Mark-1 draws heat at different temperatures, the maximum temperature being 730°C. These quantities can be plotted in a diagram, with the temperature in °C as ordinate, and the quantity of heat (Kcal/mole H<sub>2</sub>) as abscissa.

We can draw in the same diagram a similar plot for the heat carrier, and the distance between these lines will represent the  $\Delta T$  in the heat exchangers. The amounts of heat represented by these lines are indexed according to the flow-sheet of fig. 2 and to the detailed portion of it as in fig. 8. We can see in fig. 9 how the heat quantities Q<sub>12</sub>, Q<sub>11</sub>, Q<sub>40</sub>, Q<sub>34</sub> and Q<sub>33</sub> fit in the diagram. The heating fluid is represented with dotted lines. The figures refer to the production of 1 mole of H<sub>2</sub>.

With the initial temperature of the fluid at 850°C and a minimum  $\Delta T$  of 40°C we obtain the line a), with a mass-flow corresponding to a heat capacity of 540 cal/deg.C.

If we put in parallel, as it is shown in figures 2 and 9, the heat exchangers 11 and 12 we obtain line b). It is seen how the splitting of the heat carrier in two streams in the high temperature region permits a lower final temperature for the heat carrier. This is also the temperature of re-entry into the reactor, which is fairly critical due to the material problems it involves for the base of the reactor core.

Another possibility is that of bleeding part of the heat carrier and diverting it to make electricity. (fig. 9, line c). In both cases we have the possibility of producing mechanical or electrical energy for operating the auxiliaries of the plant and of the reactor.

A fixed critical point is the temperature of the hydrolysis reaction, taken as 730°C; lowering this temperature corresponds to an unacceptably low concentration of the hydrobromic acid produced in the reaction. On the contrary, the temperature levels of the heat blocks  $Q_{40}$ ,  $Q_{34}$ ,  $Q_{32}$ , can be shifted by a certain amount with respect to the values given above; the consequence of these shifts will be the variation of the pressure in some chemical steps.

These modifications may be useful for a better matching, between the heating fluid line and the Q lines, with a final lower mass-flow rate. For instance if we could raise the temperature of the reactor coolant to 900°C we could envisage a countercurrent series arrangement for the hydrolysis reaction, as it appears in fig.10, and a lowering of 50°C, from 600°C to 550°C, of the heat block  $Q_{40}$  permits the coupling indicated in fig. 11. It is evident that the slope of the dotted line is quite higher: the mass-flow is now reduced to 230 cal/deg. C and the final coolant temperature is as low as 290°C, even without bleeding.

Our heat carrier can be the primary coolant of the nuclear reactor, e.g. helium. But in order to reduce the possibility of contamination we thought it would be better to transfer the heat from the primary coolant of the reactor to an intermediate heat carrier (helium or better steam) by a heat exchanger installed in the reactor vessel. The long term objective is the use of steam both as an energy carrier and as a chemical, eliminating all the intermediate heat exchangers.

A very interesting point is that most of the heat produced by the nuclear reactor is correctly utilized in the chemical plant, so that the system is inherently a single-purpose one.

The plant rejects the degraded heat (around 50% of the input) in the form of saturated steam at 120-130°C. Expanding this steam through a turbine and condensing it permits the production of a sizeable amount of electricity to be used in the plant, especially to run the blowers of the reactor. It might eventually be used for a desalination plant or for a heavy water plant.

### ECONOMIC CONSIDERATIONS

A precise economic evaluation of the cost of the hydrogen produced by the Mark-1 process is not possible with the informations available now on the yields and on kinetics of the various reactions or the kind of materials necessary for the apparatus.

Nevertheless it is possible to fix the frame in which the process has to fit to be competitive.

E.g. we can calculate the "room for investment", that is the maximum amount of capital that can be invested in the hypothesis of a hydrogen price competitive with the hydrogen produced today by steam-reforming of natural gas. To find this we parametrise a certain number of technological data:

#### a) the cost of nuclear calorie

The cost of the nuclear heat produced by an HTGR of about 3,000 Mwth is usually indicated to be in the order of 1 mil/Mcal (18). We'll take a range between 0.75 to 1.25 mils/Mcal.

#### b) the thermal efficiency of the chemical process

This efficiency can be defined as the ratio between  $H_2$  combustion

heat and the primary heat necessary to produce it. Such definition is somehow equivocal because the heat of combustion can be assumed to include or not the condensation of the water produced, and because waste heat is released from the process as steam at temperatures still interesting for the production of electricity.

E.g. with the heat rejected from blocks 14, 22 and 23 (fig.2) by a plant equipped with the 3,000 Mwth reactor, it would be possible to operate low-pressure steam turbines for 100 + 150 Mwe. The fraction of this electricity not used inside the plant should be properly discounted from the primary heat budget.

With the heat source at 750°C, the heat sink at 25°C, and operating the water decomposition process in a reversible way, with materials (water, hydrogen and oxygen) entering and leaving the process at 25°C and 1 atm, the thermodynamical efficiency is  $\sim 0.85$  Funk (4). The temperature of 25°C means that water is liquid, i.e. that the higher value for the combustion heat of  $H_2$  (3,000 Kcal/Nm<sup>3</sup>) is taken. For our efficiency evaluations we usually assume the lower combustion heat (2,500 Kcal/Nm<sup>3</sup>), and we find actual efficiencies in the order of 0.4 - 0.6. This is the range chosen for this parameter. Electricity production is neglected.

c) the oxygen credit

The european mean price for oxygen is around \$ 6/ton; for our calculations a maximum credit of \$ 4/ton is taken, corresponding to 2.9 mils/Nm<sup>3</sup>H<sub>2</sub>.

d) heavy water credit.

By contacting the incoming water with the outgoing hydrogen in an isotopic exchange column, Deuterium can be trapped in the H<sub>2</sub> plant, e.g. at a factor of ten enrichment, and bled to a finishing plant. With current prices for D<sub>2</sub>O we have evaluated a net D<sub>2</sub>O credit of  $\sim 3$  mils/Nm<sup>3</sup>H<sub>2</sub> (Market value of the D<sub>2</sub>O produced is around 7 mils/Nm<sup>3</sup>H<sub>2</sub>).

Credits (c) and (d) can be very important in establishing the profitability of the first plants. The learning curve for the process should later take care of the diminishing value that can be allocated to these by-products, once the market will be swamped.

Fig. 12 gives the room for investment as a function of these parameters taking 12 mils/Nm<sup>3</sup> as the reference price for the hydrogen. E.g. with the nuclear calorie at 1 mil/Mcal; a thermal efficiency of 0.5 and an oxygen credit of \$ 4/ton we have 9.9 mils/Nm<sup>3</sup>H<sub>2</sub> available for fixed costs. In a conventional steam reforming plant fixed costs are around 4 mils/Nm<sup>3</sup>H<sub>2</sub>.

The sensivity of the hydrogen price in relation to these parameters is indicated in fig. 13, where the reference point assumes: fixed costs 6 mils/Nm<sup>3</sup>, thermal efficiency 0.5, cost of the nuclear heat 1 mil/Mcal and oxygen credit \$ 2/ton.

As the cost of our hydrogen is almost purely technological (uranium cost enters for less than 1 mil/Nm<sup>3</sup>H<sub>2</sub> and can be less than 0.1 mils/Nm<sup>3</sup>H<sub>2</sub> in the case of breeders), there is no rock-bottom cost, and the cost will decrease exponentially as a function of the integrated amount produced, according to a general rule valid for all the mass produced chemicals (19). This means that if we can achieve competitiveness in the chemical hydrogen market, it is only a question of time to become competitive in the energy market. This because the

cost of minerals in general and fuels in particular tends to slowly rise with time.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- 1) Philadelphia Electric - Gulf General Atomic Contract - Nucl.Eng. Vol. 16 No. 185, 874, (1971).
- 2) - A.M. Weinberg - The Coming Age of Nuclear Energy - Nuclear New - Vol. 11, No. 7, 30, (1958).  
 - R.C. Costa, P.G. Grimes - Electrolysis as a source of Hydrogen and Oxygen, Chem. Eng. Progr. , Vol. 63, No. 4 , 56 , (1967).  
 - D.W.White, H.S.Spacil, C.S.Tedmon - G E process could make cheaper hydrogen, Chem. Eng. News, Vol. 46, No. 47 (Nov. 4), 48, (1968).
- 3) D.P. Gregory, D.Y.C. Ng, G.M. Long - Electrolytic hydrogen as a fuel, in : The Electrochemistry of Cleaner Environments, Plenum Press. New York , N.Y. (1971).
- 4) J.E. Funk, R.M. Reinstrom - Energy Requirements in the Production of Hydrogen from Water - I & EC Process Design Develop. - Vol.5 - No. 3 , 336, (1966).  
 J.E. Funk - Thermodynamics of Electrolysis and Other Water Splitting Reactions - This conference - Paper 5 .
- 5) J.E. Funk , T.J.Hirt - Final Report Energy Depot Electrolysis Systems Study (U). Allison Division, General Motors, EDR 3714 , Vol. II, (1964) (Confidential).
- 6) R.M. Reinstrom et al. - Ammonia Production Feasibility Study, Final Technical Report - Allison Division - General Motors - EDR 4200 (1965).
- 7) A.R. Miller, H. Jaffe - Process for producing hydrogen from water using an alkali metal. U.S. Patent No. 3.490.871, Jan. 20, 1970.
- 8) G. De Beni, C. Marchetti - Hydrogen, Key to the Energy Market , Eurospectra - Vol. IX , No. 2 , 46, (1970).

- 9) G. De Beni - Procédé pour la préparation d'hydrogène - French Patent - No. 2.035.558 - Feb. 17, 1970 - U.S. Patent Pending - No 9.399.- Feb. 6, 1970.
- 10) More information about chemical studies can be found in EUR 4776e Hydrogen Production from Water using nuclear heat. Progress Report No. 1 ending December 1970.
- 11) P.L. Robinson, H.C. Smith, H.V.A. Briscoe - The Hydrolytic action of Low-pressure Superheated Steam on Salts of the Alkaline - Earth Metals, J. Chem. Soc., Vol. 129, 863 (1926).
- 12) L.L. Quill - The Chemistry and Metallurgy of Miscellaneous Materials - Thermodynamics - p 65, p 104 - Mc Graw - Hill Book Company, Inc. , (1950).
- 13) J.P. Coughlin - Contribution to the data on theoretical Metallurgy. 12: Heats and Free Energies of Formation of Inorganic Oxides. Bureau of Mine - Bulletin 542 , Washington 1954.
- 14) O. Kubaschewski , E.U. Evans, C.B. Alcock - Metallurgical Thermochemistry - Pergamon Press (1967).
- 15) G. Serrini, W. Leyendecker - Determinazione per via Chimica dei Prodotti risultanti dalla reazione del Mercurio con acido bromidrico - EUR 4602 i, (1971).
- 16) G.B. Taylor, G.A. Hulet, - The Dissociation of Mercuric Oxide , J. Phys. Chem. , Vol. 17 , 565 (1913).
- 17) J.W. Mellor - A comprehensive treatise on Inorganic and Theoretical Chemistry - Longmans, London (1957).
- 18) M. Kugeler - Energieprognose für die Bundesrepublik Deutschland unter Berücksichtigung des Einsatzes von Kernwärme zur Vergasung fossiler Rohstoffe - Jül - 745 - RG (1971).
- 19) D.J. Massey , J.H. Black - Predicting Chemical Prices - Chem. Eng. - Vol. 76, October 20, 150 (1969).

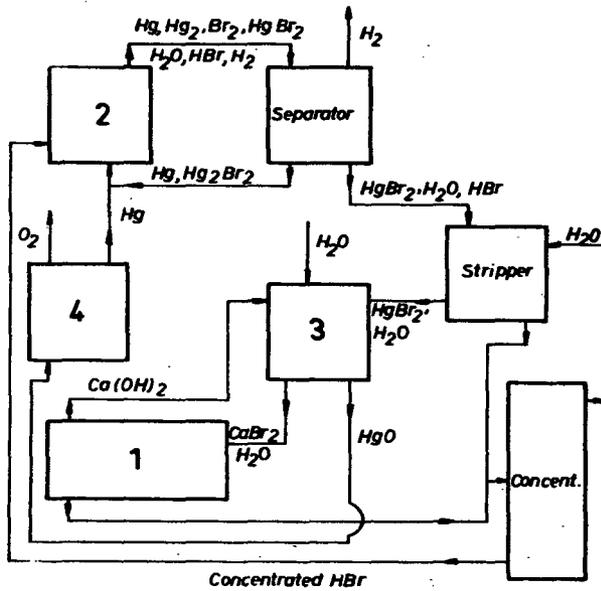


FIG. 1 Mark-1 block diagram

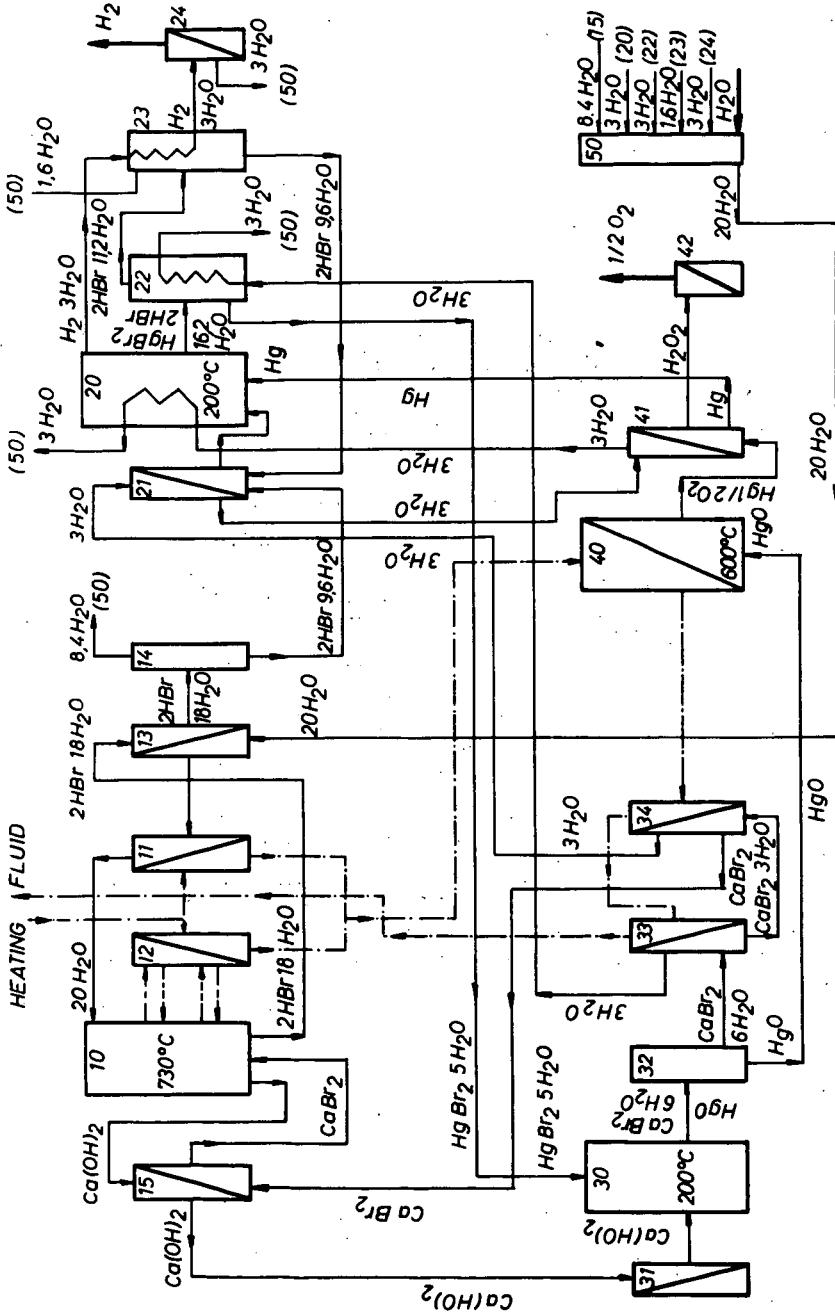


FIG. 2 Simplified flow-sheet showing materials flow and temperatures

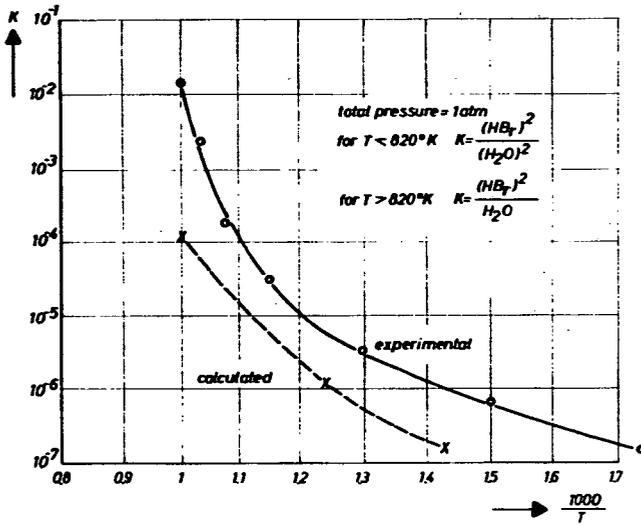


FIG.3 Hydrolysis equilibrium constants as a function of temperature

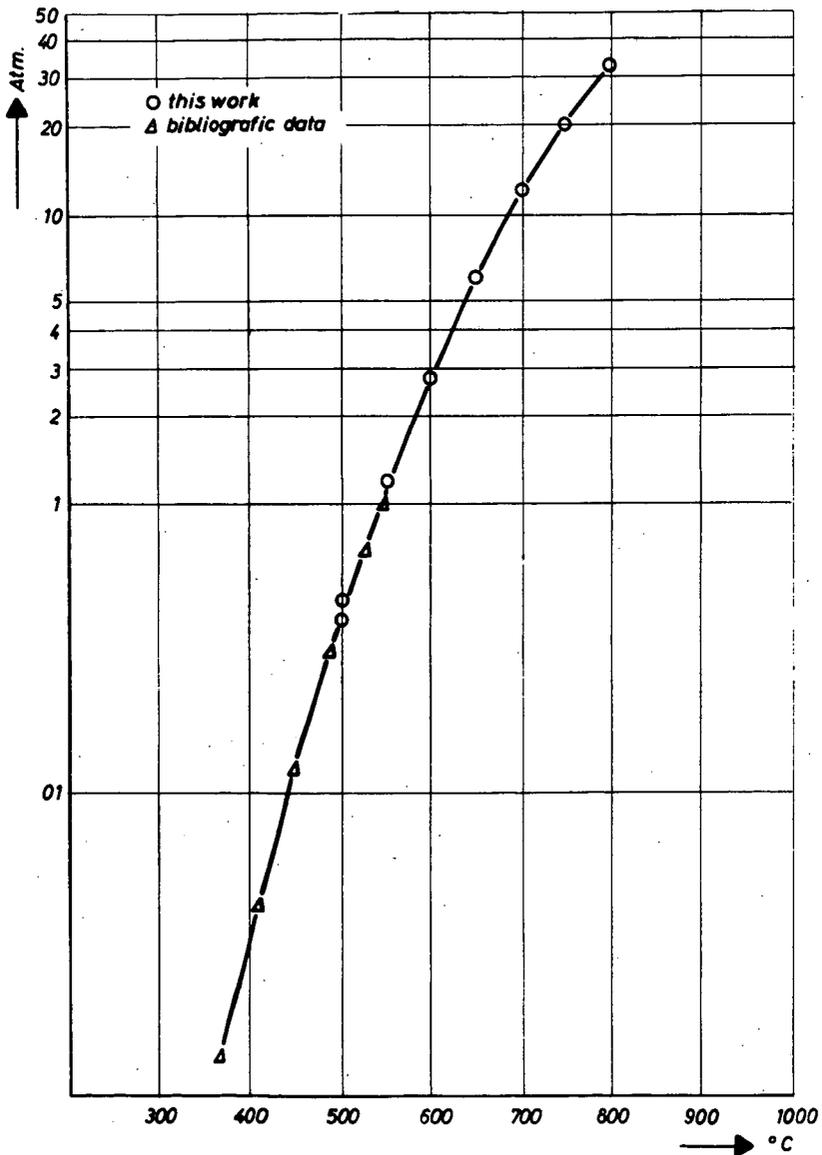


FIG. 4  $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$  Decomposition pressures

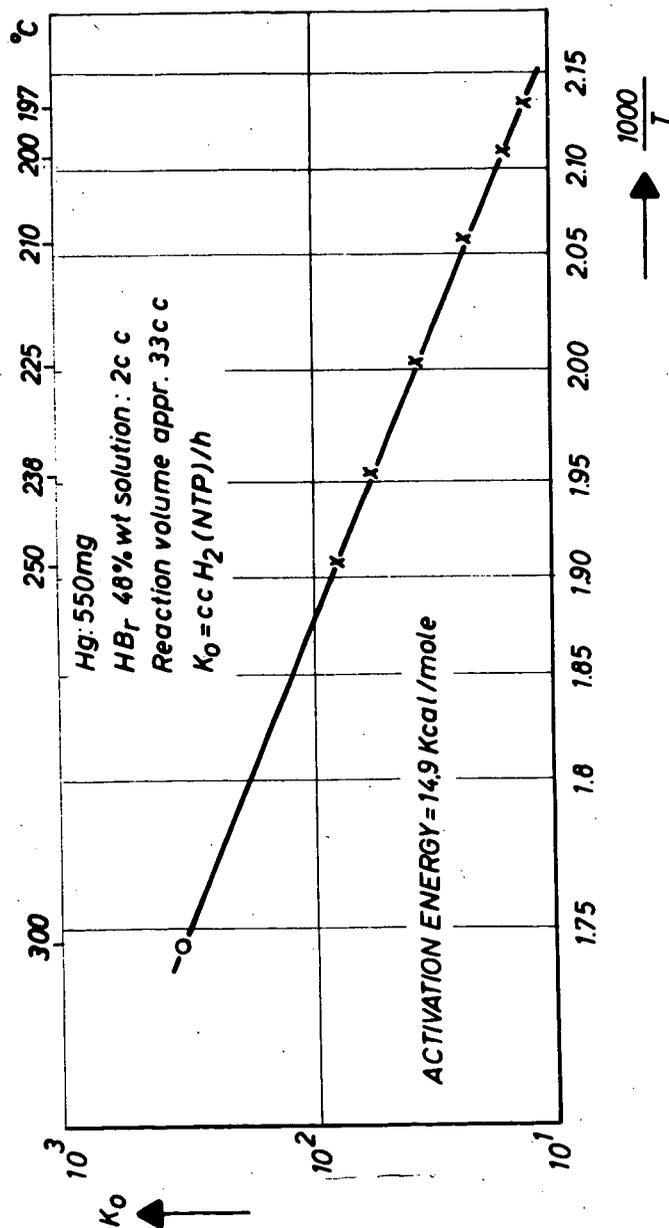


FIG. 5  $\text{Hg} + 2\text{HBr} \rightarrow \text{HgBr}_2 + \text{H}_2$  Temperature dependence  
 of rate constant.

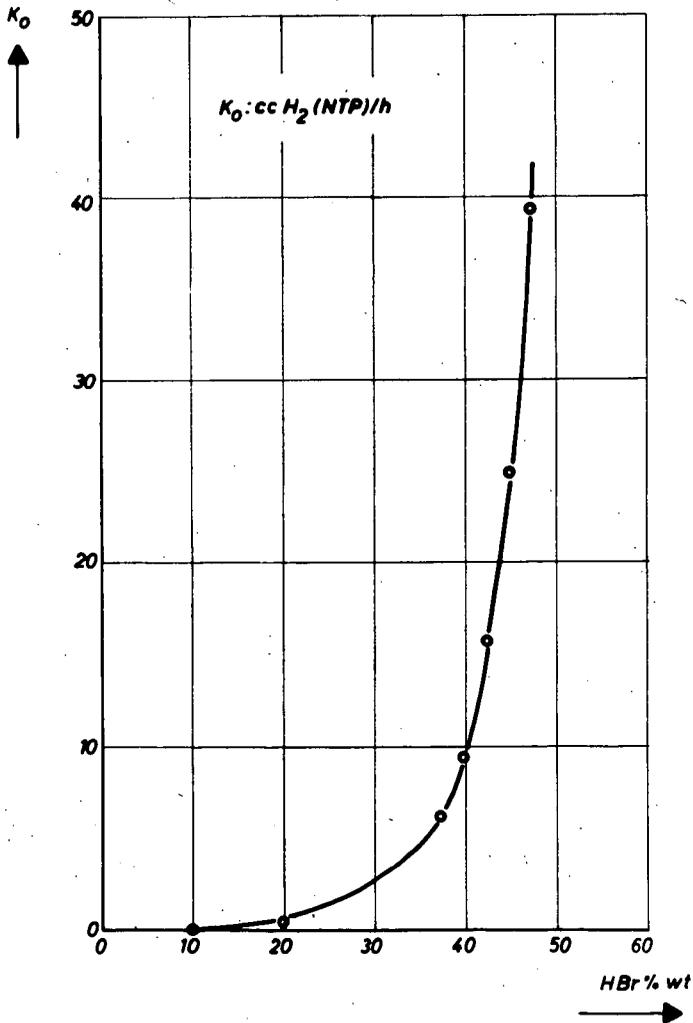


FIG. 6  $Hg + 2HBr \rightarrow HgBr_2 + H_2$  Hydrogen formation rate at 200°C influence of HBr concentration

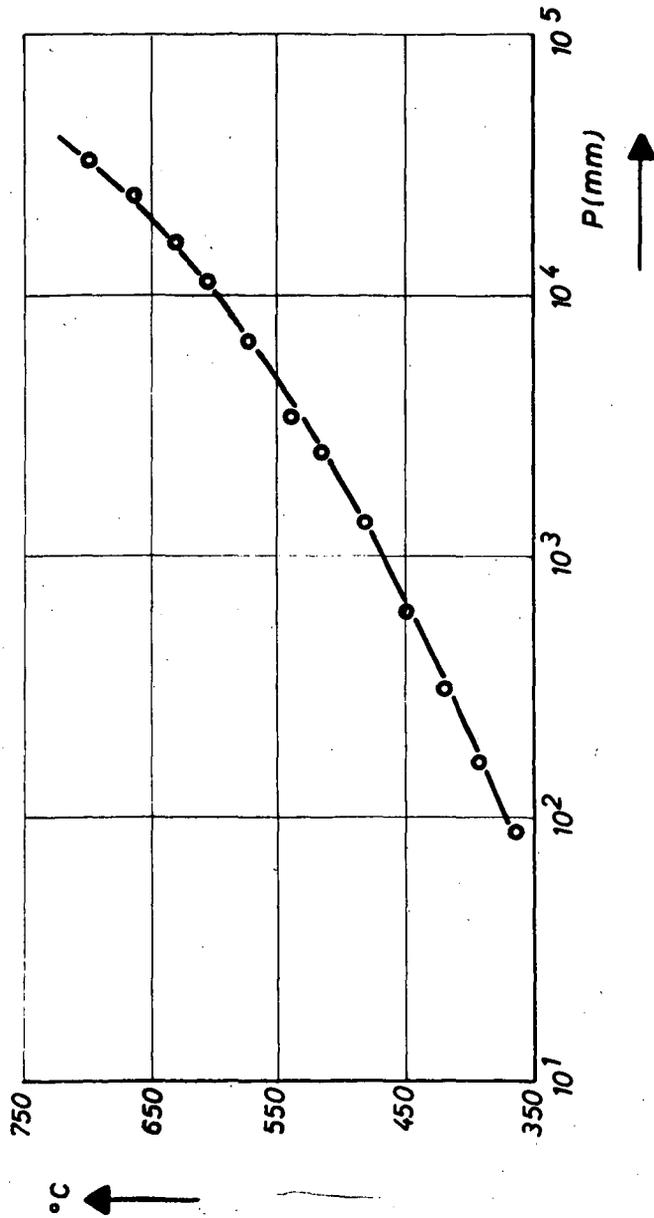
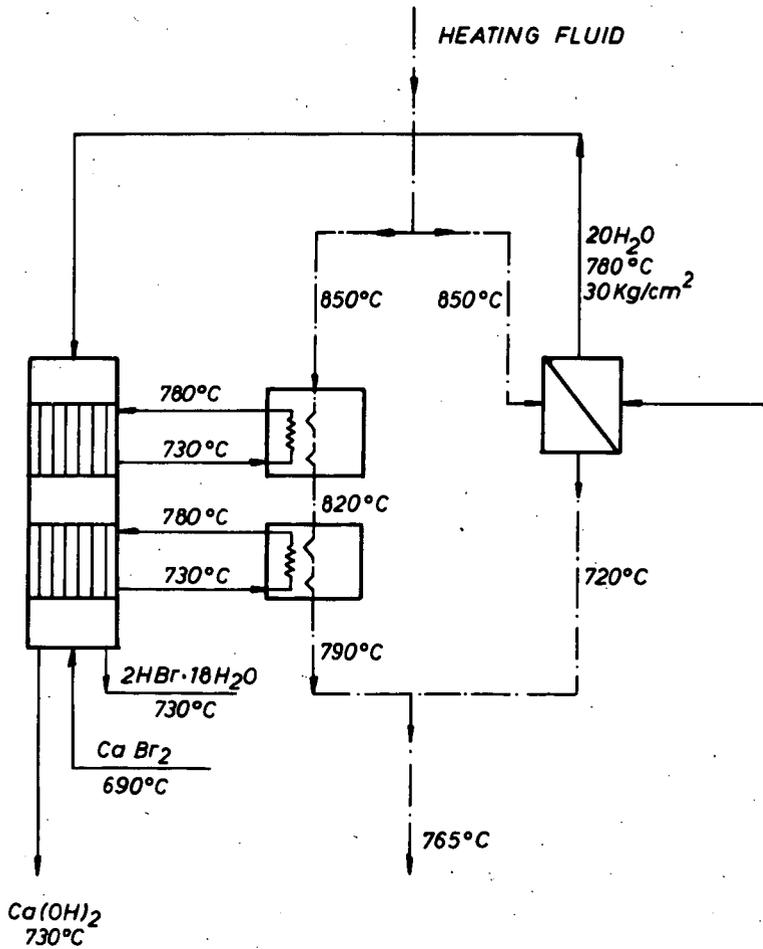
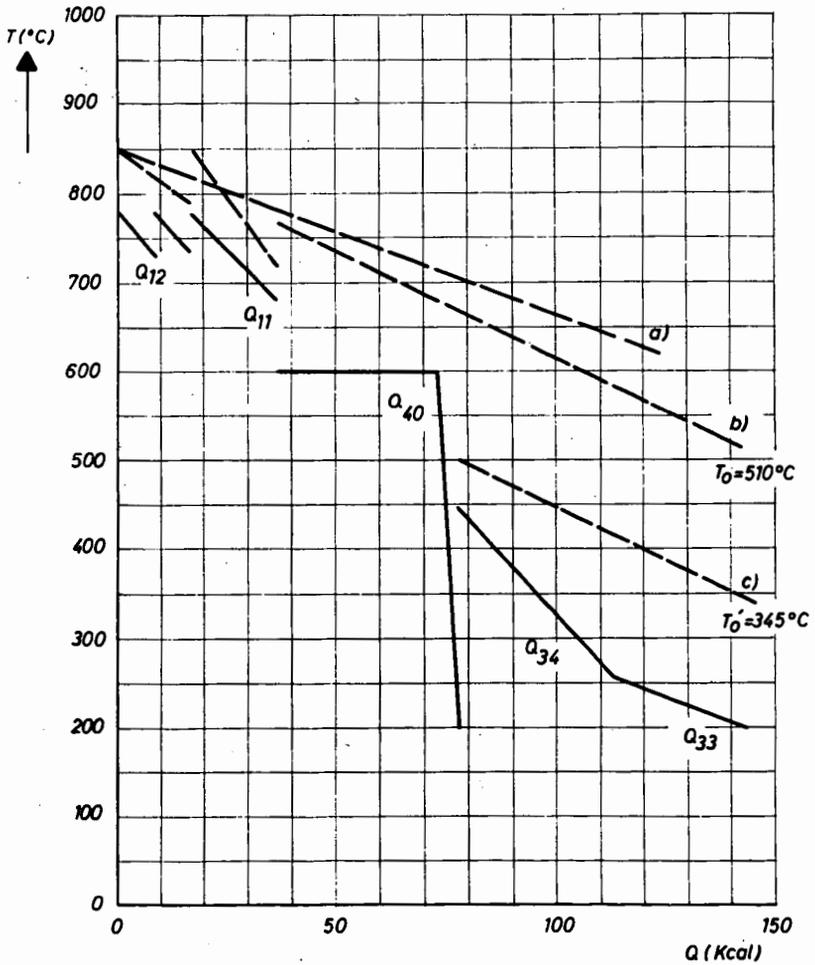


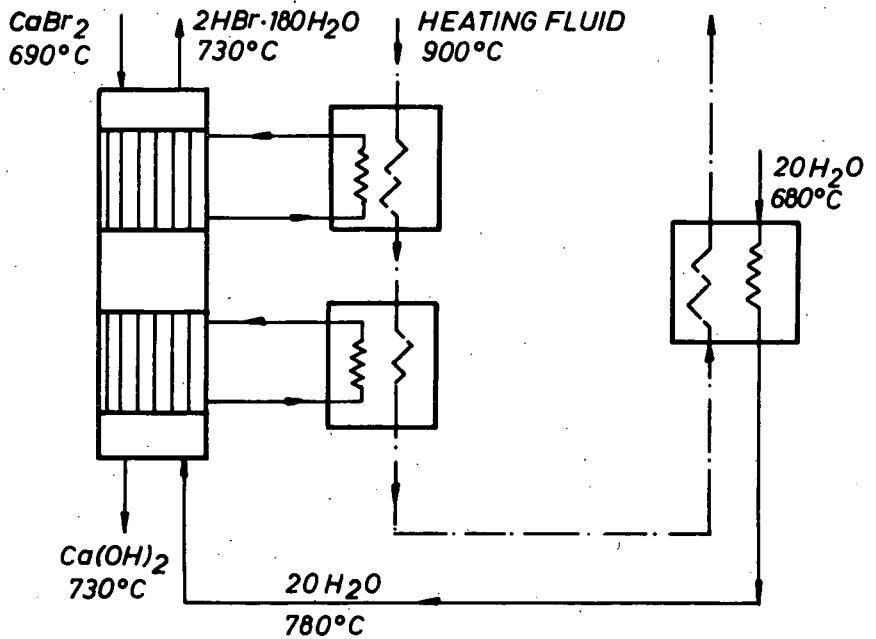
FIG. 7  $\text{HgO} \rightarrow \text{Hg} + \frac{1}{2} \text{O}_2$  Dissociation pressures



**FIG. 8** Mark-1 flow-Sheet- Detail of the hydrolysis step



**FIG. 9** Example of process thermal coupling using 850°C helium gas as primary heat carrier



**FIG.10** Mark-1 flow sheet countercurrent scheme for the hydrolysis step

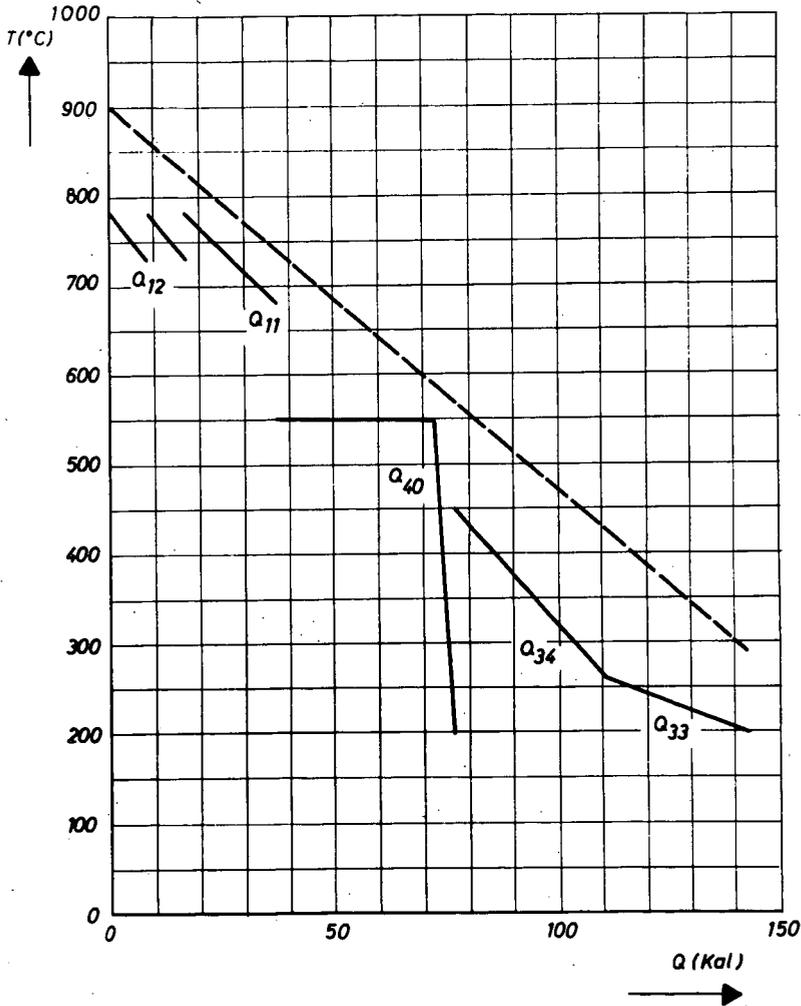


FIG.11 Example of process thermal coupling using 900°C helium gas as primary heat carrier

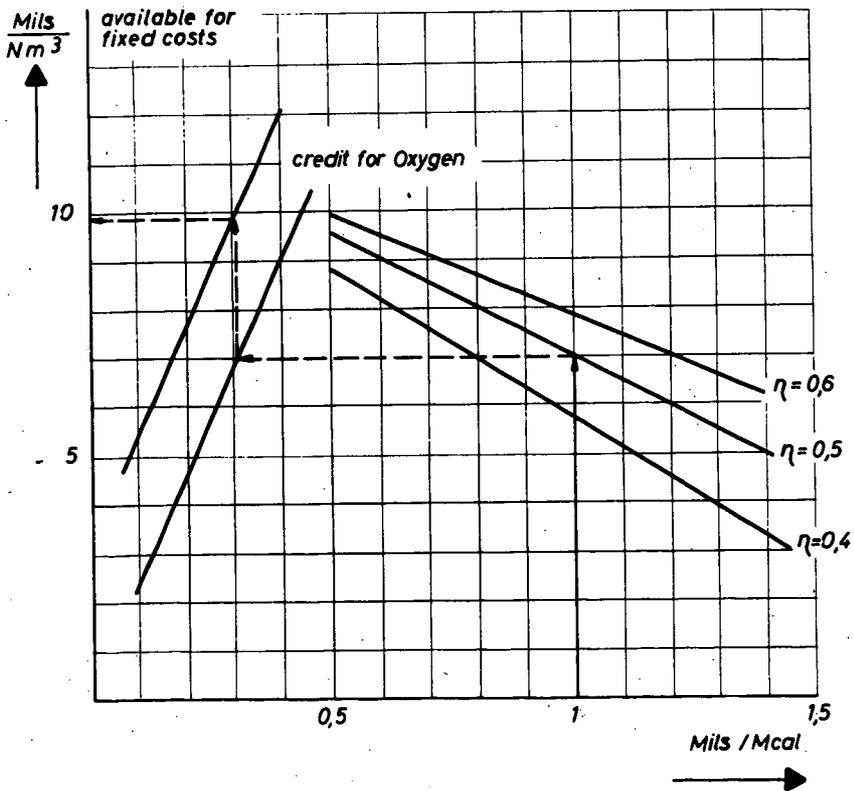
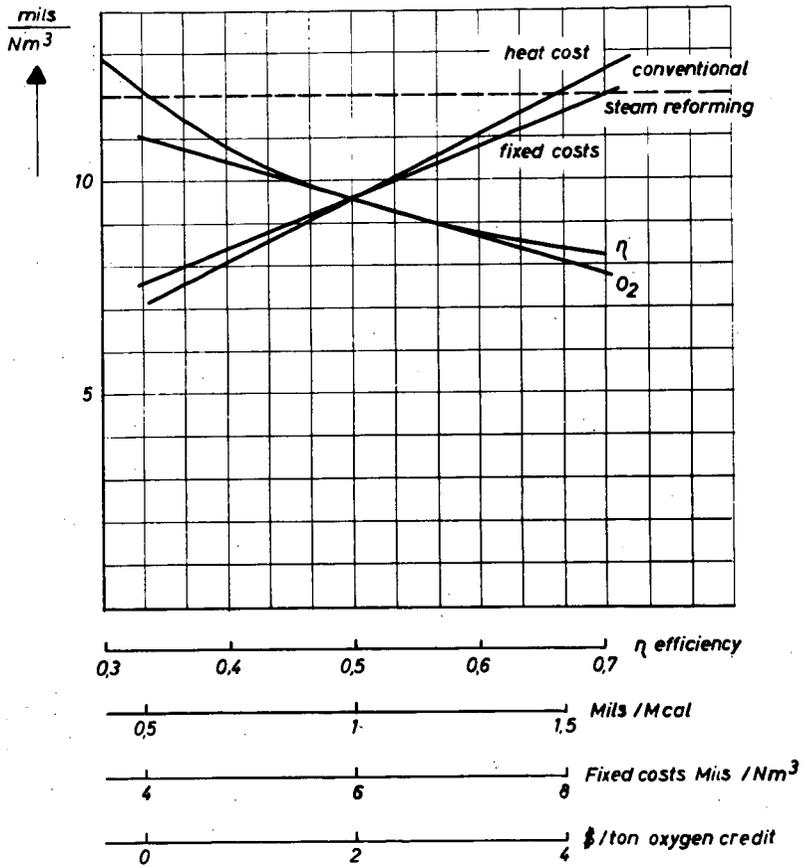


FIG.12 Abacus for fixed costs evaluation



**FIG.13** Hydrogen costs as a function of process efficiency, heat cost, fixed costs and oxygen credit

## PROSPECTS FOR HYDROGEN FUELED VEHICLES

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Modern civilization is generally said to be a consequence of the industrial revolution; a striking outward manifestation of which is the automotive vehicle. Whereas the transition from animal to mechanical means of propulsion was accompanied by an increased mobility, this transition has not occurred without some accompanying undesirable side effects. One of these, environmental pollution, is now globally recognized and presents a real challenge for its solution. Another, an impending energy crisis, is due to the insatiable appetite for energy brought about by an expanding population and a rising affluence. The two are correlative since pollution is largely attributed to an apathy for the consequences of large-scale consumption of certain forms of energy.

Some recent developments in internal combustion engine technology may have provided not only a viable solution to the environmental-energy dilemma but also a convenient mechanism for transforming to a less polluting society. The development involves a novel method of designing internal combustion engines so they can smoothly and efficiently operate on hydrogen. The purpose of this paper is to review the opportunity offered by this capability and to forecast its probably future influence. The discussion will primarily be concerned with the use of hydrogen in ground vehicles although it is obvious hydrogen can be substituted for any other fuel now in use.

## Prior Work

Early attempts to use hydrogen as a fuel in internal combustion engines were reported by Cecil in 1820<sup>1</sup> and by Barsanta and Matteucci in 1854.<sup>2</sup> However, the first significant contribution to the field waited until 1933 when Erren designed and built several engines which could operate on either hydrogen, conventional fuel, or their mixture.<sup>1, 3</sup> His major problem and one that he was unable to overcome was detonation of the hydrogen-air mixture upon ignition.

After World War II, King and associates at the University of Toronto performed an extensive study using hydrogen as an engine fuel.<sup>4</sup> They found, as did Erren, that detonation was a formidable problem which could only be overcome by painstaking cleaning of the combustion chamber at least every 12 hours of operation. Apparently, these discouraging results had reduced interest in developing a carbureted air-breathing hydrogen fueled reciprocating engine.

An effort was initiated at Oklahoma State University in 1968 to try to design around the problems of pre-ignition and detonation which had troubled earlier workers.<sup>5</sup> The design approach selected was direct cylinder injection of gaseous hydrogen in a manner similar to fuel injection in a diesel engine.<sup>6</sup> This effort has resulted in the satisfactory conversion to hydrogen of four different engines originally designed to run on gasoline. Experience with these engines including extensive performance and emissions tests with one of them has yielded the following information:<sup>7-10</sup>

1. With reference to a gasoline engine converted to run on hydrogen, it is possible to "drive" a hydrogen engine to a higher horsepower output than was possible with gasoline fuel before its conversion.
2. The only undesirable emissions of significant concentration from a hydrogen engine are oxides of nitrogen (NOX). These were found to vary with operating conditions but averaged about 2.0 grams NOX per brake horsepower-hour. This rate of NOX production is about ten times less than from its gasoline counterpart.
3. The hydrogen engine can operate smoothly with compression, glow or spark ignition. With spark ignition, it can be idled down to about one-half the minimum idle speed possible with gasoline fuel.
4. The hydrogen engine is easy to start, responds rapidly to different rates of fuel injection, and runs cooler under low to intermediate loads than its gasoline equivalent.

From the foregoing, it is concluded that an automobile properly designed to run on hydrogen should be able to meet the 1975/76 federal emission standards.

#### Basis for Forecast

This section attempts to assess some techno-economic factors and political circumstances which may influence the future pattern of automotive vehicle development. Also included in the assessment are environmental and energy resource management considerations. This is the basis for the technological forecast which is made in partial response to the challenge presented by the 1969 U. S. Senate report:<sup>11</sup> The Search for a Low Emission Vehicle.

#### Environmental Constraints

There are many instances of pollution associated with normal and accidental activities of drilling, producing, transporting, refining, distributing, and consuming conventional hydrocarbon fuels. Collectively these contribute considerably to environmental decay. Industry can and will clean itself up but must be permitted to pass such costs on to the consumer. An alternate approach is to use hydrogen fuel produced by electrolysis of water. Although such a solution would require a long-term effort, it would appear to cause less pollution overall. Of immediate significance to this alternative are the motor vehicle emissions standards prescribed by the Clean Air Act as amended. These require that automobiles achieve a 90 percent reduction from 1970 emissions levels of carbon monoxide and hydrocarbons by the 1975 model year and a 90 percent reduction from 1971 emissions of nitrogen oxides for the 1976 model year. Prescribed standards for new light-duty motor vehicles for 1973 and successive years are as follows:<sup>12</sup>

Federal Standards for Composite Emissions from Light-Duty  
Vehicles on a Driving Cycle, grams/mile

| <u>Model Year</u> | <u>Hydrocarbons</u> | <u>Carbon monoxide</u> | <u>Oxides of Nitrogen</u> |
|-------------------|---------------------|------------------------|---------------------------|
| 1973              | 3.4 (3.0)*          | 39.0 (28.0)*           | 3.0 (3.1)*                |
| 1974              | 3.4 (3.0)*          | 39.0 (28.0)*           | 3.0 (3.1)*                |
| 1975              | 0.41                | 3.4                    | 3.0                       |
| 1976 and later    | 0.41                | 3.4                    | 0.4                       |

\*Numbers in parenthesis represent standards being considered for adoption

It is significant to note that by 1976, any vehicle covered by these specifications will be permitted to emit 0.41 grams of hydrocarbons, 3.4 grams of carbon monoxide, and 0.4 grams of nitrogen oxides per mile of a typical 7.5 mile driving cycle. Thus, whether one additional person is carried in a 2-passenger vehicle, or many in a 9-passenger one, each vehicle will only be permitted to emit so much pollution to the atmosphere. Also, since large engines emit more pollutants than do smaller ones, and unless some other provisions are made, the enforcement of these regulations will cause the disappearance of vehicles with large engines. Associated automobile comforts of space, air conditioning, power equipment, safety, acceleration and speed may also have to be sacrificed. In contrast, these changes may not be necessary with hydrogen fuel.

It also appears as if the automobile industry may be unable to meet the required 1976 federal emissions standards at a cost that can reasonably be passed on to the consumer unless;

- a) the allowable pollution level is relaxed for one or more of the controlled emittants or
- b) a federal subsidy or equivalent is enacted to support a portion of the costs.

In this connection, it appears worth mentioning that sufficient technology now exists to enable the design of a reliable engine that could meet the 1976 emissions standards. The technology does not exist, however, to be able to accomplish this objective at a reasonable cost. Hence, the problem is purely one of relative economics. In this regard it will be interesting to learn of the recommendations to the EPA of the Motor Vehicle Emissions Committee of the National Academy of Sciences who have recently been charged with determining whether the automobile industry is technologically capable of designing and mass-producing a reliable engine that can meet the federal motor vehicle emissions standards.

### Energy Management

The dilemma between environmental pollution and an abundance of low-cost energy is one that will have to be resolved by the public--provided it is offered the alternative. Unfortunately, however, this antithesis can not be resolved until an abundance of energy, or at least an abundance in the form that is desired, becomes available. Since energy is the key to survival of our society, its adequacy must be insured before stringent

pollution regulations can be enforced. Accordingly, a permanent solution to the air-pollution-from-vehicles-problem can only be solved from a total energy management point of view. One such proposal is to create a Total Energy Management System (TEMS) in which hydrogen becomes the basic energy fuel.<sup>14</sup> The system proposed provides for the optimum management of our energy resources so as to place a minimum strain on the delicate ecological balance of the environment. This concept was expanded by proposing a Total World Energy Management System (TWEMS) with its primary function being to optimize energy utilization worldwide while simultaneously attempting to minimize pollution.<sup>15</sup> The creation of national and international "Energy Institutes" with similar such objectives is currently being considered at the United Nations sponsored Human Environment Conference.<sup>16</sup>

### Substitutability

Hydrogen is substitutable with any other mineral fuel currently available. Its use has already been demonstrated in reciprocating internal combustion engines and turbines. Adaptation to external combustion engines is even simpler. For energy conversion via fuel cells the technology in this area is further advanced for hydrogen than any other fuel. Its importance in air travel is shown by a companion paper at this conference proposing to use liquid hydrogen in hypersonic transport.<sup>17</sup> Finally, the roles hydrogen could play in substituting for gasoline nationwide,<sup>18</sup> or improving an urban environment,<sup>19</sup> have been assessed. In the urban environmental study, it was shown for New York City, that a) hydrogen produced with off-peak power could supply over half of the expected 1985 energy needs for transportation, b) its cost could be as low as \$0.04 per pound making it quite competitive with conventional fuels, and c) that 5,331 million pounds of pollutants would be emitted from gasoline powered 1985 vehicles as compared to 216 million pounds of emissions from those same vehicles if they were fueled with hydrogen.

Hydrogen possesses some unique physical and chemical properties which offer an advantage over conventional fuels and thus influences its substitutability. In the first place, its wide flammability limits make it an ideal motor fuel. (This was demonstrated under a no-load condition with our hydrogen engine, for example, where it was extremely difficult to get either too rich or too lean of a fuel mixture for the engine to burn. This feature could be used advantageously in the transition from fossil to hydrogen fuel if the latter is used to promote hydrocarbon fuel oxidation in the lean combustion region where the production of nitrogen oxides is least favored.) Next, its extreme volatility coupled with its flammability would make for much easier starting in cool climates. Thirdly, its ability to chemisorb with certain metals to form hydrides enables it to be conveniently stored at ambient pressure and temperature. Since the reaction is reversible, it can be released from this inactive state merely by the addition of heat. Much of the heat released by internal combustion engines could be stored if it were used thusly to release hydrogen. This energy could then be regained during the recharging of the hydride if desired.

Other characteristics of hydrogen which influence its substitutability are:

- 1) its light weight and high energy density which gives it desirable storage features of particular value in aircraft and space vehicles,
- 2) its high flame speed enabling the design against flame-out and hardware for control of the high frequency flame jets used in the engine design reported herein,
- 3) a low flame incandescence which significantly reduces radiation (accordingly affecting the overall engine temperature),
- 4) its clean burning offering an opportunity for prolonged operation without oil change

or the design of true muffler systems rather than also transporting the emissions to a location where their toxicity is unimportant (the number of deaths resulting from accidental carbon monoxide poisoning each year is considerable), and finally 5) its low activation energy which offers an opportunity for engine designs using glow ignition instead of costly and troublesome spark ignition.

Three additional time dependent factors which influence hydrogen's substitutability are its short and long-term availability, its relative safeness, and its cost. Currently, production facilities are limited with supplies primarily coming from hydrocarbons and being consumed in ore-reduction processes, chemical synthesis, and space exploration. Since hydrogen is essential in producing synthetic oil and gas from coal or oil shale, first priority for its increased production should be allocated to expanding our energy base. Furthermore, since the electrical generating facilities of the nation are hard-pressed to meet current demand, it does not appear that there will be any significant opportunity in the immediate future for the development of an excess hydrogen supply. The circumstances involved have been summarized by McKelvey and Singer:<sup>20</sup>

"In the longer term, our biggest problem will be energy and the only hope for the continuation of civilization lies in the development of nuclear breeders and fusion to maintain an inexhaustible energy supply. Many economists and bureaucrats fail to understand that major scientific developments do not come about automatically in response to price increases. Unless the necessary research and development is done early enough we may be in real trouble."

Insofar as safety is concerned, liquid hydrogen has been compared on a relative basis as being as safe as methane and gasoline.<sup>21</sup> In this comparison, the negative aspects of hydrogen's wide flammable limits, low ignition energy and tendency to detonate in air when confined were thought to be balanced by its positive factors of low heat radiation, lack of smoke to cause asphyxiation, non-toxic vapors, unlikely detonation if spilled and rapid evaporation. It would appear that hydrogen stored in the solid (hydride) form at ambient conditions, instead of as a liquid, should be even less hazardous to work with, and correspondingly easier to design safe handling systems than for gasoline.

The relative cost of hydrogen versus gasoline favors hydrogen provided it is made on a large scale as is now done with gasoline. Three separate economic studies which support this contention are contained in references 22, 23, and 24. The economic incentives for conversion to hydrogen can be expected to continue to improve as the cost of gasoline increases which it must do if the price for crude oil is allowed to swing with the supply-demand situation. An imbalance of foreign trade brought about in part by this nation's oil import program will probably continue to build up economic deficits which further increases both the short and long-term economic outlook for hydrogen.

#### Hydrogen Vehicle Forecast

One black sheep which could easily be the technological-environmental scape goat is hydrogen. This relatively unappreciated element is foreseen to play the dominant role in a "hydrogen economy" era sometime in the future. Toward this aim Weinberg<sup>25</sup> in 1959 proposed that nuclear energy be used as the fuel of the future to

power small scale mobile units with electrolytic hydrogen. Several years later, Lessing<sup>26</sup> claimed that hydrogen will be the master fuel of a new age providing first an energy source for engine (fuel cell) operation and subsequently electrical power directly from the atom via the process of controlled fusion. Hammond,<sup>27</sup> in discussing the concept of a nuclear reactor centered Agro-Industrial complex, assumed hydrogen would play an important role in producing ammonia and for reducing metal ores. Later Weinberg and Hammond<sup>28</sup> presented a very positive outlook for the prospects of cheap hydrogen.

Hydrogen's bid as a future fuel is clearly evident in the transportation sector where the demands for mobile power are flexibility and intermittent use. In the futuristic "electric economy," the energy used in any mobile power unit must have previously existed at some previous time in the form of electricity. With this in mind, an expansion of the definition of "electric auto" is proposed to include vehicles powered by batteries, fuel cells, and hydrogen fueled internal combustion engines, and turbines provided the fuel is or has been in the form of electricity at one time or another. According to this definition, a new breed of electric autos is visualized as including vehicles powered by hydrogen fueled internal combustion engines which require very little if any change in serviceability or mode of operation over their gasoline counterparts.

During the transition to hydrogen many modifications of present internal combustion engines will be made so that both fuels can be burned simultaneously. Also engines will be designed and built exclusively for hydrogen operation. The hydrogen fueled internal combustion engine is expected to power the first electric autos which receive wide acceptance because of the high degree of perfection of modern engines and their relatively low cost. Second and third generation electric autos will use electric motors along with a power supply. These may be either storage batteries or fuel cells.

Comparison of fuel cells and storage batteries immediately brings out a basic difference in their nature. Storage batteries are strictly limited in their energy storage capacity by the initial amount of reactants. For a given battery size only a predetermined amount of energy may be stored. A fuel cell on the other hand can convert an unlimited amount of energy, the cell of course being subject to wear out. It is known that the reliability of storage batteries and of fuel cells is roughly equivalent.

Electric autos using storage batteries will be used extensively. However, due to their weight and charge limitations, they will be used only in a specialized area--urban (short-range) transportation. This type of vehicle is therefore thought of as a second generation electric auto. Such a system would have a self-contained recharger relying only on a source of current, and could provide convenient, economical short-range transportation.

Ultimately a hydrogen-oxygen or hydrogen-air fuel cell will provide the motive power for the transportation sector.

#### Benefits in Conversion to Hydrogen Vehicles

More so than any other, this nation has fostered the development of a society whose per capita energy consumption can only be matched by the level of affluence offered to its citizens. Although no other society has known such opulence, the experi-

experiment has reached such proportions of acceptance that secondary effects such as environmental degradation are now of primary concern.

Rather than accepting prescribed levels of pollution as a corollary to the free enterprise system, it would appear our nation has a unique opportunity to lead in the molding of a society which maximizes the ratio of per capita energy consumption to per capita pollution. That is, if the level of affluence of a society (or its ability to use natural resources) can be measured by its per capita energy consumption, and its rate of misuse of natural resources by its per capita pollution, then it would seem desirable to its citizens to try to maximize the former while minimizing the latter. If such a direction could be accepted as a national goal, then it becomes clear in which areas legislation is needed and what the National Energy Policy currently under formulation, for example, should prescribe. If this nation does not enjoin leadership in preserving the environment or if it waits while the level of energy consumption rises in the rest of the world, then the secondary effects of pollution could become the primary concern of all humanity.

It is believed that acceptance of the concept of hydrogen fueled vehicles is one step toward avoiding such an eventuality. Once accepted, it could provide the stimulus for economic growth and national prosperity.

#### Problems Expected in Transition to Hydrogen Vehicles

The problems which must be solved before hydrogen fueled vehicles can be universally accepted are seen to be: a) the design and construction of adequate hydrogen production, handling, and distribution systems, b) the development of hardware necessary to efficiently store and utilize hydrogen as a fuel in vehicles, and c) overcoming the generally held but undeserved public attitude that hydrogen is too hazardous to use as a motor fuel. Sufficient work has already been done to demonstrate that viable solutions to these problems are already at hand.

#### Discussion

Some pertinent comparisons of a relatively conventional pollution-free hydrogen fueled vehicle with some unconventional power sources receiving prominent attention as presented by Danis<sup>29</sup> are:

1. "The hydrogen-oxygen fuel cell - fuel is the same and so is its source.
2. "The electric vehicle - in the hydrogen engine, the ultimate source of energy is the same as for charging batteries, but water is electrolyzed instead of battery chemicals being regenerated.
3. "The working fluid is steam plus air - so we would have, in effect, an internal combustion steam engine operating on the Otto cycle rather than an external combustion Rankine engine.
4. "In the global perspective, petroleum resources would shrink in importance, while nuclear energy resources would increase proportionately to meet needs of electricity for hydrogen production.

5. "Emissions are steam only, plus traces of nitric oxide formed perhaps during periods of peak power demand. This steam could form nimbus or cumulus clouds, return as rain where it could be electrolytically dissociated again.
6. "Catalysts are not required."

The fact that hydrogen will promote gasoline oxidation thus enabling combustion without misfire up to 20:1 air-fuel ratios could be utilized in the long term phasing out of gasoline and phasing in of hydrogen.

#### Conclusions

The conversion of vehicles from conventional fuels to hydrogen is forecast to fulfill a more viable long-range solution to the air pollution problem than any heretofore proposed. The prospects for development of a total energy system which produces hydrogen from an abundant natural resource, water, and replenishes this supply upon combustion in an engine whose emissions are almost pollution-free, appears to be a worthwhile effort to pursue.

## REFERENCES

1. Erren and Campbell, "Hydrogen: A Commercial Fuel for Internal Combustion Engines and Other Purposes," Journal of the Institute of Fuel, June 1933, Vol. VI, pp. 277-290.
2. Lichty, L. C., Combustion Engine Processes, McGraw-Hill, N. Y. (1967), p. 4.
3. Heinze, Edwin P. A., "Hydrogen Engines for Off-Peak Power Utilization," Power, February 1933, pp. 90-2.
4. King, R. O. et. al. "The Hydrogen Engine and the Nuclear Theory of Ignition," Canadian Journal of Research, June 1948, Vol. 26, Section F, pp. 264-276.
5. Murray, R. G. , and Schoepfel, R. J. , "A Progress Report on the Development of OSU's Hydrogen-Burning Engine." Proceedings, Frontiers of Power Technology Conference, Oklahoma State University, Stillwater, Oklahoma (1969), p. 14.
6. U. S. Patent 3,572,297, "Hydrogen Fueled Internal Combustion Engine," (March 23, 1971).
7. Murray, R.G. and Schoepfel, R.J., "Emission and Performance Characteristics of an Air-Breathing Hydrogen-Fueled Internal Combustion Engine," Proceedings, 1971 Intersociety Energy Conversion Engineering Conference, Boston, Mass., Aug. 3-6, 1971, p. 38, SAE paper No. 719009.
8. Deen, J.L. and Schoepfel, R. J. , "Hydrogen and the Electric Economy," Proceedings, Frontiers of Power Technology Conference, Oklahoma State University, Stillwater, Oklahoma, September 30-October 1, 1971, p. 10-1.
9. Schoepfel, R. J. , and Sadiq, S. , "The Role of the Power Industry in Supporting the Hydrogen Engine and Clean Air," Proceedings, Frontiers of Power Technology Conference, Stillwater, Oklahoma (October 15-16, 1970).
10. Schoepfel, R.J., and Murray, R.G. , "The Development of Hydrogen Burning Engines." Proceedings, Frontiers of Power Technology Conference, Oklahoma State University (1968), p. 12.

11. "The Search for a Low-Emission Vehicle," Staff Report, Prepared for the Committee on Commerce, U. S. Senate, U. S. Government Printing Office, Washington (1969).
12. "Exhaust Emission Standards and Test Procedures," Federal Register, Part II, Vol. 36, No. 128 (July 2, 1971).
13. Mechanical Engineering, p. 66 (December 1971).
14. Schoepfel, R. J., "Design of a Total Energy Management System for the Abatement of Air Pollution," Technical Paper SPE 2877, Gas Industry Symposium, Society of Petroleum Engineers of AIME, Omaha, Nebraska, (May 21-22, 1970).
15. Murray, R. G., and Schoepfel, R. J., "A Reliable Solution to the Environmental Problem: The Hydrogen Engine," Paper 700608, presented at SAE/AIAA/ASME Reliability and Maintainability Conference, Detroit, (July 20-22, 1970).
16. Schoepfel, R. J. "Prospects for Reducing Pollution Through Improved Energy Conversion and Utilization Processes," submitted to Energy Section, United Nations (working paper for Conference on Human Environment, Stockholm, Sweden, Spring, 1972) June 1, 1971 (Restricted).
17. Witcofski, R. D., "Hydrogen Fueled Hypersonic Transports," presented at ACS Symposium on Non-Fossil Chemical Fuels, Boston; Mass. (April 9-14, 1972).
18. Schoepfel, R. J., and Sadiq, S. "The Role of the Power Industry in Supporting the Hydrogen Engine and Clean Air," Proceedings, Frontiers of Power Technology Conference, Stillwater, Oklahoma (October 15-16, 1970).
19. Winshe, W. E., Sheehan, T. V. and Hoffman, K. C., "Hydrogen-- A Clean Fuel for Urban Areas," Proceedings, 1971 Inter-society Energy Conversion Engineering Conference, Boston, Mass. (August 3-6, 1971).
20. McKelvey, V. E. and Singer, S. F., "Conservation and the Minerals Industry--A Public Dilemma," Geotimes, p. 20 (Dec. 1971).
21. Becker, J. V. and Kirkham, F. S., "Hypersonic Transports," NASA ST-Set 292, Paper No. 25 (Dec. 4, 1971).

22. Johnson, J. E. , "Economics of Large Scale Liquid Hydrogen Production," Presented at Cryogenic Engineering Conference, University of Colorado, Boulder, Colorado (June 13-15, 1966).
23. Hallett, N. C. , "Study, Cost, and System Analysis of Liquid Hydrogen Production" NASA CR-73,226 (June 1968).
24. Costa, R. L. and Grimes, V. G. , "Electrolysis as a Source of Hydrogen and Oxygen," Chemical Eng. Progress, Vol. 63, 56-8 (1967).
25. Weinberg, A. M. , "Energy as an Ultimate Raw Material or - Problems of Burning the Sea and Burning the Rocks," Physics Today, Nov. 1959, p. 18.
26. Lessing, L. "The Master Fuel of a New Age," Fortune, May, 1961, p. 152.
27. Hammond, R. P. , "Low Cost Energy: A New Dimension," Science Journal, January, 1969.
28. Weinberg, A. M. and Hammond, R. P. , "Limits to the Use of Energy," American Scientist, Vol. 58, P. 412 (July-August, 1970).
29. Danis, L. J. , "Trends in Piston Engine Combustion Chamber Components," Presented at ASM/AWS/AIME et al Westec Conference, Los Angeles (March 1971).

## HYDROGEN FUELED HYPERSONIC TRANSPORTS

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## INTRODUCTION

Aeronautical vehicle development beyond  $M \approx 3$  has been restricted in large measure by limitations in the state of technology of high-temperature, high-strength materials; for example, application of turbojet propulsion is restricted to  $M < 3.5$  by turbine-blade temperature limits and uncooled airframes begin to require super-alloy metals at Mach numbers somewhat higher than this. Whereas, steady progress has been made in research on high-temperature materials for advanced high-speed aircraft, the most stimulating finding for the prospects of hypersonic cruise aircraft has come out of recent systems studies closely tied to continuing research in all of the disciplinary areas of aerodynamics, propulsion, and structures. This finding is the clear indication of feasibility of hypersonic cruise vehicles actively cooled over most of the airframe surface by the residual heat sink of the liquid hydrogen fuel. It is toward such projected aircraft that the present paper is primarily pointed. Results of these recent NASA studies, made in-house and under contract, will be freely drawn upon and referenced. It is significant to the future prospects for a hypersonic transport (HST) that it may avoid or overcome some of the environmental problems so critical to the decision to halt development of the U.S. SST.

One potential traffic market for the HST is indicated in Figure 1 which shows a projection of the international passenger traffic between major world areas for the year 1990 and the ranges associated with this traffic. A number of such projections have been made (refs. 1 through 3) and although there is some disagreement as to the absolute magnitude of the passenger traffic, the distribution by range of these projections is generally in good agreement. The dashed bars in Figure 1 indicate possible future exchange of travelers with the Communist countries. Two major points are made from this figure: (1) the high rate of travel predicted for the year 1990 which, from a standpoint of air traffic congestion, implies the need for aircraft with large passenger capacities (high payload), and (2) the indication that about 90 percent of this traffic will require aircraft with range capabilities between 3000 and 6000 n. mi.

From a standpoint of convenience and comfort, it is of interest to consider the duration of the flights associated with these long ranges. Figure 2 shows a comparison of the trip times (wheels rolling to wheels stopped) associated with aircraft having cruise speeds ranging from subsonic ( $M = 0.85$ ), supersonic ( $M = 3$ ) to hypersonic ( $M = 8$ ), for representative international flights. The sizable time savings available through hypersonic flight are obvious, particularly for the longer ranges.

Other factors which will influence the nature of future transport aircraft stem, for example, from the growing concern over atmospheric pollution, a fact which the aeronautical engineer must accept in designing environmental acceptability into his product. The speed, range, and environmental advantages of the HST will probably demand a premium fare; at the same time, it must fit the airway and airport systems and cannot price itself out of the market, hence must have DOC's, airframe life, and so forth, not too much different from the jumbo jets.

A distinguishing feature of the HST will be the use of liquid hydrogen fuel ( $LH_2$ ), which has 2-3/4 times the energy per pound of conventional JP fuel (ref. 4). (See Fig. 3.) The higher energy per pound of  $LH_2$  more than compensates for

the secondary effect of a reduction in aerodynamic efficiency ascribable to housing the low density fuel. The large heat-sink capacity of liquid hydrogen - 10 percent of the combustion energy - allows active cooling of the airframe (as well as the scramjet engine), offering the possibility of using conventional aluminum structures and attaining airframe lifetimes comparable to the jumbo jets.

The general appearance of one concept of an HST as illustrated in Figure 4 is noteworthy in its similarity to the current SST concepts, a fact not too surprising since, for the active-cooling approach, materials are similar and passenger windows appear feasible. Because of the low density of  $LH_2$ , the aircraft will have a large body volume which will result in a structural weight fraction higher than that for JP-fueled aircraft and a nominal increase in the aerodynamic drag of the airplane. It is likely that such an aircraft will be streamlined through blending of the wing and fuselage to get an optimum compromise between containment of the low density fuel and aerodynamic efficiency.

#### HYPERSONIC TRANSPORT PROPULSION

A primary feature of the HST will be its air-breathing, regeneratively cooled, hydrogen-fueled scramjet engines. The superior performance potential of the hydrogen burning ramjet is clearly seen in Figure 5 in terms of the propulsive efficiency factor, specific impulse (pounds of thrust per pound per second of fuel or propellant burned), as a function of Mach number. For hydrogen-oxygen rockets, values of specific impulse are limited to something less than 500 since rockets must carry their own oxidizer, but these values are, of course, available in airless space. The large increases for airbreathers over rockets is evident for both kerosene and hydrogen-fueled systems to about  $M = 10$ . For both kerosene-fueled and hydrogen-fueled air-breathing turbojets, ramjets, and supersonic-combustion-ramjets (scramjets) the downward trends with Mach number are similar with the very large advantage for hydrogen burners reflecting the higher energy per pound of hydrogen. Turbojets can be used for take-off (where ramjets are inoperable) and acceleration to  $M \approx 3.5$ . As a Mach number about this value is approached, the stagnation or ram temperature is increasing to such a value that diminishingly less fuel can be added before exceeding the permissible turbine-blade temperature, thus the thrust is dropping rapidly. In the range of Mach number, the ramjet (subsonic combustion), which has no compressor or turbine and uses only the ram pressure of flight, comes into its own. Its effectiveness survives to about  $M = 7$  at which point several factors point to the use of scramjets (supersonic combustion). By ramjet we have meant subsonic combustion; in fact, combustion is at as low a velocity as possible to minimize the entropy increase in the combustion process. For the subsonic combustion ramjet, as Mach number increases, both pressure and temperature in the combustion chamber increase, leading to high structural weight for pressure containment, high heat transfer, and large cooling requirements. Most significant, however, is the fact that the high temperatures also introduce significant dissociation of the combustion products. Most of this dissociation energy (which would otherwise be available for thrust) is lost due to lack of recombination before expansion to ambient conditions. All of these factors point to the use of supersonic combustion which lowers the pressure and temperature in the combustion chamber at some increase in entropy gain in the combustion process at higher velocities. The net effect is overall gain for the scramjet mode at  $M \approx 7.0$ . The scramjet can continue to provide thrust greater than drag for conceptual vehicles flying at Mach numbers in excess of 12.0.

#### Propulsion Technology

The use of  $LH_2$  in turbojet engines is by no means virgin territory. In 1957, NASA's Lewis Research Center successfully operated a J65 turbojet engine using

hydrogen as a fuel (ref. 5). A liquid hydrogen fuel tank and a ram-air heat exchanger were mounted on the left wing of a B-57 airplane and a high-pressure helium tank was mounted on the right wing (Fig. 6). The heat exchanger was used to gasify the hydrogen before entering the engine, and the helium was used for pressurizing the  $LH_2$  fuel tank and purging the fuel system. Take-off and climb to 49,000 feet altitude and a speed of around  $M = 0.72$  were accomplished by operating both engines on conventional JP-4 fuel. One engine was then operated on a mixture of hydrogen and JP-4 and then on hydrogen alone for approximately 20 minutes. Several flights were made without incident. Although specific fuel consumption during the flight tests was not reported, tests in ground facilities simulating flight conditions indicated that the specific fuel consumption of JP-4 fuel was 2.73 times that of hydrogen, thus realizing the gains expected from hydrogen fuel.

Returning to ramjets, extensive research over about the past 10 years has produced an advanced level of technology for applications up to about  $M = 5$ . Ramjet flight articles, primarily missiles, produced in this country and abroad, have been restricted to hydrocarbon fuels. Although limited to ground-based facilities, hydrogen-fueled ramjet engines have received considerable research effort. Both subsonic and supersonic combustion ramjet engines have been successfully demonstrated and, in most cases, the high-performance levels anticipated were achieved. A brief resume of this work is presented in reference 6. One example of the work being done in this field is the NASA Langley Hypersonic Research Engine (HRE) Project. Initially, the objectives of this project were to develop a hydrogen-burning ramjet engine for operation between Mach numbers of 3 and 8 with dual mode subsonic and supersonic combustion capability and to conduct ground-based and flight experiments which would prove design and fabrication techniques and provide needed engine research data. After the flight tests, which were to have been carried out using the X-15 research airplane as a test bed, were canceled due to the termination of the X-15 program, an expanded ground-test program was formulated and is still in progress. A simplified cross section of the HRE that evolved is shown in Figure 7. The HRE is an axisymmetric, variable geometry engine (18 inches in diameter and 84 inches long) with a translating center spike to give needed variable geometry for operation over the Mach number range; for example, the translating center body positions the shockwave from the spike on the cowl lip from Mach 6 to Mach 8, minimizing flow spillage. From the sketch, one can see that as Mach number is increased the fuel injection and combustion move forward in the engine. A so-called structural assembly model (SAM) of the HRE, which is a realistic flight weight engine (although for ground tests) incorporating subsystems, controls, and relatively sharp hydrogen-fuel-cooled leading edges for both inlet cowl and the internal struts, has been tested in the Langley 8-foot high-temperature structures tunnel (Fig. 8). This series of tests provided a solid demonstration that a flight-weight, regeneratively cooled ramjet engine could operate in the  $M = 7$  environment. Although these tests were carried out with full flight temperature, the test stream of hydrocarbon-air combustion products did not contain enough oxygen to permit combustion tests. The final phase of the HRE project will thus include tests of a "boiler plate," water-cooled, hydrogen-burning model in a new facility at our Lewis Research Center wherein true temperature air up to  $M = 7.0$  is provided, and combustion experiments can be made over a Mach number range from 5 to 7.

Under the stimulus provided by the HRE project, a number of long-range basic scramjet problems have been brought into focus for which new research has been organized. The research programs reflect the fact that efficient hypersonic cruise vehicles should capitalize on the very strong interaction among the structural, propulsive, and aerodynamic features of vehicle design. One major research objective is, for example, to develop scramjet engine concepts that minimize fuel-cooling requirements so that a maximum of the residual hydrogen-fuel heat sink is available for airframe cooling. Features of such engines that will reduce the internal heat load are readily identified as follows: supersonic combustion, nonannular ducts

having low ratio of wetted area to flow area, short combustor length (efficient fuel injectors), short cowl lengths, large combustor area ratios, reduced pressures and reduced fuel injection near the duct walls, insulation, film cooling, and the use of the aircraft body for major parts of the inlet and nozzle functions. Using all of these features except insulation, we have designed and analyzed the scramjet concept shown in Figure 9. For comparison, the cooling requirements of an annular engine were also determined and the results are given in Figure 10, which shows the large reductions in cooling requirements (integrated over the engine length) for the three-dimensional rectangular-module design (see refs. 7, 8, and 9). For this study at  $M = 6$ , the small fraction of the total fuel-flow heat capacity needed for engine cooling leaves most of the hydrogen heat sink available for airframe cooling. The large margin shown available for airframe cooling at  $M = 6$  diminishes with increasing Mach number due to growing engine-cooling requirements, however, studies have shown that actively cooled cruise vehicles may be feasible up to Mach numbers of 9 to 10.

#### HYPERSONIC TRANSPORT STRUCTURE

Before addressing the prospects for actively cooled airframes, first consider the case for "hot" structures, which dispose of a major portion of the heat load through radiation. Shown in Figure 11 is a "typical" temperature distribution for upper and lower surfaces of an  $M = 8$  HST wherein aerodynamic heating input is balanced by radiation. The feasibility of the "hot" structure rests on the fact that the radiation equilibrium temperatures of cruise vehicles tend to fall within the possible working-temperature ranges of the so-called superalloys and the refractory metals. A cross section of a radiation-cooled wing structure that has evolved from research studies is shown in Figure 12. Here the primary structure is made up of superalloys or refractory metals protected by both insulation and heat shields. Major strides toward solving the problems of thermal stress have been made through the use of nonredundant structures and corrugated shear webs (ref. 10). The thin heat shields which protect the primary structure are typically 0.01-inch to 0.02-inch thick and are attached to the primary structure by delicate clips in order to minimize conduction effects and save weight. When the heat shields expand due to high temperatures, sliding joints sealed by flexible bellows are necessary to prevent hot boundary-layer air from leaking into the substructure and causing hot spots. Whether or not aircraft structures of this type can withstand the rigorous demands of commercial aircraft operations and maintain long airframe lifetimes is yet to be determined.

Having suggested the obvious difficulties of routine airline-type operation of red-hot structures and having indicated the feasibility of scramjet engines with low cooling requirements, it remains to be stated that realistic actively cooled structures can be envisaged for the airframe of the hypersonic cruise aircraft. If it were possible to cool the skin and primary structure of the aircraft to around  $500^{\circ}\text{F}$ , it would be possible to construct the aircraft of titanium, using current materials and construction technology. Cooling the airframe to  $200^{\circ}\text{F}$  would not only allow the hypersonic aircraft design to take advantage of years of experience in building aluminum alloy airplanes, but would also open the door to the use of boron-aluminum composites. Preliminary studies (refs. 7 and 8) have in fact indicated that an airframe cooling system using a secondary coolant which is circulated internally in the airframe and used to carry the heat load from the airframe to a central hydrogen-fuel-cooled heat exchanger is feasible and could reduce the airframe temperature of a Mach 6 airplane to levels which would permit the use of titanium, and, with limited heat shielding, the use of aluminum. The secondary coolant might be a water-ethylene-glycol solution for aluminum alloy cooling or a silicone-base fluid such as Dow-Corning DC-331 for titanium alloy cooling. A typical cooled wing panel, shown in Figure 13, has been analyzed with respect to coolant-tube spacing, temperature gradients, and coolant flow rates. The studies have shown

(ref. 11) that the physical proportions of the entire cooling system are quite reasonable (Fig. 14) and that the weight of the cooling system, including the plumbing and heat exchanger, may be more than offset by the savings in the weight of the airframe, heat shields, and insulation, as shown in Figure 15. The coolant (water-glycol) and its piping constitute the principal cooling system weight. Future studies will consider design criteria and system reliability in detail and determine the optimum panel concepts and secondary coolants for a variety of airframe materials, including composites.

An area of concern to either "hot" or actively cooled structures will be the containment of the  $LH_2$  fuel at  $-423^{\circ}F$ . Two concepts being examined at Langley are shown schematically in Figure 16. As shown in the sketch at the upper right for one concept, the  $LH_2$  tank is protected by a layer of insulation. Unless air is prevented from coming into contact with the tank wall, cryopumping will occur, the air will liquify, and run down the tank wall. This condensation of the air results in high heat transfer to the fuel, reduces the effectiveness of the insulation, promotes damage due to freezing and thawing, and, due to selective liquefaction, may cause a dangerous accumulation of liquid oxygen. In order to prevent air and moisture from entering the area, the space adjacent to the outer wall is pressurized with an inert gas such as nitrogen. A portion of the insulation nearest the tank wall has a small pore size to prevent the nitrogen from flowing down the tank wall and thus minimizes cryopumping.

Another concept, shown in the lower right portion of Figure 16, utilizes internal as well as external insulation. In this case, the internal insulation maintains the tank wall above the condensation temperature of air, however, cryogenic penetration of the internal insulation must be prevented. Although not indicated in Figure 16, an inert purging gas would probably be desirable for this concept when safety aspects are considered.

## HYPERSONIC TRANSPORT OPERATIONS

### Environmental Effects

Supersonic flight of SST's over the United States was prohibited by the Congress owing to the presumed unacceptability of the "sonic boom." An examination of the sonic-boom overpressures of aircraft of the SST weight class, shown as a function of cruise Mach number (Fig. 17), gives insight into a promising HST feature. For  $M = 3$ , SST-type aircraft, sonic-boom overpressures in the range of 1.5 to 3.5 psf are estimated; for HST-type aircraft at  $M = 6$  to 8 overpressures have decreased to about 1 psf. Lower overpressures at hypersonic speeds follow principally from the higher cruise altitudes of HST's (around 100,000 ft). Should these lower sonic-boom overpressures be found acceptable when the advantages offered the air traveler by hypersonic flight are weighed against environmental aspects, overland travel would be revolutionized as shown in Figure 18. Since HST's would still have high sonic booms during the acceleration and climb to cruise altitude, these phases would be carried out over the ocean before heading overland; likewise, the HST would decelerate and descend over water. Transcontinental trips would require only one-third the time required for subsonic aircraft and a flight from Los Angeles to Paris could be made in around 2.5 hours.

Hydrogen-fueled aircraft may be more attractive than fossil-fueled aircraft from an ecological standpoint. A comparison of the environmental emissions of an HST and a hydrocarbon-fueled SST is shown in Figure 19 and is expressed in pounds of emittant per mile. The HST will emit no carbon dioxide, no carbon monoxide, no solid particles, or unburned hydrocarbons, and a smaller amount of nitric oxide than an SST - on the other hand, it will emit an amount of water vapor more than three times that for the SST. It must be stated that the effects on the environment of release of water vapor

in quantities such as those from either a fleet of high-altitude SST's or HST's is not known at the present time.

#### Economic Aspects

As was mentioned in the opening remarks, if the HST is to become a reality, it must either offer the traveler unique capabilities for which the traveler is willing to pay a premium price or it must be economically competitive from a standpoint of direct operating cost. Although the HST would offer tremendous timesavings and convenience to the traveler, it is difficult to estimate passenger preference, particularly when connected to the purse string, therefore, one needs to compare direct operating costs of large transports as is done in Figure 20 for a subsonic jet (JP-fueled), an SST (JP-fueled), and a  $LH_2$  fueled HST (ref. 4). The hashed areas represent the cost of flight crew, insurance, maintenance, and depreciation, while the open bars represent the cost of the fuel. An additional scale is shown on the right which reflects the effect of the relative price of  $LH_2$  on the direct operating cost of the HST. Clearly, the economic competitiveness of the HST will be largely a reflection of the price of  $LH_2$ . It should be pointed out that the fuel cost for the JP-fueled aircraft represent present-day prices. Consider next the fuel price situation that might exist during the time period of the 1990's when the HST might become operational. Figure 21 shows a comparison of the relative cost per Btu of  $LH_2$  as compared to JP fuel, for the past, present, and the future. With the onset of the space industry, the increasing demand for  $LH_2$  drove the price steadily downward (data supplied to author by Vic Johnson, National Bureau of Standards, and John E. Johnson, Linde Division, Union Carbide Corp.) to about 16 cents per pound at present. Economic studies of hydrogen production (for example, refs. 4 and 12) have indicated that by merely increasing the quantity of  $LH_2$  production, further sizable reductions in price would occur as shown by the hashed area. (An HST would typically use 200,000 pounds  $LH_2$  per flight.) Continual improvement in production methods will also drive the price down. Electrolytically produced hydrogen might become more economically feasible at some future date if electric-energy costs are drastically reduced. Though fossil fuel prices (ref. 13) have remained fairly constant, they are predicted to gradually rise (refs. 14 through 16) due to the depletion of our reserves, increased cost of extraction, and our growing dependence upon imports. These price increases are reflected in the hashed area representing JP fuel. The cost of hydrocarbon fuels may rise even faster than shown if pressure from environmentalists continues. In the time period of the 1990's the cost of  $LH_2$  is seen to be competitive with hydrocarbon fuel, particularly if other uses of hydrogen energy (refs. 17 and 18) continue to receive broader attention, making hydrogen the fuel of the future.

#### Technology Projection

Taken from reference 11, Figure 22 shows, from rather detailed system studies, that a hot-structure hypersonic transport weighing 750,000 pounds and carrying 300 passengers, and using current technology, would have a range of 6000 miles. Our detailed studies on the cooled structure permit realistic speculation on its potential advantages for future vehicles. It is stated in reference 11, that with cooling, a 15-percent structural weight reduction due to composites and a major reduction in cryogenic-tankage-insulation weight can be postulated. In addition, a modest 10-percent gain in lift-drag ratio (L/D) through refinements such as area ruling, twist, camber, and filleting has been included. A 12-percent increase in specific impulse is also believed to be obtainable from increases in component efficiencies over the nominal values used previously. And thus the 6000-nautical-mile range obtained with the hot vehicle could be extended to over 10,000 nautical miles through future technology, as seen in Figure 22. For comparison, the lesser gains estimated on a comparable basis for a JP aircraft are also shown. Although the additional HST performance is shown as an increase in range, which, from the previous discussion of

future travel requirements may not be needed, this performance could be traded for additional payload capability, noise suppression, and other areas of concern.

#### A HYPERSONIC RESEARCH AIRPLANE

Finally, the case for a hypersonic research airplane, as stated by Becker and Kirkham (ref. 11) is given. "Although promising new approaches are being pursued in all the disciplines, there are of course several major deficiencies, chief among which are the lack of a proven power plant and the lack of a proven practical structural concept. Probably the most serious deficiency is the absence of any real flight vehicle development. Past experience suggests that progress beyond the present stage will be slow until the development of an actual vehicle is undertaken. In previous situations of this kind where it is obviously too soon for a full-scale prototype, the research airplane has been used to great advantage to provide the necessary focus, stimulus, and resource levels. The X-15 program, for example, provided the first great impetus to hypersonics and manned space flight technology.

"Figure 23 presents a concept and specifications for a small research airplane which can be thought of as a 1/3 scale version of the hypersonic transport. Air-breathing research scramjet engines and wing panels which could embody a variety of structural concepts are principal features. The vehicle would be capable of about 5 minutes cruise at Mach 8 either on its primary rocket propulsion or with the research scramjets. Present technology would fully support the development of such a vehicle. Both the analytical and the experimental tools are available. No new national facilities would be needed.

"The technology base developed with a hypersonic research airplane would make it possible to proceed with confidence to a full-scale prototype hypersonic transport or other applications including airbreathing launch systems."

#### REFERENCES

1. Anon.: Market and System Analysis for Potential Global Transport Application of a Reusable Orbital Transport. LR 1904 (Contract NAS8-11319) Lockheed-California Co., July 29, 1965. (Available as NASA CR-67279.)
2. Metzger, William L.: An Analysis of Commercial Markets for Reusable Launch Vehicle Systems. SRI Project No. ISD-5226, Stanford Research Inst., Dec. 1964.
3. Norling, A. H.: Future U.S. Transportation Needs (Contract NASw-585) United Research Inc. (Available as NASA CR-57005.)
4. Wilcox, Darrell E.; Smith, Cynthia L.; Totter, Holden C.; and Hallett, N. C.: Future Cost of Liquid Hydrogen for Use as an Aircraft Fuel. ASME Annual Aviation and Space Conference. June 16-19, 1968.
5. Lewis Laboratory Staff: Hydrogen for Turbojet and Ramjet Powered Flight. NACA RM E57D23, April 26, 1957.
6. Henry, J. R.; and McLellan, C. H.: Air-Breathing Launch Vehicle for Earth-Orbit Shuttle - New Technology and Development Approach. Journal of Aircraft, Vol. 8, No. 5, May 1971, pp. 381-387.
7. Becker, John V.: Prospects for Actively Cooled Hypersonic Transports. Astronautics and Aeronautics, Vol. 9, No. 8, Aug. 1971, pp. 32-39.
8. Becker, John V.: New Approaches to Hypersonic Aircraft. Seventh Congress of the International Council of the Aeronautical Sciences, Rome, Italy, Sept. 14-18, 1970.

9. Henry, John R.; and Beach, H. Lee: Hypersonic Air-Breathing Propulsion Systems. NASA SP 292, paper No. 8, Dec. 3, 1971.
10. Plank, P. P.; Sakata, I. F.; Davis, G. W.; and Richie, C. C.: Hypersonic Cruise Vehicle Wing Structure Evaluation. (Contract No. NAS1-7573.) Lockheed Missiles and Space Co. (Available as NASA CR-66897, Vols. 1-3.)
11. Becker, John V.; and Kirkham, Frank S.: Hypersonic Transports. NASA SP set 292, paper No. 25, Dec. 4, 1971.
12. Hallett, N. C.: Study, Cost, and System Analysis of Liquid Hydrogen Production. Air Products and Chemicals, Inc., Contract NAS 23894 (Available as NASA CR 73,226), June 1968.
13. Anon.: Report on Crude Oil and Gasoline Price Increases of November 1970. Office of Emergency Preparedness, April 1971. (Available from U.S. Government Printing Office, Stock No. 4102-0005.)
14. Starr, Chauncey: Energy and Power. Scientific American, Vol. 224, No. 3, Sept. 1971, pp. 37-49.
15. Anon.: Experts See Grim Outlook for U.S. Energy Supplies. The Oil and Gas Journal, Oct. 4, 1971, pp. 64-69.
16. Breckenfeld, Gurney: How the Arabs Changed the Oil Business. Fortune Magazine, Aug. 1971.
17. Gregory, D. P.: A Hydrogen Energy System. American Chemical Society Meeting. Symposium on "Non-Fossil Chemical Fuels," Boston, Mass., April 9-14, 1972.
18. Schoepfel, R.: Prospects for Hydrogen Fueled Vehicles. American Chemical Society Meeting. Symposium on "Non-Fossil Chemical Fuels," Boston, Mass., April 9-14, 1972.

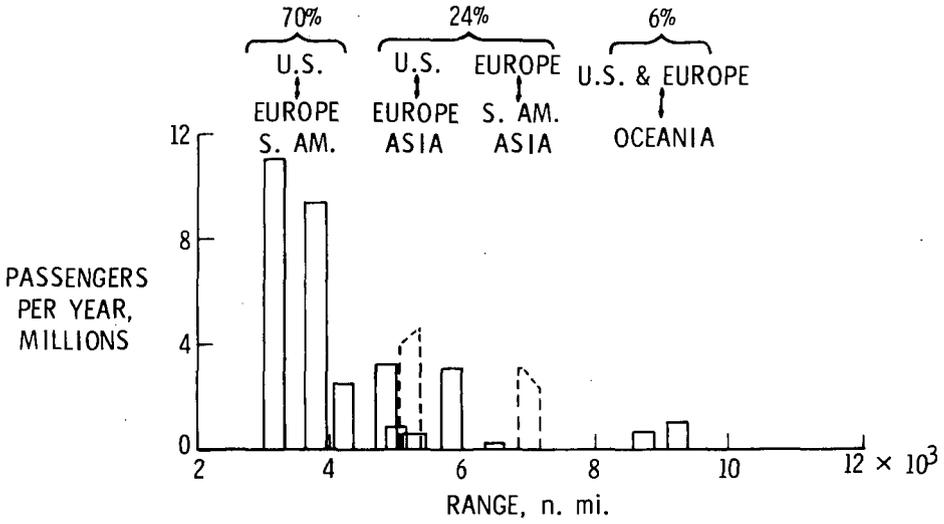


Figure 1.- Projected 1990 intercontinental air traffic.

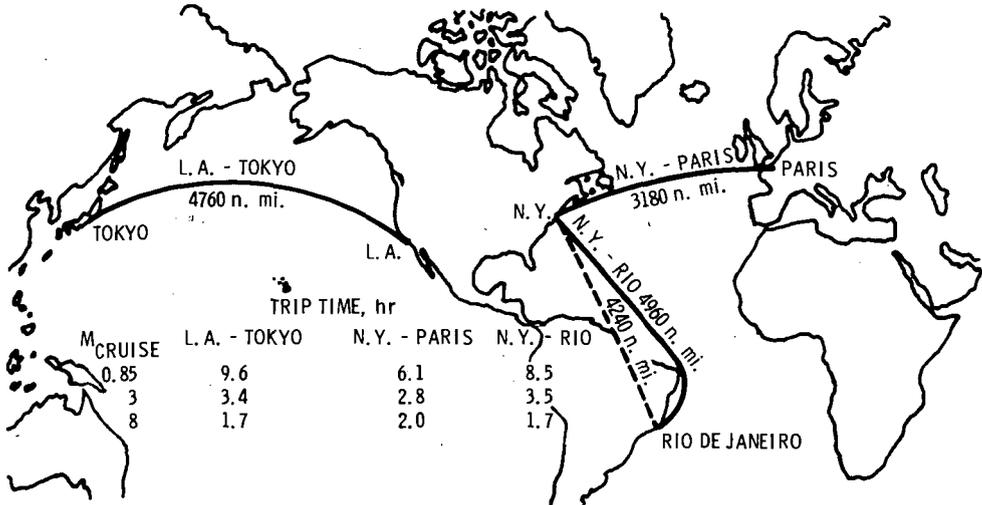


Figure 2.- Effect of aircraft speed on trip time.

| PROPERTY                                 | LIQUID   |         |        |
|--|----------|---------|--------|
|  | HYDROGEN | METHANE | JP - 4 |
| HEAT OF COMBUSTION, Btu/ lb              | 51 600   | 21 500  | 18 600 |
| HEAT SINK CAPABILITY TO 1000° F, Btu/ lb | 5 100    | 1 100   | 165*   |
| LIQUID DENSITY, lb/ ft <sup>3</sup>      | 4.4      | 26.4    | 50.0   |

\*JP - 4 HEAT SINK TO 375° F

Figure 3.- Comparison of fuel characteristics (from ref. 4).

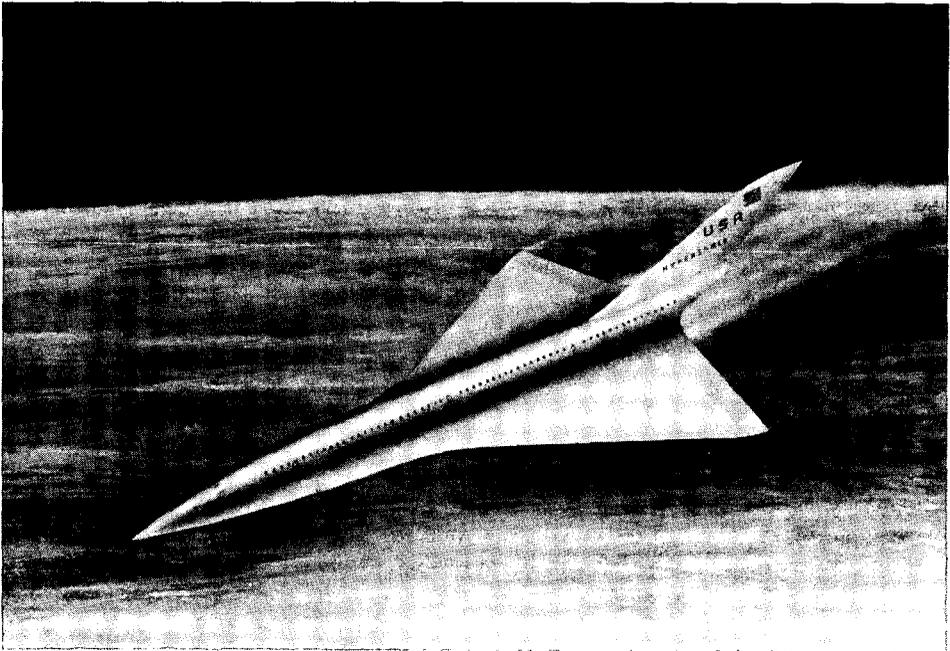


Figure 4.- Hypersonic air-breathing transport.

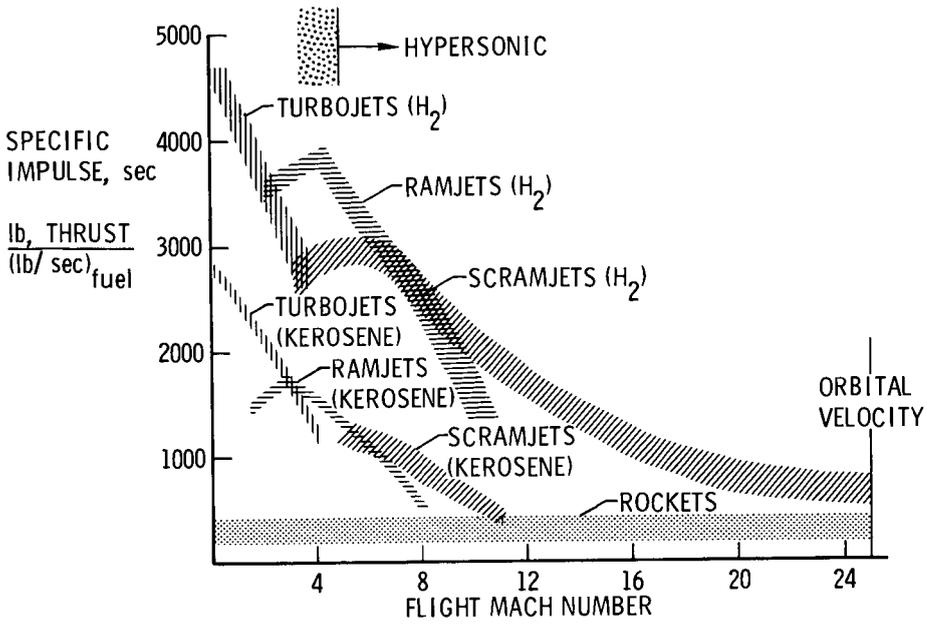


Figure 5.- Specific impulse for air-breathing engines and rockets.

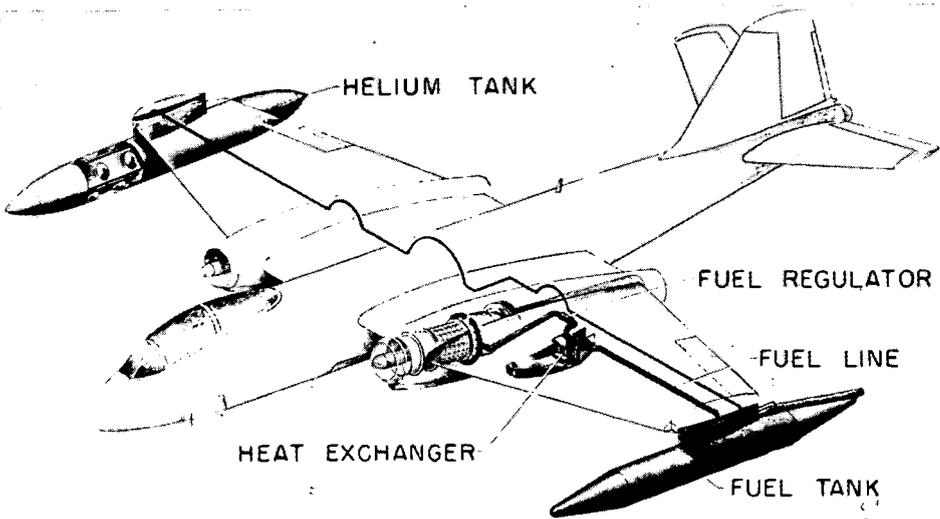


Figure 6.- Hydrogen system for B-57 airplane.

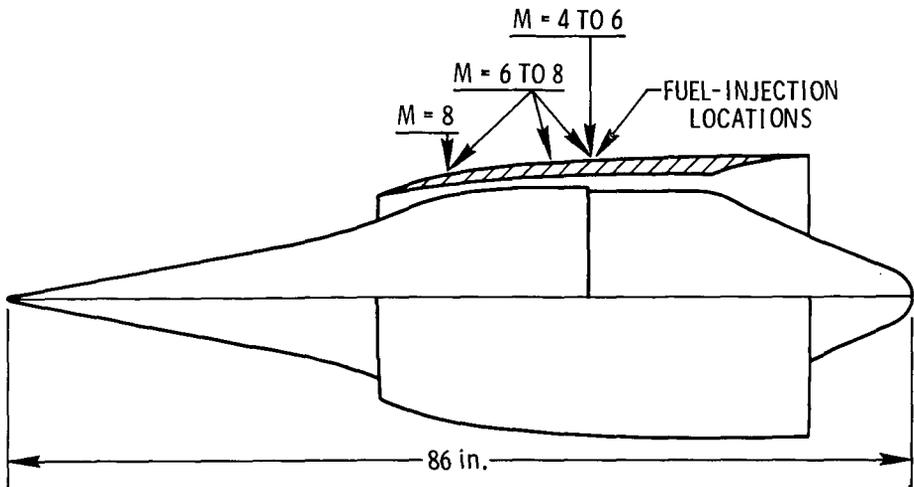


Figure 7.- Langley hypersonic research engine.

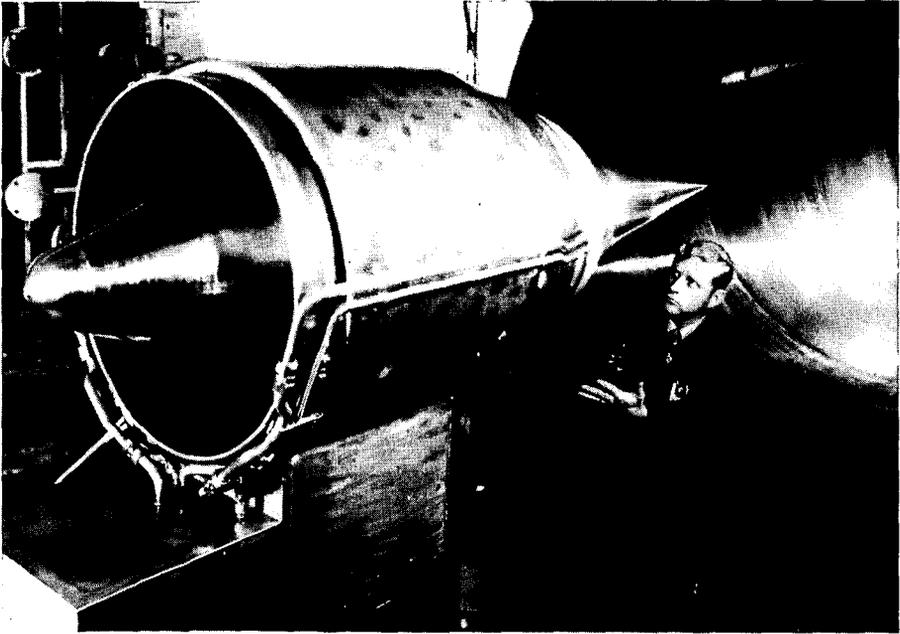


Figure 8.- HRE installed in Langley 8-foot high-temperature structures tunnel for tests.

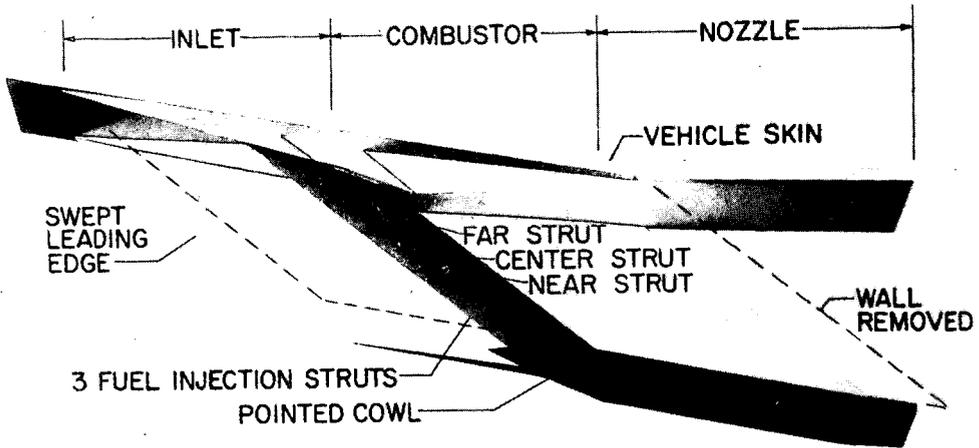


Figure 9.- Langley 3-D scramjet module.

ENGINE COOLANT REQUIREMENT  
FUEL FLOW HEAT CAPACITY

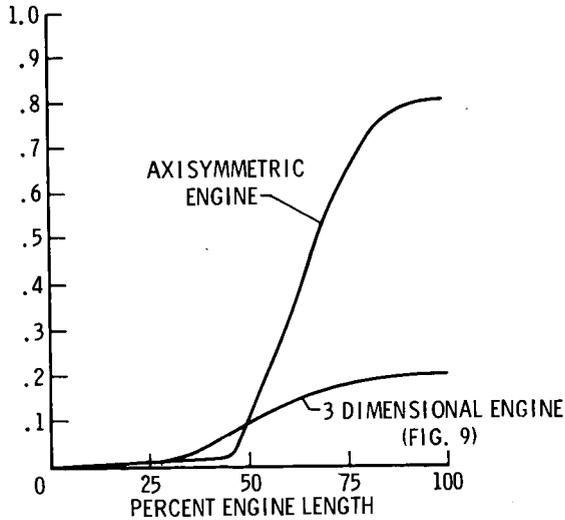


Figure 10.- Comparison of engine cooling requirements for 3-D module and axisymmetric engines. Mach 6, capture area 39.1 sq ft, altitude 112,000 ft, supersonic-stoichiometric combustion.

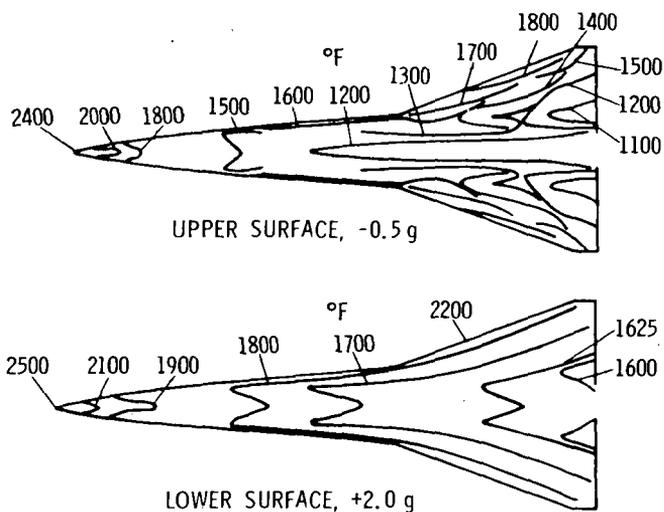


Figure 11.- Typical temperature distribution for radiation cooled hot structure. Mach 8, altitude 90,000 ft.

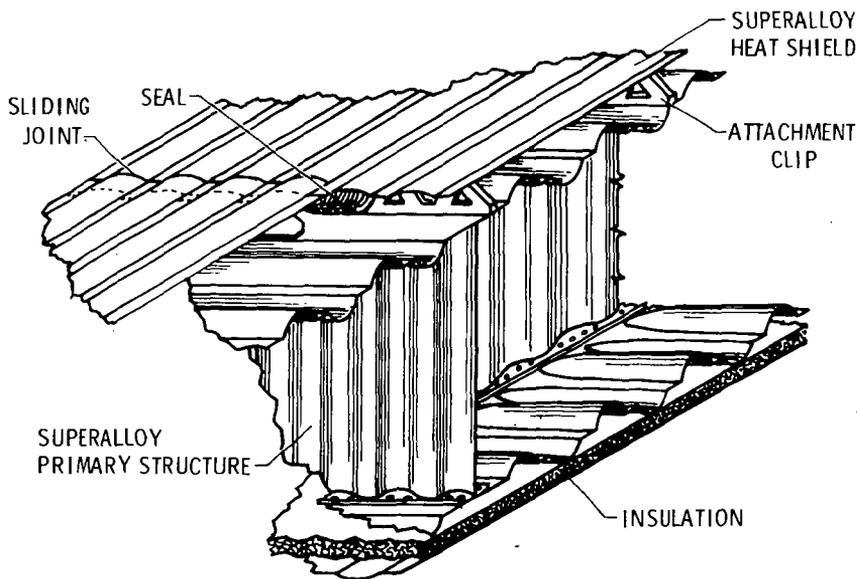


Figure 12.- Cruise vehicle hot wing structure.

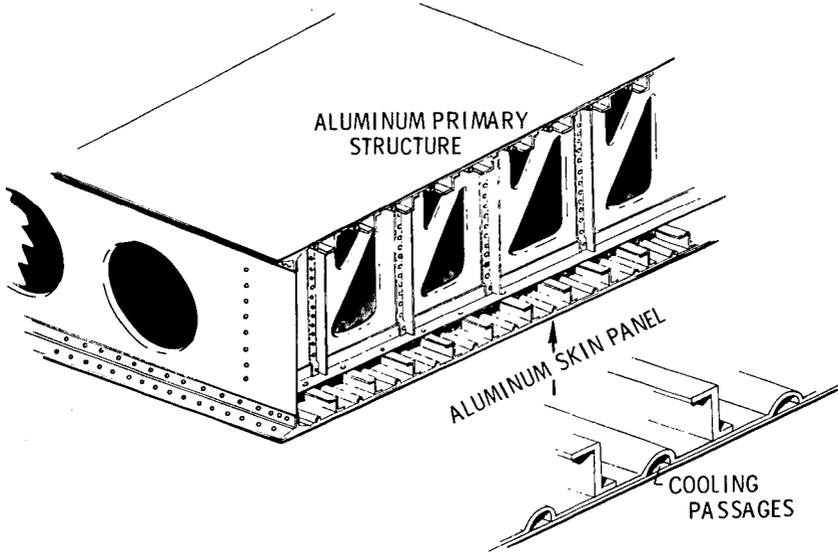


Figure 13.- Cooled wing structure.

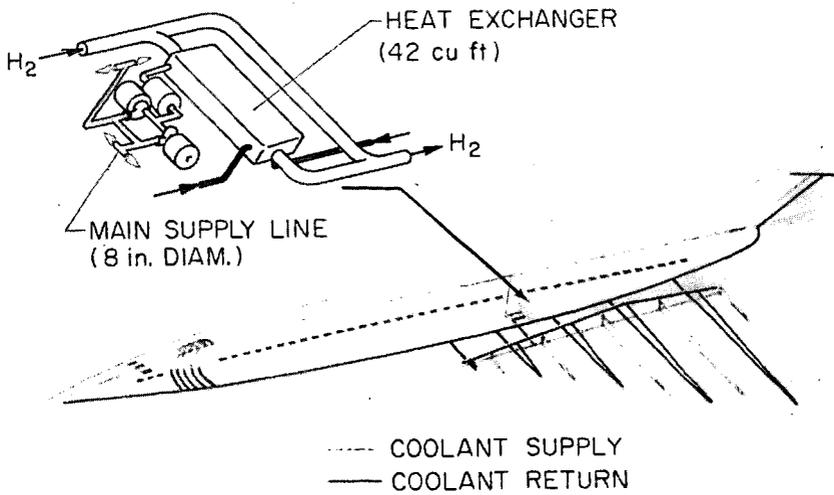


Figure 14.- Aircraft cooling system.

|                               | $W_{\text{COOLED}} - W_{\text{HOT}}$<br>kg (lb) |           |
|-------------------------------|---|-----------|
| • PIPING AND COOLANT          | +4 400  | (+9 800)  |
| • PUMPS, FUEL, MISC.          | +1 100  | (+2 500)  |
| • HEAT EXCHANGER              | +700  | (+1 600)  |
| • AIRFRAME                    | -10 100   | (-22 300) |
| • HEAT SHIELDS AND INSULATION | -6 500  | (-14 400) |
| NET CHANGE:                   | -10 400   | (-22 800) |

Figure 15.- Cooled versus hot structure - typical weight differences. (600,000 lb gross weight.)

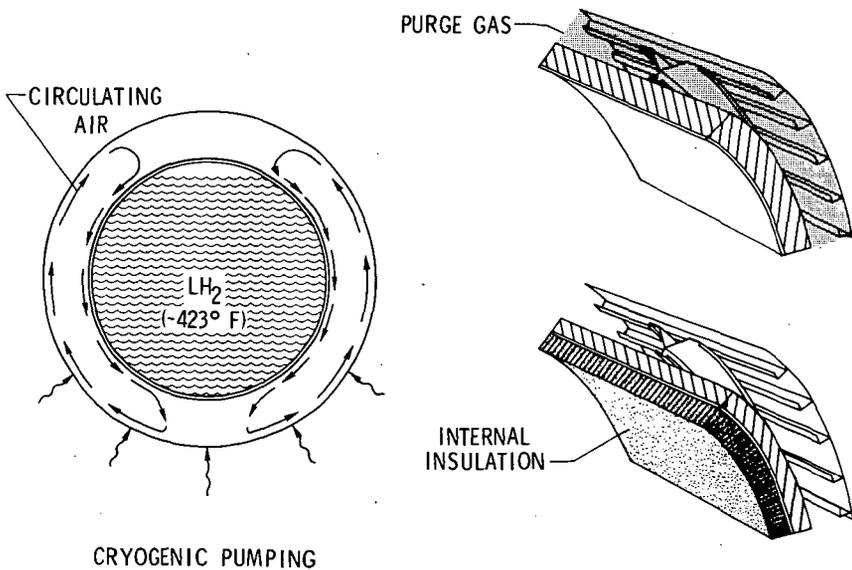


Figure 16.- Thermal protection of liquid hydrogen tanks.

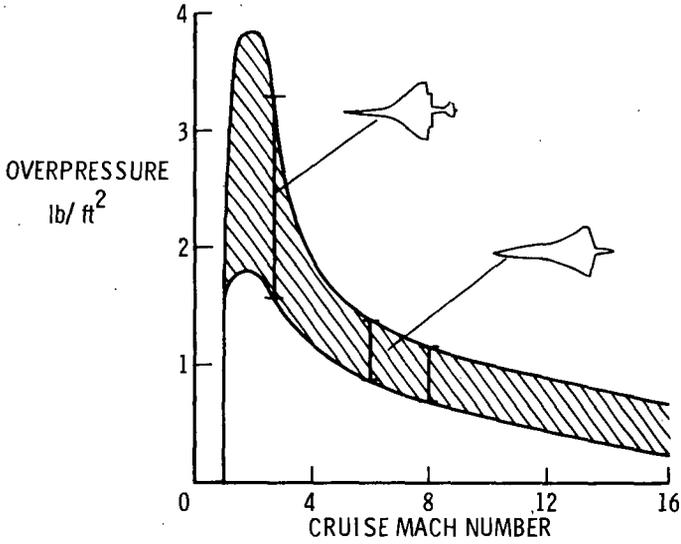


Figure 17.- Sonic-boom overpressures.

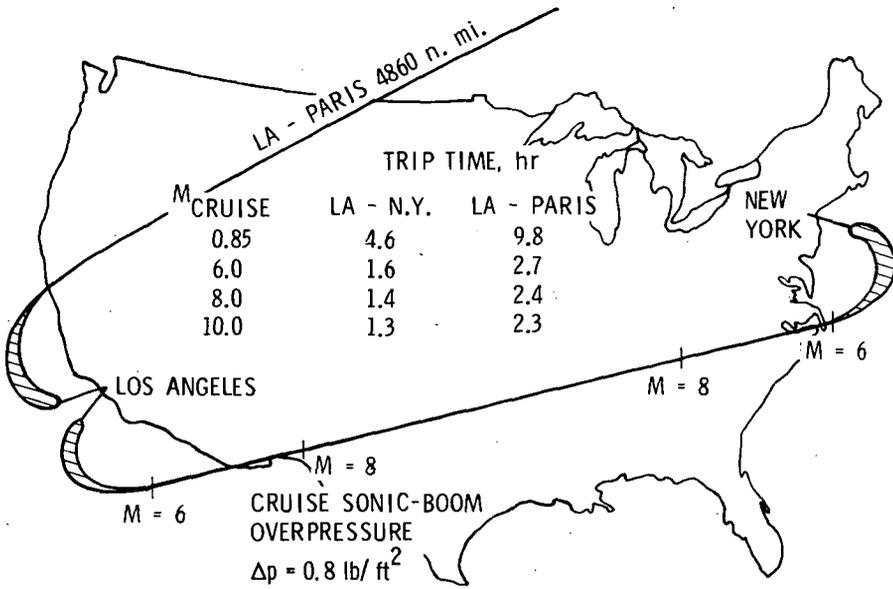


Figure 18.- Overland operation.

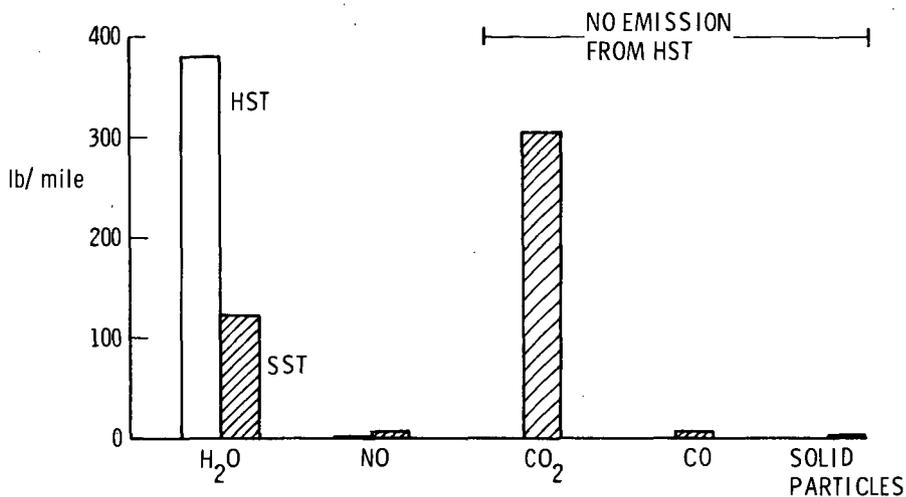


Figure 19.- Environmental emissions in cruise. (750,000 lb gross weight.)

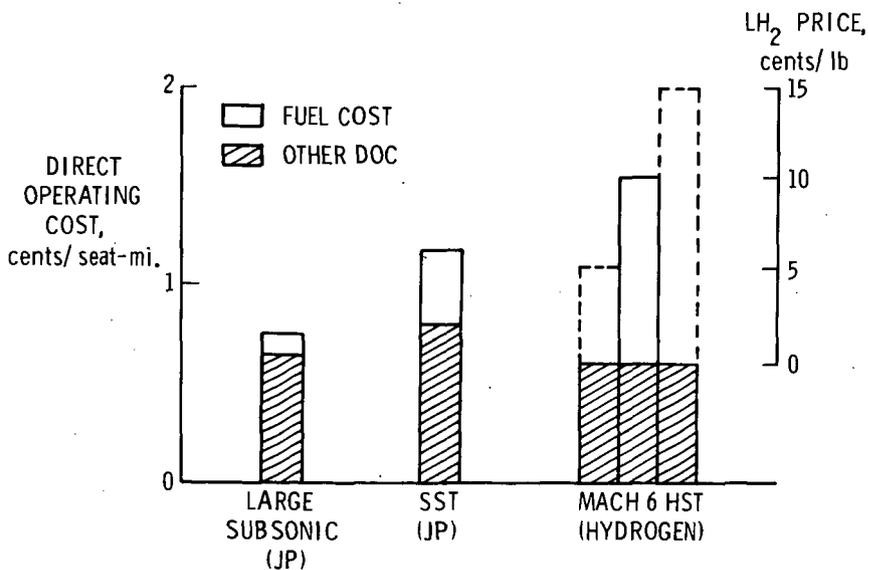


Figure 20.- Comparison of direct operating cost. Range, 4600 st. mi.

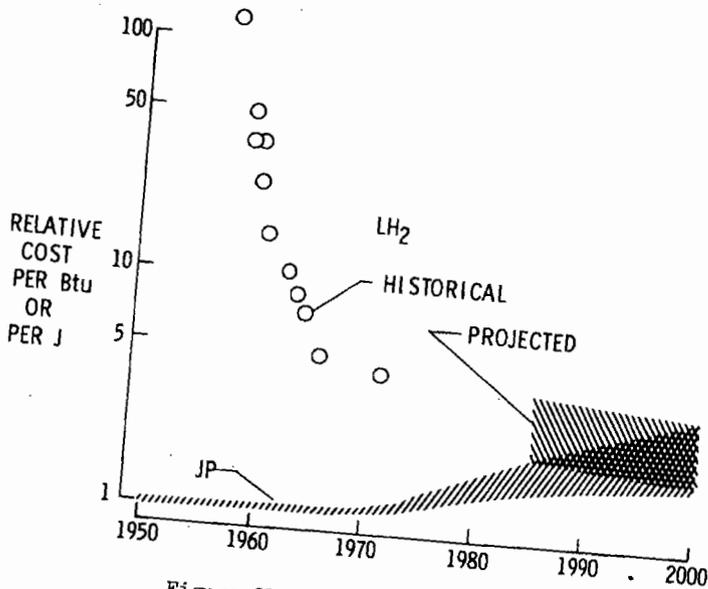


Figure 21.- Future fuel cost.

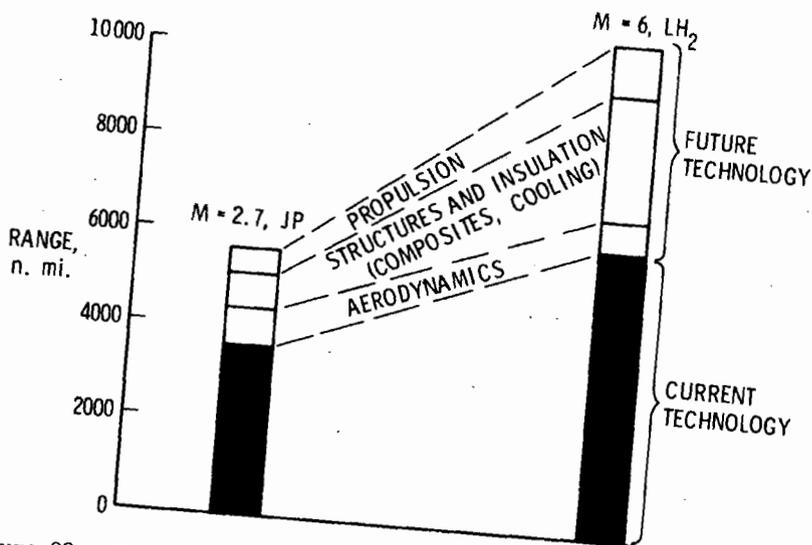
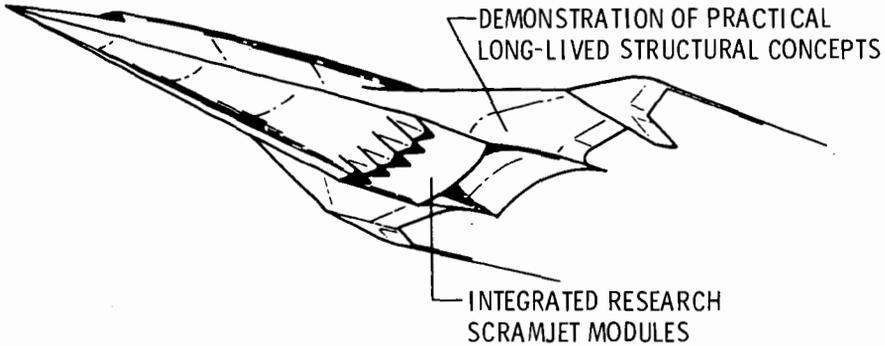


Figure 22.- Impact of future technology. (750,000 lb gross weight; 300 passengers.)



- GROSS TAKE-OFF WEIGHT  $\approx$  (80000 lb)
- LENGTH  $\approx$  (80 ft)
- CONVENTIONAL TAKE-OFF AND LANDING
- MAXIMUM SPEED,  $M = 8$  TO  $12$
- EXISTING ROCKET (PRIME PROPULSION)
- MODULAR RESEARCH AIRBREATHING ENGINES
- 5-MINUTE CRUISE AT MAXIMUM SPEED

Figure 23.- Research airplane concept and specifications.

## MEMBERSHIP IN THE DIVISION OF FUEL CHEMISTRY

The Fuel Chemistry Division of the American Chemical Society is an internationally recognized forum for scientists, engineers, and technical economists concerned with the conversion of fuels to energy, chemicals, or other forms of fuel. Its interests center on the chemical problems, but definitely include the engineering and economic aspects as well. Further, the Division is strengthening its coverage of areas of air and water pollution, gasification, and related areas.

Any chemist, chemical engineer, geologist, technical economist, or other scientist concerned with either the conventional fossil fuels, or the new high-energy fuels--whether he be in government, industry, or independent professional organization--would benefit greatly from participation in the progress of the Fuel Chemistry Division.

The Fuel Chemistry Division offers at least two annual programs of symposia and general papers, extending over several days, usually at National Meetings of the American Chemical Society. These include the results of research, development, and analysis in the many fields relating to fuels which are so vital in today's energy-dependent economy. Members of the Division have the opportunity to present papers of their own, or participate in discussions with experts in their field. Most important, the Fuel Chemistry Division provides a permanent record of all of this material in the form of preprints, which are sent free to all members several weeks before each meeting.

Symposia of significant content and broad interest have been published as part of the Advances in Chemistry Series and by other scientific book publishers. Landmark symposia on Fuel Cells, Advanced Propellant Chemistry, Gasification, and Spectrometry are already in print. When these volumes are available they are usually offered first to Division members at greatly reduced cost.

In addition to receiving several volumes of preprints each year, as well as regular news of Division activities, benefits of membership include: (1) Reduced subscription rates for "Fuel" and "Combustion and Flame," (2) Reduced rates for volumes in the "Advances in Chemistry Series" based on Division symposia, and (3) The receipt card sent in acknowledgment of Division dues is good for \$1.00 toward a complete set of abstracts of all papers presented at each of the National Meetings.

To join the Fuel Chemistry Division as a regular member, one must also be or become a member of the American Chemical Society. Those not eligible for ACS membership because they are not practicing scientists, engineers, or technical economists in areas related to chemistry, can become Division Affiliates. They receive all benefits of a regular member except that they cannot vote, hold office, or present other than invited papers. Affiliate membership is of particular value to those in the information and library sciences who must maintain awareness of the fuel area. Non-ACS scientists active in the fuel area and living outside of the United States are also invited to become Division Affiliates.

Membership in the Fuel Chemistry Division costs only \$4.00 per year, or \$11.00 for three years, in addition to ACS membership. The cost for a Division Affiliate, without joining ACS, is \$10.00 per year. For further information write to:

Dr. Harold L. Lovell  
Secretary-Treasurer  
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Pennsylvania State University  
109 Mineral Industries Building  
University Park, Pennsylvania 16802  
Telephone: Area 814 - 865-2372

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| <u>Volume</u>                    | <u>Title</u>  | <u>Presented At</u>                  |
|----------------------------------|---|--------------------------------------|
| Vol. 14, No. 1                   | Symposium on Coal and Coal Based Carbons<br>Symposium on Petrographic, Chemical, and<br>Physical Properties of Coal | Toronto, Canada<br>May, 1970         |
| Vol. 14, No. 2                   | Symposium on Coal Combustion in Present and<br>Future Power Cycles  | Toronto, Canada<br>May, 1970         |
| Vol. 14, No. 3                   | Synthetic Fuels Symposium No. 3 - Economics<br>of Solid Fuel Conversion Processes<br>General Papers                 | Chicago, Illinois<br>September, 1970 |
| Vol. 14, No. 4<br>Parts I and II | Symposium on Hydrogen Processing of Solid<br>and Liquid Fuels   | Chicago, Illinois<br>September, 1970 |
| Vol. 14, No. 5                   | Symposium on High Temperature and Rapid<br>Heating Reactions of Fuels   | Chicago, Illinois<br>September, 1970 |
| Vol. 15, No. 1                   | Symposium on Shale Oil, Tar Sands and<br>Related Materials  | Los Angeles<br>March, 1971           |
| Vol. 15, No. 2                   | Symposium on Combustion<br>Symposium on Pollution Control in Fuel<br>Combustion, Mining and Processing              | Washington, D. C.<br>September, 1971 |
| Vol. 15, No. 3                   | Symposium on Gasification of Coal<br>General Papers   | Washington, D. C.<br>September, 1971 |
| Vol. 16, No. 1                   | Symposium on Quality of Synthetic Fuels,<br>Especially Gasoline and Diesel Fractions,<br>and Pipeline Gas           | Boston, Mass.<br>April, 1972         |
| Vol. 16, No. 2                   | Symposium on Preparation and Properties of<br>Catalysts for Synthetic Fuel Production<br>General Papers             | Boston, Mass.<br>April, 1972         |
| Vol. 16, No. 3                   | Symposium on Modern Methods of Fuel Analysis  | Boston, Mass.<br>April, 1972         |
| Vol. 16, No. 4                   | Symposium on Non-Fossil Chemical Fuels  | Boston, Mass.<br>April, 1972         |

DIVISION OF FUEL CHEMISTRY

PROJECTED PROGRAMS

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| <u>Environmental Pollution Control - Part I. Removal of Oxides of Sulfur and Nitrogen from Combustion Products</u><br>James<br>Robert M. Jameson | New York, N. Y.<br>August, 1972 |
| <u>Environmental Pollution Control - Part II. Removal of Sulfur from the Fuel</u><br>Robert M. Jameson   | New York, N. Y.<br>August, 1972 |
| <u>Storch Symposium</u>  | New York, N. Y.<br>August, 1972 |
| <u>General Papers</u><br>Wendell H. Wisner   | New York, N. Y.<br>August, 1972 |
| <u>Symposium on the Power Industry of the Future - Fossil and Fission Fuels</u><br>Joint with IEC Division - Develop by IEC                      | New York, N. Y.<br>August, 1972 |
| <u>Novel Combined Power Cycles</u><br>S. Fred Robson   | Dallas, Texas<br>April, 1973    |
| <u>Fuel from Waste Products</u><br>H. R. Appell  | Dallas, Texas<br>April, 1973    |
| <u>Carbon Monoxide Production and New Uses</u><br>J. S. Mackay   | Dallas, Texas<br>April, 1973    |
| <u>Synthetic Fuel Gas Purification</u><br>H. S. Vierk  | Dallas, Texas<br>April, 1973    |
| <u>Coal Gasification</u><br>L. G. Massey   | Dallas, Texas<br>April, 1973    |
| <u>General Papers</u><br>F. Schora   | Dallas, Texas<br>April, 1973    |